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Natural cement as the precursor of Portland cement: Methodology for its identification

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Abstract

When cements appeared in the 19th century, they took the place of traditional binding materials (lime, gypsum, and hydraulic lime) which had been used until that time. Early cements can be divided into two groups, *natural* and *artificial* (Portland) cements. Natural cements were introduced first, but their widespread usage was short-lived as they were quickly replaced by artificial cements (Portland), still the most important and predominant today. The main differences between natural and artificial cements arise during the manufacturing process. The final properties of the cements are greatly influenced by differences in the raw materials and burning temperatures employed.

The aim of this paper is to assess the efficiency of traditional analytical techniques (petrographic microscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR)) used to differentiate natural and artificial cements.

Keywords: Natural cement; Ordinary Portland cement; Old mortars; SEM-EDX; Belite

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1. Introduction

The precursor of today's ordinary Portland cement (OPC) was natural cement. Natural cements are not hydraulic limes [1–3]. The great innovation of natural cements was that they used quick-hardening and water-resistant hydraulic binders. This made them indispensable in satisfying the construction needs of the 19th century Industrial Revolution. Natural cements first appeared in England in 1796 when James Parker patented his "Roman cement." However, the importance of natural cements was eclipsed by the appearance of Aspdin's ordinary Portland cement in 1824 [2]. Because of its higher rigidity and hardness, Portland cement soon replaced natural cements in mortars (Fig. 1).

The raw material of natural cement manufacture was marl (75–60% of carbonates and 25–40% of clay), burnt at a temperature of 800–1200 °C for between 8 and 20 h. The innovations and advantages provided by natural cements over traditional hydraulic binders (pozzolanic cements and hydraulic limes) are, first of all, that hydration and setting processes take place simultaneously, and, second, the cement is fast-setting (<12 h) [3,4]. Natural cement began to be manufactured in Spain in large quantities in the middle of 19th century, and was mainly used in construction projects (ports, channels, drains and water supply networks, etc.). Natural cements can be classified as [3]:

a) *Rapid natural cements (RNC)*. These cements were manufactured using marls with low clay content (25–30%). Burning temperatures ranged between 1000 and 1200 °C, for 12–20 h. These cements were lime-rich and set fast (< 30 min).
b) *Slow natural cements (SNC)*. Marls with high clay content (40%) were used as raw materials. Calcination lasted for 8–12 h at 800–1000 °C. These cements were silica-rich and set more slowly (30 min–12 h).

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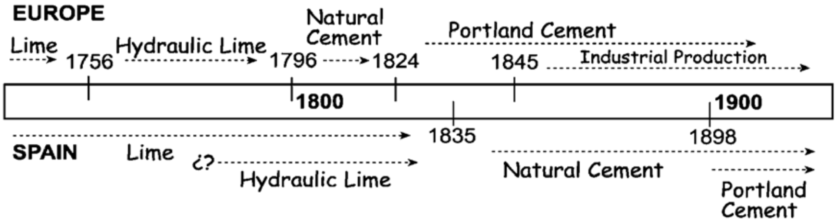


Fig. 1. Chronological evolution of mortar binders in Europe and Spain.

Technological improvements and advances in natural cement production rapidly led to the appearance of "ordinary Portland artificial cements"—harder, more rigid, and waterproof. These Portland cements (OPC) were obtained by the calcination of a dosed admixture consisting of pure limestones (80–75%) and clays (20–25%), at temperatures >1300 °C, for shorter periods of time (< 8 h). Their setting time is longer than that of RNC (> 1 h) [3,4].

The characteristic mineralogy–calcium silicates and aluminates–of both types of cements (natural and Portland) is the product of burning clays and carbonates containing lime, silica, alumina, and iron oxides together at $\geq$ 900 °C. Burning dehydrates and decomposes clays (<800 °C), and decomposes the carbonates (800–1000 °C) found in marls, limestones, and clays to produce calcium silicates and aluminates. While C_2S (dicalcium silicate, belite) is the major hydraulic phase in natural cement–with some C_3S (tricalcium silicate, alite) due to localized "hot spots"–C_3S is the major phase in ordinary Portland cement. C_2S originates, and is stable, at a temperature between 900 and 1200 °C, while C_3S forms above 1300 °C (surpassing the melting point) [1,5–7]. Gehlenite (C_2AS, Ca–Al silicate) is another typical mineral, formed at temperatures below 1200 °C. Hence, the presence of gehlenite is a major factor in differentiating natural cements from ordinary Portland cements [5], as shown in cases studied so far in the research [5,8].

To date, there has been limited research on the identification and characterization of natural and ordinary Portland cements in old mortars. Interest in the systematic study of old cement mortars is relatively new [5,9–11]. The use of modern cements for the restoration of structures that contain natural and ordinary Portland cements of different periods can lead to problems of materials incompatibility. Such incompatibilities are due to the comparatively higher strength, rigidity, and impermeability of modern cements. The original properties of hardness, rigidity, and impermeability of old cements deteriorate with time. Modern cements, manufactured with improved technology, are more resistant. Therefore, before embarking on restoration projects of structures more than 100 years old, it is necessary to study the cement mortars (natural and Portland cements).

Our aim in this research is to characterize and determine mineralogical and chemical differences between the natural cements (both slow and rapid natural cements) used in Spain at the end of the 19th century and the first artificial cements of Portland type that appeared in Spain at the beginning of the 20th century. Such knowledge will allow cements that have survived until the present day to be typed and will facilitate appropriate restoration.

2. Materials and instrumental techniques

2.1. Materials

A comparative study of the old mortars made from natural cement and Portland cement was done. Samples were taken from two buildings:

- A drinking water supply tank (1914–1915), located in Salamanca (Spain), constructed using the first Portland cement produced in this country. Samples used were hydraulic concrete (SA-1) from the main wall of the tank and a rendering mortar on the external wall (SA-2).
- The Pantheon of Illustrious Men (1892–1899), a historic building in Madrid (Spain) belonging to the National Heritage. The existing historical documentation shows the use of two types of natural cement mortars: rapid natural cement ss and slow natural cement. Samples of rapid natural cement (M-1) were taken from rendering mortars, and samples of slow natural cement (M-2) were collected from joint mortars. These mortars were from the interior of the building.

