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Natural Cement in Portugal: Context in Cement Production and Architectural Use

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Abstract: Natural cement, also known as "Roman cement", was used across Europe during a historic period, mainly in many building facades, due to its hydraulic properties and aesthetic qualities. In Portugal, the use of natural cement occurred in buildings from the second half of the 19th century to the beginning of the 20th century, a period during which the use of lime binders decreased and before the massive use of Portland cement. Recent conservation and rehabilitation actions resulting from necessary interventions in heritage buildings from this period have played an important role in revealing evidence of the use of natural cement and clarifying the lacunae of information about this material. Due to the inadequate use of reparation materials in previous conservation and rehabilitation interventions, this study summarizes the historical production, study, and use of natural cement in Portugal. Natural cement results from the calcination of clay-rich limestone (marlstone) without any compositional changes after extraction, distinguishing itself from hydraulic lime due to its higher clay content and allowing for the formation of higher quantities of hydraulic reactive phases without free lime. Although this topic has been approached at a European level, mainly focusing on the production and use of natural cement in Central Europe, in Portugal, it is still necessary to produce and disseminate information on this specific subject. Therefore, this study focuses on the evolution of cement production in Portugal and an analysis of the existing knowledge of the binders used in architectural heritage based on the scientific and historical bibliography.

Keywords: natural cement; architectural heritage; 19th and 20th centuries; historical bibliography

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1. Introduction

In recent years, the rehabilitation and conservation of historic buildings have played a fundamental and growing role in civil construction, which has been motivated by the observation of the progression of heritage building degradation. The growing interest in heritage building recovery requires knowledge of both the techniques and original materials used to ensure the compatibility, durability, and quality of conservation actions.

Generally, air lime was the predominant binder found in renders, plasters, and aesthetic elements in old and heritage buildings [1]. However, the need to intervene in more recent buildings has emphasized the relevant issue that other types of binders were also used from the 19th century onward. Recent interventions in Portuguese heritage buildings have revealed the use of different binders, such as hydraulic lime, Portland cement, and slag, among others, and it is thought that binders based on natural cement may also have been used. Natural cement, also known as "Roman cement", is thought to have been used for a substantial period of time in many buildings' facades in Europe [2,3] due to its hydraulic properties and aesthetic qualities throughout. It is thought that the name "Roman Cement" has its origins in the time of the Roman Empire due to the quality of concrete produced at this time, as clearly mentioned by the Roman Vitruvius, whose books have been spread worldwide [4], and the well-known scholar Jean-Pierre Adam [5]. In

Portugal, as in other European countries, natural cement manufacturing occurred between the second half of the 19th century and the beginning of the 20th century [6].

Natural cement results from the burning of limestones with 20 to 40% clay content (marlstone) at temperatures below the sintering point (750–1200 °C) [7,8], and this material was introduced to some European countries in the late 18th century [9]. In Portugal, the production progress of building materials is not as well known. Moreover, the specific periods of natural cement use and the transition to the use of modern cement have not been well defined. According to Mascarenhas and Castro (2018), the effective industrial Portuguese production of natural cement began in 1866 in Alcântara, Lisbon. Before this, in 1858, there was some evidence of the existence of two kilns in Pataias; however, production was not intense. Afterward, other companies appeared, and industrial production began. Gradually, Portland cement replaced a range of artificial cement, including "Roman cement", primarily due to its more resistant and durable properties [10]. This modern artificial cement appeared in England in 1824, and its industrial production started in 1845 [11]. It is an artificial hydraulic agglomerate resulting from the burning of a mixture of pure limestone and clays at temperatures above 1300 °C, leading to the formation of clinker 1845 [11].

In this study, we intend to establish the period of natural cement production through an analysis of the evolution of the cement industry in Portugal and recreate the historical information between the end of the 19th century and the mid-20th century. In order to improve the knowledge of this binder and obtain information on the materials from this period, examples such as Teatro Nacional de São João (TNSJ) and Mercado do Bolhão (Porto) are presented to exemplify the use of natural cement in Portuguese buildings.

2. The Chronological Use of Hydraulic Binders: An Overview

2.1. Initial Hydraulic Mortars

It is believed that the Greeks were probably the first civilization that used lime as a binding agent for the execution of renders. This material could develop hydraulic properties in specific mixes and was, in this context, useful in the construction of the sea ports of Greek civilization. The Chinese also used lime mortars to build the famous Great Wall of China (700–500 BC). However, it was the Romans who applied this material most effectively. In the 15th century BC, the eruption of Thera (Santorini, Greece), which destroyed part of Santorini, and, later, the eruption of Mount Vesuvius (Bay of Naples) were responsible for the appearance of a large amount of ash used in the formulation of mortars by Roman civilization. The ashes located in the Bay of Naples next to the village of Pozzuoli are known as pozzolan, a name that, nowadays, reflects a category of materials. The Roman civilization modified and improved the mixture of Roman lime-based mortars, adding pozzolans to improve the characteristics of mortars. The construction of several pieces of infrastructure, such as aqueducts, bridges, and large buildings, employing these materials occurred at that time [12,13]. The Colosseum and Pantheon in Rome, as well as the Pont du Gard aqueducts (in the south of France), reveal the durable properties of Roman lime-based mortars mixed with pozzolans.

Mortars with pozzolanic additions allowed the construction of large structures, such as the vault arches and vaults of Roman architecture. These pozzolanic materials are believed to improve the quality of mortars and may be found in various forms, such as volcanic sand, artificial pozzolan, and kaolinitic clay (800 °C) [14]. Opus Signinum was usually constituted of crushed ceramics, and it was often used in cisterns, water tanks, and fountains [14], attesting to its hardening under water.

Between the 5th and 7th centuries, there was a general downgrade of lime-based mortars when compared to Roman mortars [14]. Subsequently, around the 8th century, gypsum plaster was introduced by the Arabs in Europe, with a relevant use as a material for interior renders (or exterior use in arid areas due to its degradation when in contact with water).

2.2. The Advent of Natural Cement

In the 18th century, the development of hydraulic binders (Figure 1) occurred due to the need to build in maritime areas using products with the ability to harden underwater. The use of natural cement emerges from this need for faster-hardening binders for application in marine and humid environments [15]. These materials should have high mechanical resistance and waterproof properties.

