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Microstructure of Historical Lime and Lime – Hydraulic Mortars: from Setting to Corrosion

Introduction

The present work aims at the review of micromorphological features of lime and, less so, hydraulic mortars. Their components (filler and binder) were analysed, mistakes in their preparation were traced, and corrosion phenomena were identified and documented.

Lime and hydraulic mortars, along with gypsum ones, were widely used in Central Europe. They are composed of a filler of determined parameters, and lime or hydraulic cement, acting as a binder, with or without admixture of the organic compounds. Lime, after firing, undergoes a process of slaking and later on in mortar, is calcified in a setting process; intermediate structural and compositional phases appear, influenced by technological and environmental factors, like e.g. amount of water used during slaking, temperature, dampness (Mora et al. 1983, 47–55).

When „used", mortars are affected by numerous phenomena, e.g. corrosion processes, their mechanical strength is weakened and colour changed – mostly due to the increase in porosity and evolution of pores shapes (long, permeable pores and caverns tend to appear), crystallization of new phases with new properties (e.g. volume, dissolution rates), penetration by microorganisms and their metabolites, enrichment of a porous water with aggressive components, like chloride, sulphate, nitrate ions, and sometimes occurrence of colouring iron and copper compounds.

Origin of corrosive agents has roots in three basic areas: technology of mortar production (e.g. improper filler-to-binder ratio, mineral composition of filler, accuracy of binder preparation), environmental factors (temperature changes, dampness), contemporary anthropogenic factors (pollution of soil and atmosphere). Corrosion of historical mortars has not been studied so far, contrary to the contemporary building materials (e.g. Kurdowski 1991, 323–341).

The component that is principally present in lime mortars is calcium carbonate in its most abundant polymorphic variety[1], calcite.

[1] A substance, with a given chemical composition, that has various crystallographic order.

Quite often, natural admixtures of limestone occur: clay minerals and quartz, and they may, after firing, transform to alumosilicates and silicates, partially (or entirely) active as hydraulic components, reacting with lime. Quartz may remain chemically unchanged, though, structurally, in 573°C it transforms into metastable high-temperature variety, quickly recrystallising to a low-temperature one. Volume changes are involved in this phenomenon. In hydraulic mortars, due to reaction of unslaked lime (CaO) with abundant alumosilicates and silicates, added purposely, numerous lime silicates, alumosilicates and other phases appear (Kurdowski 1991). It is supposed that all components of mortars transform from colloidal to fine crystalline form (Mora et al. 1983, 40). Added organic compounds are adsorbed on carbonate crystals surfaces (Frye, Thomas 1993) and may influence either their morphology or composition (Doerner 1975, 172).

Material and methods

Material that illustrates microstructural features of mortars and plasters as well as corrosion phenomena is represented by 14^{th} and 16^{th} century mortars from ruins of Czudec Castle near Rzeszów (Podkarpacie Province SE Poland) (Trąbska et al. 2005); plasters from the Chapel of Hatshepsut in Deir-el-Bahari, Egypt (Pawlikowski et al. 2006), mortars from the selected mediaeval churches in Lower Silesia (SW Poland) (Trąbska 1998, 80–100) and mortars from Pompei.

To illustrate the phenomena of our interest, two methods were applied: polarising microscopy for transmitted light (PLM), Carl Zeiss Jena LMA 10 type, and scanning microscopy with X-ray microanalyser (SEM-EDS), Jeol 5200 with Link-Isis microanalyser.

Experimental part

1. Filler

Requirements for a filler quality were rigorous; it is enough to look at Vitruvius' recipes (1999, 54) confirmed by modern researchers and restorers (e.g. Doerner 1975, 172; Mora et al. 1983, 53). They point at application of pure quartz sand; a source of weathered feldspars, mica scales or clay minerals that change their volume in wet conditions is then eliminated. Sea sand was not suggested either: a potential source of easily soluble salts (e.g. gypsum). Contemporary practitioners propose rectangular sand grains or crushed stone, e.g. limestone *(op. cit.)*, though Vitruvius does not neglect river sand. Microscopic observations enable to confirm or exclude features mentioned (comp. Fig. 1) above,

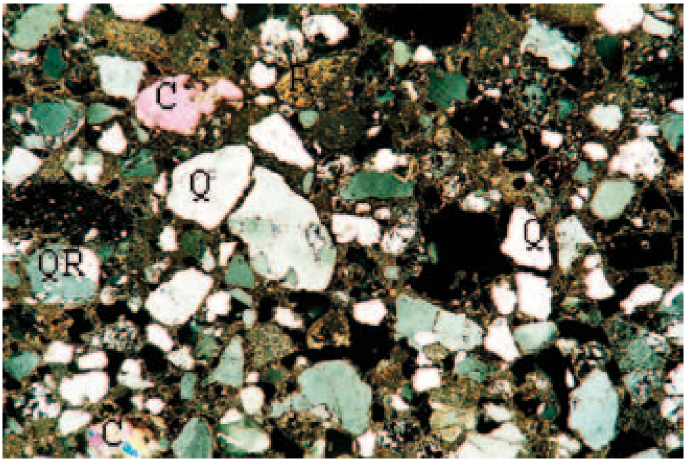


Fig. 1. 14th century mortar from the ruins of Czudec Castle. Filler grains are composed of quartz (Q), calcite (C), fragments of quartz rocks (QR), fragments of other rocks (R). Black areas are caverns, pores and cracks. Filler grains are rounded in various degree, they may be groupped in two fractions: around 0.2 mm and around 0.5 mm and coarser. Crossed polars, magn. x 25, Phot. M. Doktor.

Ryc. 1. Zaprawa XIV-wieczna z ruin zamku w Czudcu. W skład ziaren wypełniacza wchodzi kwarc (Q), kalcyt (C), fragmenty skał kwarcowych (QR). Czarne obszary to kawerny, pory i spękania. Ziarna wypełniacza są obtoczone w różnym stopniu; grupują się w dwie frakcje: około 0,2 mm oraz około 0,5 mm i grubsze. Polaryzatory skrzyżowane, pow. 25x. Fot. M. Doktor.

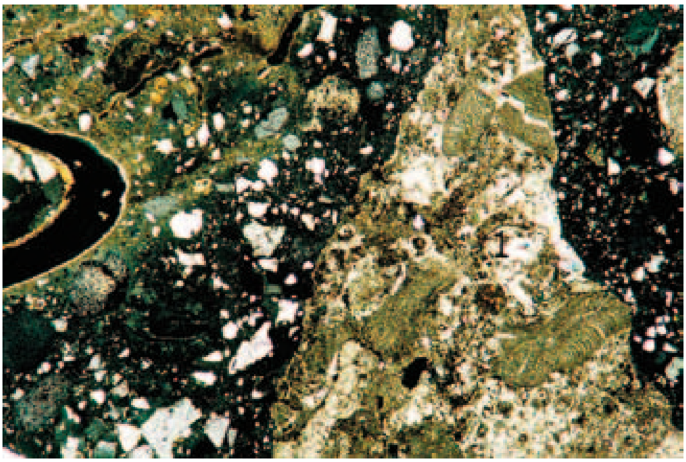


Fig. 2. 16th century mortar from Czudec Castle. A large filler grain of Miocene *Lithothamnium* limestone (1), most probably also a raw material for lime production (comp. Fig. 7, p. 4). Left part: an empty space remaining after fired (?) organic structure. In the background: fine filler grains. Crossed polars, magn. x 25. Phot. M. Doktor.

