THE POSSIBILITY OF USING ROMAN CEMENT AS A BINDER OF REPAIR MORTARS TO RESTORE POROUS STONES

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Abstract

Repair mortars, which could be successfully employed to restore sculptures and architectonical details made of porous stones, such as the sandstone or light limestone, were the subject-matter of numerous researches, which examined both mineral and organic binders (Domasłowski, W., 1966; Łukaszewicz, J.W., 2002; Obajtek, M. 1993). However, till today this issue remains unsolved. The following study covers the problem of the potential use of Roman cement, whose technology was re-developed in the frames of the European project ROCEM (Adamski, G., Bratasz, Ł., Mayr, N. *et al*. 2009; Weber, J., Gadermayr, N., Kozłowski, R. *et al*. 2007), as a binder of repair mortars to restore stone monuments with a porous structure, particularly from the light limestone.

The scope of the research includes a determination of the influence of the following factors on the qualities of the mortar: sort, size and amount of the aggregate used to formulate a repair mortar. Moreover, the influence of the citric acid employed as the setting retarder was examined. Ready-to-use casting mortar produced in The Division of Glass and Building Materials in Cracow, Pińczów limestone and Żerkowice sandstone were employed as the reference materials for comparison. In the frames of the study following properties of the formulated mortars were examined: workability, linear contraction, setting time, the capability of capillary water transport, density, water absorption, porosity, compressive and tensile strength, resistance to decay mechanisms, therein to water and soluble salts.

As a result of those investigations, the possibility of employing Roman cement in art conservation as a binder of repair mortars, especially for the light limestone, can be concluded.

Keywords: mineral binders, repair mortars, Roman cement, porous stones, sandstone, light limestone

1. Introduction

Filling losses in stone monuments, especially in those made of porous stones being exposed in external conditions, should be considered as a treatment of a special significance, determining the final effect of the whole conservation process. Two methods of filling losses are commonly in practice: employing natural stone and repair mortars based on organic or mineral binder. Such mortar should be characterised by the following features: proper application qualities (workability, plasticity, consistency, capability of adhesion and binding in a layer of any thickness, adequate working time) and proper aesthetic qualities (colour and texture). While setting, repair mortar should show no contraction and produce no harmful for the stone substances (such as acids or soluble salts). After setting, water absorption, porosity and primarily the capability of capillary water transport of the repair mortar should be comparable to the original material and slightly higher. Also tensile and compressive strength of the mortar should be comparable to the stone, but slightly lower. High corrosion resistance of the repair mortar is desirable.

Due to the re-appearance of the Roman cement on the conservation market, researches aiming to determine whether this binder fulfils above-mentioned criteria were carried out.

Roman cements were commonly employed in the architecture of European Historicism and Art Nouveau (second half of the 19th century/ beginning of the 20th century) as binders in stucco mortars and elements decorating façades of many buildings. During years, in places where Roman cement mortars were being exposed to prolonged performance of rain water, the deterioration of the material was becoming more and more advanced and conservation treatment became a necessity. However, the problem of obtaining the original binder occurred, due to the decline of the manufacturing of Roman cements in 1950s. The need for carrying out restoration work of the built heritage from this period was underlying the researches and it was performed in the frames of European projects ROCEM and ROCARE (Hughes, D.C., Weber, J., Kozłowski, R. 2010), which aimed at re-developing the technology of producing high quality Roman cements and at formulating the composition of mortars, putties and paints. Currently, those are being produced in The Division of Glass and Building Materials in Cracow, Institute of Ceramics and Building Materials in Warsaw.

2. Materials and methods

2.1 Materials

Mortar: ready-to-use casting mortar, self-formulated repair mortars
Binder: Roman cement
Aggregates: quartz sand (size : 0.125-0.25 mm, 0.25-0.5 mm, 0.5-1.25 mm, 1.25-2.0 mm), pulverised Pińczów limestone (size: 0.125-0.25 mm, 0.25-0.5 mm)
Additives: citric acid (0.4% of the weight of the cement)
Water-to-cement ratio: 0.6, 0.7, 0.8, 0.9, 1.0, 1.1
Cement-to-aggregate ratio: 1:2, 1:3, 1:4, 1:5, 2:1, 1:1, 1:2
Stones (as the reference materials): Żerkowice sandstone, Pińczów limestone

Both, ready-to-use casting mortar and Roman cement binder were produced in The Division of Glass and Building Materials in Cracow. Ready-to-use casting mortar was used to formulate samples to determine optimal curing conditions. The paste was produced according to technical specifications at the following proportion: 0.35l of water to 1 kg of ready-to-use dry casting mixture.