2.2. Instrumental techniques

Qualitative mineralogical and chemical compositions were obtained by means of the following techniques:

a) X-ray powder diffraction analysis (XRD) (Philips PW-1752, copper anode tube, $2°\theta$, and PC-ADP diffraction software) to identify the mineral crystalline phases of the mortars (binder plus aggregate).
b) Fourier transform infrared spectroscopy analysis (FTIR) (Nicolet Magna-IR750 Series II, KBr pellets) for gathering qualitative information on the chemistry of some of the characteristic substances contained in mortars (calcium carbonate, gypsum, silicates, water, etc.).
c) Optical microscope examination of thin sections (Zeiss, Axioskop, Alizarin staining) for the petrographical–mineralogical characterization of the mortars' constituents (binder and aggregate).
d) Scanning electron microscopy (SEM) (JEOL JSM 6400, graphite sputtering) with energy dispersive X-ray spec-

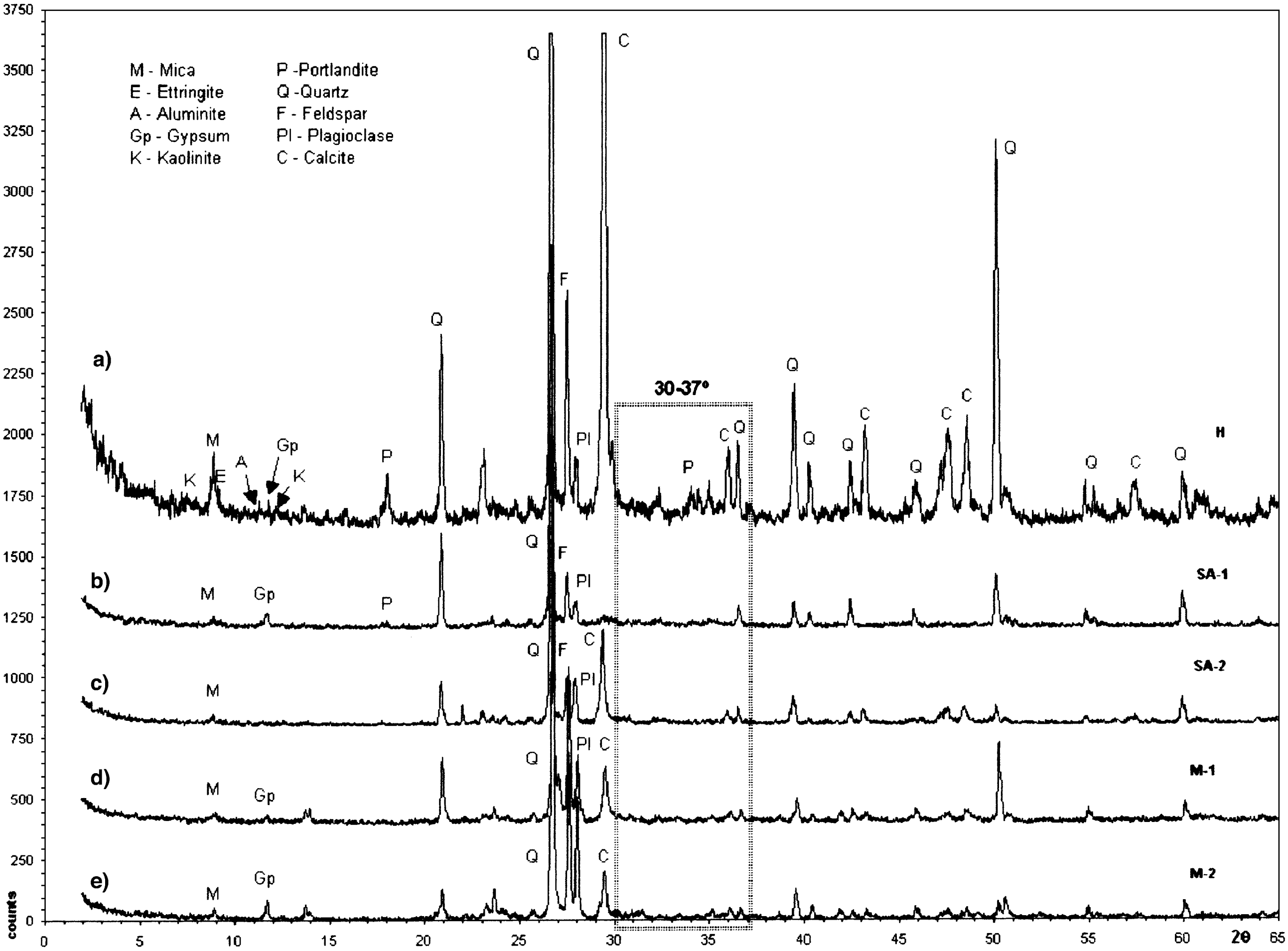


Fig. 2. X-ray diffractograms (powder fraction of the whole sample) of the cement mortars studied.

