

Natural cement and stone restoration of Bourges Cathedral (France)

Cimento natural e restauro de pedra na Catedral de Bourges (França)

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Abstract

Natural cement, also called “Roman cement”, was invented at the end of the 18th Century and played an important role in the development of civil engineering works until the 1860s. More surprisingly, it was also used to restore historic buildings, such as gothic cathedrals. This paper deals with the mineralogy and the durability of natural cement, in the particular case of the Bourges Cathedral in France. This study illustrates the interest of this material particularly adapted in stone repair or substitution. Contrary to traditional mortars, the present samples are made of neat cement paste, revealed by the absence of mineral additions as quartz or carbonate sand. Several combined techniques (SEM-EDS, TGA, XRD) were carried out to determine the composition of the hydraulic binder rich in calcium aluminate hydrates. The raw marl at the origin of the cement production contains oxidized pyrites which consist in a potential source of sulphate pollution of the surrounding limestone. The exposition of the cement in urban environment leads to some weathering features as atmospheric sulphation. Finally a petrophysical approach, based on water porosity, capillary sorption and compressive strength, has been performed to demonstrate the durability and the compatibility of roman cement applied as a restoration mortar of historical building.

Keywords

Bourges Cathedral; durability; mineralogy; natural cement.

Resumo

O cimento natural, ou “cimento romano”, foi inventado no final do século XVIII e desempenhou um papel importante no desenvolvimento de obras de engenharia civil até à década de 1860. Surpreendentemente, foi também utilizado no restauro de edifícios históricos, incluindo catedrais góticas. O presente artigo incide sobre a mineralogia e a durabilidade do cimento natural, no caso particular da Catedral de Bourges, em França. Este estudo ilustra o interesse deste material, particularmente adaptado à reparação ou substituição de pedra. Ao contrário de argamassas tradicionais, as presentes amostras foram executadas com pasta de cimento limpa, revelada pela ausência de adições minerais como areias de quartzo ou calcário. Foi utilizada uma combinação de diversas técnicas (SEM-EDS, TGA, XRD) para determinar a composição do ligante hidráulico, rico em hidratos de aluminato de cálcio. As margas cruas que originaram o cimento continham pirites oxidadas, que constituem potenciais fontes de contaminação por sulfatos para o calcário circundante. A exposição do cimento em ambiente urbano levou a algumas características de alteração como a sulfatação atmosférica. Finalmente, foi conduzida uma abordagem petrofísica, baseada na porosidade acessível à água, absorção capilar e resistência à compressão, para demonstrar a durabilidade e a compatibilidade do cimento romano quando aplicado como argamassa de restauro em edifícios históricos.

Palavras-Chave

Catedral de Bourges; durabilidade; mineralogia; cimento natural.

■ Introduction

Natural cements, sometimes called “Roman Cements” were discovered at the end of the 18th Century in England [1,2]. Those hydraulic binders, originating from the calcination of marl stones, were used principally for works where rapid set and waterproof properties were required. Their discovery spread quickly all over Europe, where several quarries were found out during the 19th Century. Their properties made these cements of great help in buildings construction, particularly in civil engineering applications, until the development of artificial Portland cements in the 1870s. A minor use emerged in the field of restoration of historic buildings because of specific properties of natural cement, as strong as stone, with a similar colour, but cheaper, at a time when restoration campaigns increased in scale. Some architects were also eager for experiments with new materials and techniques. Dating from the 13th Century and located in central France, the cathedral of Bourges is one of the best examples of the use of natural cements. The cements came from the first quarries discovered in France, in 1824 at Pouilly-en-Auxois and in 1830 at Vassy-les-Avalon (Burgundy). These cements and particularly the one from Vassy, were employed from 1824 to the 1860s, for basement waterproofing masonry, stones repointing mortar and sculpture repair [3].

The literature [4-11] reveals many scientific studies on the different materials employed in the 19th Century. Table 1 gathers several data on the chemical composition of different natural cements, compared to limes and Portland cements. From table 1, Vassy and Pouilly cements show a homogeneous aluminium oxide Al_2O_3 content close to 10 %, while the content of calcium and silica oxides (CaO and SiO_2) are more fluctuating, according to the production sites. The process of natural cement required the firing of marl stones at a temperature estimated between 1000 and 1100°C [3]. The variations in the oxides composition in table 1 may originate from the nature of local marl banks used for the cement production as well as from the quality of the firing process. The other French production sites provide natural cements with a constant composition in the main oxides. Whereas SiO_2 and Al_2O_3 contents are consistent with the Vassy and Pouilly ones, the significant difference resides in the CaO content, slightly lower for the other

origins of natural cement. The European and US natural cements are characterized by a large dispersion in silica and calcium. These fluctuations between the European productions sites reveal an actual requirement of gathering and standardization of limes and cements composition, as initiated in France by Vicat, from 1818.

The literature mentions Portland cements as slow cements in comparison with natural cements, called rapid cements. The opposition in this nomenclature is linked to the setting time of the respective binders. Indeed, Portland cement setting time is controlled by the addition of a small amount of calcium sulphate (less than five percent weight of cement is substituted by gypsum). In contrary, natural cements are not added with calcium sulphate, implying a very quick set. By pursuing table 1, Portland cements differ from natural cements by the Al_2O_3 content, slightly lower in the first case (from 5 to 10 %) and, secondly, by a more controlled CaO amount (from 65 to 70 %) in Portland cement.

Research into natural cements as materials used in the monumental restoration is a new subject, because the use of such materials has been recently rediscovered and their historicity has been taken into account. At Bourges, the presence of natural cement on central and southern portals (figures 1 and 2) has been revealed the last decade [12, 13], during successive preliminary studies for the occidental facade restoration. In 2005, the French Laboratory of Research of Historical Monuments (LRMH) has worked out a scientific study of this cement

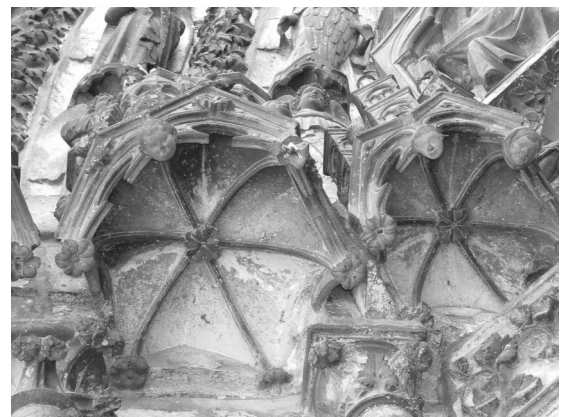


Fig. 1 Head and flower shape ornamentations made in natural cement, under a dais (cl. C. Gosselin 2005). In the centre, apparent iron bar shows the sealing system using plaster.