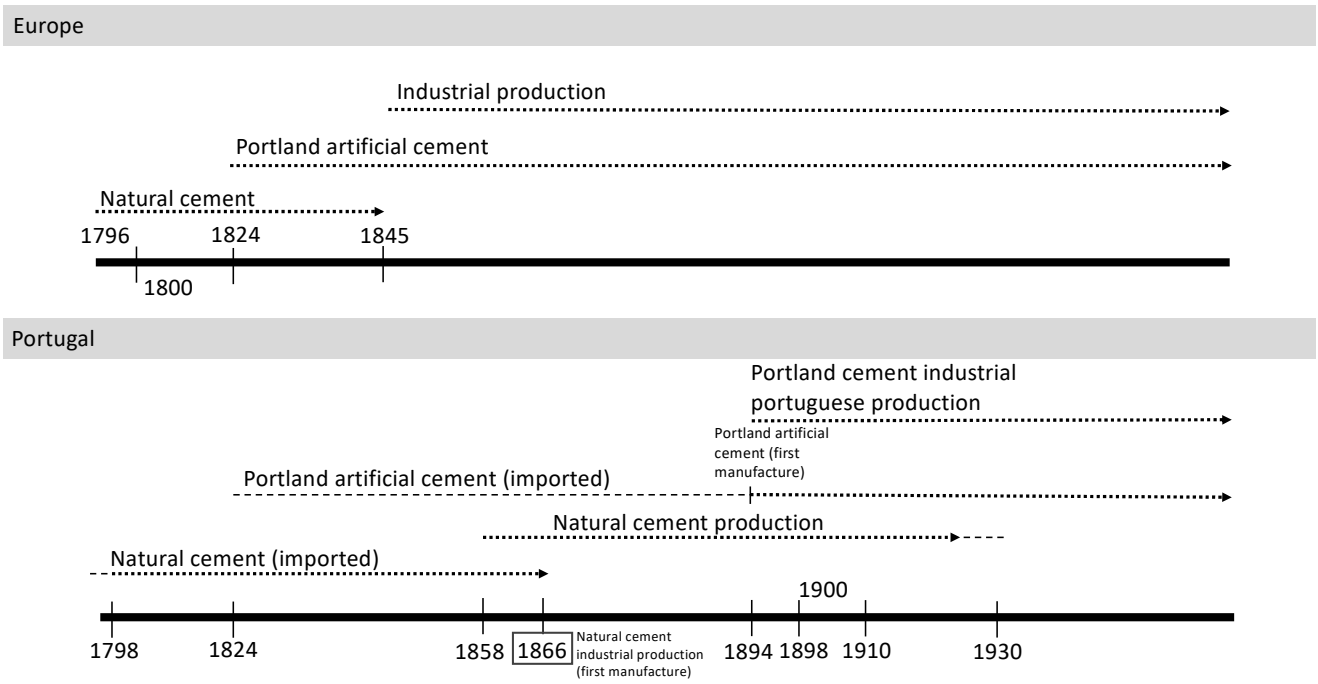


Figure 1. Evolution of cement production in Europe and Portugal (adapted from [11], accessed on 3 December 2023).

Natural cement was first produced in England. In 1796, James Parker patented a natural cement called "Roman" cement. When it was first produced, the manufacture involved the calcination of clay–limestone rocks or marl with clay content (25–40%) at moderate temperatures (lower than 1200 °C).

The dissemination of natural cement, known as Parker cement or Parker & Wyatt cement after the sale of the patent in 1798 to Samuel and Charles Wyatt, throughout North America and Europe contributed to the opening of several production locations. This type of cement was commonly designated as Roman cement, as confirmed by publicity flyers [16].

2.3. From Natural to Portland Cement

During the Napoleonic Wars, France showed interest in cement manufacturing (1815). The mechanism of the production of hydraulic materials and their properties began to be studied by Vicat (1786–1861) in an attempt to develop the production of these binders. Vicat studied the hardening of mortars, supported by scientific analysis methods, and following this, the production of artificial binding materials (artificial cement, hydraulic lime, and Portland cement) began [16]. Portland cement appeared in England in 1824 at the hands of Vicat and Joseph Aspdin (1778–1855). The production of artificial cement was made possible due to a furnace system that worked at high temperatures to produce clinker. In general terms, the main evolution in cement manufacturing leading to modern Portland cement involved a change in the production temperatures required for the sintering of raw materials and the formation of cement clinker. Together with the development of this artificial cement using limestone mixed with clay-based raw materials to the required

proportion in order to obtain the desired properties, this period is also marked by the development of natural cement, obtained exclusively from one type of stone. The production of Portland cement requires temperatures above 1300 °C, while the production of natural cement uses temperatures between 750 °C and 1200 °C, avoiding the formation of alite and creating predominantly belitic cement that is characterized by its mechanical strength and durability [16,17].

France was quick to attain knowledge of the production of these artificial binders; as a consequence, in 1853, the production of French cement began. This cement came from the first quarries discovered in France in 1824 [17]. The discovery of rock deposits located in Pouilly (1820) and Vassy (1830) ensured the production of natural cements, which contributed to the reduction in imports from England and to the definitive commercial exploitation of French natural cement and the beginning of its exportation. The mineral resources present in the Grenoble region were also explored, leading to the start of natural cement production in several plants, such as Porte de France (1842), Vif (1858), and Voreppe (1874). Between 1855 and 1885, several manufacturers began to explore the limestone deposits in Boulogne and Vassy, and the products were sold by the Société Anonyme des Ciments de Vassy [16]. In 1882, there were thirty-two cement companies producing natural cement. In the 20th century, Voreppe cement was still available on the market [16].

In the mid-nineteenth century, Germany was the main center for the development of studies on this type of cement production, resulting in significant improvements in kilns. Around this time, in Spain, the manufacture of natural cement was starting (1835), later followed by the industrial production of Portland cement, which occurred from the end of the 19th century onward [11].

2.4. Evolution of Cementitious Materials in Portugal

In Portugal, the use of natural cement can be traced to a transition period between the use of lime-based binders and the common use of modern Portland cement. Compared to other countries, the introduction of cements, including natural cement, was posterior—between the end of the 19th and the beginning of the 20th century. Before cement's local industrial production starting in 1866, Portugal had been importing Portland cement since 1824. By the late 19th century, Portugal imported artificial cement mainly from England and Vassy (Paris, France).