Ryc. 2. Zaprawa XVI-wieczna z zamku w Czudcu. Duże ziarno wypełniacza mioceńskiego wapienia litotamniowego (1). Był to najprawdopodobniej także surowiec dla wyrobu tej zaprawy (por. Ryc. 7, 4). W lewej części fotografii widoczna jest pusta, podkowiasta przestrzeń po wypalonej (?) substancji organicznej. W tle widoczne drobne ziarna wypełniacza. Polaryzatory skrzyżowane, pow. 25x. Fot. M. Doktor.

and additionally, discover rarely encountered minerals, e.g. zircon crystals (Zr [SiO_4]), an accesory mineral of sands (Fig. 3). Either rounded shards or iron lumps of natural origin can be noted (Fig. 21) and criteria of their recognition should be worked out. Rounded grains of calcite, most probably pieces of a former calcite vein (Fig. 1, C) and a large grain of Miocene *Lithothamnium* limestone (Fig. 2, p. 1) are an example of potential drawback in the usage of chemical separation method, where all calcareous components would have been dissolved in HCl (Casadio et al. 2005).

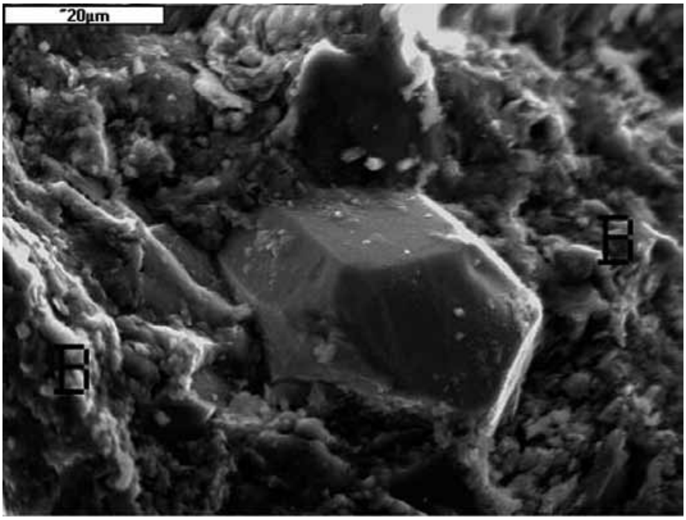


Fig. 3. 14th century mortar from Czudec Castle. Automorphic grain of zircon, a common component of sands. Another phenomenon that should be noted here is a good, close contact of crystal walls and sourrounding lime binder (B). Magn. x 1500.
Ryc. 3. Zaprawa XIV-wieczna z zamku w Czudcu. Automorficzne ziarno cyrkonu, pospolity składnik piasku. Warto zwrócić uwagę na dobry kontakt ścian kryształu i otaczającego spoiwa węglanowego (B). Pow. 1500 x.

2. Mortars

2a. Microstructure

Slaked lime, first composed of tiny, long crystals of $CaCO_3$, creates with time – unfortunately it is not exactly known, how long, though it has been stated that around six weeks (Mora et al. 1983, 47–55) – fine grained, homogeneous structure, in which no apparent crystals forms are visible any longer[2]. Lime mortar is microcrystallinic (comp. Fig. 3, B; 6, p.2), like hydraulic mortars (Figs. 4, 6). Due to this homogeneous, fine-grained structure, mortars posess their good mechanical properties. A good illustration of similarity (if not identity) of the two phases is a mixed hydraulic-lime mortar from mediaeval church in Kondratów (Lower Silesia) (Fig. 6), with "nests" of hydraulic mortar (1) that neighbour with pure lime parts (2). Other microstructures that should be compared here are depicted in Figs. 3B, 4, 10 and 14.

Sometimes in lime mortars, small areas of "triangle"crystal forms are observed; their surface is flat (Fig. 5). Similar crystals, though ten times smaller, were found in natural contemporary calcareous secretions in mineralized waters from Tylicz (Kostecka 1993, 32, 33)[3]. Flat

[2] Very fine occurrences, around 2 micrometers, are called collomorphic (Kostecka 1993, 28).

[3] Identical structure was found by the authors in a white painting layer of a Baroque ceiling painting in the church in Kurów Wielki (Lower Silesia Voivodeship) (Trąbska et al. 1994).

surfaces are interpreted as a result of crystallization on the contact air/solution (Binkley et al., 1980; fide Kostecka 1993, 33), or within a thin film of solution, just beneath its surface (Kostecka *op. cit.*). In salinated ground water (75:25% of ground water *vs.* salinated one) "triangle" crystals grown experimentally (Hanor 1978, 493) are exactly of the size observed in our mortars. Thus, their presence may be interpreted as a result of crystal growth in areas of locally increased water concentration, but as for salts concentration in the used water, the phenomenon should be observed further.

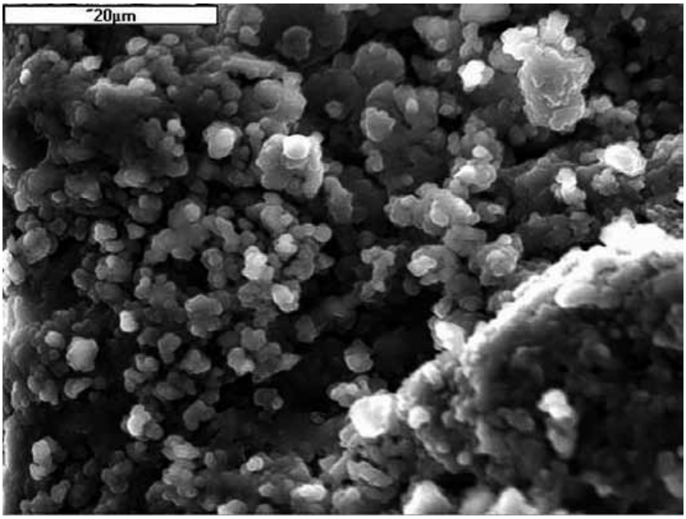


Fig. 4. Pompei. Hydraulic mortar of fine grained, homogeneous structure. Magn. x 2000.
Ryc. 4. Pompeje. Zaprawa hydrauliczna o drobnokrystalicznej, homogenicznej strukturze. Pow. 2000x.

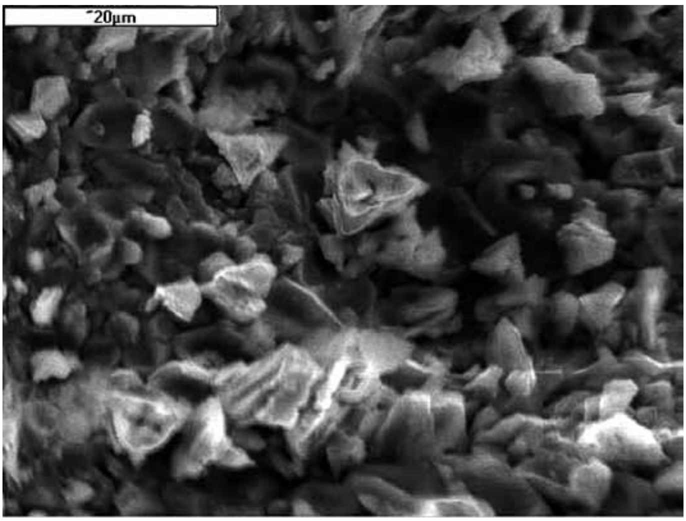


Fig. 5. Lime mortar of unknown age, Czudec Castle. Acicular calcite crystals, grown just beneath surface of solution; further explanation in the text. Magn. x 2000.
Ryc. 5. Zaprawa wapienna nieznanego wieku z zamku w Czudcu. Specyficzny pokrój kryształów kalcytu jest rezultatem krystalizacji tego minerału tuż pod powierzchnią roztworu; dalsze objaśnienia w tekście. Pow. 2000x.