Table 1 Chemical composition of different hydraulic binders used for construction in the 19th Century, after [4-11]

Nature of hydraulic binder		Origin, plant and authors	Oxyde Composition (weight %)						
			CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	Fe ₂ O ₃	SO ₃
Natural cement Vassy and Pouilly	1	Vassy-les-Avallon [9]	59.60	6.80	17.75	-	-	7.35	4.08
	2	Pouilly en Auxois [9]	49.60	10.00	26.00	-	-	5.10	0.69
	3	Vassy-les-Avallon [8]	56.60	6.90	21.20	1.10	13.70	-	-
	4	Vassy [5]	52.05	8.40	20.00	0.95	5.70	-	2.29
	5	Vassy-les-Avallon [10]	50.90	9.30	20.30	0.30	5.50	-	2.86
	6	Vassy-a [7]	52.69	8.90	22.60	1.15	5.30	-	2.65
	7	Vassy-b [7]	50.68	8.76	23.50	1.80	5.65	-	3.29
	8	Vassy-c [7]	44.12	7.00	24.80	2.08	4.80	-	2.94
	9	Vassy-d [7]	52.20	9.60	22.40	1.44	4.76	-	3.13
	10	Pouilly [7]	46.10	10.39	26.80	1.72	4.61	-	1.42
	11	Vassy (plant Dumarcet) [11]	48.06	10.14	20.26	0.90	-	4.44	2.87
	12	Vassy (Rotton) [11]	46.70	9.64	20.14	1.10	-	4.86	2.86
	13	Vassy (Faure) [11]	43.46	10.80	22.82	1.60	-	4.24	1.80
	14	Vassy (plant Millot) [11]	49.90	10.52	20.10	1.06	-	4.00	3.18
	15	Vassy (plant Voyot) [11]	46.04	9.66	21.16	0.97	-	5.12	2.58
	16	Vassy (plant Prevost) [11]	50.14	9.76	19.74	1.18	-	4.94	2.89
	17	Vassy (plant Bougault) [11]	49.46	8.76	19.70	0.86	-	4.98	3.31
	18	Vassy (plant Détang) [11]	42.34	12.32	26.52	1.54	-	3.92	1.34
Other French natural cements	19	L'Albarine (Ain) [4]	47.95	9.25	23.45	1.45	-	3.83	0.57
	20	Argenteuil (Seine-et-Oise) [4]	47.50	8.35	29.55	3.85	-	4.10	1.10
	21	La Bédoule (Bouches-du-Rhône) [4]	49.05	11.60	23.45	1.05	-	4.75	1.02
	22	Cahors (Lot) [4]	50.65	10.75	28.20	1.05	-	3.50	1.71
	23	Champréau (Yonne) [4]	52.05	8.40	21.00	1.00	-	5.10	2.04
	24	Chanaz (Savoie) [4]	46.50	8.95	23.25	1.60	-	4.15	1.14
	25	Chouard-Angély (Yonne) [4]	47.70	12.90	23.40	1.05	-	3.30	2.69
	26	Courterolles (Yonne) [4]	49.15	9.15	22.15	0.7	-	5.45	2.00
	27	Fresnes (Seine) [4]	46.05	7.95	29.05	2.80	-	3.75	0.90
	28	Guétary (Basses-Pyrénées) [4]	53.80	8.85	25.10	1.15	-	3.05	0.94
	29	La Valentine (Bouches-du-Rhône) [4]	47.85	10.85	24.55	1.60	-	5.20	1.31
	30	La Valentine La Méditerranée (Bouches-du-Rhône) [4]	48.60	12.50	29.10	1.70	-	4.65	1.55
	31	La Valentine Ile du Rocher Bleu (Bouches-du-Rhône) [4]	50.45	11.35	24.65	1.15	-	5.25	1.02
	32	Vimines (Savoie) [4]	49.70	9.50	25.50	2.55	-	4.35	1.14
	33	Warcq (Ardennes) [4]	48.70	4.10	27.40	0.65	-	3.75	0.78
	34	Boulogne [9]	49.29	9.58	28.02	2.58	5.73	-	0.42

Nature of hydraulic binder	Origin, plant and authors	Oxyde Composition (weight %)						
		CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	Fe ₂ O ₃	SO ₃
European and US natural cements	35 Krienberg (D) [6]	58.38	6.40	28.83	5.00	-	4.80	-
	36 Sheppey (GB) [6]	55.50	6.96	25.00	1.73	-	6.63	-
	37 Tarnowitz (P) [6]	47.83	1.50	5.80	24.26	-	20.80	-
	38 Hausbergen (Alsace) [6]	58.88	7.24	23.66	2.25	-	7.97	-
	39 Medina Parker Nouveau [9]	43.45	5.60	19.50	13.95	-	12.15	0.65
	40 Zumaya (ES) [7]	33.04	7.82	30.80	0.93	-	5.13	2.37
	41 San Sebastien (ES) [9]	38.34	17.53	37.65	0.00	-	-	2.73
	42 Cumberland (US) [7]	36.12	10.66	29.40	2.42	-	5.37	1.55
	43 Rosendale (US) [7]	33.02	7.16	27.50	19.50	-	4.64	1.09
	44 Lehigh (US) [7]	48.24	9.12	24.10	2.42	-	3.18	1.34
	45 Kentucky (US) [7]	43.40	4.82	23.00	12.80	-	3.18	1.81
	46 Podolski, société Moscou [7]	40.15	0.00	16.66	18.19	-	6.84	1.83
Low hydraulic limes	47 Ablancourt (Marne) [4]	59.50	4.90	12.20	0.90	-	2.50	-
	48 Beaume (Côte-d'Or) [4]	60.90	1.75	13.85	0.70	-	1.35	0.16
	49 Les Côtes d'Alun (Haute Marne) [4]	61.70	5.65	13.35	1.43	-	2.75	0.16
	50 Malain (Côte d'Or) [4]	65.85	4.45	10.60	0.50	-	1.35	0.65
	51 Fresnes (Seine) [4]	59.00	5.80	11.63	0.30	-	2.05	0.73
	52 Les Ormes (Vienne) [4]	64.50	3.05	9.80	0.80	-	1.30	-
	53 Cardalou (Tarn) [4]	67.30	3.60	13.60	3.20	-	2.35	0.49
	54 Doué (Maine-et-Loire) [4]	63.85	2.90	14.35	0.80	-	2.20	0.33
	55 Echoisy La Grave (Charente) [4]	59.20	4.60	11.70	1.40	-	2.30	-
	56 Massay (Cher) [4]	64.75	2.40	10.30	0.85	-	1.45	0.73
Hydraulic limes	57 Les Pomets (Var) [4]	62.40	4.75	12.15	0.75	-	1.60	0.57
	58 Argenteuil (Seine et Oise) [4]	56.80	5.20	17.85	1.35	-	2.40	1.06
	59 Bar sur Seine (Aube) [4]	59.20	5.20	17.30	1.90	-	2.60	-
	60 La Bédoule (Bouches-du-Rhône) [4]	58.80	3.45	16.80	0.85	-	3.45	0.57
	61 Beffes (Cher) [4]	61.35	4.25	13.50	1.05	-	3.20	0.37
	62 Bougival (Seine et Oise) [4]	57.80	5.00	16.35	1.00	-	2.10	0.09
	63 Les Cordeliers (Vienne) [4]	60.60	6.25	13.65	1.45	-	2.35	0.78
	64 Cruas (Arcèche) [4]	65.80	2.00	21.60	0.35	-	1.25	0.12
	65 Saint Astier (Dordogne) [4]	62.25	1.35	21.85	1.05	-	2.83	0.41
	66 Saint Michel (Savoie) [4]	62.20	5.40	14.20	2.40	-	2.10	-
High hydraulic limes	67 Lafarge du Teil (Ardèche) [4]	63.76	1.72	23.13	0.97	-	0.73	-
	68 Albi (Tarn) [4]	49.40	6.30	19.60	5.75	-	2.60	0.29
	69 Bertaucout (Ardennes) [4]	47.85	4.20	19.35	0.60	-	3.45	1.31
	70 Chanaz (Savoie) [4]	54.85	7.85	18.10	1.30	-	2.50	0.78