The history of natural cement production in Portugal is not well known; however, it is believed to have occurred between 1858 and 1930, according to the appearance and development of production companies during that period. In 1890, the production of Portland cement was consolidated by the spread of international and national scientific findings, and chemical and economic studies led to the construction of the first company in 1892. As a consequence, the interest and improvement in technology led to the production of Portland cement. Thus, the industrial Portuguese production of Portland cement started in 1894 and has since continued, being used mostly in renders, plasters, and finishes as a hydraulic binder, replacing hydraulic lime and hydrated lime [14]. Clearly, during the first decade of the 20th century, the use of natural cement transitioned to the use of Portland cement, eventually being completely replaced by the latter.

3. Portuguese Geological Raw Materials

During the first half of the 19th century, the natural cement used in Portugal was imported from England and Vassy. As the production of natural cement requires the extraction and burning of unchanged raw materials, one of the most important steps in the manufacturing process is to access and extract limestones and marl. Portugal is rich in these raw materials, and that fact enabled the initiation of cement production and the subsequent development of a national lime and cement industry.

Figure 2 shows the most relevant geological features of continental Portugal, presenting the country's high diversity of geological resources. The most common raw rock types

used in cement production are limestone, clay, marl, or shale, as well as other supplementary materials, such as sand, fly ash, or ironstone.

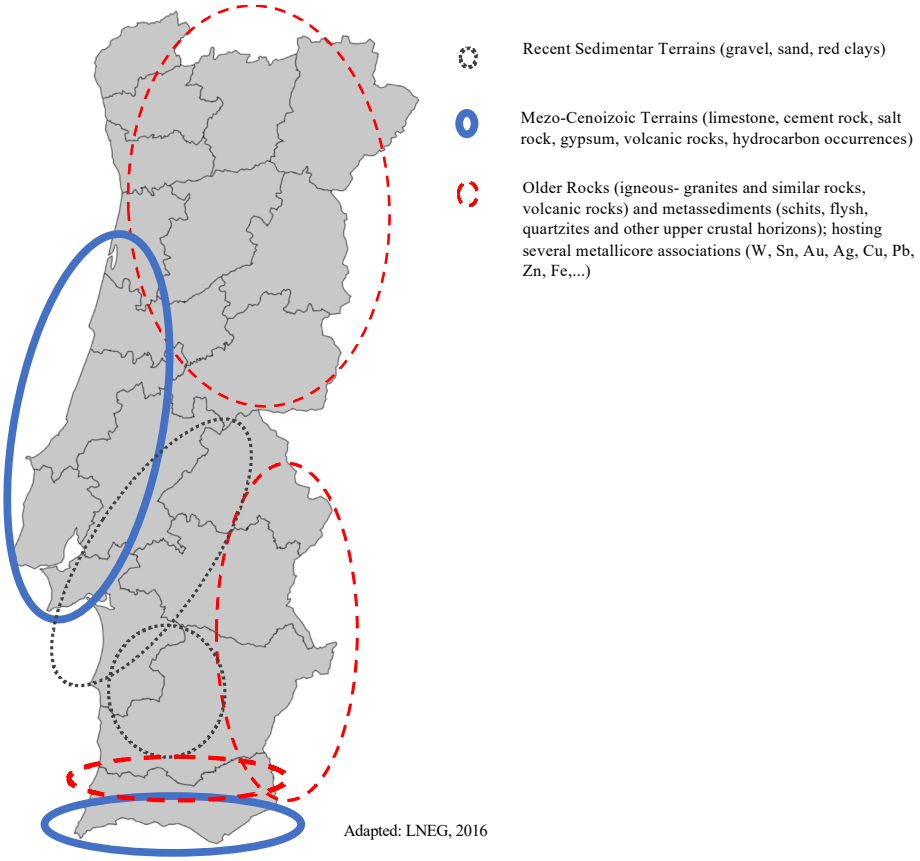


Figure 2. Geology of Portugal. Adapted by LNEG, 2016 (http://www.aniet.pt/fotos/editor2/jt/lneg_for_aniet_9_nov_2016_v1.pdf, accessed on 4 April 2022).

In Portugal, the existence of raw materials to supply the manufacture of cement, such as limestone and clays/marl, is widespread in the Meso-Cenozoic basins. Although raw materials for cement production are distributed across the entirety of the continental Portuguese territory, the main limestone massifs are located in the center and south of Portugal—Condeixa-Sicó-Alvaiázere-Tomar, Estremenho, Montejunto, Arrábida, and Algarve. The limestone and clay–limestone formations extend to the center of Portugal, namely, to the Aveiro area (Anadia and Mealhada, Portugal) and Coimbra (Cantanhede, Coimbra, Figueira da Foz, Verride, and Montemor-o-Velho, Portugal). Also located in the center of the country are the main known formations, located in Maceira and Pataias, Serra d'El Rei-Nazaré (Leiria, Portugal), Vila Nova de Ourém, Alcanede, Rio Maior, Benedita, Turquel, and Alcobaça. Lisbon has outcrops of limestone near Montejunto and Alenquer-Vila Franca de Xira. Other relevant outcrops can also be found in the Setubal Peninsula and Alentejo (Santiago do Cacém, Portugal).

In general terms, the most relevant production regions are located in the proximity of deposits, such as Foz do Sado, the Sado river mouth in the southern region of Portugal, which is a geologically rich zone in terms of sediments and also the location of the first cement factory (1866–1877). In the center of the country, the main production regions are Cabo Mondego, near Figueira da Foz, Pataias, S. Pedro de Moel, and Maceira. In the Cabo Mondego region, the production of hydraulic lime and natural cement was enhanced by the existence of the necessary raw materials, similar to Pataias and S. Pedro de Moel deposits, in which clayey limestone was explored to produce natural hydraulic materials, such as hydraulic lime and cement. Maceira, located in Leiria, also produced those products using locally sourced marly limestones [18,19].

4. Production and Imports of Cement by the Portuguese Industry

4.1. First Stage of Industrial Production (1866–1895)

4.1.1. Production Units

Although, in Europe, the industrial production of Roman cement occurred between the end of the 18th century and the end of the 19th century, in Portugal, the interest in this material only began in the second half of the 19th century, but the exact period of natural cement use in Portugal is not clearly defined [7]. The 18th century marks the beginning of the industrial revolution in Europe, with the main change being the replacement of artisanal production with industrial processes and equipment.