Samples used to examine the influence of the sort, size and amount of the aggregate on repair mortars were formulated from Roman cement binder and respective aggregate. The pastes were produced at the water-to-cement (w/c) ratio varying from 0.6 to 1.1. The value of w/c ratio was determined by the workability of the pastes. The quartz sand of the following sizes: 0.125-0.25 mm, 0.25-0.5 mm, 0.5-1.25 mm, 1.25-2.0 mm and the pulverised limestone Pińczów of the sizes: 0.125-0.25 mm, 0,25-0,5 mm were used as aggregates and the cement-to-aggregate (c/a) ratio was from 1:2 to 1:5 and from 2:1 to 1:2 by weight for the quartz sand and the limestone respectively. Furthermore, the influence of the citric acid employed as setting retarder was examined in relation to the mortar with the limestone aggregate. The percentage was 0.5% in water, which corresponds to 0.4% related to the weight of cement (Bayer, K., Gurtner, Ch., Hughes, D.C. *et al*. 2006; Szeląg, H., Garbacik, A., Pichniarczyk, P. *et al*. 2008). Pińczów limestone and Żerkowice sandstone were employed as the reference materials for comparison.

2.2 Methods

For all measurements, prismatic specimens of 16x4x4 cm were cast in steel modules in accord with PN-EN 196-1:2006 standard. All the samples were demoulded after 48 hours and cured for 14 days. The specimens with quartz sand aggregate were cured in a cotton cellulose compress, which was being alternately wetted in distilled water and left for drying. After curing period the samples were cut into 4x4x4 cm cubes and left for 28 days in laboratory conditions to reach constant weight. The specimens with limestone aggregate were cured in a climatic chamber allowing the vapour transport, i.e. near 95% relative humidity. After curing period the samples were cut into 4x4x4 cm cubes and left for 21 days in laboratory conditions to reach constant weight. Curing period and methods were chosen basing on preliminary tests on ready-to-use casting mortar.

Following properties were determined for the mortar samples: workability, linear contraction (in accord with PN-55/H-104189 standard), setting time (PN/B-04300 standard), the time of capillary water transport, density, water absorption and porosity (PN-54/B-04100 and PN-54/B-04101 standards), tensile strength (using a RMU Testing Equipment SRL M052), compressive strength (using a ToniPRAX Zwick/Roell, in accord with EN 196, ISO 679 and ASTM C 109, C 349 standards), freeze-thaw resistance (PN-54/B-04102) and resistance to the soluble salts. The workability of mortars was determined basing on the observation of the freshly formulated pastes. The time of capillary water transport was measured on 4x4x4 cm mortar cubes immersed at the depth of 1 cm in water. The resistance to the soluble salts was examined on the specimens, which were being alternately for 24 hours immersed in 10% $Na_2SO_4 \times 10H_2O$ water solution, for 24 hours placed in a laboratory drier at 378.15K and for 24 hours placed in desiccator with silica gel. Those cycles of examination were being conducted repeatedly until the samples were destroyed.

3. Results and discussion

The following features of the mortars formulated according to a given technology after curing period (in the aforesaid conditions) and reaching constant weight were examined: the time of the water capillary rise, water absorption, porosity, tensile and compressive strength. Moreover, the freeze-thaw resistance and resistance to the soluble salts were determined. The results are presented in charts and discussed therein under.

3.1 Influence of the size of the aggregate on the qualities of Roman cement mortar

Four types of mortars formulated using the quartz sand aggregate of the following sizes: 0.125-0.25 mm, 0.25-0.5 mm, 0.5-1.25 mm and 1.25-2.0 mm were examined. The cement-to-aggregate was 1:3 by weight and w/c ratio varied from 0.6 to 0.8.