2b. Phase unhomogeneity

Lime binder observed by us was sometimes actually composed of two groups of phases lime and lime-(alumo)silicate (hydraulic). Phase inhomogeneity of a binder should always be conspicuous as a potential source of trouble due to variations in mechanical and chemical mortar properties. This phenomenon was noted in mediaeval mortar in Kondratów church (Fig. 6). Though microstructure of a lime and hydraulic part is the same, separation areas, seen as narrow crack are present. Another example of this phenomenon is illustrated in Fig. 7; grey parts of a binder and a lump are not composed of lime, but of siliceous phases, which are most probably reaction products of lime and silica. Nevertheless, it has to be stated that in other (though not so numerous) cases such phenomenona were not observed (Fig. 15).

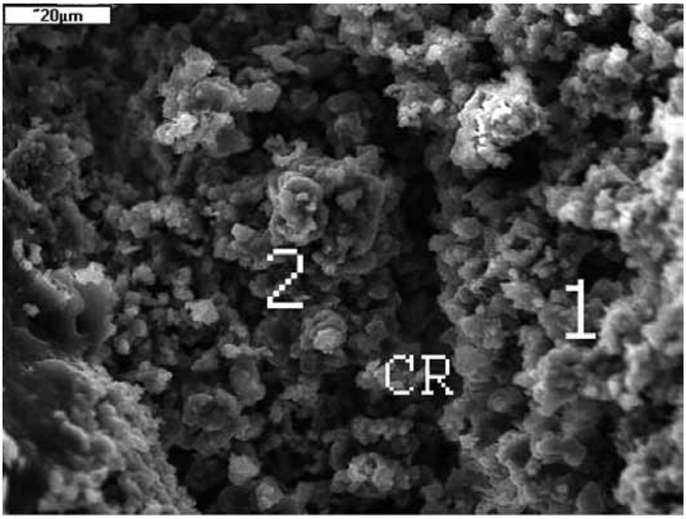


Fig. 6. Mediaeval mortar from Kondratów church near Jawor, Lower Silesia. Hydraulic mortar (1) with nests of pure lime component (2): micromorphologies, and thus, mechanical features, are identical. An unexplained phenomenon is a crack between the two areas (cr). Magn. x 2000.

Ryc. 6. Średniowieczna zaprawa z kościoła w Kondratowie koło Jawora, Dolny Śląsk. Spoiwo hydrauliczne (1) z gniazdami czystego składnika węglanowego (2). Mikromorfologia obu części jest identyczna, co wpływa na bardzo zbliżone własności mechaniczne. Przyczyna powstania szczeliny między tymi obszarami (cr) jest nieznana. Pow. 2000x.

2c. Lumps within a binder

In historical mortars quite often fine-crystalline, lime (Fig. 8) or „hydraulic" (Fig. 7) lumps are observed. Their internal structure and composition may be identical with a surrounding binder but they are more or less sharply separated from it. Lumps with sharp boarders (Fig. 8) are interpreted as having been appeared either during lime slaking with poor access of water (then certain volumes remain unslaked and are transformed to calcium carbonate later; Mora et al. 1983, 51), or as a result of uneven conditions of firing processes, with remaining lumps of not utterly fired limestone. In the latter case certain primary features

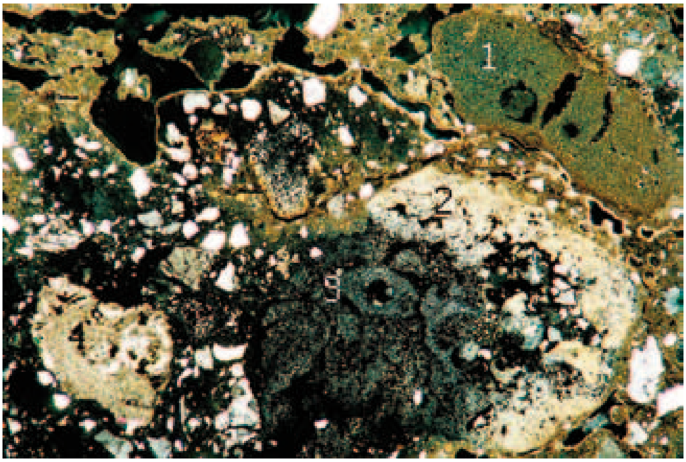


Fig. 7. 16th century mortar from Czudec Castle. Lumps (1), resulting from mistakes in production of mortar, sharply separated from surrounding binder, are cracked themselves, prone to dissolution. Dark-grey, large lump in a lower part of the photography, is composed of lime-silica phases (lime: 2; hydraulic: 3); reaction product of silica and lime. It is "a nest" of hydraulic component within a lime mortar. The lump in the left, lower part of the photography (4) is probably, due to its structure, a remnant of not completely fired raw material (comp. Fig. 2). Black areas: pores, caverns and cracks. Crossed polars, magn. x 25. Phot. M. Doktor.

Ryc. 7. Zaprawa XVI-wieczna z zamku w Czudcu. Grudki (1), powstałe wskutek błędów w procesie wytwarzania zaprawy, wyraźnie odseparowane od otaczającego spoiwa, są spękane, podatne tym samym na rozpuszczanie. Duża, ciemnoszara grudka widoczna w dolnej części fotografii składa się z faz o charakterze krzemianów wapnia (3): produktu reakcji krzemionki i wapna gaszonego. Jest to „gniazdo" składnika hydraulicznego w obrębie zaprawy węglanowej. Grudka w lewej, dolnej części fotografii (4) jest prawdopodobnie pozostałością niecałkowicie przepalonego surowca (por. Ryc. 2). Czarne obszary: pory, kawerny, spękania. Polarzatory skrzyżowane, pow. 25x. Fot. M. Doktor.

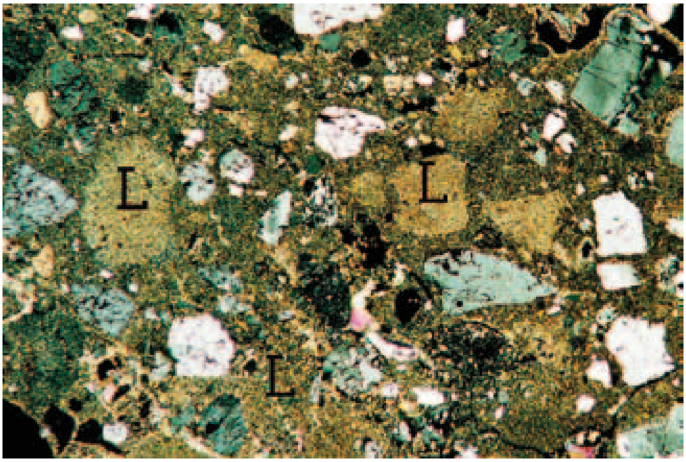


Fig. 8. 16th century mortar from Czudec Castle. Lumps (L), separated from binder. Their origin is explained in the text. Crossed polars, magn. x 25. Phot. M. Doktor.