It has been stated that, until the 1890s, Portugal imported most of its cement [20], despite the fact that the effective start of Portuguese natural cement production was in 1866, when cement companies began to appear. However, the importation of binding materials continued due to some key factors, such as product quality and competitiveness.

In 1866, the official industrial cement production Company of Lime and Cements of Rasca was founded in Alcântara, Lisbon. Available raw materials to produce natural cement were abundant in the region, as the location of these industries depended essentially on the proximity to the local mines and quarries from where the necessary raw materials were extracted. Rasca Company used limestone extracted from the quarries of Vale de Alcântara and also marly limestone extracted from Serra da Pedra Branca in Quinta da Rasca. During this time, the first Roman cement production occurred; however, several tests attributed negative properties to this material, claiming that shortly after mixing and setting, the cement would exfoliate and crumble [21]. Maybe due to this aspect, the company operated only for eleven years [21]. From then onward, interest in the cement industry increased and was widespread among several companies, such as the Mining and Industrial Company of Cabo Mondego, Cement Company of Tejo, Company of Maceira-Liz, Company of White Cements (Pataias), Company of Northern Cement, and Company of Southern Cement, which originated the current cement companies Cimpor SGPS and SECIL. Figure 3 shows the timeline of the foundation of the most relevant Portuguese cement companies.

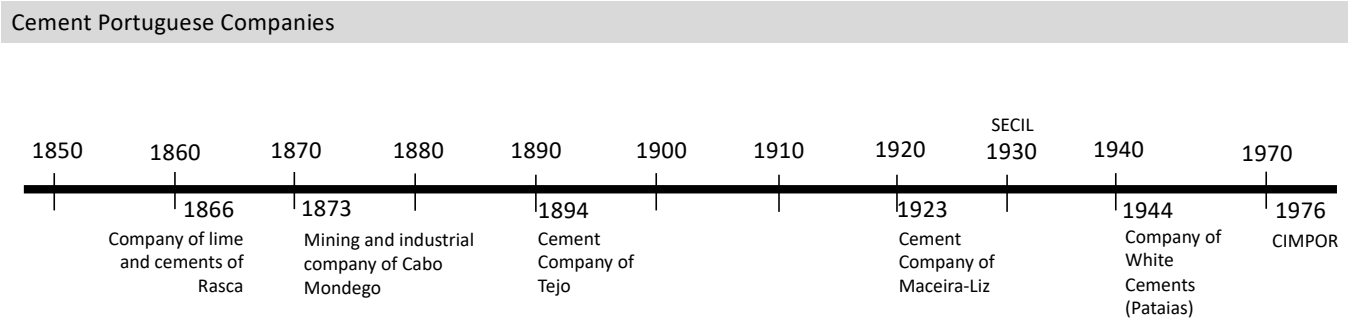
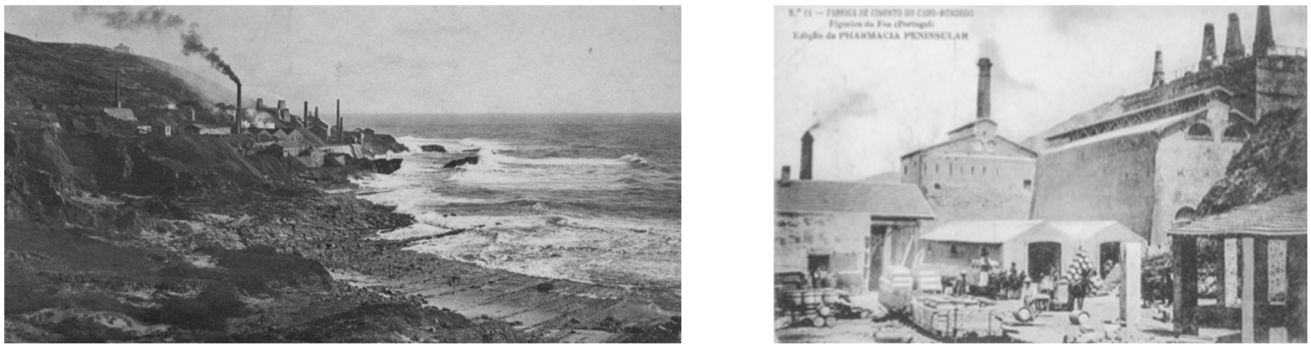


Figure 3. Timeline of establishment of industrial cement companies in Portugal.

In 1873, a new industrial company—Cabo Mondego—appeared near Figueira da Foz, in the Central Region of Portugal, and also engaged in the production of natural cement. Cabo Mondego Company also started to explore bituminous coal and the margo-carbonated formations available in the Cabo Mondego region. Despite the different types of industries installed in the region of Cabo Mondego, the most important industrial production occurred in hydraulic lime and natural cement plants due to their contribution to the local economy [22]. It is a historical fact that, from 1884 onward, the industries of Cabo Mondego produced not only very pure lime but also natural hydraulic lime and natural cement (Figure 4) [19].



(**a**) (**b**)

Figure 4. (**a**) Cabo Mondego coal mine and (**b**) Cabo Mondego natural cement kilns (1890) [22].

Notwithstanding the advances in the manufacture of cement in Portugal, many technical difficulties still existed. The high extraction costs and the poor quality of coal maintained the practice of importation from France and the United Kingdom [23]. Furthermore, soon after, as Portland cement appeared in Europe, Portugal began making several attempts to produce it.

4.1.2. Studies and Quality Control

During the late 19th century, different geological studies were performed on the qualities of marl and limestone and their potential for the manufacture of hydraulic lime and cement [24]. These studies would encourage the emergence of new kiln plants for Roman cement and natural hydraulic lime production. These materials were often combined with pozzolana from the volcanic islands of Azores [24]. The increase in interest in the production of hydraulic binders can be explained by the existence of relevant public works, such as railways, harbors, and roads [24].

Between 1880 and 1930, David Xavier Cohen, a military engineer and officer of the Portuguese Army at the service of the Ministry of Public Works and the director of the Companhia Nacional de Construções (Lisboa, Portugal), published Bases para Orçamentos. These publications had an important role in the context of the use of cement. Bases para Orçamentos was released in four editions, the first of which was published in 1880. Composition formulas and references to prices are described for construction works, such as roads, bridges, railways, buildings, and others, with the presentation of the "caderno de encargos"/specifications, legislation, and regulations on works.

