Abstract Starting in the late 18th century, the age of industrialisation brought about a huge number of new technologies, amongst which novel binder systems of hydraulic nature were meant to answer the demand for improved mortar strength even at moist conditions. Such mortars form an important part of our today’s architectural heritage and are therefore frequently encountered either as primary materials or as historic restoration mortars, when historic objects are studied in the course of restoration. Their proper identification, a prerequisite for any sound diagnosis and therapy, may be complicated by the fact that those building materials later on either ran out of use, or developed into more modern systems. The paper deals with the basic features of a choice of those cementing materials which were “novel” at their time: Sorel cements, iron hammer scale mortars, and natural Roman as well as early Portland cements. The analytical approach followed is based on light and scanning electron microscopy, believed to provide primary tools to identify the mortars and to understand some of their key properties.

1 Methods

Samples were studied on thin sections and polished sections by means of polarising microscopy (PM) at transmitted and incident light. The same sections were eventually observed by scanning electron microscopy (SEM), using back-scattered electron (BSE) facilities. Several instruments were employed both at high and at low vacuum, thus no apparatus specifications are given. In all cases was energy-dispersive X-ray systems (EDX) used for chemical analyses.
Microstructures of the matrix of a sample were studied preferentially on fresh fracture faces, using both secondary electron (SE) and BSE detectors.

2 Sorel cement mortars

Magnesia cement, also called Sorel cement after its inventor Stanislas Sorel, is in fact no cement according to today’s terminology, since it is not resistant to water. The binder was first produced in 1867. In the late 19th century and probably until after World War I, Sorel cement was used for a wide range of applications, such as e.g. artificial stones, floorings, grindstones, repair mortars and even glues for broken stone parts. Today’s use is mostly in the field of floor screeds for industrial purposes. More data related to this application are given e.g. in [1].

Sorel cement belongs to the class known as acid-base binders, with caustic magnesia, MgO, produced from calcining magnesite, MgCO\(_3\), to which magnesium chloride, MgCl\(_2\), is added either as solution or in the solid state [1]. The resulting salt is reported to be a magnesium oxychloride hydrate of the formula 3MgO·MgCl\(_2\)·11H\(_2\)O [2], probably in intimate mixture with magnesium hydroxide, Mg(OH)\(_2\), precipitated in a colloidal form [3]. The binder starts to set after approx. 40 min and should be hard after 9 hrs at relatively low shrinkage. The final strength of a floor screed is impressive, with tensile strengths from 5 to 20 MPa and compressive strengths from 20 to 100 MPa. The low resistance to the action of moisture has however limited the application of Sorel cements.

Mortars and grouts from Sorel cement may contain considerable amounts of almost any kind of filler, and the use of wooden fibres in that context, increasing the thermal insulation capacity of a floor, has led to the name of *xylolith*.

Sorel cement mortars have been identified by the authors in a number of cases ranging from repair mortars and stuccoes for marble sculptures, glues for archaeological stone objects, inlays for structured façade renders, and floors. Some of those findings were related to outdoor applications where the material was strongly weathered but still in place.

Thin-sections under the polarising microscope show a brownish matrix which cannot be identified further, apart from several characteristic phases of residual or secondary nature. These comprise residual carbonates, brucite, Mg(OH)\(_2\), in aggregates of tiny crystals, and hydromagnesite, Mg\(_5\)[(OH)\(_2\)/(CO\(_3\))\(_4\)]·4H\(_2\)O, as spherical grains of radial-fibrous appearance.

The mortar structure is largely dependant on type and amount of filler adjusted to the mode of application. Fig. 1 shows a *xylolith*-type flooring mortar with high internal porosity due to the abundant wood fibres and frequent air voids caused by the liquid consistency. Fig. 2 illustrates a 19th century stone repair mortar applied to a marble sculpture outdoors. Its abundant filler consists of limestone fragments; the lower water:cement ratio is reflected by residual periclase, MgO, and the air voids are filled with secondary hydromagnesite.
The microstructure of the Sorel cement matrix provides additional information to understand the high mechanical strength attributed to these mortars. The crystals of magnesium oxychloride appear in prismatic shapes from tiny acicular to coarser pillared, sometimes intergrown with platy crystals. The porosity within the matrix varies from fairly high, with pore sizes in the range of $<5\mu$m (Fig. 3), to relatively low, with just a few air voids in an otherwise compact structure (Fig. 4).