Table 1. Influence of the size of the aggregate on the qualities of Roman cement mortar

Type of the sample	Size of the quartz sand aggregate [mm]	Density [g/cm^3]	Time of the water capillary rise [3 cm] [min]	Water absorption [%]	Porosity [%]	Tensile strength [MPa]	Compressive strength [MPa]
Roman cement repair mortar	0.125-0.25	1.51	38	16.69	25.05	0.65	1.97
	0.25-0.5	1.54	25	18.15	27.82	0.67	2.06
	0.5-1.25	1.59	19	15.43	24.55	0.52	1.63
	1.25-2.0	1.55	15	14.56	22.53	0.65	1.60
Limestone	-	1.71	25	14.24	24.84	-	10.48
Sandstone	-	1.97	8	6.68	12.48	-	25.31

The best workability was observed for the mortar with the quartz sand 0.25-0.5 mm and the worst – for the 1.25-2.0 mm mortar. A linear contraction of mortars was in the range of 0.23% (for 1.25-2.0 mm mortar) to 0.8% (0.125-0.25 mm mortar). Thereby, the linear contraction increases pro rata with the increase of the w/c ratio. A setting time was between 1.5 hour for 1.25-2.0 mm mortar and 27 hours for 0.125-0.25 mm mortar. This correlation could be also explained by lower w/c ratio for the mortars formulated with the aggregate of a bigger size.

The water absorption of the examined samples (14.56-18.15%) and the limestone (14.24%) were comparable, as well as their porosity (22.53-27.82% for mortars and 24.84% for the limestone). Both values, water absorption and porosity were the lowest for the mortar with the biggest size of the aggregate employed. Thereby, an inversely proportional correlation could be observed between size of the aggregate and value of water absorption and porosity of examined Roman cement mortars. All four types of tested samples were characterised by good capability of capillary water transport (the time of capillary water transport at the height of 3 cm was 15-38 min, while for the limestone this time was measured 25 min).

The examined mortars were obtaining relatively low tensile (0.52-0.67 MPa) and compressive strength (1.63-2.06 MPa), with the highest values for the mortar with 0.25-0.5 mm aggregate, while the limestone was characterised by a compressive strength of 10.48 MPa.

3.2 Influence of the amount of the aggregate on the qualities of Roman cement mortar

Four types of mortars formulated using quartz sand aggregate of the 0.125-0.25 mm size and following c/a ratios: 1:2, 1:3, 1:4, 1:5 by weight were examined. The value of w/c ratio was determined by workability of the pastes and varied from 0.7 to 1.1 (for 1:2 and 1:5 mortars respectively).

Table 2. Influence of the amount of the aggregate on the qualities of Roman cement mortar

Type of the sample	C/a ratio	Density [g/cm^3]	Time of the water capillary rise [3 cm] [min]	Water absorption [%]	Porosity [%]	Tensile strength [MPa]	Compressive strength [MPa]
Roman cement repair mortar	1:2	1.56	53	17.25	26.77	0.80	4.08
	1:3	1.43	2	23.17	33.00	0.45	1.36
	1:4	1.42	4	22.64	31.95	0.35	1.15
	1:5	1.53	5	18.82	28.72	0.40	0.02
Limestone	-	1.71	25	14.24	24.84	-	10.48
Sandstone	-	1.97	8	6.68	12.48	-	25.31

The best plasticity and workability of the pastes was noticed for samples with the smaller amount of the quartz sand (1:2 and 1:3 by weight). Those properties were declining with an increase of the amount of the aggregate employed. The linear contraction of examined mortars was in the range of 0.35% to 0.47% and setting time between 25 hours for 1:2 mortar to 51 hours for 1:5 mortar.

Both, the water absorption and porosity of the tested mortars were higher than in a previous group and amounted to respectively 17.25-23.17% and 26.77-33.0%. Among specimens examined in this group 1:2 mortar was indicating capillary properties the most compatible with the limestone and sandstone tested as the reference material. Nonetheless, its time of capillary water transport at the height of 3 cm was 53 min, while for sandstone and limestone this measure was adequately 8 min and 25 min.

Depending on the amount of the aggregate mortars were indicating tensile strength between 0.4 MPa to 0.8 MPa and compressive strength in the range of 0.02 MPa to 4.08 MPa. The highest values revealed 1:2 mortar and the lowest were observed for 1:5 mortar.

3.3 Influence of the sort of the aggregate on the qualities of Roman cement mortar

The pulverised Pińczów limestone was chosen as an aggregate due to its common occurrence in architecture monuments and aesthetic considerations (the mortar based on Roman cement and pulverised limestone could successfully imitate natural stone). Four types of mortars were prepared, three of them were formulated with the aggregate of a mixed size (1 part by weight 0.125-0.25 mm and 1 part by weight 0.25-0.5 mm) and fourth was formulated with 0.25-0.5 mm limestone. It was expected, that using the aggregate of a mixed size could effect in the increase of the mechanical strength of the mortar. The cement-to-aggregate ratio was 2:1, 1:1, 1:2 by weight for the samples with limestone of a mixed size and 2:1 by weight for the sample with the 0.25-0.5 mm aggregate. Due to a porous character of the pulverised limestone, pastes required bigger amount of water to obtain desirable workability and w/c ratio was from 0.6 to 0.9.