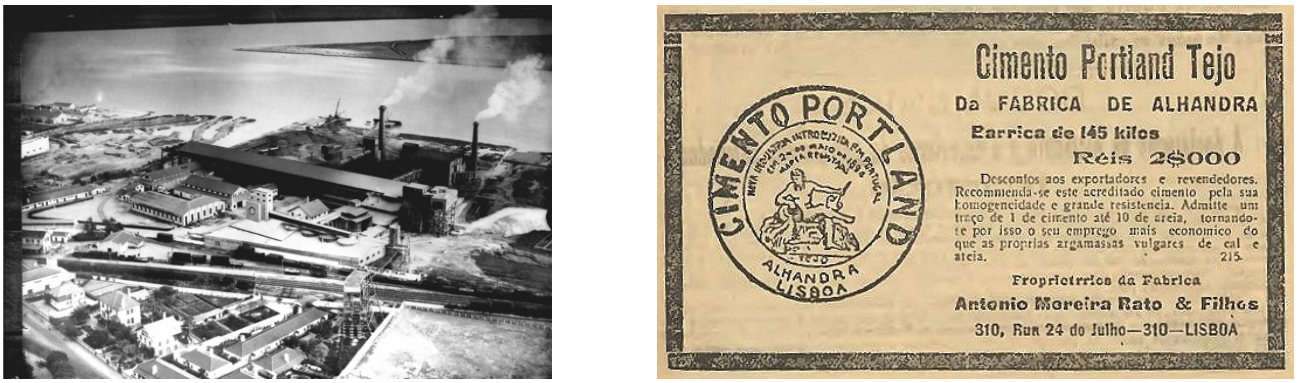
In relation to the use of materials, the first edition presents the caderno de encargos/specifications (first part) referencing several binders, such as lime, pozzolana, and cement. In the second part of caderno de encargos, dedicated to the construction process, a division by mortar type is presented: "Lime slaking", "Mortars", "Portland cement mortars", and "Vassy cement mortars". In this publication, natural cement is referred to by the designation of "Vassy Cement".

Starting in 1881/1882, a scientific approach to the study of cement was a task performed by engineers from the Military School, who created the Secção de Estudos sobre resistência de Materiais (Section of Studies on the Resistance of Materials) subject and the Mechanics of Materials Department of the Directorate of Lisbon Port Works (1886) [24]. José Paixão Castanheira das Neves (1849–1922) was its first director, performing various studies on Portuguese construction materials and producing the first guidelines for Portuguese Portland cement [24].

In 1887, the increase in industrial production of building materials and the need to evaluate and control their quality led to the development of the first official quality control laboratory (Figure 5). Castanheira das Neves, the engineer responsible for the laboratory, published a relevant study on Portuguese natural cements [19,24]. This study divided Portuguese natural cements into two groups: slow-setting natural cements (Rasca and

Cabo Mondego) and quick-setting cements (Pataias, Maceira and São Pedro de Moel) [24]. Moreover, Castanheira das Neves published various studies about Portuguese construction materials in Revista de Obras Públicas e Minas (1891). Between 1891 and 1894, several studies followed, with a focus on the production of hydraulic lime, Roman cement, and the characteristics of the materials available on the national market during this period. As a consequence, there was increased interest and improvement in technology, and the first company producing artificial Portland cement was founded in 1892. This company, Cimento Tejo, is currently named CIMPOR. It was established in Alhandra, which is located only a few kilometers from Lisbon, by António Teófilo de Araújo Rato (Figure 6). This unit had a Hoffman kiln and a production capacity of 6000 tons [24]. The inauguration license was assigned in 1894, marking the start of 10 years of exclusivity for the production of Portuguese Portland cement.

Figure 5. Laboratory for cement studies used by Castanheira das Neves [25].



(**a**) (**b**)

Figure 6. Cimentos Tejo Company: (**a**) the company and (**b**) dissemination of information.

4.2. Second Stage of Production (1895–1994)

4.2.1. Production Units

In 1894, the industrial production of artificial cement began in Portugal [26]. Two years later, in 1896, Jacques Monet and Herculano Galhardo, the director of the Alhandra plant, proceeded to test both pavement and a beam made from reinforced concrete using

artificial cement as a binder. In 1898, the building Moagens do Caramujo flour mill was the first construction built entirely with reinforced concrete using the Hennebique system [24], following François Hennebique's system, which was very popular during this period of time and applied in a variety of countries [26].

In 1904, the Companhia de cimentos de Portugal was established due to the increase in demand for Portland cement. This was a society formed between Garcia Machado (Bosse & Cie) and Belgian technicians, and it was situated at the Sado river mouth. In 1906, the Fábrica do Outão—the previous Rasca Company—restarted its production (Secil: História 2020). This manufacturer was located at Serra da Arrábida, near Jurassic limestone and clay–limestone formations. Rasca, currently known as Secil, improved manufacturing with similar technologies and techniques to those used at the Alhandra production unit, a fact that led to artificial cement production in two variants named "Tenaz" and "Audaz".

Later, in 1912, the Moreira Rato family sold the Cimento Tejo company to a public company owned by several capitalists from Porto (Neves 2007). Six years later, the annexed buildings were acquired by the Companhia Geral de Cal e Cimento (Lisboa, Portugal). In 1925, those buildings were rented to the Sociedade de Empreendimentos Comerciais e Industriais Lda., from which the current name—SECIL—originated (Neves 2007).

In central Portugal, in July 1919, Henrique Sommer founded the Empreza de Cimentos de Leiria, the effective production of which began three years later. During the third decade of the 20th century, this industry dominated cement production, which represented 81,000 tons of material.

Nearby, in Maceira (1923), the production of Portland cement began at the Fábrica de Cimentos de Maceira-Liz. In Portugal, it was the first official industrial manufacturer to produce Portland cement. Additionally, it manufactured hydraulic lime, natural cement (slow-setting), and hydraulic lime with more resistance (lime–cement) [21].

On the 20 July 1944, Joaquim Matias, manager of the company of hydraulic tiles and artificial marble (SCIAL), founded the Companhia Portuguesa de Cimentos Brancos, S.A.R.L., in Pataias, although production only started later, in 1949 [16].

