

STUDY OF THE FIRST BOULOGNE-SUR-MER CEMENTS USED FOR A HISTORIC AQUEDUCT FROM THE 19TH CENTURY

ŠTUDIJA CEMENTOV BOULOGNE-SUR-MER, UPORABLJENIH V ZGODOVINSKEM AKVADUKTU IZ 19. STOLETJA

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Natural and Roman cements are generally considered as the first binders of the 19th century concrete but their widespread usage was short-lived as they were quickly replaced by artificial cements (Portland), still the most important and predominant today. The Boulogne-Sur-Mer area in the North of France is one of the cradles of the French cement industry where the first French natural cement was produced in 1802 and the first French Portland cement at around 1850. These cements, natural and artificial, quickly gained a national and international fame. This paper presents a case study of a 19th century aqueduct, still in operation, with a focus on identifying the binders of concretes and mortars. Several combined techniques – optical microscopy (OM), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) and X-ray diffraction (XRD) – were carried out to characterize and determine the compositions of the binders present in the aqueduct. Phenolphthalein tests were carried out in order to evaluate the depth of carbonation in the concrete. Several concrete and mortar samples, from pinkish to greyish ones, were taken from the outer and inner parts of the aqueduct. Results show several clinker morphologies and compositions, and different types of hydrates. They also reveal important differences in the microstructure between natural and Portland cement, dated from an early period of the cement industry in France. The concomitance of the use of natural and Portland cement, and good durability of these materials highlight the know-how of the engineers in the 1860s on cement performances and characteristics.

Keywords: natural cement, Portland cement, optical microscopy, scanning electron microscopy

Naravni in romanski cementi so splošno znani kot prva veziva v betonu iz 19. stoletja. Njihova široka uporaba je bila kratkotrajna, saj so jih hitro nadomestili umetni portlandski cementi, ki še danes prevladujejo v betonih. Območje Boulogne-Sur-Mer v severni Franciji je eno od zibelk francoske cementne industrije, kjer je bil prvi francoski naravni cement proizveden leta 1802, prvi francoski portlandski cement pa okoli leta 1850. Tako naravni kot umetni cementi iz Boulogne so hitro pridobili sloves dobrega proizvoda, na nacionalni in mednarodni ravni. Prispevek predstavlja študijo primera akvadukta iz 19. stoletja, ki je še vedno v uporabi, s poudarkom na identifikaciji veziva v betonih in maltah. Za karakterizacijo in določitev sestave veziv iz akvadukta je bila uporabljena kombinacija različnih tehnik optične mikroskopije OM, vrstičnega elektronskega mikroskopa sklopljenim z energijsko disperzijsko spektroskopijo SEM-EDS in rentgensko difrakcijo XRD. Globino karbonizacije smo ocenili s testom s fenolftaleinom. Različne vzorce betona in malte, katerih barva je bila od roza do sive, smo odvzeli iz notranjih in zunanjih delov akvadukta. Rezultati analiz so pokazali prisotnost različnih sestav in morfologij klinkerja ter različne vrste hidratacijskih faz. Rezultati prikazujejo tudi pomembne razlike v mikrostrukturi hidratacijskih faz med naravnimi in Portland cementi, ki so bili proizvedeni v zgodnjem času cementne industrije v Franciji. Sočasna uporaba naravnega in portlandskega cementa in dobra obstojnost teh materialov kažeta na visoko kvaliteto znanja in izkušnje inženirjev v 1860-ih letih, o lastnostih in zmogljivosti cementov.

Ključne besede: naravni cement, portland cement, optična mikroskopija, vrstična elektronska mikroskopija

1 INTRODUCTION

In 1796, James Parker discovered a clayey limestone nodule that sets with water after burning at a low temperature (1000 °C) in traditional vertical kilns. He patented his discovery and sold his cement under the name of "Roman cement".¹ Parker's patent activated the research of chemists in Europe. The French engineer Louis Vicat was the first to prove, in 1812, that the hydraulic proper-

ties of these binders were the result of a simultaneous combustion of limestone and clay in very specific proportions, depending on the chemistry of the materials. However, he published his results without filing a patent.