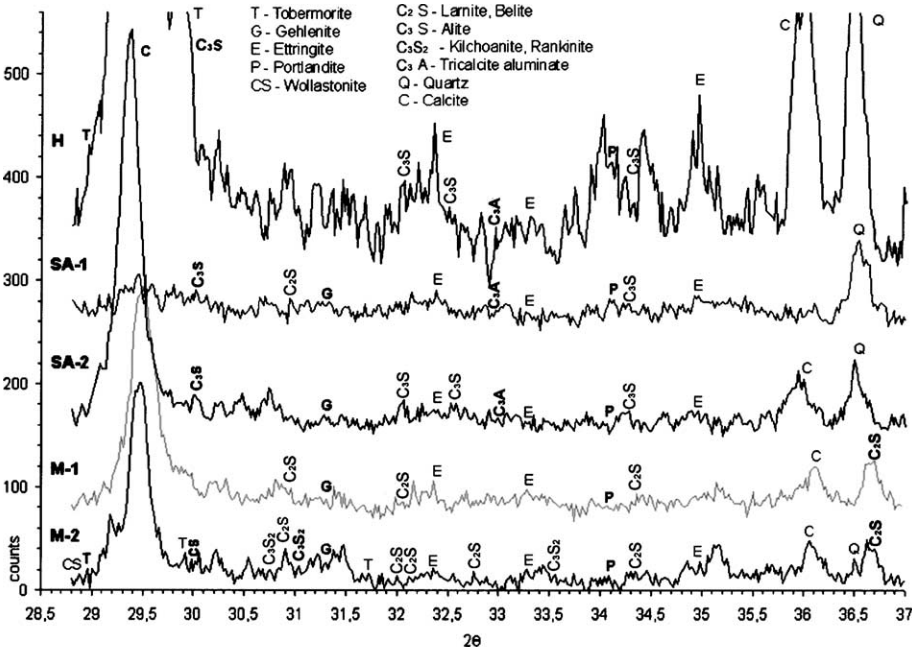


Fig. 3. X-ray diffractograms (powder fraction of the whole sample) of the cement mortars studied, along the interval 30–37°.

trometer (EDX) (Oxford-Link Pentafet). This last technique was mainly used for binder analysis. SEM-EDX analysis in the backscattering electrons (BSE) mode on polished sections was used for elementary semi-quantitative chemical study of the binder components. SEM-EDX analysis in the secondary electrons (SE) mode on small pieces was used for microscopic observations of the microstructure and the texture of the binder components.

3. Results and discussion

3.1. X-ray diffraction (XRD)

Qualitative XRD analysis has shown the presence of (Fig. 2) quartz (3.34Å), K-feldspar (3.24Å), plagioclase (3.19Å), clay–micas (8.87Å), and calcite (3.03Å). The first four minerals correspond to the sandy aggregates of the mortars, whereas calcite may come from the binder constituents. It is formed when calcium hydroxide (portlandite, $Ca(OH)_2$) is produced during hydration of cement carbonates in the presence of atmospheric CO_2.

Galán et al. [12], have studied the mineralogy of cement binders between 30 and 37° (2θ) (2.97Å–2.42Å), and reported the presence of calcium and calcium–aluminium silicates (Fig. 3). These silicates provide hydraulic properties to the binder:

a) In the natural cement binders (M-1 and M-2; Fig. 3), C_2S (belite or larnite), C_2AS (gehlenite), and calcium silicate hydrate (CSH, tobermorite) have been detected. However, in the SNC sample (M-2), CS (wollastonite) and C_3S_2 (rankinite or kilchoanite) were also found, and more C_2AS (gehlenite) than in the RNC (M-1).

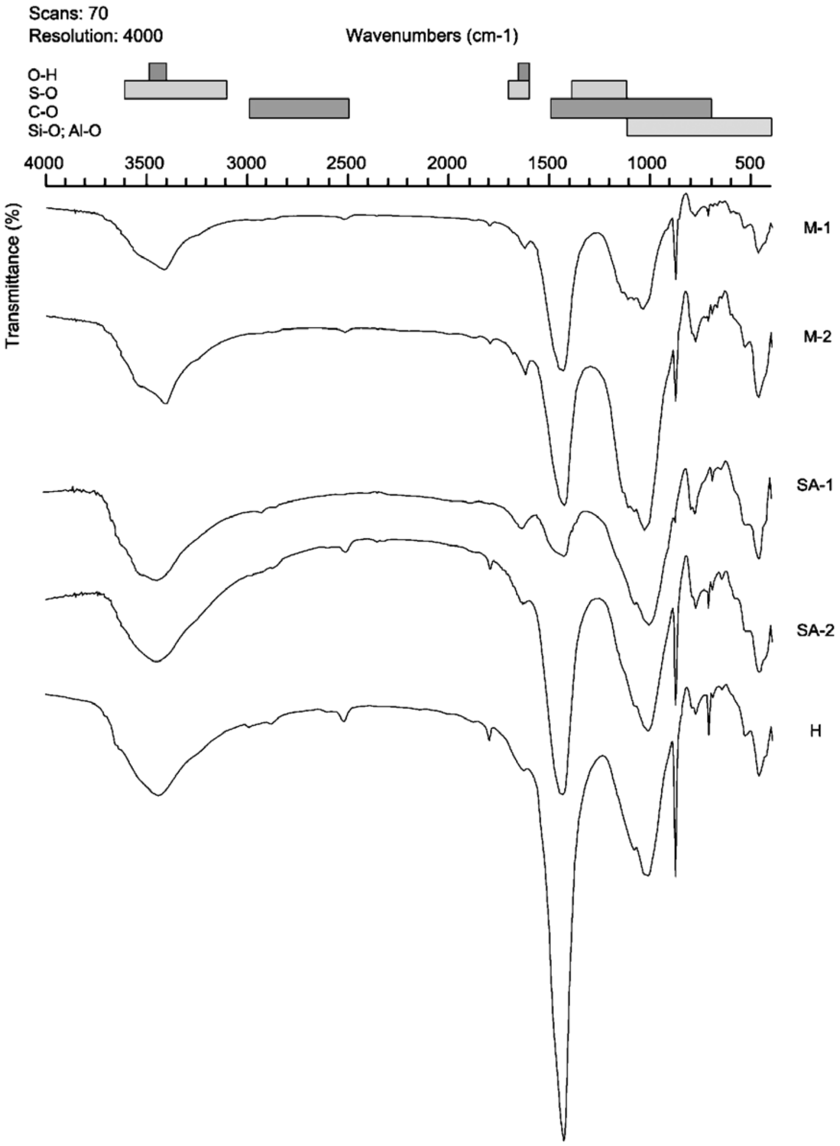


Fig. 4. FTIR spectra of the mortar samples studied.

b) In the older Portland cement binders (SA-1, SA-2; Fig. 3), calcium silicate minerals are present as described earlier, although there is more calcium. As more siliceous CS disappears, more calcium-rich silicate (C_3S, alite) appears. As is mentioned earlier, alite is a typical phase of OPC, while gehlenite is absent.