3 Iron hammer scale mortars

High strength lime mortars of reddish to dark red colour can be found as 19th century materials for stone and masonry repair as well as for rejointing e.g. brick walls. The presence of iron in metallic form or as oxides can be suspected by visual inspection or sometimes even by the magnetic properties. Even if in the restoration community they are well known as hammer scale mortars, not much knowledge seems to exist about their properties and the mechanisms leading to the
strength they develop. Only few historic sources mention these mortars [4] which should not be confused with other types of putty prepared from iron cuttings.

Hammer scale is a waste product from iron smithing which consists mainly of tiny flakes of iron converted to iron oxides such as magnetite, Fe₃O₄, or haematite, Fe₂O₃. According to [4], the scale was ground and admixed to lime to prepare a mortar which was reported to harden considerably, particularly in moist places. The same article in [4] offers an explanation for the hardening of hammer scale mortars by addressing the well-known fact of rust subjected to volume expansion when forming from iron through the action of moisture and atmospheric acid.

The analysis of hammer scale mortars by means of microscopy and SEM supports the above hypothesis. Fig. 5 from a 19th century pointing mortar shows flakes of a dark grey iron phase, either haematite or magnetite. Both oxides have formed at high temperatures. Occasionally, metallic iron is still preserved in the core of such fragments (Fig. 6). Inert fillers such as e.g. quartz are also present.

![Fig. 5](image1.png) **Fig. 5** Iron hammer scales with “rusty” haloes in a 19th cent. pointing mortar; incident light

![Fig. 6](image2.png) **Fig. 6** Iron hammer scale with metal surrounded by iron oxide; SEM-BSE

![Fig. 7](image3.png) **Fig. 7** Lime matrix surrounding hammer scale, densified by iron compounds; SEM-BSE

![Fig. 8](image4.png) **Fig. 8** Needles of iron compound (goethite?) around a binder pore; SEM-BSE

Most of the iron oxide scales are surrounded by irregular areas of red colour, where iron hydroxides and hydrated oxides have caused densification of the calcite matrix (Fig. 7). No evidence for the formation of a calcium ferritic phase could be found, and small needle-shaped crystals growing within the matrix (Fig. 8) contain just iron and no calcium and are hence likely to represent a
mineral of the goethite type, FeO(OH)·H₂O. Even if an exact mineralogical identification of the phases involved has not been performed in the present study, the principles of reaction are clear: the oxidation – rusting – of the scales is accompanied by the migration of colloidal iron hydroxides into the lime matrix where they precipitate and crystallise in the binder pores, causing significant compaction. Similar effects by an analogous process had been described for crystalline marble whose cracks were “healed” by iron hydroxides having migrated from rusting iron rebars [5].

4 Roman cements

Several papers, e.g. [6, 7, 8, 9, 10, 11, 12, 13], have recently dealt with Roman cements (RC) - natural cements produced at temperatures well below sintering, i.e. in the range of about 800 to 900°C. These hydraulic binders played an important role in building construction and façade decoration especially in Western and Central Europe.

When analysing historic RC-mortars it should be kept in mind that they differ from Portland cement or NHL-mortars not so much in their chemical composition as in respect to mineral content and appearance of the residual clinker, along with the microstructure of the hydrated cement matrix. The nature of the raw feed, typically argillaceous limestone, and the low temperatures of calcination lead to the formation of characteristic cement compounds and binder microstructures. Their identification must be primarily based on microscopy and SEM. Weber and Gadermayr in [11] have presented the range of residual phases typically present in RCD-mortars, as well as their visual appearance under the polarising microscope and SEM. Fig. 9 shows a 19th century RC-mortar at low magnification, where the brownish colour and the abundant binder nodules form the primary features of distinction. The nodules mark areas of incomplete or non-ideal hydration due to non-reactive phases formed by either sub- or super-optimal calcination, both conditions being inherent to the process of production. The sub-optimal nodules are characterised by incomplete decomposition of carbonate and/or insufficient reactions with the silicates, while the super-optimal grains typically contain coarse belite, C₂S of the β-form, gehlenite, C₂A₂S, and sometimes even products of local melting (Fig. 10). Both nodule types seem to play an essential role as inert fillers.