Nature of hydraulic binder		Origin, plant and authors	Oxide Composition (weight %)						
			CaO	Al ₂ O ₃	SiO ₂	MgO	FeO	Fe ₂ O ₃	SO ₃
French Portland cements	71	Charleville (Ardennes) [4]	47.85	4.55	21.85	0.75	-	3.75	0.86
	72	Chatenoy (Haut-Rhin) [4]	57.90	9.25	21.95	0.25	-	3.20	0.08
	73	Côtes d'Alun (Haute-Marne) [4]	54.00	7.75	16.30	0.30	-	1.65	2.49
	74	Sigonce (Basses-Alpes) [4]	55.65	3.70	20.80	0.25	-	1.95	0.94
	75	Virieu-le-Grand (Ain) [4]	56.10	5.75	19.90	1.50	-	2.70	0.82
	76	Argenteuil (Seine et Oise) [4]	57.90	8.50	24.50	1.50	-	4.25	0.65
	77	Bassin Paris (Seine) [4]	59.80	9.35	22.30	1.15	-	3.90	0.41
	78	Boulogne-sur-Mer (Pas-de-Calais) [4]	59.40	7.20	24.10	0.95	-	3.35	0.43
	79	Campbon (Loire Inférieure) [4]	51.80	9.65	18.75	12.95	-	3.80	0.49
	80	Charleville (Ardennes) [4]	51.30	4.70	23.65	0.25	-	4.35	1.39
	81	Chouard-Angély (Yonne) [4]	49.40	9.05	22.60	0.90	-	5.95	2.82
	82	Frangy (Yonne) [4]	63.70	7.53	21.61	1.22	-	3.17	0.50
	83	Marseille (Bouches-du-Rhône) [4]	53.00	7.60	19.90	1.20	-	3.60	0.65
	84	Saint-Bazille (Hérault) [4]	60.85	9.55	22.10	1.30	-	4.25	0.78
	85	Lafarge du Teil (Ardèche) [4]	59.10	3.25	25.70	0.95	-	1.40	0.24
	86	Tenay (Ain) [4]	53.25	6.90	24.30	1.70	-	3.85	0.57
	87	La Valentine (Bouches-du-Rhône) [4]	50.45	8.60	21.25	2.05	-	4.20	1.35
	88	Candlot [11]	63.70	8.30	19.50	0.74	-	3.30	0.51
	89	Sollier [11]	64.03	6.03	22.30	0.97	-	2.94	0.65
	90	plant A [11]	63.23	7.80	22.03	0.97	-	2.57	0.76
	91	Couronne [11]	64.33	6.26	21.70	1.10	-	2.47	0.71
	92	Darsy [11]	60.35	9.30	21.35	0.90	-	2.30	0.98
	93	Cambier [11]	63.05	7.80	20.75	0.75	-	3.03	0.61
	94	Delbende [11]	63.40	8.30	21.07	1.10	-	2.47	0.54
	95	Cie Nouvelle [11]	62.68	8.32	22.00	0.80	-	2.23	0.53
	96	plant B [11]	62.95	8.15	22.05	0.85	-	2.40	0.74
	97	Quillot [11]	64.00	8.30	20.00	1.65	-	2.15	0.29

applied in Bourges Cathedral [14, 15]. The characterization aimed at better understanding the composition and physical properties of the material, in order to select the most appropriate restoration product and procedure for both natural cement and adjacent stones in the Bourges monument.

■ Sampling and experimental techniques

■ ■ Sampling

By the end of the 20th Century, many fragments of decayed stones and mortars were about to fall on the cathedral forecourt [12]. Due to long lasting and severe stone and mortar decay, many pieces of repointing mortar and sculptures made of natural cement were

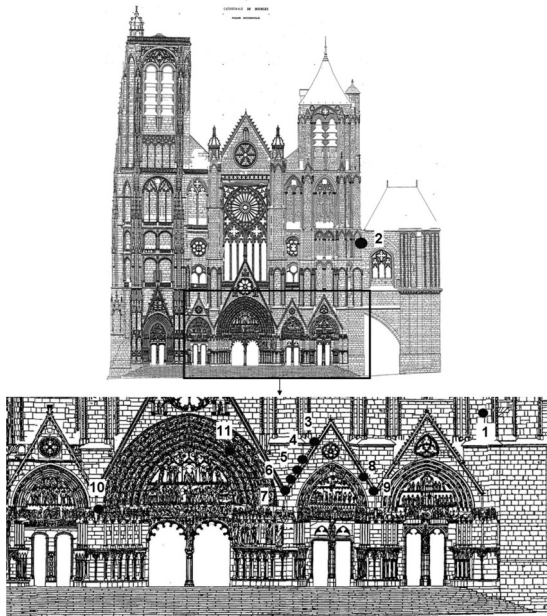


Fig. 2 Location of samples on the occidental façade (scheme from Société Française de Stéréotopographie 1969). The view of central and southern portals is detailed to locate the samples.

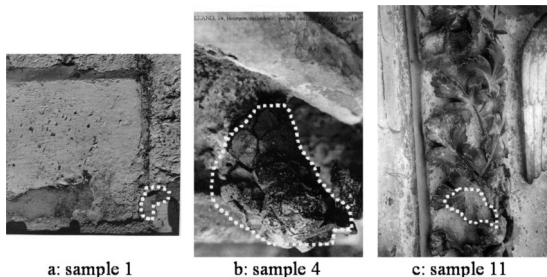


Fig. 3 Different natural cement applications on the cathedral: a-stone repointing (cl. O. Rolland 2001), b-hook shaped sculpture (cl. O. Rolland 2001), c-leaf shaped sculpture (cl. V. Verges-Belmin 2003).

removed in 2001 within the frame of a safety removal campaign. The present 11 samples were selected amongst the pieces collected during this campaign and are located in figure 2.

Sample 1 (Fig.3-a) is a fragment of repointing mortar while samples 3 to 11 come from ornamentation sculptures standing on the third portal gable (Fig.3-b) or on the central portal vaults (Fig.3-c). Only one sample of lime-stone (sample 2) comes from a hook shaped sculpture.

Experimental techniques

The present experimental procedures are inspired from the literature on historical mortars characterization [16-19]. Preliminary phenolphthalein (concentration 1 %) was pulverized on freshly fractured samples to distinguish carbonated from non carbonated areas. The latter were then preferentially studied, in what concerned the mineralogy of the cementitious matrix, because their content of calcium carbonate is lesser [20].