In the natural and ordinary Portland cements analysed, apart from a siliceous mineralogy, some other minerals are also detected: a) C_3A is scarce in old cement mortars: it is absent in the natural cements studied here and only slightly present in OPC (SA-1, SA-2); b) portlandite is present in all the cements, but it is more abundant in mortar samples that have not been in contact with the environment (SA-1) and consequently have not been carbonated (to calcite); c) gypsum is more common in SNC mortars (M-2) than in OPC mortars, due to their manufacturing process, while in ordinary Portland cements, gypsum was added in small quantities after calcination to control its setting [4] and, in natural cements gypsum, is produced during the calcination process of the raw materials (marl) with lignites; d) ettringite (Ca–Al sulphate), which is a mineral originated by degradation processes, is scarce in both types of cements, due to the fact that atmospheric pollution degree (S) is negligible; e) calcite is present in all the cement mortars, although its presence is more noticeable in the OPC mortars exposed to the environment. Due to the fact that calcite is the result of the carbonation processes of the binder, its presence will depend on the original carbonate content (of 80–75% in Portland cements and 75–60% in natural cements) in the raw materials.

The oldest Portland cement's higher calcite content (carbonation), and differences in its portlandite, ettringite (sulphation), and aluminium mineral content (kaolinite, aluminite) (Fig. 3) clearly distinguish it from modern Portland cement (H).

3.2. Fourier transform infrared spectroscopy (FTIR)

Fig. 4 shows the spectra of five cement mortar samples. These spectra show four large regions where the main vibration and deformation bands of Si–Al, S, Ca, and OH are concentrated [13–15]. Their variability allows some interesting differences:

Fig. 5. Photomicrograph (crossed nicols) of a thin section of SNC mortar. Matrix dissolves the edges of skeletal grains (alkali–aggregate reaction).

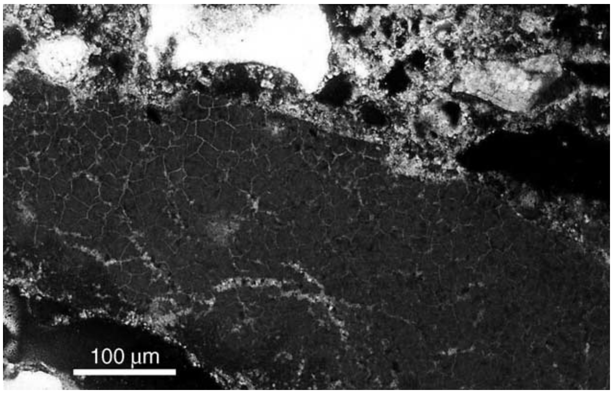


Fig. 6. Photomicrograph (crossed nicols) of a thin section of RNC mortar. The rapid curing of the mortar leads to the cracking of the matrix (binder).

1- In the 1100–400 cm^{-1} region, vibrational bands corresponding to Si (Si–O and Si–O–Si) and to Al (Al–O and Al–O–Al) are detected. This region is clear in the SNC mortar (M-2), diminishes in RNC (M-1), and is similar to equivalent regions in the OPC mortars (old-SA-1, SA-2- and recent-H-; Fig. 4). This region is

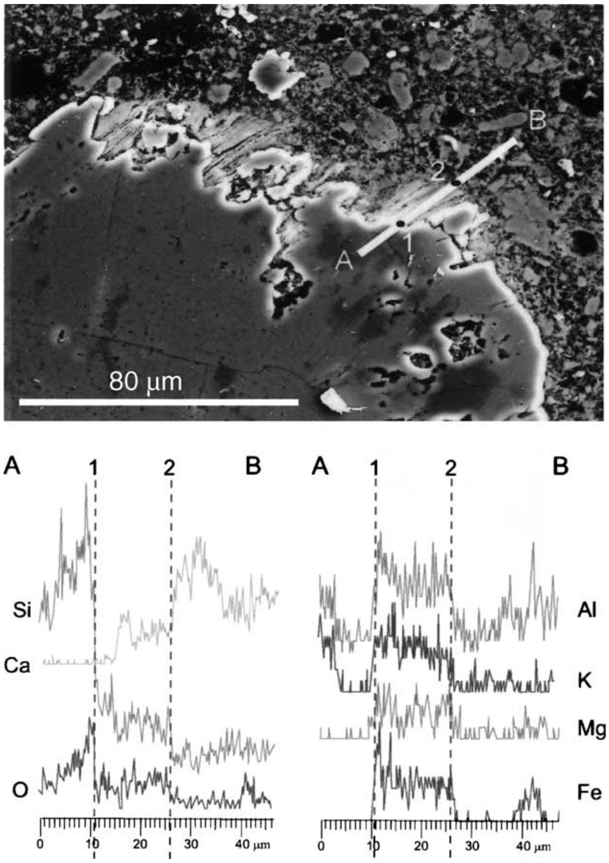
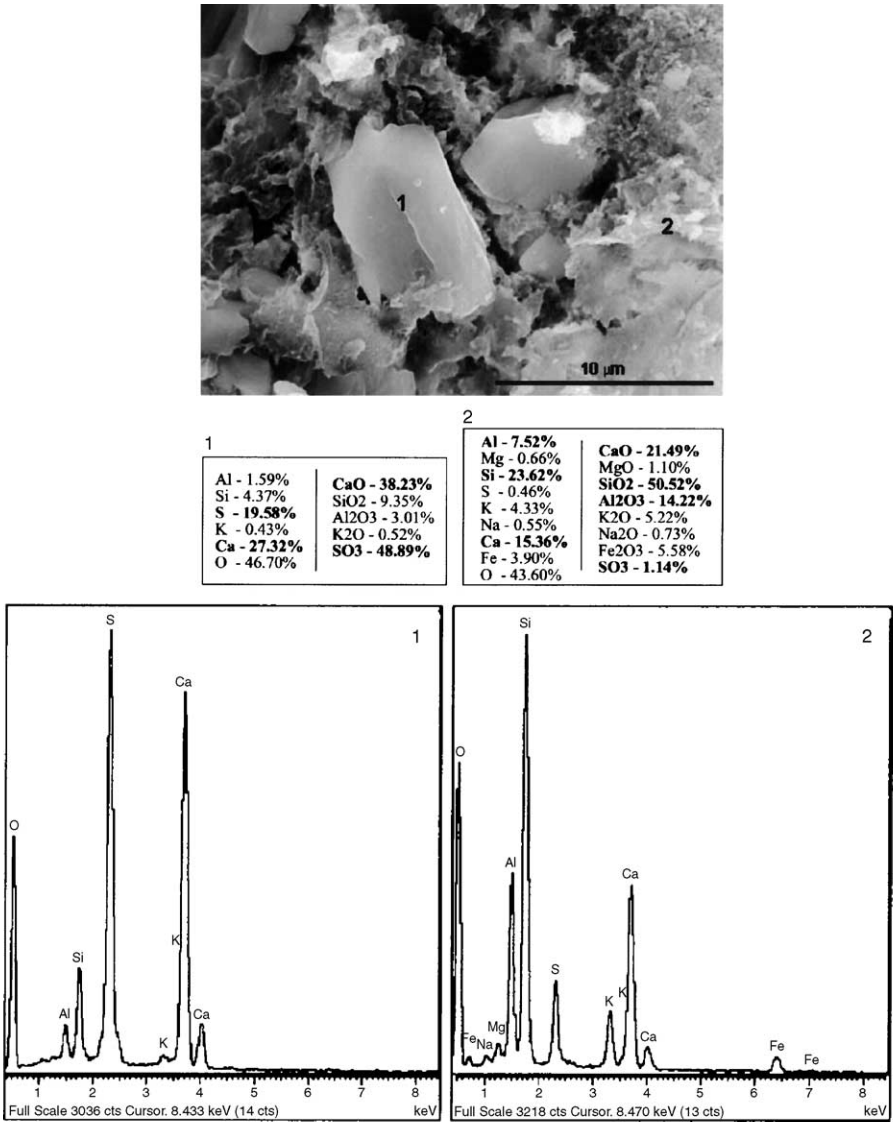