Ryc. 8. Zaprawa XVI-wieczna z zamku w Czudcu. Grudki (L) wyraźnie oddzielające się od spoiwa. Ich powstanie objaśnione jest w tekście. Polaryzatory skrzyżowane, pow. 25x. Fot. M. Doktor.

of a rock would have been expected to be preserved (Fig. 7, p. 4). Lumps with "cloudy", not very apparent boarders appear due to secondary corrosion (dissolution-recrystallisation) processes or unevenly mixed organic substances (comp. Doerner 1975, 171–176), (Fig. 9). Besides ne-

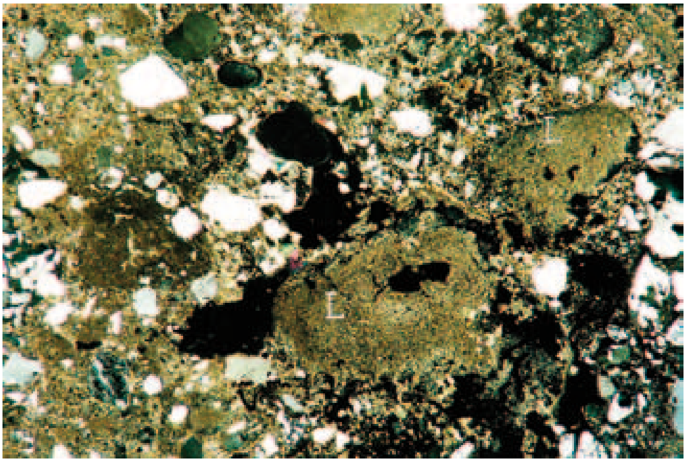


Fig. 9. 14th century mortar from Czudec Castle. Lumps with cloudy, not very sharp contact with surrounding lime. Lumps, being of "alien" structure, of mechanical properties different from the rest of binder, are prone to separation, cracking and dissolution. Black areas: pores, cracks and caverns. Origin of the lumps explained in the text. Crossed polars, magn. x 25. Phot. M. Doktor.

Ryc. 9. Zaprawa XIV-wieczna z zamku w Czudcu. Grudki (L) o rozmytym kontakcie z otaczającym spoiwem. Ich dmienność morfologiczna wpływa na pogorszenie własności mechanicznych zaprawy i intensyfikacją procesów korozji. Czarne obszary: pory, spękania, kawerny. Pochodzenie grudek objaśnione w tekście. Polaryzatory skrzyżowane, pow. 25x. Fot. M. Doktor.

gative aspects of lumps presence there are some positive ones: it is stated that they help in slower and more homogeneous calcification of slaked lime, thus acting as filler (*op. cit.*). Structurally, some lumps tend to separate from a wet binder whilst others remain an integral part of it (Fig. 7, 9 and 8).

2d. Other structures of binders

In historical mortars (Mora et al. 1983, 51) lumps of metastable aragonite (a polymorphic variety of $CaCO_3$) and even unreacted $Ca(OH)_2$, portlandite, which in the usual conditions is unstable, very fast transforming into calcite, are often observed; they remain unchanged even after some hundred years. It is due to absorbtion of water by freshly slaking lime, increase of its volume, and tightening pores and closing nests of fresh lime (*op. cit.*). Aragonite identified in Czudec Castle mortars may be of twofold origin: either earlier caverns were secondarily filled due to the migration of water, enriched with calcium and carbonate ions, or it appeared in the course of processes described in this passage (Figs. 19, 21).

2e. Primary pores and cracks

Emergence of the primary pores and cracks results from inhomogeneities in binder density and viscosity, thus uneven contact with filler grains. Dessication cracks also appear (Fig. 11). It also results from mistakes in mortar production, e.g. adding water during slaked lime and sand mixing: an effect is now observed as pores around whole or some parts of filler grains.

Mistakes in mortar production, e.g. adding water during slaked lime and sand mixing, result in appearing of the empty spaces around the filler grains or its parts (Doerner 1975, 72) (Fig. 1).

Primary pores, even of very low diameter, like in hydraulic mortar from Pompei, are permeable for capillary water action (Fig. 10) (Tokarski, Wolfke 1969, 96).

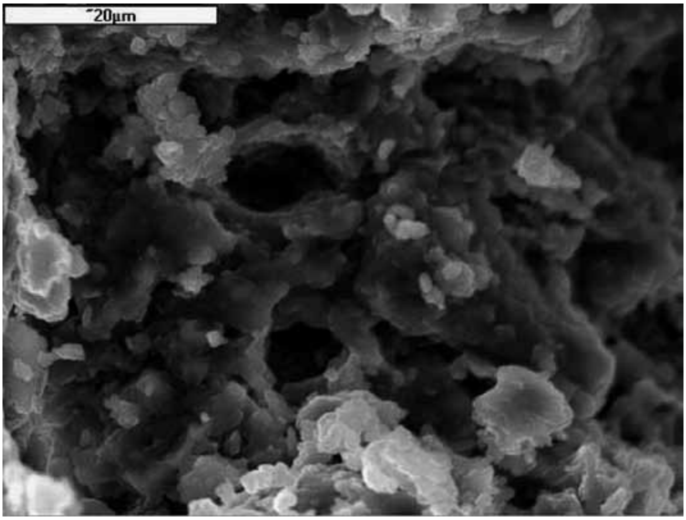


Fig. 10. Pompei, hydraulic mortar with pores open for capillary water. Magn. x 2000.
Ryc. 10. Pompeje, zaprawa hydrauliczna. Porowatość kapilarna. Pow. 2000x.

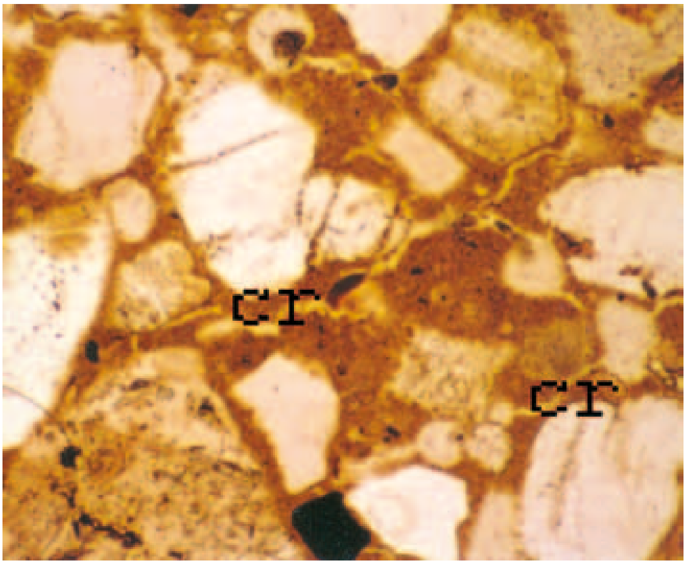


Fig. 11. Desiccation cracks (cr) in mediaeval plaster from the church in Kondratów near Jelenia Góra, Lower Silesia. One polar, magn. x 40.
Ryc. 11. Szczeliny z wysychania (cr) w średniowiecznej węglanowej zaprawie gruntującej (gruncie) z kościoła w Kondratowie koło Jeleniej Góry, Dolny śląsk. Polaryzatory równoległe, pow. 40x.

2f. Petrified microorganisms

Microorganisms may find their niche in mortars from the moment of setting up to now (Fig. 23); they could appear, let's say, one hundred or fifty years ago, and then become calcified.

Thus, they cannot be regarded as a proof for an 'old age' of mortars. Calcification of organic remnants is a result of percolation of water (either of internal or external, environmental origin) rich in calcium and carbonate ions. Other minerals than calcite may also replace microorganisms, like iron oxides noted in mediaeval mortar (Fig. 12).