During the 1970s, the engineer Mário Gaspar, owner of Somapre, founded Cisul. The factory was located in Loulé, with the first kiln starting in September 1973. After that, the Queirós Pereira family founded Cinorte, located in Sousela, with two kilns starting in 1974 and 1975, respectively.

In 1976, CIMPOR was founded. The company emerged from the nationalization of the Cimentos Tejo, Cimentos de Leiria, Cibra-Pataias, Cisul, Cinorte, and Cabo Mondego companies.

The company Cimentos Maceira e Pataias (CMP) was founded in 1992 as a result of the privatization of the cement industry. The origin of this company was the Fábrica da Maceira-Liz and Fábrica Cibra-Pataias (Secil: História 2020). In 1994, Secil became a private company and was acquired by CMP.

4.2.2. Studies and Quality Control

The evolution of production techniques and application procedures was closely accompanied by science and engineering as a form of ensuring quality and safety. Tests were performed by Reynaud & Cia, the Cottancin license holder (1892), on reinforced concrete pavement at the School of Medicine in Lisbon in 1898 in the presence of Paul Cottancin, who was a pioneer in the use of reinforced brickwork and concrete. After 1898, the use of reinforced concrete was enhanced by the initiation of teaching modules, the appearance of journals on the subject—such as Construção Moderna (1900)—and numerous articles on the use of reinforced concrete. In 1902, a new journal—Revista de Engenharia Militar—presented several studies about different military caserns in which reinforced concrete was used in immersion tanks, lavatories, and mangers. During this period, the Military School (Lisbon, Portugal) also carried out studies on the properties of concrete, limestone, and cement (1896–1904).

Meanwhile, Cohen produced his second and third editions, which were published in 1896 and 1913, respectively, updating the technical information on the prices applied

to different types of construction works and referring to the materials used by various stakeholders during this period. In the second edition, the cement designations had already evolved to hydraulic quick-setting cement mortars and slow-setting hydraulic cement mortars.

The technical literature and the work of scientists such as Castanheira das Neves [19] referred to the use of reinforced concrete and presented the advantages of this material: improved physical, chemical, and mechanical properties and the flexibility of use in a great variety of applications. The consolidation of the use of cement and reinforced concrete resulted from these international and national scientific findings and studies, allowing the development and consolidation of the Portuguese industry. The standardization of cementitious materials and related building systems were also important contributions, with several patents and industrial companies continuing to appear in this specific area.

A few years later (1908), the progressive appearance of new techniques and materials in construction led to the creation of a new journal, "A Arquitetura Portugueza", which published, during its initial years, papers on other different construction materials, such as metallic elements and concrete bricks. This journal also referred to the works and names of important architects of the time.

At this time, António Vicente Ferreira (1874–1953) wrote one of the most relevant structural handbooks, Tabelas Técnicas, which was the first book published in Portugal on the subject of reinforced concrete. Somewhat later, in 1913, Cohen's previously referenced third edition presented "hydraulic mortars and Voreppe Roman cement". This was manufactured by Thorrand & C. in Voreppe, and it was considered the best French natural cement product. In this edition, seven types of mortars with natural cements were presented—including one without the addition of sand. The fourth edition was published in 1930, after Cohen's death. This fourth edition referred to a new type of cement called "Slag cement" (incorporating blast-furnace slag), which was defined as a more economical cement [16]. It should be noted that, in 1918, the first Portuguese regulation for reinforced concrete was approved and implemented [24].

During this period, in Portugal, the University of Lisbon and the University of Porto were founded, with Cimento Armado—reinforced concrete—as the first module to be taught in this new context at the Technical Faculty of the University of Porto by the engineer Theotonio Rodrigues.

4.2.3. Application in Architectural Heritage

Between 1902 and 1905, Bernardo Joaquim Moreira de Sá (1879–1919), a Portuguese engineer known for being one of the major drivers of the use of reinforced concrete in Portuguese construction works, and, later, the company Moreira de Sá & Malevez were responsible for the development of several construction elements using reinforced concrete (terraces, balconies, staircases, and others). Between 1909 and 1913, more projects with these techniques and materials were executed [24] and developed, supported by scientific research.

According to Júlio Appleton [26], during the mid-twentieth century, several relevant Portuguese constructions in reinforced concrete were built, such as the Tagus Canal (1932–1940), including elements such as tunnels, canal bridges, and pipes; the IST building (1936); and the Duarte Pacheco viaduct in Lisbon, completed in 1944. During the intense period of war, great infrastructures were developed, such as the pavement of the first Portuguese highway that started in Lisbon, the National Stadium (1942–1944), the viaduct on the same highway (1939–1944), the Santa Luzia arch dam, and the large University Hospital of Santa Maria (1940–1953).

5. Natural Cement in Portuguese Architectural Heritage

Historical Records of the Use of Natural Cements: Buildings and Architectural Elements

The beginning of the 20th century was characterized by a process of urban industrialization in the Portuguese territory. Cities such as Porto and Lisbon led the accelerated

progression of industrial evolution and population growth. This consequently led to the introduction of new construction techniques and materials that can be currently perceived in the specific characteristics of buildings, which provide a singularity that demands the necessary protection and conservation of this heritage. Historical records are a fundamental basis in terms of understanding the construction evolution that took place with the use of Roman cement and Portland cement, although, at the moment, the information is somewhat dispersed.

This period brought about significant changes in architectural expression, implemented by a considerable number of architects who transitioned toward modernism and the use of new building materials. However, this process was not direct, and the use of a variety of binders at the beginning of the 20th century is still obvious [9]. Examples of this diversity are Casa Barbot, built in the Art Nouveau style, in which a mixture of air lime, hydraulic lime, Portland cement, and blast-furnace slag coexist [27]. At Mirante da Quinta da Azeda [28], the use of Portland cement is clear, notwithstanding the fact that renders continued to be made with air lime. A notable architect from the 20th century, Raúl Lino (1879–1974), with over 700 projects, employed a mixture of air lime and pozzolana (from the Azores islands) to ensure the quality of renders [29].

Another architect with a large impact in the region of Porto at the beginning of the 20th century was José Marques da Silva (1869–1947). He carried out significant duties as the architect for Porto's city council and also the director of the School of Fine Arts of Porto and was largely responsible for the transition from eclecticism to modernity in this city [16]. This also had an impact in terms of a change in the choice of building materials. Over the years, Marques da Silva amplified his knowledge during his numerous international journeys and composed his library with various architecture books, construction manuals, journals, project documents, and other varied works. This archive currently constitutes the Fundação Instituto Marques da Silva, which has been maintained by his family since his death.