Historical data indicate that the applications of these cements were very broad (building constructions and the industrial field). However, numerous kinds of natural cements produced during the 19th century could also be of very different qualities, especially due to the variations in the composition of the original stones.² Their colors generally varied from brown to beige.³

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Figure 1: Historic aqueduct from the 19th century

Vicat's discovery also facilitated the development of their industrial production. Thus, following his work, many cement factories appeared. In France, similar stones were discovered at Boulogne-sur-Mer, leading to the first cement production. The product was known as "plâtre ciment". This expression recalls the properties of workability of plaster and the setting/resistance of the cement despite the obvious contradiction between both binders in the same product.⁴

Artificial Portland cement, obtained from a precise mix of clay and limestone extracted separately appeared in parallel with the development of natural cements. This development of artificial Portland cements led to a progressive decrease in the production of natural cements.² Today, Vicat is the only company to produce and market fast-setting natural cement, "prompt cement".

In France, the Portland cement manufacture began in 1846 in Boulogne-sur-Mer by Mr. Dupont and Mr. Demarle, and at around 1870 in Genevrey-de-Vif near Grenoble with vertical shaft kilns directed by Joseph Vicat (son of Louis Vicat). On May 1853, Mr. Dupont filed the first patent on the production of natural Portland cement. A fifteen-kiln factory was opened in 1859, located on the banks of Liane close to Boulogne-sur-Mer.⁵

The main differences between the two types of cements lie in the manufacturing process:

Natural cement – its lithology indicates 75–60 % of carbonates and 25–40 % of clay, which is crushed into tiny blocks between two temperatures, 800 and 1200 °C.

Early Portland cement – the raw feed, the so-called "cement stone", containing pure limestone (80–75 %) and clays (20–25 %) used to be mixed with water in big pools, and pressed into bricks before being burnt. The

composition of historical PCs always suggests a very heterogeneous heat distribution (800–1400 °C) during the firing.⁶

Many applications of Boulogne-sur-Mer cements have been identified in the constructions of buildings (bridges, aqueducts, etc.). According to old documents, several military, civil and cultural engineering works have used these cements, the most famous being the Eiffel Tower foundations.⁷ Unlike other historical French types of cement⁸, these types remain relatively unknown, and few studies have been devoted to them. In addition, their compositions and setting mechanisms are not well known.

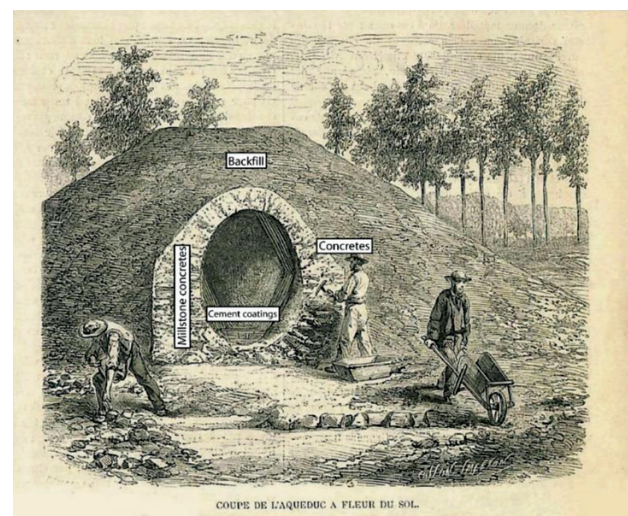


Figure 2: Section of the historic aqueduct from the 19th century (illustration from 1865)⁹

This paper presents a case study of a historic aqueduct from the 19th century where Boulogne-sur-Mer cement was used. This study aims at characterizing and identifying the binder of mortars used in the construction of the aqueduct from the 19th century, with a focus on anhydrous-grain characterizations. Such knowledge will allow an appropriate restoration of the cement-based materials that have survived until the present day.

The historic aqueduct from the 19th century was built with Boulogne-sur-Mer cements, from 1863 to 1865 at the request of Napoleon III (1808–1873) to convey water from the north-east of the Parisian area to Paris (**Figure 1**). The aqueduct is covered with a 10-meter wide grassy strip and vegetation on both sides, forming a true ecological corridor. The total length of the aqueduct is 128.61 km. The water circulation is allowed by a natural slope, using the "siphon" effect with a flow of 230 liters of water per second. This aqueduct is built of rough stone blocks. Both the interior and exterior are protected by cement and concrete linings (**Figure 2**).