Mortar macrostructure was observed on thin and polished sections, using natural or polarised reflected light optical microscopy (Leica DM) equipped with a digital camera.

The microstructure was observed by scanning electron microscopy (JEOL JSM 5600 LV) and analysed by electron probe microanalysis. Backscattered electron technique (Low Vacuum 17 Pa, 15 kV acceleration voltage) on polished sections was used for elementary chemical analysis. Secondary electron imaging, on carbon coated fresh fractures (High Vacuum, 25-30 kV acceleration voltage), provided high resolution images of the microstructure morphology.

Crystallized phases were determined by X-ray diffraction, using a Brücker D8 Advance diffractometer (100µm sieved fraction powder method, Cu tube, 2theta = 5-65°) with long time acquisition parameters (step size = 0.01°, step time = 10s, rotation speed = 10 rpm).

A complementary mineralogical analysis was performed by the LERM in Arles. This includes a chemical analysis of the acid soluble fraction (HNO₃ 1:50) according to the protocol described in [18]. A complementary thermogravimetric/differential thermal analysis (TGA/DTA Netzsch), until 1000°C and under N₂ atmosphere is used. These coupled methods aim at determining the mineralogical composition of the mortar. The computation principle is based on oxides Bogue calculation and the results are expressed in weight percent of binder, aggregate and carbonated fraction [21]. This qualitative and quantitative approach, usually known as "Calcul Minéraux LCPC" method, was applied only on sample 8.

The separation of aggregates from hydraulic binder was performed using diluted (1:3) HCl acid etching [16]. After etching, the filtrate was rinsed with distilled water, dried and weighted before optical observation and XRD analysis.

Petrophysical characterization of cement and limestone has been comparatively done on prismatic specimens. The total porosity N_t , the 48 hours porosity N_{48} and the kinetics of capillary rise were measured according to the Rilem recommendations [22].

Finally, compressive strength tests were performed using an Instron 5500R hydraulic press, and managed at a controlled displacement rate of 0.5 mm/min.

In this article, the chemical formulas of phases are simplified using the cementitious notations for oxides: C: CaO; \bar{C} : CO₂; S: SiO₂; \$: SO₃; A: Al₂O₃; H: H₂O.

■ Results

■ ■ Macroscopic observations

Cement samples present common weathering forms, such as biological colonization (lichens, mosses) or black crusts, as a signature of rich sulphur urban atmosphere on calcareous materials [23]. Some samples present a network of deep cracks but no corrosion products have been observed, especially in the casting marks of the copper sealing rebars.

The samples present an original aspect and show a very fine, beige coloured and homogenous texture. In most cases a sub-millimetre thick brownish oily-aspect layer underlines the surface, as previously observed by Weber [24] on roman cement mortars sampled from European monuments. Traditional repair mortars contain mineral additives (sand, stone powder, pozzolans and/or tile fragments) but the matrix of our samples does not contain any of these coarse inclusions. Given these preliminary observations, all available specimens seem to come from the same restoration campaign. While the general texture looks similar for every sample, some nuances of colour are distinguishable in the matrix. After pulverising phenolphthalein solution on fresh fractures, this difference coincides with carbonated and non carbonated areas.

■ ■ Microstructure

The microstructure has been investigated using optical and scanning electron microscopy on thin and polished sections. From optical examination, the matrix is com-

posed of a binder including distinct and small inclusions. The porosity is defined by spherical and oblong pores with a large range of sizes, from 50 µm to 1 mm, and with a mean diameter estimated at 200 µm. The few microcracks, probably originating from preparation artifacts, are isolated and do not constitute a well defined network.

Optical microscopic exams are performed on polished sections etched by borax. This etching method reveals the major mineral phases like clinker grains not reacted with water during or after the mixing of mortar. Figure 4 shows two types of anhydrous grains of cement (50 to 200 µm size) present in the matrix. The first type of encountered cement grains, illustrated in Fig 4-a, is composed of blue to brown spherical and oblong particles in a white matrix. These spherical particles represent mainly dicalcium silicate grains (C₂S) contained in a white colored solid solution composed of calcium-aluminates such as tetra-calcium-alumino-ferrite (C₄AF) [25, 26]. The second type of anhydrous clinker grain is illustrated in Fig. 4-b. These grains are only composed of calcium-aluminates such as tricalcium-aluminates (C₃A, grey coloration) or tetra-calcium-alumino-ferrite (C₄AF, white coloration).

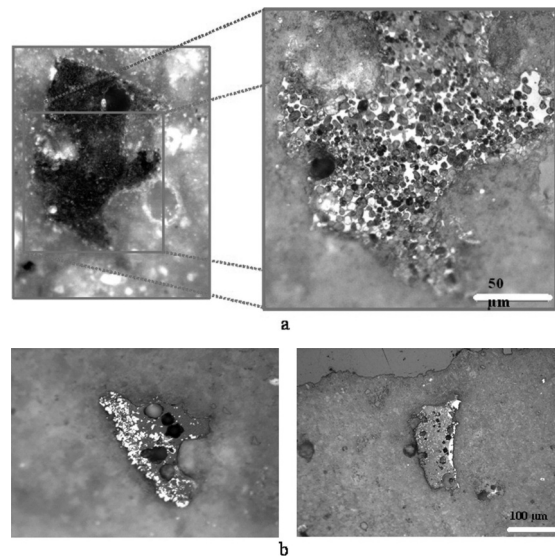


Fig. 4 Photomicrograph of anhydrous grains of clinker on etched polished section – a/: reflected natural light (left) and reflected polarized light (right) to show rounded C₂S grains in a (white) rich C₄AF matrix – b/: reflected polarized light view (grey) C₃A and (white) C₄AF rich grains clinker.

The rarity of clinker grains in the matrix shows a high degree of hydration of the cement. The heterogeneous nature and form of clinker grains could originate from a non optimized process of marls firing. Indeed, the kiln temperature must be constant to obtain a constant composition of clinker.

■ ■ Analysis of aggregates

Optical microscopy examination of thin sections confirmed the naked eye observations on the absence of quartz sand or stone fragments in the mortar. As a complementary investigation, we proceeded to an acid etching of the bulk mortar that allowed separating siliceous inclusions from the binder. Filtrate residue (which represents

Table 2 Results of XRD semi quantitative analysis of carbonated and non carbonated (7, 8, in bold) samples: significant (+++), average (++), weak (+), trace (t) conformity of diffraction peaks according to reference file.