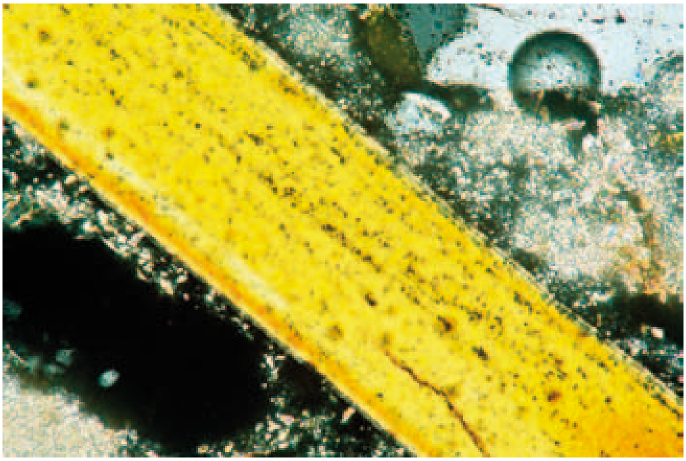


Fig. 12. 14th century mortar from Czudec Castle. Fragment of a microorganism, filled with secondary iron compounds. Crossed polars, magn. x 400. Phot. M. Doktor.
Ryc. 12. Zaprawa XIV-wieczna z zamku w Czudcu. Fragment mikroorganizmu wypełnionego wtórnymi związkami żelaza. Polaryzatory skrzyżowane, pow. 400x. Fot. M. Doktor.

2e. Organic compounds added to filler

Straws, ash, charcoal were added to mortars purposedly, to modify mechanical strenght and regulate dampness during calcification of mortars (Ślesiński 1983, 30, 59; Wirska-Parachoniak, 1974, 20). In most cases they may be identified macroscopically but they are also noticeable in microscopic image. Not rarely they are also calcified, due to the reasons described above.

2f. Organic compounds added to binder

Addition of organic compounds (blood, egg yolks, milk, etc.) was justified to improve mechanical strenght and plasticity of mortars. The most efficient method to identify them is chromatography, nevertheless scanning microscopy may also bring interesting information. Mortars and plasters with organic additions to binder have specific, "thick", crusty, smooth surface (Trąbska 1998, 237–257) (Fig. 13) and their presence is confirmed by EDS analysis, pointing at enormously high level of carbon. The same microchemical analysis was conducted for hydraulic mortar from Pompei: shape of lime-organic (?) phases (Fig. 14) does not resemble fine grained inorganic occurrences (comp. Figs. 6, 15).

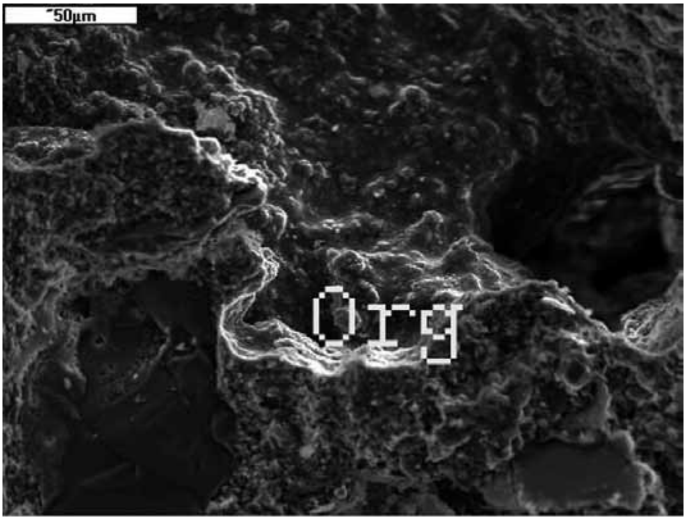


Fig. 13. 14th century mortar from Czudec Castle. In the central part of the photography the mortar's surface is smooth and thick (Org), giving evidence for the presence of organic components. Magn. x 500.

Ryc. 13. Zaprawa XIV-wieczna z zamku w Czudcu. W środkowej części obrazu (Org) spoiwo jest zbite i gładkie, co wskazuje na obecność składników organicznych. Pow. 500x.

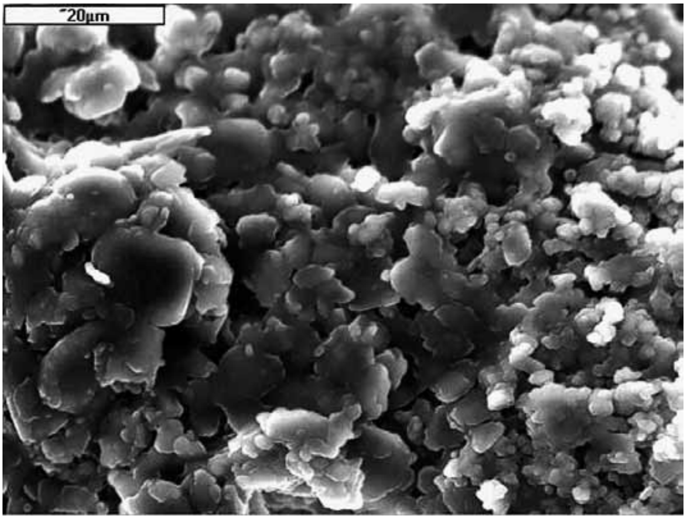


Fig. 14. Pompei. Hydraulic mortar. Flaky structures with irregular and rounded edges, enriched with organic compounds, as the EDS analysis shows they are most probably organic-lime phases. Magn. x 2000.

Ryc. 14. Pompeje. Zaprawa hydrauliczna. Płatkowe skupienia o nieregularnych i zaokrąglonych brzegach, wzbogacone są w substancje organiczne, najprawdopodobniej fazy o charakterze organicznych soli wapnia. Pow. 2000x.

3. Filler-binder contact

A feature that, among others, enables to determine whether a mortar was produced carefully or not is a contact between a filler grain and binder. Empty spaces between them let water permeate and widen open spaces. An interesting phenomenon was observed in mortars from Czudec Castle: certain surfaces of the sand grains adhered strongly to a binder (Fig. 15), wheres others, even in a very close vicinity were not (Fig. 1). This difference was observed also for a one grain. It is exactly a result of careless preparation of mortar: water was added unnecessarily to slaked lime and sand mixture (Doerner 1975, 172).

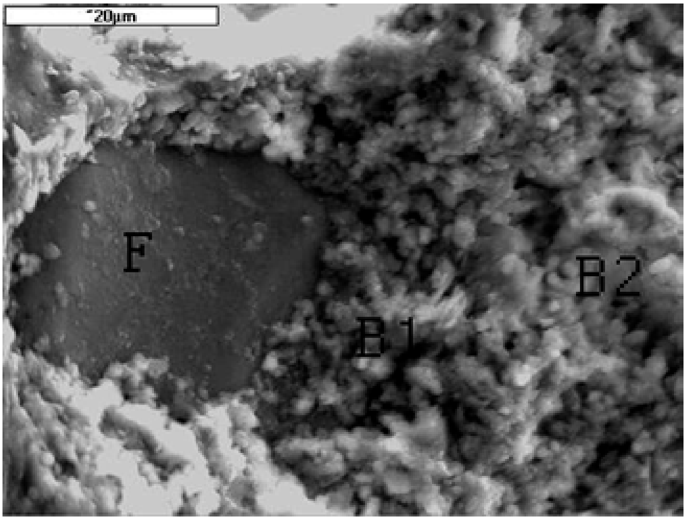


Fig. 15. 14th century mortar from Czudec Castle. A binder (B1) contacts very well with a grain of filler (F). Microstructure of the binder is typical for the old lime mortar: very fine grained and homogeneous. The B1 binder is a silica-lime phase (a hydraulic one), whilst the B2 phase is composed of pure lime, as it was revealed by EDS microchemical analysis. Magn. x 2000.