2 EXPERIMENTAL PART

2.1 Sampling

Several representative locations were selected for the sampling. Three pinkish-colored concretes sampled at different levels were referred to as:

- sample B1 from the inner section of the vault,
- sample B2 from the intrados (inner curve of an arch) face,
- sample B3 from the bottom of the aqueduct.

Additional sample B4 (rather grey) was taken from the external face of the aqueduct vault.

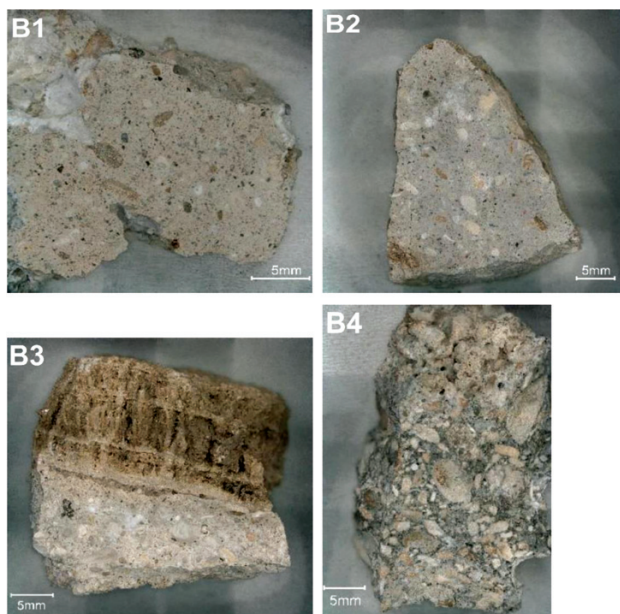


Figure 3: Presentation of the ancient-concrete samples from the historic aqueduct

2.2 Analytical methods

In order to characterize the concretes from the selected locations and, in particular, to identify the binders used, several types of analyses were carried out. Preliminary phenolphthalein (1 % concentration in ethanol) was sprayed on freshly fractured samples to distinguish carbonated from non-carbonated areas. Then, crystallized phases were determined with X-ray diffraction, using a Bruker D8 with long-time acquisition parameters (a step size of 0.02°, step time of 2 s). The analysis was carried out on powders of crushed cement paste, obtained after the separation of the cement matrix from the aggregates by sieving and hand picking (the samples were gently crushed, then the aggregates were sieved and separated from the cement paste under the microscope).

Mortar microstructures were observed on polished sections, using a reflected light optical microscope (Leica DMRXP) and a scanning electron microscope equipped with an EDX detector (JEOL IT 300). The polished plane sections were prepared from the samples impregnated under vacuum with a low-viscosity epoxy resin.¹⁰ The SEM-EDX analysis in the backscattering electron (BSE) mode was used on polished sections to determine their elemental composition at a working distance of 10 mm.

3 RESULTS

3.1 Macroscopic observations and phenolphthalein tests

To identify the non-carbonated areas of concrete, phenolphthalein spraying was performed in situ on the samples taken. Due to phenolphthalein, the treated samples became pink. It allowed us to identify the more basic pH areas corresponding to the non-carbonated domains. The B4 sample is essentially composed of a sandy fraction completed by large aggregates. On the other hand, the three pinkish samples (B1, B2 and B3) show much smaller sandy fractions than the other loca-