Fig. 7. SEM-EDX analysis (BSE mode) on polished section of the reaction fringe matrix–skeletal grain (alkali–aggregate reaction).

dominant in those mortars elaborated from slow setting cements. The mineralogy determined in this interval is mainly siliceous: quartz, pozzolans, and calcium silicates. Quartz (1080 cm^{-1}) corresponds to sandy aggregates. Pozzolans (1035–1030 cm^{-1}) are abundant in natural cement mortars, mainly in SNC mortars. They constitute an additional source of reactive SiO_2 and Al_2O_3 and are the ashes produced by the simultaneous calcination of coal (lignites) and cement raw materials [1,3,4,16]. The concentration of these ashes is higher in the slow cements because during their manufacture burning time and temperature are lower, thus creating a higher proportion in residues (ashes). In the case of Portland cements, pozzolans disappear due to a complete melting of the raw materials during manufacture, when calcination temperatures exceed 1300 °C. Calcium silicates, components of cements, are also present in this region (1010–1000 cm^{-1}, 930 cm^{-1}) and in a secondary region in which carbon of calcite vibrates as well (2930–2920 cm^{-1} and 2855–2850 cm^{-1}) [15]. These calcium silicates are present in all the cements studied, although their vibrational bands are more intense in the Portland cements (1010–1000 cm^{-1}).

2- Sulphur (S) shows vibrational bands (S–O) in three regions: 1300–1100 cm^{-1}, 1685–1620 cm^{-1}, and 3600–3100 cm^{-1}, with gypsum being the best represented mineral in these mortars. Gypsum is mainly detected in the natural cement mortars and is more abundant in SNC (M-2), which is produced during natural cement manufacture. S is a residual product, resulting from the calcination of raw materials (marls) by coals.

3- In the 1500–700 cm^{-1} region, there are C-vibrational bands (C–O), although secondary bands also exist in the 3000–2500 cm^{-1} region. The best represented mineral is calcite, with a mineralogy that is a result of cement carbonation. Its presence is high in Portland cements,



1

Al - 1.59%
Si - 4.37%
S - 19.58%
K - 0.43%
Ca - 27.32%
O - 46.70%

CaO - 38.23%
SiO2 - 9.35%
Al2O3 - 3.01%
K2O - 0.52%
SO3 - 48.89%

2

Al - 7.52%
Mg - 0.66%
Si - 23.62%
S - 0.46%
K - 4.33%
Na - 0.55%
Ca - 15.36%
Fe - 3.90%
O - 43.60%

CaO - 21.49%
MgO - 1.10%
SiO2 - 50.52%
Al2O3 - 14.22%
K2O - 5.22%
Na2O - 0.73%
Fe2O3 - 5.58%
SO3 - 1.14%

Fig. 8. SEM-EDX analysis (SE mode) on a fragment of binder of SNC mortar (M-2). (1) Gypsum; (2) calcium silicates.

with recent Portland cements (H) presenting the highest content.

4- Vibrational and deformation bands of constitutive water (O–H) appear in the 3450–3400 cm^{-1} and 1650–1620 cm^{-1} regions. Natural cement mortars (M-1 and M-2) present narrow bands located nearer lower values (3414–3409 cm^{-1}), which indicates anhydrous conditions. Conversely, OPC mortars (SA-1, SA-2) give broader bands with higher values (3446–3441 cm^{-1}), indicating less anhydrous conditions. Hydrated minerals, such as portlandite (3650 cm^{-1}) and tobermorite (3630 cm^{-1}), are also detected.

3.3. Petrographic microscopy

The cement mortars analysed (natural and Portland) are composed of skeletal grains (aggregates) surrounded by a matrix (binder). Their petrographic study shows few mineralogical differences. Most significant was the detection of reactions between both components and how this leads to structural and textural changes.