Table 3. Influence of the sort of the aggregate on the qualities of Roman cement mortar

Type of the sample	Sort of the aggregate	C/a ratio	Size of the aggregate [mm]	Density [g/cm^3]	Time of the water capillary rise [3 cm] [min]	Water absorption [%]	Porosity [%]	Tensile strength [MPa]	Compressive strength [MPa]
Roman cement repair mortar	pulverised limestone	2:1	0.25-0.5	1.36	295	24.67	33.15	1.40	5.84
		2:1	1 part 0.125-0.25 1 part 0.25-0.5	1.37	30	24.82	32.88	1.33	6.71
		1:1		1.56	245	20.54	31.09	1.85	8.47
		1:2		1.35	30	27.66	33.96	0.88	1.94
	quartz sand	1:2	0.125-0.25	1.56	53	17.25	26.77	0.80	4.08
Limestone	-	-	-	1.71	25	14.24	24.84	-	10.48
Sandstone	-	-	-	1.97	8	6.68	12.48	-	25.31

A rapid decay of plasticity was observed for all the pastes after few minutes. The linear contraction was between 0.06-0.67% and the setting time was in a range of 20 min for the 2:1 mortar with the mixed-size aggregate to 6 hours for the 2:1 mortar with 0.25-0.5 mm limestone.

The examined mortars revealed higher water absorption (20.54-27.66%) and porosity (31.09-33.96%) than mortars with quartz sand. As predicted basing on a porous character of a limestone, samples containing less aggregate were showing lower values of water absorption and porosity. The time of capillary water transport at the height of 3 cm was between 30 minutes and almost 5 hours.

The tensile strength of the tested mortars was in a range of 0.88 MPa to 1.85 MPa and their compressive strength between 1.94-8.47 MPa. The best mechanical resistance was noted for the 1:1 mortar with the mixed-size aggregate, which was the highest result throughout the research. The samples with the higher c/a ratio were obtaining better tensile and compressive strength test outcomes.

3.4 Influence of the citric acid employed as setting retarder on the qualities of Roman cement mortar

The last part of the research was an attempt to improve workability and plasticity of a Roman cement mortar with the pulverised limestone. The 1:2 mortar with the mixed-size aggregate (1 part by weight 0.125-0.25 mm and 1 part by weight 0.25-0.5 mm) was chosen as the one obtaining relatively good results in earlier tests. Citric acid was employed as setting retarder at the percentage of 0.5% in water, which corresponds to 0.4% related to the weight of the cement and w/c ratio was 0.9.

The setting retarder considerably improved workability and plasticity of a paste and the setting time was prolonged to 25 min (for the non-modified mortar it was 20 min). The linear contraction raised from 0.06% to 0.18%.

The water absorption was slightly lower (25.15% for modified and 27.66% for non-modified mortar), while its porosity increased (from 33.96% to 35.72%). The time of capillary water transport was prolonged from 30 to 43 minutes.

The citric acid influenced substantially mechanical properties of a mortar. The tensile strength declined from 0.88 MPa to 0.58 MPa, while compressive strength waned from 1.94 MPa to 1.11 MPa.

3.5 Resistance to the decay mechanisms (freeze-thaw resistance and resistance to the soluble salts)

In the first group of examined samples (1:3 mortars with the quartz sand aggregate of a size varying from 0.125-0.25 mm to 1.25-2.0 mm) the best freeze-thaw resistance was observed for the mortar with 0.25-0.5 mm aggregate. The first changes in the appearance of the samples of this type were noticed in a fifth cycle of the test and the destruction of the specimens occurred in the last, 20th cycle. General regularity that mortars with the bigger size of the aggregate are more prone to low freeze-thaw resistance could be concluded. No changes were observed throughout the examination time neither for the limestone, nor for the sandstone. All types of mortars were characterised by general good resistance to the soluble salts, comparable to the limestone, which revealed first changes in the appearance of a sample in the second cycle of examination. The mortars with bigger size of the aggregate employed revealed slightly better resistance. This could be explained by the bigger diameter of their pores, which permit longer crystallisation of the salts without exerting pressure on the walls of the mortar itself.