The reactive portion of a RC “clinker” is known to consist of an amorphous phase and highly reactive α’-belite mixed with less reactive β-belite [7, 8]. Historic Roman cement mortars combine high strength with high porosity in the capillary range. This specific feature is even more pronounced for mortars with very low amounts of aggregate. SEM-studies of the matrix help understand the mentioned properties. As already stated e.g. in [8] and [11], the calcium silicate hydrates formed in a Roman cement paste is of an unusual coarse nature
with card house-like intergrowth (Fig. 11). Abundant calcite crystals formed in most of the historic mortars upon carbonation yield additional strength.

**Fig. 9** 19th century RC-mortar with characteristic binder nodules; the red grain is a brick fragment; transmitted light in bright field (BF) and dark field (DF)

**Fig. 10** RC binder residues with silica grains to which diffusion of Ca and alkalis has caused zoning with even local melting (right). Matrix with partially hydrated belites, C2S; SEM-BSE

**Fig. 11** Matrix of historic RC-mortar with coarse calcim silicate hydrate, C-S-H; SEM-SE

## 5 Early Portland cements

When dealing with early Portland cement (PC) mortars, it should be kept in mind that their binders differ from today’s OPC. Analyses of early PC raise the suspicion that, for a period of probably about hundred years, the usual peak kiln temperatures were rather in the range of about 1200°C – the temperature of sintering for most raw feeds – than 1450°C as for OPC. The main clinker phase of modern PC (see e.g. [14]), i.e. alite, C3S, is thus unlikely to occur in early cements, while the other phases of significance, such as belite, C2S, aluminate, C3A, and ferrite, C4AF, would form before or as soon as the above point of sintering is reached.

Most early Portland cements lack therefore C3S in favour of C2S. It would be misleading, however, to consider them as binders similar to Roman cements, and
in fact all historic handbooks make a clear distinction between both cements, pointing to the slower set, more rapid strength gain, and higher final strength of PC (e.g. [15]). From the point of view of the clinker composition, the difference between early PC and RC can be explained by several factors: first, belite present in an early PC was most probably of the $\beta$-type in contrary to the $\alpha'$-polymorph typical for RC; second, not the amorphous phase present in RC, but rather $C_3A$ was the phase responsible for the onset of stiffening and early strength in PC pastes; finally, the higher temperatures of PC calcination would have caused higher rates of reaction within the raw feed, leading to coarser crystals, less solid solutions, and thus less binder residues in the final product as compared to RC.

A distinctive feature in sections of early PC-mortars viewed under the microscope is therefore the low amount or even lack of brownish binder nodules. As soon as, with temperatures of calcination exceeding about 1.100 °C, iron starts to be incorporated in the ferrite phase, the colour of the cement turns from yellowish-reddish to greenish-greyish. Fig. 12 and Fig. 13 show examples.

From modern PC mortars the early ones can be distinguished by their much coarser clinker residues – in the range of 200 µm or more as compared to 20 µm - and by the lack of $C_3S$ in them.

Viewed by SEM on fractures, the microstructure of the hydrated matrix of historic Portland cement can be described as more compact than in Roman cements (Fig. 14), with C-S-H forming a dense framework even if some areas remain more open-porous. The hydrates are, however, much coarser than in modern cements (Fig. 15); when growing inside larger voids, they tend to develop acicular shapes. Rhombohedral crystals of calcite can be found quite frequently, since all of the samples investigated revealed full carbonation.

Fig. 12 early PC-mortar with coarse clinker residues with interstitial ferrite; transmitted light in bright field (BF) and dark field (DF)  
Fig. 13 early PC binder residues with small silica (dark grey), belite and ferrite, surrounded by a dense matrix of hydrates; SEM-BSE
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7 References