	Carbonated samples								Non carbonated samples	
	1	3	4	5	6	9	10	11	7	8
Calcite CC	+++	+++	+++	+++	+++	+++	+++	+++	++	++
Vaterite CC	++	++	++	++	++	++	++	++	-	-
Quartz SiO_2	++	++	++	++	++	++	++	+	+	+
Calcium silicate hydrate $\text{C}_2\text{SH}_{0.5}$	-	-	-	-	-	-	-	-	++	++
Hydrogarnet C_3AH_6	-	-	-	-	-	-	-	-	++	+
Hydrocalumite C_4AH_{13}	-	-	-	-	-	-	-	-	++	++
Gypsum $\text{C}\$ \text{H}_2$	+	+	+	+	-	t	t	+	++	+++
Ettringite $\text{C}_3\text{A}.3\text{C}\$ \text{H}_{32}$	-	-	-	-	-	-	-	-	+++	+

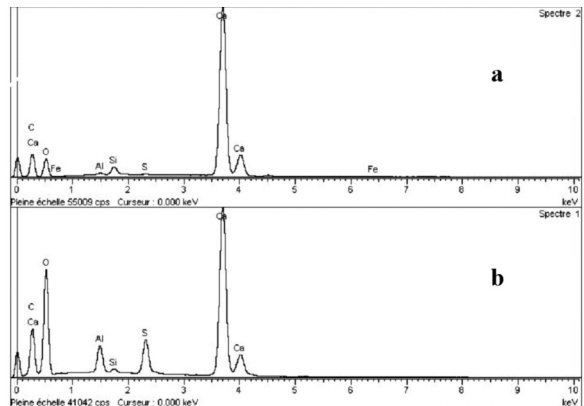
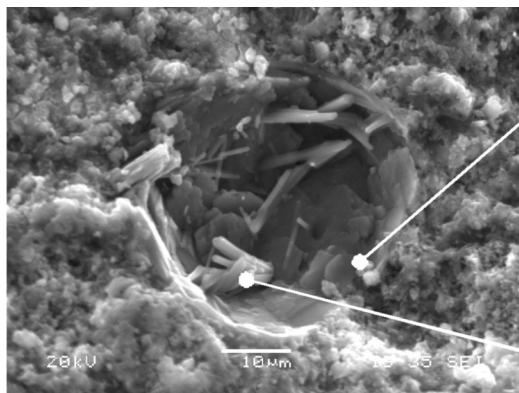


Fig. 5 SEM-EDS analysis of a pore recovered by portlandite (EDS spectrum a) and ettringite needles (EDS spectrum b).

12 to 15 % of bulk mortar mass) is composed of fine grains (5 to 10 μm) or grains groups (20 to 50 μm). XRD analysis gives the following crystallographic nature of these grains: quartz SiO_2 , tridymite SiO_2 and goethite FeOOH .

■ ■ XRD Analysis

The main crystallized phases of the samples are detected by XRD and the results are given in table 2.

As mentioned above, calcite and vaterite are the two major phases detected in carbonated samples. Among the main crystalline phases characterizing the binder, calcium silicate hydrate is a long term hydration product of C_2S , known to be slowly reactive. Then C_4AH_{13} is a member of hydrocalumite minerals and results from the hydration of calcium aluminates, such as C_3A grains observed on thin sections. This reaction is favoured in presence of Portlandite CH [27]. The latter seems to be weakly crystallized because undetected by XRD even within non carbonated samples. However, SEM-EDS examinations reveal the presence of CH in very small pores (Fig. 5).

Hydrogarnet C_3AH_6 is a stable phase corresponding to the complete thermodynamical conversion of C_4AH_{13} . Finally, ettringite and gypsum indicate a reaction between sulphates and the calcareous binder as commented below.

■ ■ TGA/DTA results

The TGA/DTA results are given in table 3. This method allows the quantification of hydrated phases and calcium carbonate, for which the thermal decomposition corresponds to distinct ranges of temperature. In case of sample 8, 15.6 % of mass is attributed to hydrated phases (ettringite and calcium aluminate hydrates) and 12.7 % is related to calcium carbonate.

■ ■ Chemical composition

The nitric acid etching of sample 8 confirms that the mortar contains a low amount of insoluble fraction (7 %). The analysis of the soluble fraction, expressed in wt % of oxides is given in table 3. The high loss on ignition could confirm the high degree of carbonation but as well the high degree of hydration of the cement. By combining

Table 3 Thermal analysis (bound water and decarbonation) of sample 8 and chemical analysis (expressed in wt. % of oxides) of its soluble fraction after nitric etching.

	Elements	% weight
Thermal analysis	Free water (<60°C)	0.2
	Bound water (60 to 550°C)	15.6
	from ettringite	3.3
	from hydrated aluminates	6.1
	Loss for 550 to 1000°C	12.7
	CO_2 from calcite	11.6
	corresponding calcite	26.4
	Total loss	28.4
Chemical analysis	SiO_2	13.83
	Al_2O_3	5.49
	Fe_2O_3	2.13
	CaO	40.87
	MgO	0.94
	SO_3	1.48
	P_2O_5	0.16
	Na_2O	0.04
	K_2O	0.10
	TiO_2	0.14
	MnO	0.19
	Cr_2O_3	0.01
	SrO	0.06
	Cl	0.01
	Insoluble fraction	6.15
	Loss ignition	28.40
	Total	100.00

chemical and thermal results, a calculation is carried out to approximate initial mortar composition: hydraulic binder 60.2 %, siliceous fraction 7.0 % and carbonate fraction 30.5 %. Concerning the siliceous fraction, this composition corresponds to the preliminary observations of insoluble residue after HCl (1:3) etching and confirms the presence of quartz only in raw marl stones.

Concerning the carbonated fraction, results of mineral computation have to be taken into account carefully. Indeed, this method is limited for highly carbonated materials because the distinction between calcite from calcareous aggregates and matrix carbonation is impossible at this stage of investigation. Moreover, the calcareous fraction could also correspond to incompletely burnt marl fragments but no typical grains of calcite, from limestone aggregates, have been observed on thin sections.

Table 3 shows a high content of SO_3 in the binder. Sulphates are linked to the presence of ettringite and gypsum (table 2 and section 3-7) but also to unfired marl blocks or combustibles used for cement production. From table 1, among all French natural cements, Pouilly and especially Vassy cements contain a high amount of sulphate, with an average of 2.8 % SO_3 , much higher than for French Portland cements (0.75 %) and hydraulic limes (0.48, 0.48 and 0.94 % respectively for low, medium and high hydraulicity).

■ ■ Source of sulphates

The hydrated phases containing sulphur are significantly detected as gypsum and ettringite. Those two phases are secondary formation products coming from the effect of sulphur or sulphates sources on calcium and aluminium hydrates phases of cement. Gypsum is present in bulk mortar (XRD results) as well as on external subsurface (revealed by elemental EDX mapping of Ca and S, performed on polished sections where the external border was covered with a thin black crust). Ettringite is mainly present in the pores of the matrix and shows different degrees and forms of crystallization.

Concerning the internal sources of sulphur, several grains of pyrite (iron sulphur FeS_2) have been observed enclosed in the cement matrix. Pyrites originate from the raw marl stones used for the cement process. Figure 6 displays a grain of oxidized pyrite using optical microscopy (left) and the corresponding SEM image (right). X-Ray mapping illustrates the repartition of iron Fe, sulphur S and oxygen O in such oxidised pyrite grain. More generally, the pyrites observed under SEM present different degrees of oxidation.