Ryc. 15. Zaprawa XIV-wieczna z zamku w Czudcu. Kontakt spoiwa (B1) i ziarna wypełniacza (F) jest bardzo dobry. Mikrostruktura spoiwa jest charakterystyczna dla historycznych zapraw węglanowych. Spoiwo B1 jest złożone z faz typu krzemianów wapnia (komponent hydrauliczny), spoiwo B2 składa się wyłącznie z węglanu wapnia. Pow. 2000x.

4. Multilayer structure of mortars and plasters

Multilayered structure is commonly observed on mortars, evened by plasters, sometimes followed by painting layers. A number of subsequent layers may be quite high, but in this example (Fig. 15) only one is detectable. Tracing the layers of mortars and plaster is a fascinating work in the studies of mortar's stratigraphy.

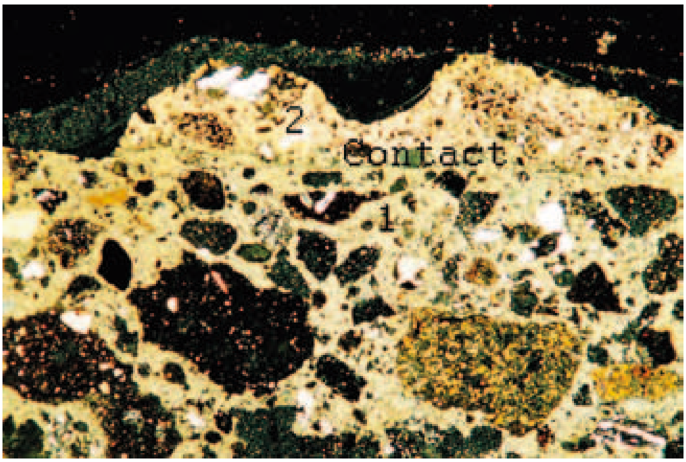


Fig. 16. Pompei. Two layers of mortars are noticeable, lower, with coarse grains of filler (1) upper, with little amount of filler (2) contact between them is marked. Crossed polars, magn. x 25. Phot. M. Doktor.

Ryc. 16. Pompeje. Widoczne są dwie warstwy zaprawy (lub gruntów); dolna z gruboziarnistym wypełniaczem (1), górna z niewielką jego ilością (2); zaznaczono kontakt między nimi. Polaryzatory skrzyżowane, pow. 25x. Fot. M. Doktor.

Depended on local customs and accessible raw materials, mortar's layers may be composed of filler grains of various proportions, kinds and diameters, or may be completely devoid of it.

Corrosion phenomena in microstructure of historic mortars

1. Filler

Despite rigorous recipes, quality of filler was quite often far from the theory and results were usually miserable. Impured sand, rich in feldpars and micas, which are weathering easily (Figs. 17, 18) in clay minerals, was a source of phases, easily changing their volume in the presence of water, thus weakening the structure of the whole mortar. Other minerals, like amphiboles or pyroxenes (Fig. 16) weather to chlorites,

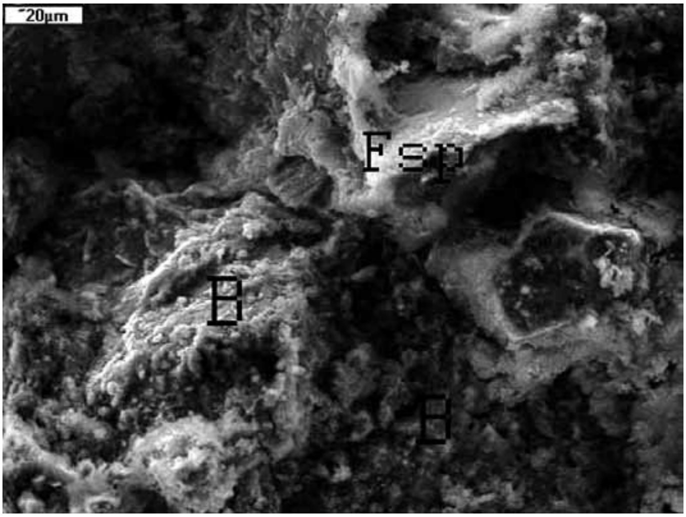


Fig. 17. Mortar from Czudec Castle, of unknown age. Heavily corroded grain of feldspar (Fsp), a source of clay minerals, immersed in surrounded lime binder (B). Magn. x 750.
Ryc. 17. Zaprawa z zamku w Czudcu, wiek nieznany. Silnie zwietrzałe ziarno skalenia (Fsp) staje się źródłem minerałów ilastych. Ziarno zanurzone w spoiwie węglanowym (B). Pow. 750x.

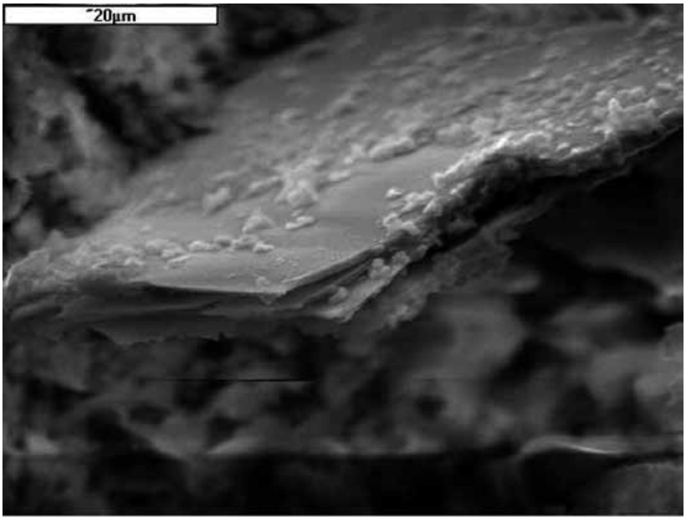


Fig. 18. 14th century mortar from Czudec Castle. Mica crystal, a potential source of clay minerals. Magn. x 2000.
Ryc. 18. Zaprawa XIV-wieczna z zamku w Czudcu. Blaszka miki, potencjalne źródło minerałów ilastych. Pow. 2000x.

carbonates and iron oxides (Borkowska, Smulikowski 1973, 269, 361), that differ from primary substances either in volumetric and colour parameters or in solubility. Other components of impured sands may dissolve and recrystallize (e.g. gypsum, encountered often in arid climate). Additionally, clay minerals and iron oxides, due to their high specific surfaces, are prone to absorbtion of the harmful substances from environment (Trąbska 1998, 236–257). Thus, suggestions for the use of pure quartz sand are more than justified.

2. Binder

2a. Secondary salts

Presence of secondary, easily soluble salts, e.g. nitrates, sulphates, chlorides of natrium, potassium, calcium or magnesium, leads to their multistage dissolution and recrystallization, quite often with intermediate, changeably hydrated phases, exerting high pressure on walls of cracks and pores. All these processes depend on kind of ions and their activity[4], dependent on dampness and temperature, presence of other ions, and permeability of mortars. Visual effect is noticeable in a plaster from the Chapel of Hatshepsut, in which among fine grained lime components of a plaster, crystals of halite appear. They used to be automorphic or their habit is difficult to precise clearly, sometimes the crystals are fiber-like or skeleton-like (Fig. 19; Pawlikowski et al. 2006, 19). This particular shape results from stronger growth of crystals on corners and edges; when influx of a solution is not sufficient, then crystal interior will not be completely built up (see also Bolewski et al. 1990, 103–105).