Figure 4: 3D rendering of the ettringite crystals in the pores

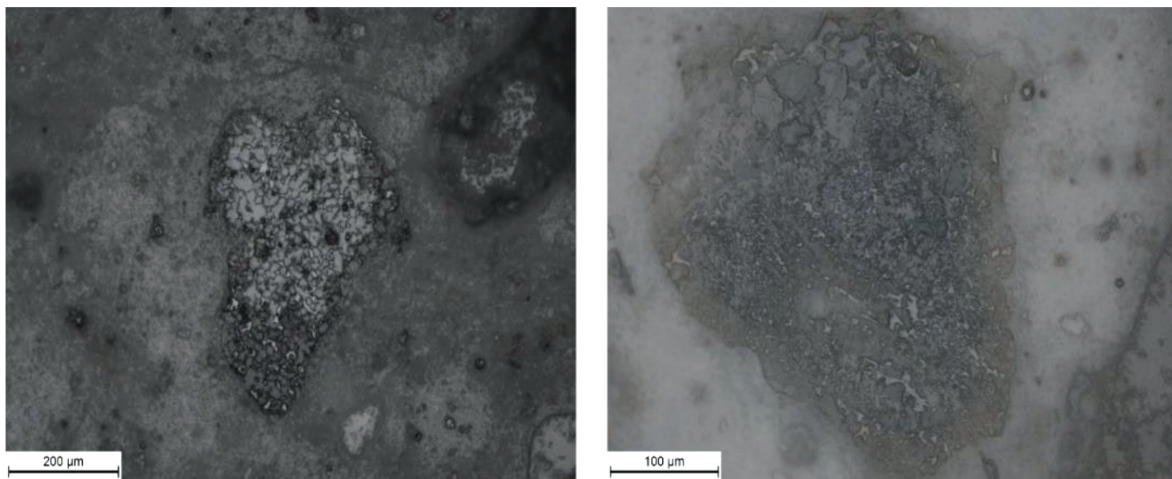


Figure 5: OM view using reflected light; anhydrous grains of clinker on a polished section; B1 sample

tions. These samples have a very rich binder with small quartz grains, compared to the grey cement samples (Error! Reference source not found.). Ettringite crystals (Figure 4) were observed in the pores of sample B1. Ettringite was predominantly in the form of fibers, but scattered needles were also identified.

3.2 Crystallized phases determined with the XRD analysis

The crystallized phases of different samples were identified with X-ray diffraction. The results of these analyses are shown in Table 1 below. According to these analyses, the nature of the identified minerals is almost identical for all the pinkish concretes (B1, B2 and B3). All four samples are non-carbonated. The non-carbonated zones of these four samples are composed mainly of calcite, ettringite and other calcium aluminates, commonly found in the B1, B2 and B3 samples. Gypsum was not detected in the four samples. The anhydrous phases present in the pinkish samples are rankinite, C₂S, C₄AF and C₃A with a high Al content. Alite is absent

Table 1: Crystallized phases identified for each sample

	B1	B2	B3	B4
Carbonation	no	no	no	no
Calcite CC	++	++	++	+++
Quartz SiO ₂	++	++	++	+++
Larnite C ₂ S	++	++	++	+
Alite C ₃ S	∅	∅	∅	++
Browmillerite C ₄ AF	+	+	+	+
Hydrocalumite C ₄ AH ₁₃	+	+	+	∅
Ettringite C ₆ A ₃ H ₃₂	++	++	++	+
Portlandite Ca(OH) ₂	∅	∅	∅	++
Anorthite CaAl ₂ Si ₂ O ₈	+	+	+	∅
Rankinite C ₃ S ₂	+	+	+	∅

Note: significant presence (+++), average presence (++), traces (+), absence (∅)

from the B1, B2 and B3 samples. On the other hand, in the grey cement concrete (B4), alite and belite crystals were detected. The B4 sample is characterized by an important presence of portlandite, which is absent from the pinkish samples.