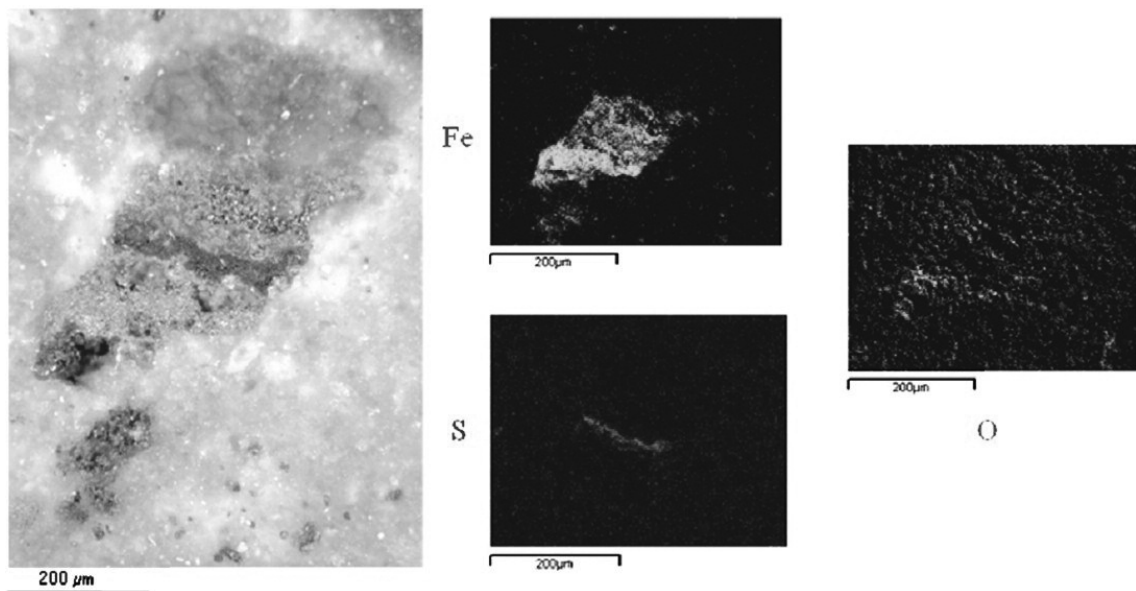


Fig. 6 Grain of oxidised pyrite: left/ reflected natural light OM exam to see rusty aspect of oxidised pyrite in cement – right/ X-ray mapping of the same grain to show repartition of iron, sulphur and oxygen.

■ ■ Petrophysical and durability properties

Comparative petrophysical tests have been performed on cement mortars and limestone specimens to measure the porosity, the capillary sorption and evaluate the properties of fluid transfers within each material. This characterization evaluates the compatibility of natural cement applied as a repair material on a calcareous substrate. Table 4 gives results of cement and limestone samples presenting appropriated dimensions to prepare prismatic specimens.

The amount of water absorbed by a dried rectangular section of a sample in contact with a free water surface follows the relation $m = A \cdot t^{1/2}$, where m is the amount of water ($\text{g} \cdot \text{cm}^{-2}$) and t is time. The constant A is called water absorption coefficient ($\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1/2}$). Simultaneous measurement of the water level raised by capillarity is operated to determine the rate of water sorption following the relation $h = B \cdot t^{1/2}$, where h is height of water uptake, B the

water sorption rate ($\text{g} \cdot \text{cm}^{-2}$) and t time. N_t and N_{48} are defined as the amount of water absorbed under vacuum respectively during 24 and 48 hours. The ratio between N_t and N_{48} is called Hirschwald coefficient S_{48} .

The solid density of all cement specimens is homogeneous, while the bulk density differs significantly. The fluctuations in the water/cement ratio used during the preparation of the cement paste are involved in the variation of the bulk density. Furthermore, the cement specimens present a higher total porosity (25-30 %) than the limestone (15-20 %) ones. Capillary sorption results reveal that the cement matrix presents a capacity (A) and kinetics (B) coefficients significantly higher than the calcareous substrate. This tendency is convenient in term of hygroscopic transfers between the two materials. High capillary sorption within the mortar avoids the water retention, especially at the stone/mortar interface and limits the risks of crystallisation of damaging salts.

Table 4 Capillary water uptake, water porosity, and density on limestone (†) and natural cement (*) specimens, complemented with compressive strength of cement sample 10.

Sample	Value A ($\text{kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1/2}$) and correlation R^2	Value B ($\text{cm} \cdot \text{h}^{-1/2}$) and correlation R^2	N_t (%)	N_{48} (%)	Hirschwald Coefficient (S_{48})	Bulk density ($\text{g} \cdot \text{cm}^{-3}$)	Solid density ($\text{g} \cdot \text{cm}^{-3}$)	Ultimate compressive strength (MPa)
1-1 *	-	-	28.62	20.10	0.70	1.80	2.52	-
1-2 *	-	-	16.31	15.00	0.92	2.28	2.72	-
2-b †	1.07 ($R^2=0.9835$)	1.04 ($R^2=0.998$)	14.41	15.49	0.93	2.28	2.69	-
2-c †	0.45 ($R^2=0.9984$)	0.71 ($R^2=0.980$)	17.93	16.47	0.92	2.19	2.67	-
2-d †	0.78 ($R^2=0.9907$)	0.61 ($R^2=0.994$)	20.67	18.75	0.91	2.28	2.88	-
2 †	-	-	19.88	-	-	2.14	2.66	-
3 *	-	-	24.78	-	-	1.86	2.47	-
4-a *	-	-	27.24	-	-	1.80	2.48	-
4-b *	-	-	30.01	-	-	1.70	2.43	-
10-a *	8.56 ($R^2=0.999$)	2.32 ($R^2=0.989$)	49.86	49.10	0.96	1.32	2.63	15.34
10-b *	9.25 ($R^2=0.999$)	2.38 ($R^2=0.989$)	48.21	46.46	0.96	1.34	2.59	12.88
10-c *	9.03 ($R^2=0.998$)	2.50 ($R^2=0.994$)	47.24	45.36	0.96	1.39	2.63	15.50
10-d *	-	-	48.01	46.37	0.97	1.35	2.60	17.17
10-e *	-	-	49.23	47.20	0.96	1.33	2.63	-
11 *	-	-	27.46	-	-	1.78	2.46	-

Table 4 gives compressive strength results measured on the most porous sample of cement mortar (sample 10). The mean compressive strength is about 15 MPa with a low standard deviation (1.7 MPa). Comparatively, six months compressive strength has been evaluated in 1903 by the Laboratoire de la Ville de Paris [10] on different samples of Vassy cements coming from several plants (table 5). Those results were measured on neat cement paste (equal part of water and cement, without sand). By comparing the strength (17.6 MPa at 6 months and 15 MPa at around 160 years), we can conclude that the natural cement, mixed and applied in those conditions, would have passed through time without any loss of strength. This conclusion, based on petrophysical properties of a porous sample (50 %), could well be drawn to all natural cement specimens present on the façade of the edifice.

Table 5 Six months compressive strength results on Vassy cement paste coming from several plants, from [10].