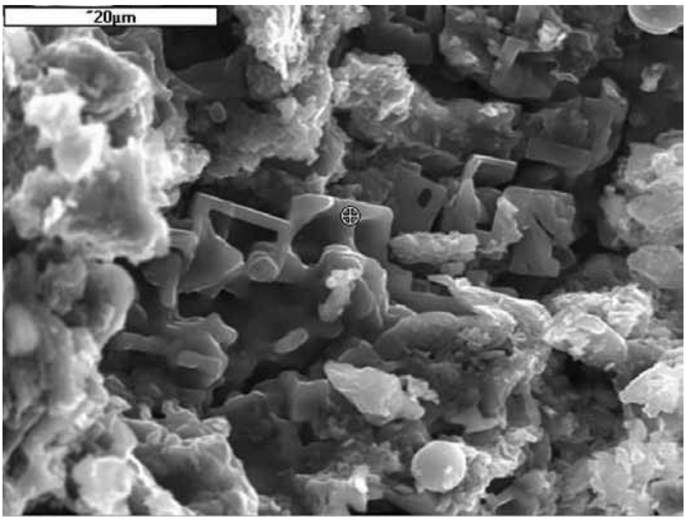


Fig. 19. Halite (NaCl) skeleton crystals in a plaster from the Chapel of Hatshepsut, Deir-el-Bahari, Egypt (Pawlikowski et al. 2006). Their origin is explained in the text. Magn. x 2000.

Ryc. 19. Szkieletowe kryształy halitu (NaCl) w zaprawie gruntującej (gruncie), ze świątyni Hatszepsut, Deir-el-Bahari, Egipt (Pawlikowski i in. 2006). Objaśnienia w tekście. Pow. 2000x.

[4] Activity is defined as „an active concentration" (Lipiec, Szmal 1980, 38).

Another, less comfortable situation is also possible: even under several thousand times of magnification no phases are observed and yet chemical analysis gives evidence for the presence of "corrosive" ions. Examples are numerous; one of them is a plaster from under the Gothic painting layer in the Kurów church (Lower Silesia Province), where sulphur was detected due to the microchemical analysis (Fig. 20)[5]. This phenomenon was well confirmed by the experimental works (Trąbska 1998, 236-257).

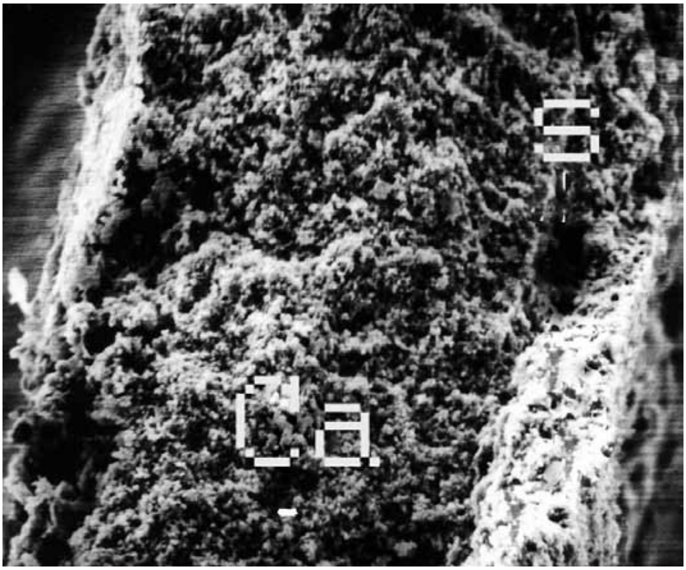


Fig. 20. Mediaeval plaster from under a wall painting from the church in Kurów Wielki near Głogów, Lower Silesia. Sulphur is concentrated on a contact between plaster and painting layer and within painting layer, without any visible crystalline forms. Magn. x 1100.
Ryc. 20. Średniowieczna zaprawa gruntująca (grunt) spod malowidła ściennego w Kurowie Wielkim koło Głogowa, Dolny śląsk. Na kontakcie warstwy gruntu i malowidła koncentrują się związki siarki, nie tworząc wyraźnie widocznych skupień. Pow. 1100x.

2b. Secondary cracks

Secondary cracks appear due to the partial dissolution of binder and widening a primary cracks net. They appear also on boundaries of lumps and binder, within lumps (Figs. 7, 9). Caverns of irregular shape are an effect of partial binder dissolution (Fig. 9), they may also be filled with secondary carbonates or other salts (Fig. 21, p. 1).

2c. Recrystallization (rebuilding) of a binder without an influx of new elements

Compounds of lime and hydraulic mortars may partially dissolve and recrystallize to a substance of the same chemical, and, usually, phase composition. It is not easy to discern recrystallized secondary carbonates, resulting from dissolution of a lime binder, from the ones that have appeared due to percolation of "environmental" calcium and

[5] This photography was taken by Mr Janusz Stępiński, University of Mining and Metallurgy.

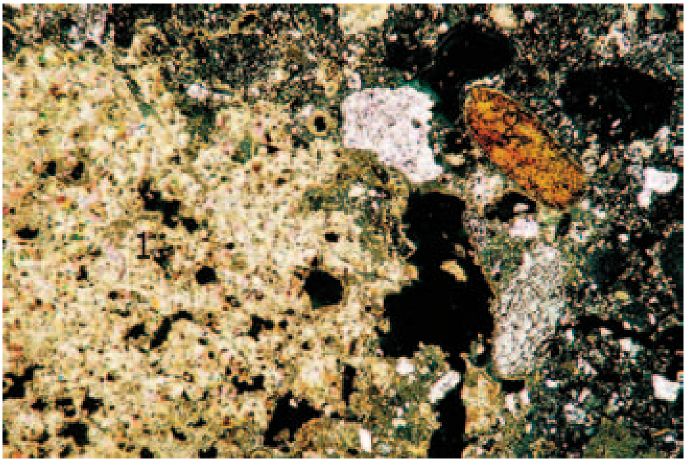


Fig. 21. Czudec Castle mortar of unknown age. A cavern filled with secondary carbonates (1). Brown, rounded grain (2) is of problematic origin: either this is a natural occurrence of iron oxides or a rounded shard. Crossed polars, magn. x 25. Phot. M. Doktor.
Ryc. 21. Zaprawa z zamku w Czudcu, wiek nieznany. Kawerna wypełniona wtórnymi węglanami (1). Owalne, brązowe ziarno (2) stanowi albo naturalne skupisko związków żelaza albo jest zaokrąglonym fragmentem skorupy. Polaryzatory skrzyżowane, pow. 25x. Fot. M. Doktor.

carbonate ions. Only the examination of both: environment and general features of examined mortars may help here. Structurally, secondary carbonates in a lime mortar are different from primary, homogeneous structures: they constitute veins and fine-crystalline (with detectable crystals) pore fillings (Fig. 21).