The aggregate is the same in all the mortars. It is a siliceous aggregate (mono- and polycrystalline quartz, muscovite, biotite, feldspar and quartzite, schist and granite fragments), with an angular, large skeletal grain size and corroded edges. Such corrosion is due to the dissolution reaction of the surrounding matrix (binder) (Fig. 5). The high alkalinity of the matrix interacts with the acid of the siliceous aggregate.

In general terms, the binder (matrix) is a dense mass, massive, and micro- and crypto-crystalline, where no mineral or even crystalline structures are recognized. However, differences within this component allow the different analysed cement mortars to be distinguished:

a) The binder of the RNC mortar (M-1) shows an opaque appearance, with a carbonated composition and porosity created by dissolution phenomena. Moreover, the contraction processes undergone by the rapid drying of these cements lead to the cracking of the matrix (crazing; Fig. 6).

b) The binder of the SNC mortar (M-2) is translucent, lumpier, and less carbonated than the binder of the rapid cement (Fig. 5). This matrix shows a significant amount of porosity brought on by dissolution, and, when in contact with the skeletal grains aggregate, by fissuring.

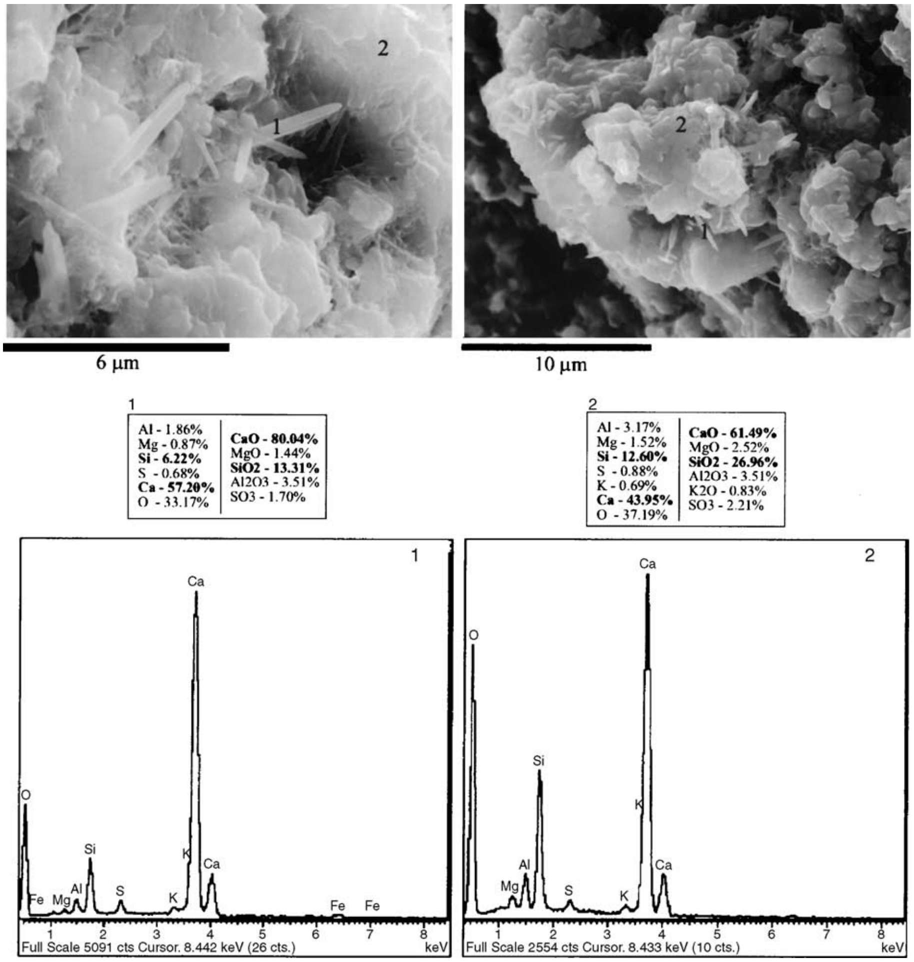


Fig. 9. SEM-EDX analysis (SE mode) on a fragment of binder of RNC mortar (M-1). (1 and 2) Calcium silicates.

Separation between skeletal grains and matrix provokes the disintegration of these types of mortars. This is a consequence of the high content in argillaceous materials of the aggregate. It must be indicated also that the matrix has a large number of opaque minerals, corresponding to the ashes added to this cement during its manufacture.