It was observed that the cement-to-aggregate ratio was determining freeze-thaw resistance of the tested mortars. The samples formulated with the lower content of the quartz sand were indicating better resistance while examined. The 1:2 mortar revealed the first changes in the appearance in the sixth cycle of the test and did not undergo destruction throughout 20 cycles of the examination, while for the 1:5 mortar decay processes started in the fourth cycle and samples survived only until 16th cycle of the test. The resistance to the soluble salts of the examined mortars with the quartz sand and c/a ratio varying from 1:2 to 1:5 is comparable with limestone. During the test binding qualities of the samples were decreasing and specimens started to disintegrate. No direct correlation between the amount of the aggregate in the sample and its resistance to the soluble salts could be concluded.

The sort of the aggregate was also influencing the freeze-thaw resistance of the mortars. The samples with the pulverised limestone were more prone to the destructive action of water than the specimens formulated with quartz sand, which could be concluded basing on the porous character of the aggregate. However, mortars with a higher c/a ratio (2:1, 1:1) did not get destroyed throughout 20 cycles of the test. All sort of samples with the limestone aggregate showed relatively good resistance to the soluble salts. General good density of the mortars was noticed during the examination. Deep cracks (Figure 1.) were observed on the surface of all the samples in the fourth cycle of the examination.

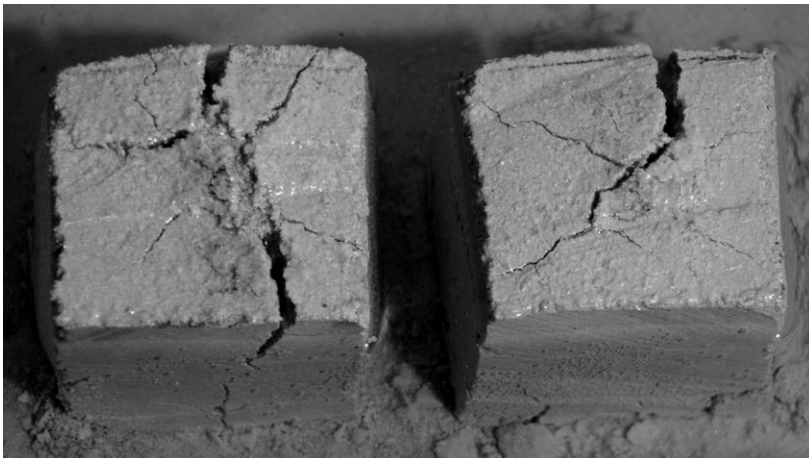

Figure 1. Deep cracks observed on the surface of the samples of the Roman cement repair mortar with the pulverised limestone, the fourth cycle of the resistance to the soluble salts examination

A good freeze-thaw resistance of the mortar with setting retarder was observed. Only in the 13th cycle of the examination first changes appeared on the surface of the sample, while for the non-modified mortar they were noted already in the third cycle. Specimens with setting retarder did not get destroyed throughout the 20 cycles of the examination. However, lower resistance to the soluble salts was observed. The samples get damaged in the second cycle of the test in a very characteristic way: walls of the cubes were spalling and the inside of the sample was dilapidating (Figure 2.). This mechanism could be the effect of the non-homogenous fast binding process.

Figure 2. The destruction of the samples of the Roman cement repair mortar with setting retarder, the second cycle of the resistance to the soluble salts examination

4. Conclusions

The results obtained in the frames of this research allow to state that following factors: sort, size and the amount of the aggregate used to formulate a repair mortar influence its later qualities, as well as employing the citric acid as a setting retarder. Among all examined types of the Roman cement repair mortars two seem to represent the most promising qualities: the 1:3 mortar with 0.25-0.5 mm quartz sand and the 1:2 mortar with the mixed-size pulverised limestone (1 part 0.125-0.25 mm and 1 part 0.25-0.5 mm, by weight). Presented test results lead to conclusion, that both of mentioned mortars could be employed to restore sculptures and architectonical details made of light and porous stones, particularly of limestone characterised by low mechanical strength and high water absorption. However none of those mortars could be considered as a material, which fulfils all the requirements, that conservators impose on the ideal repair mortar. One can hope, that further researches will help to eliminate those negative properties of mortars, which could be an obstruction to their common use in stone conservation.

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