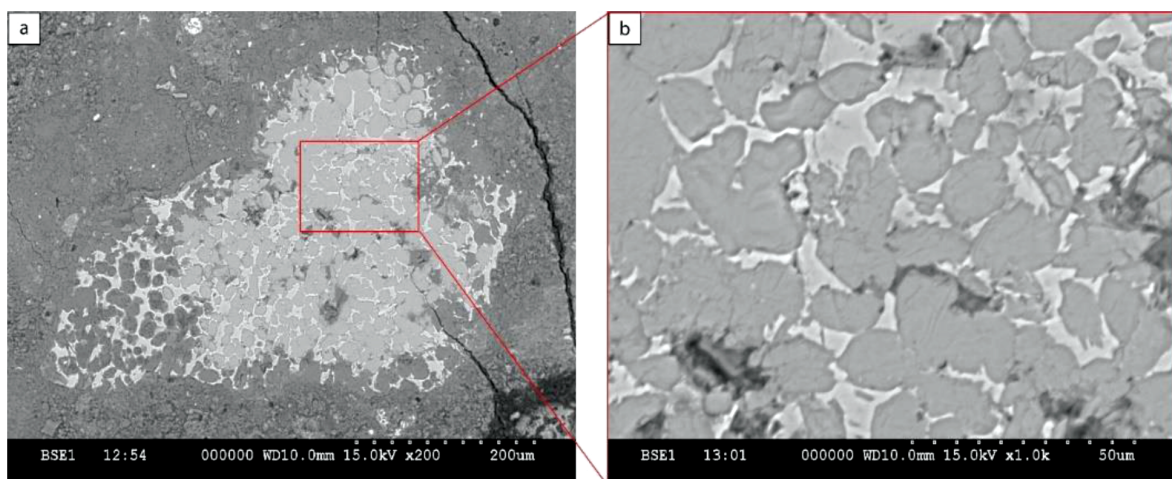


Figure 6: BSE-SEM of B1 sample: a) clinker grains; b) clinker-grain details

3.3 Identification of the anhydrous grains

3.3.1 Pinkish-colored concretes

The anhydrous grains shown in **Figure 5** are the most representative of the pinkish-colored concrete. They measure about 200–500 μm . They are mainly composed

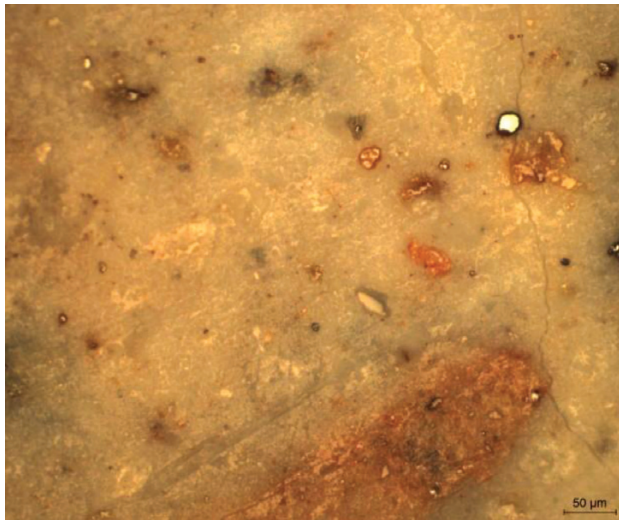


Figure 7: OM view using reflected light; iron-bearing compounds; B1 sample

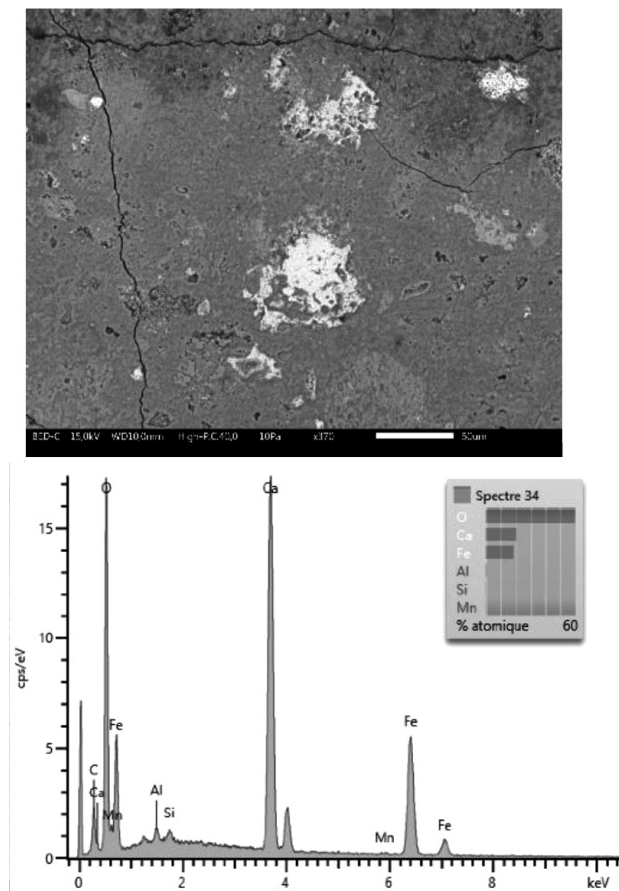


Figure 8: BSE-SEM view; iron-bearing compounds; B1 sample

of weakly crystallized calcium silicates, with more or less visible contours. The binding matrix is a mono-phase and it is very clear. It is only rich in iron. These grains present very few binding phases. SEM observations coupled with EDS (**Figure 6**) confirm the presence of C_2S . The crystallizations of these grains are irregular and heterogeneous.