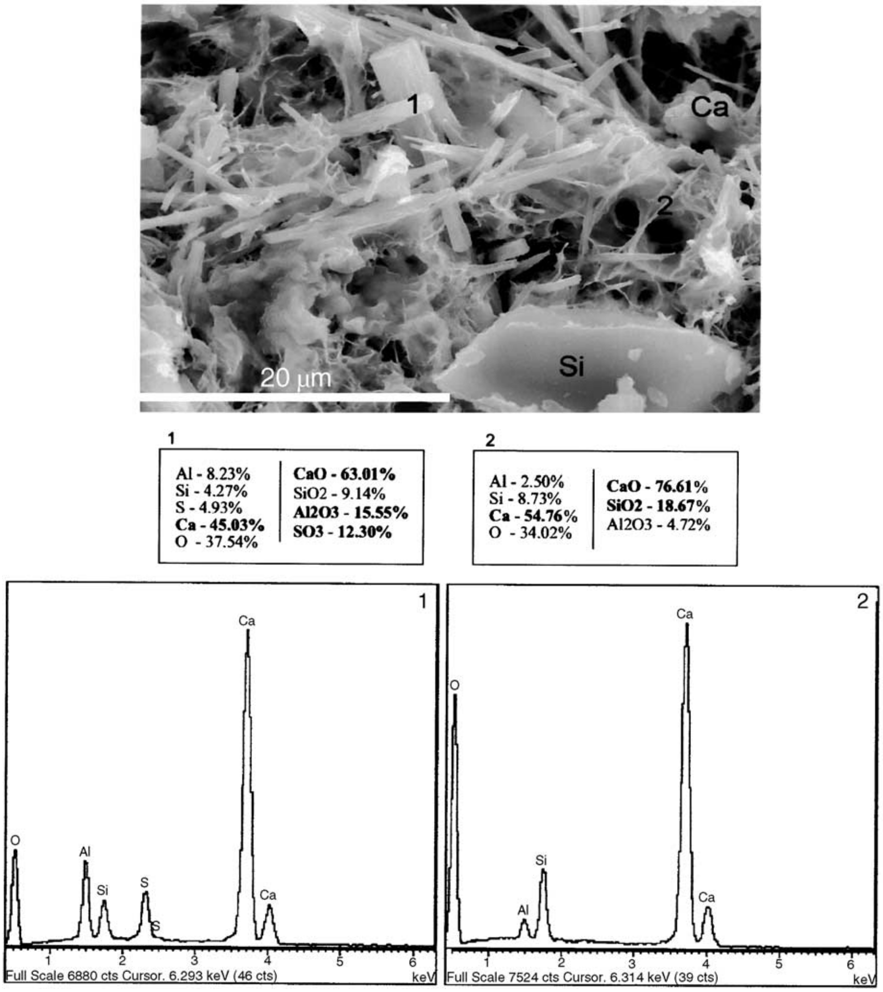
c) The binder of the old OPC mortars shows varying levels of carbonation depending on the type of sample; sample SA-2 is highly carbonated because it is a rendering mortar, thus favouring the existence of porosity caused by dissolution. On the other hand, sample SA-1 is not carbonated because it is an internal mortar that has not been in contact with the atmosphere, turning the matrix into a compact, non-porous, or very slightly porous mass. The fact that the matrix is not carbonated explains its high degree of alkalinity because calcium is present as CaO and $Ca(OH)_2$, leading to very aggressive reactions with the aggregate. Such reactions affect not only the edges of the skeletal grains but also their internal areas.

The mortars employed as renders (M-1, SA-2) show a very carbonated matrix and a high porosity due to the dissolution processes linked to their alteration by carbonation. Mortars used in the masonry (interior; M-2, SA-1) show lower carbonation and porosity, since their contact with atmospheric CO_2 is more limited. This is the reason the matrix is highly alkaline and reacts with the aggregate dissolving it (alkali–aggregate reaction).

3.4. Scanning electron microscopy (SEM) + X-ray dispersive energy microanalyser (EDX)

The use of SEM + EDX is essential for the characterization of old cement mortars. It highlights the clear morphological and chemical differences between the binders of natural cements (slow and rapid) and Portland cements.

In general, the corrosion of the aggregate edges of all the mortars has been detected, caused by the alkaline nature of the binder (Fig. 7). Such corrosion appears in the form of



1

Al - 8.23%
Si - 4.27%
S - 4.93%
Ca - 45.03%
O - 37.54%

CaO - 63.01%
SiO2 - 9.14%
Al2O3 - 15.55%
SO3 - 12.30%

2

Al - 2.50%
Si - 8.73%
Ca - 54.76%
O - 34.02%

CaO - 76.61%
SiO2 - 18.67%
Al2O3 - 4.72%

Fig. 10. SEM-EDX analysis (SE mode) on fragments of binders of two old Portland cement mortars (SA-1 and SA-2). (1) Ettringite; (2) alite.

radial morphologies, which consist of a transition reaction zone between the skeletal grain that is being broken down by dissolution and the matrix that decomposes the skeletal grain. Chemical elements of both components (mainly Si, O, and Ca) coexist in this transition area but in different proportions. Si and O content increases when reaching the edge of the skeletal grain and then sharply decreases near the transition area. In this area, Si continues to decrease slightly, O stays the same, and Ca content increases. This occurs up to the border of the transition area, where Si and O give way to the Ca of the matrix (binder). The analysis of other elements (Al, K, Mg, and Fe) shows the maximum concentration in this transition area and minimal or very small concentrations in contact areas, both with the skeletal grain or with the matrix (Fig. 7).

The SNC binder shows a mineralogy rich in Si (Si > Ca) and irregular morphologies (lump and leaf shaped; Fig. 8). The presence of hexagonal crystals corresponding to gypsum and the absence of carbonates (calcite) is significant. Conversely, the RNC binder presents a mineralogy rich in Ca (Ca > Si) and spherical/globular and acicular morphologies (Fig. 9). The acicular shapes are isolated needles of C_3S and C_4S, and the spherical ones, more abundant, are C_2S (belite or larnite). The carbonation that affects this cement also shows globular shapes with a composition of CaO > 80%. The needle-like morphology and the C_3S and C_4S composition make these minerals similar to alite. According to Klenner et al. [17], C_3S forms when the raw materials are overheated during the production of this cement.

The older Portland cement binders show a better defined mineralogy than the natural cements. Their morphologies are fibrous and acicular. The compositions are rich in Ca (Fig. 10). Fibres correspond to tricalcium silicates (alite), and acicular crystals to sulphates of the ettringite type.

From the point of view of their chemistry (Fig. 11): a) SNC shows a mineralogy rich in Si and Al; b) the RNC binders present a mineralogy in which Ca is more abundant than Si and Al; and c) old Portland cements can be placed in the middle of both natural cements, tending to be more similar to RNC than to SNC. Portland cements show mineralogy rich in Ca, although they also have significant amounts of Si.