Huntite (Fig. 22), not extremely rare in Egyptian plasters, may have crystallized, as it seems to us, either due to an influx of 'external' Mg ions, as the mineral crystallizes easily under the action of meteoritic waters rich in magnesium ion percolating into calcium carbonates (Skinner 1958, 159), or due to the activation of Mg, structurally in-

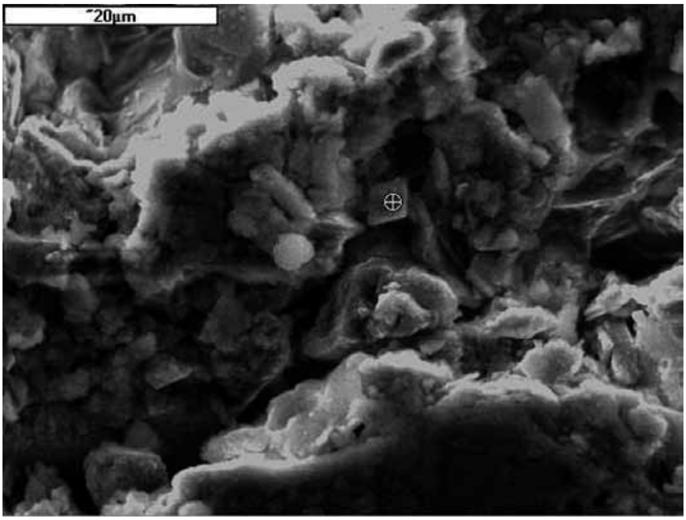


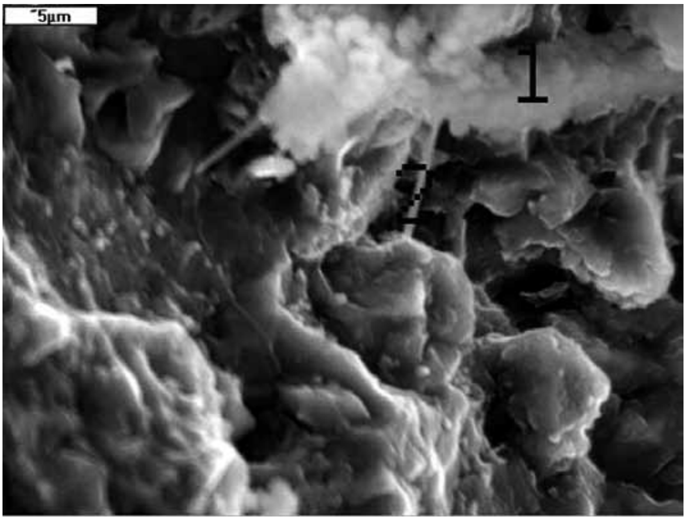
Fig. 22. Recrystallization of binder, most probably without an influx of new elements. A crystal of Ca-Mg carbonate; either dolomite or huntite (point). The Chapel of Hatshepsut, Deir-el-Bahari, Egypt (Pawlikowski et al. 2006, 19). Magn. x 2000.
Ryc. 22. Rekrystalizacja spoiwa, prawdopodobnie bez dopływu pierwiastków z zewnątrz. Kryształ węglanu wapniowo-magnezowego: dolomitu lub huntytu (punkt). świątynia Hatszepsut, Deir-el-Bahari, Egipt (Pawlikowski i in. 2006, 19). Pow. 2000x.

cluded in the plaster (see also EDS analyses in Pawlikowski et al. 2006, 19). A mixture of automorphic calcite and aragonite in Czudec Castle mortars may have been of similar origin, i.e. dissolution of lime and recrystallization to the two minerals, though it cannot be excluded that aragonite[6] appeared in course of uneven mortar calcification. We rather believe that, due to presence of it within cracks and pores, aragonite crystallized rather as secondary mineral (Fig. 21).

2d. Former and present microorganisms

Everyday observations demonstrate negative results of microorganisms' action in the surfaces of buildings, i.e. retention of dampness, colour changes and weakening of structure. The problem was studied long time ago (Silverman, Ehrlich 1964; Smyk, Ettlinger 1963) in the aspect of stone deterioration. Now, fauna and flora of mortars are waiting for their explorers. Penetration of microorganisms into historic mortars and plasters is a fact (Fig. 23), here a calcified part of a microorganism was documented (1), but still it is not clear whether other parts (2) are biologically active.

Fig. 23. 16th century mortar from Czudec Castle. Calcified microorganism (1), with elements of present (?) biological activity (2). Magn. x 3500.
Ryc. 23. Zaprawa XVI-wieczna z zamku w Czudcu. Skalcyfikowany mikroorganizm (1), ze strukturami znamionującymi współczesną (?) aktywność biologiczną (2). Pow. 3500x.



[6] This polymorphic variety of $CaCO_3$ was affirmed due to infrared spectrophotometry analyses (FTIR) (Trąbska et al. 2005).

Conclusions

We have identified and described components of historical mortars as well as corrosion phenomena resulting from careless manufacture and environmental impact.

Features of local workshops can be exhibited due to determination of the phase composition of a filler (e.g. Carpathian sands or tuff material; Fig. 1 and 16), its roundness, size diameter and general degree of care provided to its preparation (e.g. harmful components of the unwashed sand, Fig. 17). Binder reveals also numerous information about: an "echo" of firing processes (Fig. 7, p. 4), slaking and setting conditions (e.g. Figs. 5, 8, 10), process of a mortar production (Figs. 1, 15). All careless actions can be revealed, starting from filler composition through binder features, to structures of filler/binder contact. They were all documented on the photographs. Differences between e.g. mortars from Czudec Castle and Pompei buildings are striking and possible to explain by an analysis of their microstructure.

Carelessness and technological mistakes resulted in the development of corrosion processes and they were, as well as the ones of "environmental" origin, documented, e.g. primary (Fig. 11) and secondary cracks of a binder (Fig. 21), also as a results of phase varieties in binder composition (Fig. 6), penetration by secondary salts (Fig. 21), seconary reconstruction of a binder (Fig. 22), action of microorganisms (Fig. 23).

Subtle features of the structure, pointing at specific condition of setting the lime (excess of water, its possible enrichment with salts) were also detected (Fig. 5).

Further research of mortars should be extended to observations on their other types (e.g. gypsum ones) and should concentrate also on the solution of detailed, microsctructural problems, like identification of iron oxides and rounded shards and criteria for distinction of the secondary from the primary carbonates (if it is structurally unclear). Experimental works might cast some light on the appearance of lumps and their structural features, thus indicating the working habits of the masons.

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Mikrostruktury historycznych zapraw wapiennych i cementowo-wapiennych: od procesu wiązania do korozji

Mikrostruktury historycznych zapraw niosą liczne, a wciąż niedoceniane informacje na temat cech technologicznych oraz procesów korozji materiału wiążącego. Dane te dotyczą zarówno cech lokalnych warsztatów, specyfiki i staranności wykonywania zapraw, jak również zaawansowania procesów korozyjnych.

Cechy lokalnego warsztatu mogą być określone dzięki identyfikacji wypełniacza (np. piaski karpackie lub wulkaniczny tuf, ryc. 1, 16), staranności jego doboru, przejawiającej się odpowiednim obtoczeniem i średnicą ziaren, pozbawieniem ich szkodliwych domieszek przez przepłukanie (ryc. 17), warunkami dołowania wapna (ryc. 5, 8, 10), starannością łączenia ziarna i spoiwa (ryc. 1, 15). Bardzo wiele uchybień w rzemiośle można uchwycić w mikroobrazie; różnice między zaprawami z zamku w Czudcu a zaprawami z Pompejów są dobrym przykładem.

Niestaranność wytwarzania zaprawy skutkuje rozwojem procesów korozji, pogłębianej przez czynniki środowiskowe. Przejawami jej są pierwotne (ryc. 11) i wtórne szczeliny (ryc. 21) obecne w spoiwie wskutek niehomogeniczności fazowej spoiwa (ryc. 6), penetracji przez wtórne sole (ryc. 21), wtórne procesy przebudowy spoiwa (ryc. 22), działanie mikroorganizmów (ryc. 23).

Subtelne cechy mikrostruktury odzwierciedlają specyficzne warunki wiązania zaprawy, np. nadmiar wody, możliwe wzbogacenie w chlorki sodu, ewentualnie magnezu (ryc. 5).

Dalsze badania, w tym obserwacje mikrostruktur innych typów zapraw (np. gipsowych) oraz prace eksperymentalne z pewnością pozwolą na rozwiązanie wielu niejasnych jeszcze zagadnień, związanych w szczególności z procesami wiązania spoiwa zapraw.