There are twenty-four works that mark the city of Porto designed by Marques da Silva. The first relevant project was Estação de São Bento (1896–1916), and between 1910 and 1920, the São João National Theater (TNSJ) was designed and built. Until 1943, the architect remained connected to projects in Porto. Serralves Villa (1925–1943) is one of the major architectural works and resulted from the contribution of several architects; however, somehow, Marques da Silva's "temperate modernist" characteristic is noticeable.

TNSJ (Teatro Nacional de S. João) is the main theater in Porto, located in the city center and built in 1918 [30] (Figure 7). This project by Marques da Silva used hydraulic binders and, more specifically, natural cement [30] for the execution of external ornaments and decorative elements with variable shapes and sizes, depicting floral elements, facial masks, and simple patterns of mortar in which a steel frame was used to create complex forms [17,30]. There are records suggesting innovation in the selection of materials, evolving from the traditional air lime to cement [30]. This possibly occurred in other prominent buildings, such as the Bolhão Market building (Figure 8) and other buildings of the same period. Bolhão Market was built shortly beforehand, in 1914, in the heart of the city of Porto and is characterized by its monumentality, architecture, and the evident influences of the "École de Beaux Arts" on the work of Marques da Silva.

Figure 7. São João Theatre (Teatro Nacional São João), built in 1918, Porto [18].

Figure 8. Bolhão Market (Mercado do Bolhão), built in 1914, Porto [31].

6. Conclusions

Natural cement, used in a transitional period that occurred before the general replacement of lime with Portland cement, is present in important elements of the built heritage across Europe. In Portugal, natural cement is understood to have been used between the end of the 19th century and the beginning of the 20th century. This is supported by the literature, scientific studies, and current research that confirms its presence in important heritage buildings, such as Teatro Nacional São João.

The cement industry in Portugal appeared later in time when compared to Central Europe and was initially based on imports. The first cement production company was established in 1866 under the name of Rasca. The location of the production units is noticeably related to the availability of raw materials in the surrounding areas. Portuguese natural cements designated as slow-setting natural cements are associated with the Rasca and Cabo Mondego sites (between the 1860s and 1890s), and quick-setting cements were produced by Pataias, Maceira, and São Pedro de Moel factories (early 20th century).

Commercial competition, technical improvements, and the introduction of technology increased the production and quality of materials and promoted the evolution of cement properties. Thus, the development of an artificial material that showed better properties, such as high durability, high mechanical resistance and greater impermeability, resulted in increased interest in modern cement production. Natural cement was unable to compete with these materials and was gradually replaced with Portland cement in mortars and concrete. At the same time, important changes in architecture also occurred, and buildings

started to exhibit fewer ornamental elements, in which natural cement was predominantly important, resulting in simpler and purer designs.

The manufacture of Portland cement expanded with its use and the help of scientific research in the development and improvement of its properties for different kinds of structures and applications. It is possible to trace the chronological period of the main advances in the Portuguese cement industry between 1866 and 1945.

Nowadays, the increase in conservation and restoration actions in buildings from this period implies the use of materials with mechanical, physical, and chemical properties that must be compatible with the original materials. Therefore, the impact of the use of binders and mixtures in the built heritage is undeniable. In order to comply with the great diversity of materials and mortar compositions used during this period, conservation/restoration actions should encompass a complete mortar characterization toward the use of compatible materials.

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References

1. Veiga, M.R.; Santos Silva, A. Mortars. In *Woodhead Publishing Series in Civil and Structural Engineering, Long-Term Performance and Durability of Masonry Structures*; Ghiassi, B., Lourenço, P.B., Eds.; Woodhead Publishing: Sawston, UK, 2019; Volume 6, pp. 169–208. ISBN 9780081021101. [CrossRef]
2. Weber, J.; Mayr, N.; Bayer, K.; Hughes, D.C.; Kozłowski, R.; Stillhammerova, M.; Ullrich, D.; Vyskocilova, R. Roman Cement Mortars in Europe's Architectural Heritage of the 19th Century. *J. ASTM Int.* **2007**, *4*, 1–5. Available online: http://www.astm.org/DIGITAL_LIBRARY/JOURNALS/JAI/PAGES/JAI100667.htm (accessed on 3 December 2022). [CrossRef]
3. Pintér, F.; Vidovszky, I.; Weber, J.; Bayer, K. Mineralogical and microstructural characteristics of historic Roman cement renders from Budapest, Hungary. *J. Cult. Herit.* **2014**, *15*, 219–226. [CrossRef]
4. Vitruvius. On Architecture: Bks. I-X. In *Dover Architecture*; Dover Publications, Inc.: Garden City, NY, USA, 2000; ISBN 9780486206455.
5. Adam, J.P. *Roman Building: Materials and Techniques*, 1st ed.; Routledge: London, UK, 1994; ISBN 0-203-98436-6.
6. Andrejkovičová, S.; Maljaee, H.; Rocha, D.; Rocha, F.; Soares, M.R.; Velosa, A. Mortars for Conservation of Late 19th and Early 20th Century Buildings—Combination of Natural Cements with Air Lime. *Materials* **2022**, *15*, 3704. [CrossRef] [PubMed]
7. Gerardo, S.; Gonçalves, T.; Flores-Colen, I. Cimento natural. In Proceedings of the História e Perspetivas de uso na Conservação de Edifícios em Portugal, Conferência Património Industrial, Tradição, Inovação, Conservação, LNEC, Lisboa, Portugal, 25 September 2015.
8. Elsen, J.; Balen, K.; Mertens, G. *Hydraulicity in Historic Lime Mortars: A Review*; Historic Mortars RILEM Bookseries; Springer Proceedings: Berlin/Heidelberg, Germany, 2012. [CrossRef]
9. Trout, E. The History of Calcareous Cements. In *Lea's Chemistry of Cement and Concrete*, 5th ed.; Hewlett, P.C., Liska, M., Eds.; Butterworth-Heinemann: Oxford, UK, 2019; Volume 1, pp. 1–29. ISBN 9780081007730. [CrossRef]
10. Singh, V.K. Overview of cement and cement industry, The Science and Technology of Cement and Other Hydraulic Binders. In *Woodhead Publishing Series in Civil and Structural Engineering, The Science and Technology of Cement and Other Hydraulic Binders*; Singh, V.K., Ed.; Woodhead Publishing: Sawston, UK, 2023; Volume 1, pp. 1–9. ISBN 9780323950800. [CrossRef]
11. Varas, M.J.; de Buergo, M.A.; Fort, R. The origin and development of natural cements: The Spanish experience. *Constr. Build. Mater.* **2007**, *21*, 436–445. [CrossRef]
12. Margalha, M.G. Argamassas—Conservação e Recuperação do Património. Master's Thesis, University of Évora, Évora, Portugal, 2007.