Vassy cement Plant	Pure paste compressive strength (MPa)
Bougault	18.30
Dumarcet	20.50
Faure	17.58
Millot et Cie	16.58
Prévost	16.80
Rotton	17.00
Voyot	16.42
Mean	17.60

Discussion

At Bourges, the natural cement mortar is distinguished from traditional ones by the absence of mineral admixtures such as siliceous and carbonates aggregates. The insoluble residue size is too small for any addition of siliceous aggregates to be considered. This indication reveals a deficiency on the mix design. Indeed, the use of pure cement paste can promote successively thermal and mechanical shrinkage. This is confirmed by the archives mentioning a premature cracks network formed on the mortar surface, only two years after the end of the works [3].

The quartz and tridymite present in the insoluble residue led us to raise some questions on the temperature of marl stones calcination. During this process, α -quartz undergoes successive transitional phases: α -quartz at 573°C, (minor, short and unstable phase), tridymite (unstable phase between 867 and 1450°C) and cristobalite (stable phase above 1450°C) [27]. Moreover, according to literature, the natural cement process required marls firing at temperature estimated between 1000 and 1100°C [3]. Within this range of temperature, only tridymite would be present in the insoluble residue. The simultaneous presence of very fine grains of tridymite and quartz in the samples shows a heterogeneous firing of marl blocks. Consequently quartz originates from unfired marl fragments while tridymite is a residue of completely burnt stones. The presence of incompletely burnt marl stones reflects the heterogeneity of calcination temperatures, directly linked to weakly optimized process of firing. The use of shaft kiln was probably the main reason of such fluctuations in the cement production. From 1824, the development of Portland cements [28] has undergone similar defaults in the process of fabrication. Through the 19th Century, successive improvements in cement industry resulted, from the late 1870s, in the continuous production using rotary kiln and ball milling to grind the cement.

The main anhydrous phase of the cement is a bicalcium silicate C_2S , obtained for a temperature range of 900-1100°C. Above this temperature, tricalcium silicates C_3S would be the main reactant of the cement. The absence of C_3S confirms thus the data from the literature [3] on the cement calcination (1000 to 1100°C). At this range of temperature, the formation of C_4AF and C_3A depends on the sufficient amount of Al_2O_3 and Fe_2O_3 in marls before its calcination. According to the literature [4-11], the chemical composition of Vassy cement gives 9.20 % and 5.58 % respectively for Al_2O_3 and Fe_2O_3 amount, allowing the formation of significant amounts of C_4AF and C_3A in the clinker.

The determination of hydrated phases details the nature of raw marl used for the cement production. Vicat estimated a minimum clayey fraction of 27 to 30 % in marl stones destined to natural cement production [9]. In Bourges cement, highly argillaceous limestone is exhibited by a binder rich in calcium aluminates hydrates. C_4AH_{13} is clearly detected and partially con-

verted into the stable form C_3AH_6 . The binder rich in calcium aluminate confers to the material a high reactivity and rapid setting time. These properties are generally linked to a great heat of hydration and a consequent thermal shrinkage, as mentioned above. Additionally to calcium aluminate phases, poorly crystalline CSH implies the hydration of C_2S .

The chemical and mineralogical results retain attention on the high amount of sulphur in the cement samples. The influence of sulphur on Vassy cement has been notified from the earliest applied chemistry handbooks [4]. In 1885, Durand-Claye discussed the quality of those cements despite of their good hydraulic index – i.e. as defined by Vicat in 1856, the ratio between oxides from clay and lime fractions in raw marls, $i = (SiO_2 + Al_2O_3) / CaO$. Earlier in 1857, Vicat [29] attributed the high sulphur content to accidental presences of calcium sulphate coming from sedimentary marls layers or combustibles used for cement manufacture. This initial sulphate content was qualified as a defect by Vicat and the concerned cements were avoided for marine structures, subject to aggressive saline environment.

In the present samples, the combination of sulphur and calcium on the subsurface results typically from a sulphation of hydrated phases (CH , C_4AH_{13}), anhydrous grains (C_3A), or calcium carbonate, by soluble atmospheric SO_2 . The mechanisms of calcareous stones are well identified [23] but the atmospheric sulphation of mortars and concretes need more understanding. Recent studies [30] have explored the process of concrete sulphation by sulphur dioxide in urban and industrial sites. This type of sulphate attack in such conditions promotes mainly the formation of gypsum and ettringite in the porosity and the matrix of cementitious materials. Ettringite is thus a product of reaction between gypsum and anhydrous cement grains (such as C_3A and C_4AF) or hydrated calcium aluminates phases (C_4AH_{13}). Depending on the concentration of available sulphates and calcium aluminates, ettringite can expand with high pressure of crystallization generating internal mechanical stress. In particular conditions (location of ettringite growth, space availability), this pressure can lead to damage of the cement matrix.

Additionally to atmospheric soluble SO_2 , plaster, applied to seal natural cement pieces [3, 12], is an external source of SO_3 .

The oxidized pyrites implicate an internal source of sulphate, originating from raw marl to process the cement. Originally, the alteration of pyrites in marls can occur from a sedimentary process. This hypothesis would imply that goethite $FeOOH$, product of pyrite oxidation and identified in the acid insoluble fraction, should have been totally decomposed during the calcination stage and transformed into hematite Fe_2O_3 from a temperature of $250^\circ C$. Consequently, the presence of $FeOOH$ corresponds to a secondary alteration occurring beyond the cement production or hydration. In this case, sulphuric acid released from pyrite alteration would react with calcium aluminates of the binder to produce gypsum and ettringite [31]. However, such reaction rims have not been observed in the surrounding of pyrite grains.

The two sources of sulphates (external from atmospheric SO_2 and internal from oxidized FeS_2) figured out in this study are potential sources of limestone pollution, when solubilised sulphates migrate to the calcareous matrix. Recent works [32], based on the dosage of sulphur and oxygen stable isotopes, are currently being carried out to characterize the different sources of sulphates in Bourges cathedral samples (healthy or decayed stone, plaster, roman cement). This isotopic approach aims at comparing the sulphatic signature of cement with the sulphates present in decayed stones, in order to evaluate the potential of pollution of natural cement on the edifice stones.

Although the natural cement used in Bourges constitutes a potential source of sulphates due to the high level of pyrites oxidation, its compatibility with limestone has been clearly demonstrated. The high porosity and the possibility of water evaporation characterize the natural cement as particularly adapted to substitute and repair the stones, in respect with proper fluids transfers and prevention of sulphate salts crystallisation.

■ Conclusions

This article gives new results on the characterization of natural cements produced in France during the 19th century. Their special application in monumental stones restoration is studied by means of mineralogical and petrophysical approaches. Through the determination of

the cement composition and durability properties, the knowledge on natural cement process (nature of clayey marls stones, calcination temperature) and the state of art of stone restoration is enhanced. As the most of calcareous materials exposed in urban environment, natural cements undergo atmospheric sulphation leading to it superficial weathering (black crust). The several grains of oxidized pyrites have been identified as an internal source of sulphate. The soluble sulphates can react with calcium aluminate phases of the cement to form ettringite and gypsum. A secondary reaction involves the soluble sulphates migration through the cement to the calcareous substrate, leading to potential damage of the edifice stones. On one hand, the salt migration could be promoted by the high porosity of the cement matrix. But on the other hand, the high porosity and capillary transfer of the cement allow the evaporation of water and the crystallization of salt at the interface cement-stone. This property, complemented with consistent long term compressive strength, demonstrates the durability and the compatibility of natural cement to restore monumental stones.