Iron-bearing compounds are also noted. The OM observations showed the presence of red-colored iron oxides, as shown in **Figure 7**. SEM observations coupled with the EDS chemical analysis of these compounds show that they contain mainly iron and calcium oxides with low contents of Si, Mn and Al (**Figure 8**).

3.3.2 Grey-colored concrete

Three types of anhydrous grains were observed and characterized on sample B4.

Type-1 grains are mainly composed of bi- and tri-calcium silicates (**Figure 9a**). It should be noted that C_2S are more or less circular, with parallel striations, thus this is type II of C_2S crystals.¹¹ Type-2 grains are mainly composed of aluminate phases in platelets and poorly crystallized calcium silicates. Optical and scanning electron microscope observations are presented in **Figure 9b**. Finally, important amounts of C_3A and C_4AF were observed in type-3 grains (**Figure 9c**).¹²

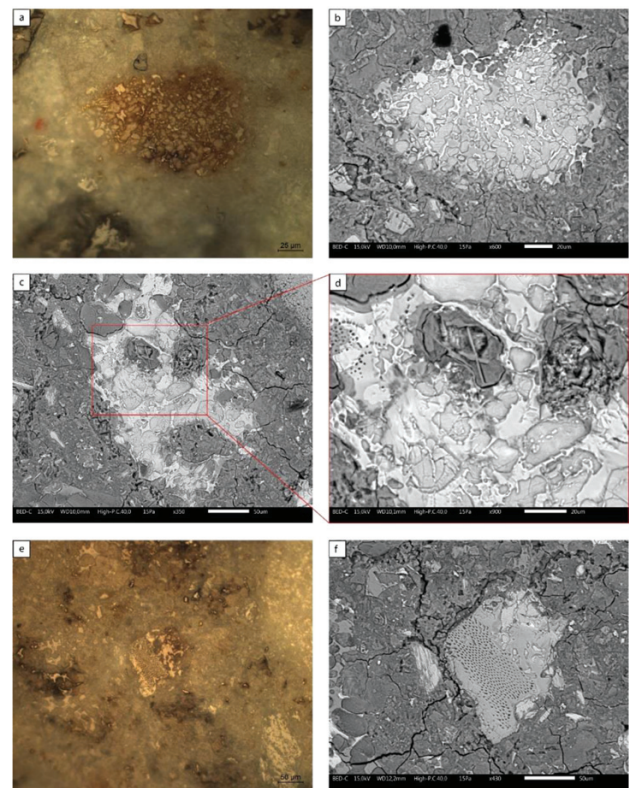


Figure 9: Photomicrographs of anhydrous grains of clinker on the polished section, B4 sample: a) OM view, type-1 clinker grains; b) BSE-SEM view, type-1 clinker grains; c) BSE-SEM view, type-2 clinker grains; d) BSE-SEM view, type-2 clinker-grain details; e) OM view, type-3 clinker grains; f) BSE-SEM view, type-3 clinker grains