13. Fernandes, P. Vigas de Grande Vão Prefabricadas em Betão de Alta Resistência Pré-Esforçado. Ph.D. Thesis, Universidade de Coimbra, Coimbra, Portugal, 2005.
14. Alvarez, J.; Sequeira, C.; Costa, M. Ensinamentos a retirar do Passado Histórico das Argamassas. In Proceedings of the 10 Congresso Nacional de Argamassas de Construção, FIL, Lisboa, Portugal, 24–25 November 2005.
15. Maravelaki-Kalaitzaki, P.; Bakolas, A.; Moropoulou, A. Physico-chemical study of Cretan ancient mortars. *Cem. Concr. Res.* **2003**, *33*, 651–661. [CrossRef]
16. Vale, C.P.; Figueiredo, C.; Velosa, A.; Veiga, R. O Cimento Natural em Portugal. Registos de uso entre o final do século XIX e o Primerio Quartel do Século XX. In Proceedings of the 3o Congresso Internacional de História da Construção Luso-Brasileira, Salvador da Bahia, Brazil, 3–6 September 2019.
17. Gosselin, C.; Verges-Belmin, V.; Royer, A.; Martinet, G. Natural cement and monumental restoration. *Mater. Struct. Mater. Constr.* **2009**, *42*, 749–763. [CrossRef]
18. Rocha Vizinho, D. Argamassas de Cimento Romano Utilizadas em Edifícios do Início do Século XX. Master's Thesis, University of Aveiro, Aveiro, Portugal, 2015. Available online: https://ria.ua.pt/handle/10773/16867 (accessed on 22 September 2022).
19. Neves, J.C. 1984. Estudo sobre cimentos estrangeiros importados em Portugal. In *Revista de Obras Públicas e Minas, 295 and 29*; Associacão dos Engenheiros Civis Portugueses: Lisboa, Portugal, 1894; pp. 265–371.
20. Diogo, M. *Indústria e engenheiros no Portugal de fins do século XIX: O caso de uma relação difícil', Scripta Nova*; Revista Eletrónica de Geografía y Ciencias Sociales: Barcelona, Spain, 2000; Volume 69, ISSN 1138-9788.
21. Martins, P. The History of Cimpor (Portuguese Cement Company): A Contribution to the History of Science. *Int. J. Eng. Manag. Res.* **2018**, *8*, 157–161. [CrossRef]
22. Brandão, J.; Callapez, P.; Soares, J. O carvão do Cabo Mondego e os Caminhos de Ferro do Estado: Cinco perguntas e um parecer. *Geonovas* **2016**, *29*, 53–70.
23. Callapez, P.; Pinto, J.; Santos, V.; Brandão, J. A Mina de Carvão do Cabo Mondego: 200 anos de Exploração E a Paleontologia Portuguesa, "Memórias do Carvão" é o Tema que Norteia a Organização do Programa das Jornadas Internacionais 11–13 de Setembro, Porto de Mós e Batalha. 2014. Available online: http://repositorio.lneg.pt/handle/10400.9/2855 (accessed on 7 August 2023).
24. Mascarenhas-Mateus, J.; Castro, C. The Portland cement industry and reinforced concrete in Portugal, Building Knowledge. In *Constructing Histories*, 1st ed.; Imprint CRC Press eBook: Boca Raton, FL, USA, 2018; Volume 2, ISBN 9780429446719.
25. Neves, P.; Grandes Empresas Industriais De Um País Pequeno: Portugal. Da Década De 1880 À 1a Guerra Mundial, Doctoral Thesis, ISEG. 2007. Available online: https://www.repository.utl.pt/bitstream/10400.5/525/1/TesePedroNeves.pdf (accessed on 7 August 2023).
26. Appleton, J. Construções em Betão–Nota Histórica Sobre a Sua Evolução, Instituto Superior Técnico. 2005. Available online: https://www.civil.ist.utl.pt/~cristina/GDBAPE/ConstrucoesEmBetao.pdf (accessed on 4 September 2023).
27. Maljaee, H.; Silva, A.S.; Velosa, A. Characterization of Mortar from Casa Barbot (Portugal), a Case Study from the Beginning of the 20th Century. *Buildings* **2023**, *13*, 232. [CrossRef]
28. Almeida, L.; Santos, A.R.; Santos Silva, A.; Veiga, M.R.; Velosa, A. Characterization of Mortars and Concretes from the Mirante da Quinta da Azeda, Setúbal (Portugal). In *A Case Study from the Beginning of the 20th Century*; RILEM Bookseries; Springer Proceedings: Berlin/Heidelberg, Germany, 2023; Volume 42, pp. 243–257. [CrossRef]
29. Silva, H.; Lourenço, T. Do papel para a matéria os cadernos de encargos como fontes para a interpretação da obra arquitetónica. In *Cinco Construçes de Raul Lino Cadernos do Arquivo Municipal*; 2.ª Série N.º 17: Lisboa, Portugal, 2022; pp. 27–51. ISSN 2183-3176. Available online: https://journals.openedition.org/arquivomunicipal/427 (accessed on 4 September 2023).
30. Velosa, A.; Rocha, F.; Costa, A.; Coroado, J.; Fragata, A.; Paupério, E. Characterization of the Conservation State of the Façade of Teatro Nacional de S. João, Porto. In Proceedings of the International Conference on Durability of Buildings Materials and Components, FEUP, Porto, Portugal, 12–15 April 2011.
31. Direção-Geral do Património Cultural, (n.d.) Sistema de Informação para Património Arquitetónico (SIPA). Available online: https://www.monumentos.gov.pt/Site/APP_PagesUser/SIPA.aspx?id=5473 (accessed on 11 March 2020).