4. Conclusions

The combination of several traditional analytical techniques allows the differentiation and characterization of two types of cement (natural and Portland) used in the manufacture of old mortars (Table 1), the mineralogy of which has not been well-defined until now. Of all the

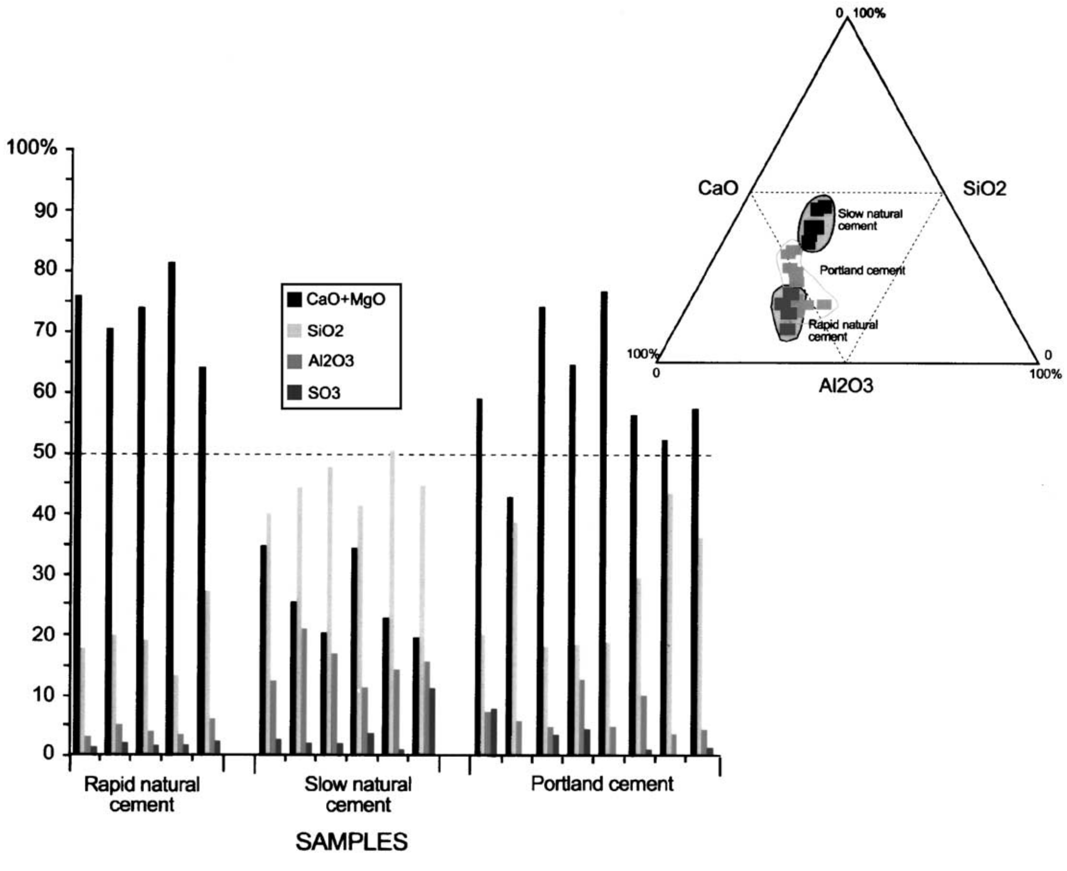


Fig. 11. Comparative chemical evolution (EDX) of old cements studied.

Table 1
Results of the techniques used for the analysis of natural and Portland cements

Techniques	Natural cements		Portland cements (20–25% clay content)	
	Slow (SNC) < 40% clay content	Rapid (RNC) > 25% clay content	Old	Recent
SEM	Leaf and lump-shaped	Acicular and globular shapes	Fibrous shapes	
EDX	Si $\gg$ Ca gypsum	Ca $\gg$ Si	Ca > Si ettringite	
XRD	Gypsum, CS, C_3S_2, gehlenite	C_2S, calcite, gehlenite	C_3S, calcite	Calcite, ettringite, aluminates, C_3S
FTIR	> Ashes (pozzolans)	< Ashes (pozzolans)	Hydration	Hydration
Petrographic microscopy	Fissuring (< carbonation, > porosity)	Crazing (> carbonation, < porosity)		

techniques, SEM + EDX has been the most effective for the chemical and morphological characterization of the mineralogy of these old cements.

Portland cement mortars can be distinguished from those of natural cement mainly by the presence of C_3S (alite), and by their higher degree of carbonation and sulphation. Among the natural cements, the main differences are related to the silicon/calcium and gypsum contents, and to the carbonation and sulphation degree.

The SEM study and EDX analysis show that SNC mineralogy is rich in Si (CS and C_3S_2), with leaf and lump-like morphologies. Gypsum is also a significant compound in these cements. RNC mineralogy is richer in calcium with acicular (C_3S, C_4S) and spherular (C_2S) shapes. These cements undergo carbonation easily. Old Portland cements are similar to RNC. Their mineralogy is highly calcic with fibre-like shapes (C_3S) and abundant ettringite (Ca–Al sulphate, acicular morphologies).

The XRD analysis, in the 30–37°θ range (2.97Å–2.42Å), and the FTIR study define the typical mineralogy of the cement mortars and also allow differentiation between old and recent cement mortars. These techniques reveal that natural and old Portland cements are poorer in aluminium than recent Portland cements, and for this reason, the presence of aluminates and ettringite is minimal. Moreover, recent Portland cements also undergo carbonation and sulphation more readily than the old cements.

FTIR shows the presence of pozzolans in natural cements. These pozzolans are abundant in SNC and absent in Portland cements. Hydration processes are slightly higher in Portland cements.

The petrographic microscope helps to determine that the old mortars studied are composed of a siliceous aggregate and a dense, massive, and micro- and cryptocrystalline binder. The natural (rapid) and Portland cement binders used for rendering purposes show a high degree of carbonation and porosity. Natural (SNC) and Portland cements that are set in the masonry are less carbonated and less porous. The RNC binder shows shrinking fissures (crazing) due to its rapid setting, while the SNC binder shows fissuring around the skeletal grain aggregates, possibly because of the high content in argillaceous compounds of the aggregates. In general terms, in all the cement mortars (natural and Portland), dissolution by corrosion of the edges of the skeletal grain aggregates has been detected. Such corrosion is caused by the alkaline nature of the surrounding matrix (binder). The less carbonated a matrix is, the more alkaline it tends to be (alkaline–aggregate reaction; masonry mortars).

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