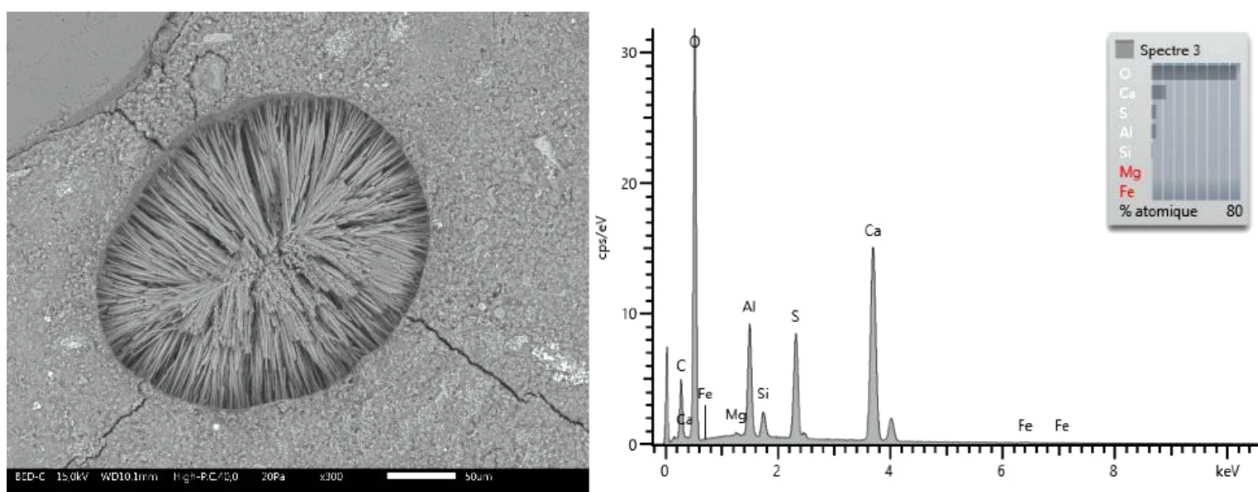


Figure 10: BSE-SEM view, ettringite, B1 sample

3.4 Hydrated phases

SEM observations of the non-carbonated zone were carried out on the B1 concrete sample. Numerous ettringite crystallizations are mainly located in the paste and in the pores. **Figure 10** shows ettringite crystals in the form of well-crystallized needles, in the pores of the B1 sample.

4 DISCUSSION

Microstructural and physical characterizations of these concretes from the selected locations were carried out. The main phases identified with the XRD analyses for the pinkish samples (B1, B2 and B3) of the historical aqueduct are similar.

Indeed, the XRD analyses indicated the presence of rankinite, C_2S , C_3A and C_4AF in the three concretes (samples B1, B2 and B3). Alite was not detected. According to Rankin and Wright¹³, rankinite is formed at temperatures below 1200 °C. Hydrocalumite C_4AH_{13} was also identified through XRD in the pinkish-colored concretes (samples B1, B2 and B3). In terms of hydrated phases, the XRD analysis and SEM observations revealed the presence of ettringite in samples B1, B2 and B3. Ettringite is localized in the paste and in the pores. Optical microscopic observations and scanning electron microscopic analyses identified anhydrous grains mainly composed of C_2S , C_3A and C_4AF . Their structure is poorly crystallized. Alite crystals were not detected. The shape of C_2S is very irregular. During firing, dicalcium silicate (C_2S) crystallizes between 900 °C and 1200 °C.¹³ All these analyses showed that the pinkish-colored concretes were based on fast-setting natural cement.

The grey concrete (B4) is poorer in aluminium (hydrocalumite was not detected) than the concretes based on natural types of cements (B1, B2 and B3). In the B4 concrete, the anhydrous phases are mainly composed of C_3S , C_3A , C_4AF and some C_2S whereas in the

natural-cement concretes (B1, B2 and B3), C_2S , C_3A and C_4AF were mainly observed. Concerning the hydrated phases, the presence of portlandite was mainly detected with the XRD analysis in sample B4 and few ettringite crystals were identified. On the contrary, the hydrated phases observed in natural cements (B1, B2 and B3) correspond to the ettringite crystallization while portlandite was not detected. So, according to these analyses, the cement used in the B4 concrete corresponds to Portland cement.

5 CONCLUSION

This article provides new findings on the microstructural and physical characterization of the cements produced in the first French plants during the 19th century. The structures were built with Boulogne-sur-Mer cement. The location and identification of these buildings were identified with the help of the indications given in old documents. This article presents a case study of a historic aqueduct from the 19th century using this cement. Samples were taken from the interior (B1, B2 and B3, pinkish-colored concretes) and exterior of this aqueduct (B4, grey-colored concretes). Microstructural and physical analyses of the concretes from selected locations were presented. Several characterization techniques were used: SEM observations, optical microscopy and X-ray diffraction. These analyses revealed mainly two categories of the binder: natural cements and cements close to the Portland type.

The absence of portlandite, a strong presence of the ettringite zone, the presence of rankinite, limited presence of alite and poorly crystallized anhydrous grains clearly indicated that the binder used in the pinkish-colored concretes (B1, B2 and B3) was a natural cement, rich in aluminates, and the calcination temperature was lower than 1200 °C.

In the case of the B4 concrete, the co-existence of three types of anhydrous grains, as well as the presence

of portlandite and alite confirmed that the binder used in this concrete was close to Portland cement.

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