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References

- Hughes, D. C.; Sugden, D. B.; Jaglin, D.; Mucha, D., 'Calcination of Roman cement: A pilot study using cement-stones Whitby', *Construction and Building Materials* **22**(7) (2008) 1446–1455.
- Hughes, D. C.; Swann, S.; Gardner, A., 'Roman cement: Part One: its origins and properties', *Journal of Architectural Conservation* **13**(1) (2007) 21–36.
- Royer, A., 'Le ciment romain en France: un matériau du XIXe siècle méconnu', *Monumental* **2** (2006) 90–95.
- Durand-Claye C. L., 'Chimie appliquée à l'art de l'ingénieur', in *Encyclopédie des travaux publics*, Baudry et Cie, Paris (1885).
- Debauxe, A., *Procédés et Matériaux de Construction*. Tome 3, Dunod et Vicq, Paris (1886).
- Wagner, R.; Fischer, F.; Gautier, L., *Traité de Chimie Industrielle*. Tome 2, Masson, Paris (1903).
- Candlot, E., *Ciments et chaux hydrauliques, Fabrication Propriétés Emploi*, 3rd ed., Paris et Liège, Paris (1906).
- Claudiel, J.; Laroque, L., *Pratique de l'Art de Construire. Maçonnerie*, Carilian-Goeury et Vor Dalmont, Paris (1850).
- Vicat, L. J., *Traité pratique et théorique de la composition des mortiers, ciments et gangues à pouzzolanes et de leur emploi dans toutes les sortes de travaux, suivi des moyens d'en apprécier la durée dans les constructions à la mer*, Maisonneuve, Grenoble (1856).
- Le ciment de Vassy*. Revue des Matériaux de Construction et de Travaux Publics, Paris (1905) 290–292.
- Simonet, E., *Maçonneries*, Librairie des Ponts et Chaussées, des Mines des Chemins de Fer. Dunod et Vicq, Paris (1897).
- Rolland, O., '18, Bourges, Cathédrale, portail occidental, rapport de relevé de fissures et de mise en sécurité', unpublished report, Direction régionale des affaires culturelles de la région Centre, Orléans (2001).
- Di Matteo, C., 'Etudes et essais de traitement des sculptures de la cathédrale de Bourges', in *La conservation de la pierre monumentale en France*, ed. J. Philippon, D. Jeannette, R.-A. Lefevre, CNRS Editions, Paris (1992) 272.
- Gosselin, C., 'Le ciment romain: une source potentielle de sulfates dans la dégradation des pierres de la Cathédrale de Bourges', Master Thesis, University of Paris VII, Paris (2005).
- Verges-Belmin, V.; Gosselin, C., 'Le ciment romain: une source potentielle de sulfates dans la dégradation des pierres de la Cathédrale de Bourges', *Monumental* **2** (2006) 96–99.
- Callebaut, K., *State of the Art of Research/Diagnostics of Historical Building Materials in Belgium*, Advanced Research Centre for Cultural Heritage Interdisciplinary Projects, Prague, 4–10 February 2002, http://www.arcchip.cz/w09/w09_callebaut.pdf.
- Palomo, A.; Blanco-Varela, A. M. T.; Martinez-Ramirez, S.; Puertas, F.; Fortes, C., *Historic Mortars: characterization and durability. New tendencies for research*. Advanced Research Centre For Cultural Heritage Interdisciplinary Projects, Prague, 4–10 February 2002, http://www.arcchip.cz/w09/w09_palomo.pdf.
- Martinet, G.; Quenee, B., 'Proposal for a useful methodology for the study of ancient mortars', in *Proceedings of the International RILEM Workshop on Historic Mortars: Characteristics and Tests*. Paisley, 12–14 may 1999 (2000) 81–93.
- Van Hees, R. P. J.; Binda, L.; Papayianni, I.; Toubmakari, E., 'Characterisation and damage analysis of old mortars', *Materials and Structures* **37**(9) (2004) 644–648.
- Baroghel-Bouny, V., *Caractérisation des Pâtes de Ciment et des Bétons. Méthodes, Analyses, Interprétations*, LCPC, Paris (1994).
- Deloye, F. X., 'Le calcul minéralogique: application aux monuments anciens', *Bulletin de Liaison des Laboratoires des Ponts et Chaussées* **175** (1991) 59–65.
- RILEM, 'Recommended tests to measure the deterioration of stone

- and to assess the effectiveness of treatment methods', *Materials and Structures* **13**(6) (1980) 175-253.
- 23 Verges-Belmin, V., 'Altération des pierres mises en œuvre', in *Géomécanique Environnementale, Risques Naturels et Patrimoine*, ed. B. Shrefler, P. Delage, Hermes, Paris (2001) 191-235.
- 24 Weber, J. ; Gadermayr, N. ; Bayer, K. ; Hughes, D. ; Kozłowski, R. ; Stillhammerova, M. ; Ullrich, D.; Vyskocilova, R., 'Roman Cement Mortars in Europe's Architectural Heritage of the 19th Century', *Journal of ASTM International* **4**(8) (2007).
- 25 Campbell, D. H., *Microscopical Examination and Interpretation of Portland Cement and Clinker*, 2nd ed., Portland Cement Association, Skokie (1999).
- 26 Cailleux, E.; Marie-Victoire, E.; Sommain, D.; Brouard, E., 'Microstructure and weathering mechanisms of natural cements used in the 19th Century in the French Rhône-Alpes region', in *Proceedings. Repair mortars for historic masonry. Rilem workshop, pre-prints, Delft, 26-28 January* (2005).
- 27 Taylor, H. F.W., *Cement Chemistry*, 2nd ed., Academic Press, London (1997).
- 28 Blezard, R. G., 'The history of calcareous cements', in *Lea's Chemistry of Cement and Concrete*, 4th ed., Arnold, London (1998) 1-23.
- 29 Vicat, L. J., *Recherches sur les causes chimiques de la destruction des composés hydrauliques par l'eau de mer, et sur les moyens d'apprécier leur résistance à cette action*. 2nd ed., Valmont, Paris (1958).
- 30 Sabbioni, C.; Zappia, G.; Riontino, C., 'Atmospheric deterioration of ancient and modern hydraulic mortars', *Atmospheric Environment* **35**(3) (2001) 539-548.
- 31 Marion, A. M.; Daube, J.; Smits, R., 'The stability of pyrite in calcareous aggregate: investigations in old concrete structures', in *Proceedings of the 23rd International Conference on Cement Microscopy, Albuquerque, New Mexico, April 29 - May 4* (2001) 146-164.
- 32 Vallet, J. M.; Gosselin, C.; Bromblet, P.; Rolland, O.; Verges-Belmin, V.; Kloppmann, W., 'Origin of salts in stone monument degradation using sulphur and oxygen isotopes: first results of the Bourges cathedral (France)', *Journal of Geochemical Exploration* **88**(1-3) (2006) 358-362.