ORIGINAL ARTICLE

A review on the evolution of Portland cement and chemical admixtures in Brazil

Uma revisão da evolução do cimento Portland e das misturas químicas no Brasil

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Abstract: Over the years, Portland cement concretes have undergone increasing demands for constructability, cost, quality, and environmental impact. These demands were met, mainly, through changes in the cement composition and the introduction of chemical admixtures. In this sense, through a literature review, the authors sought to create a collection of information on the evolution of these materials and their standards from 1937 to 2020 in Brazil . This work is part of a research project that aims to elaborate a dating protocol for Brazilian concretes. From the review conducted, the authors observed that the absence of systematic records in the Brazilian civil construction sector hinders the attempt to create a chronology of the development of concrete in the country. In addition, we concluded that the knowledge of the evolution of Portland cement and chemical admixtures is relevant information that can assist in concrete dating processes. The reliable comparison data, posteriorly combined with microstructural characterisation techniques, may lay the basis for an effective dating methodology.

Keywords: Portland cement, chemical admixtures Brazil, cement industry, review, concrete dating.

Resumo: Ao longo dos anos, os concretos de cimento Portland têm sofrido demandas crescentes em termos de construtibilidade, custo, qualidade e impacto ambiental. Essas demandas foram atendidas, principalmente, por meio de mudanças na composição do cimento e introdução de aditivos químicos. Nesse sentido, por meio de uma revisão da literatura, os autores buscaram criar um conjunto de informações sobre a evolução desses materiais e seus padrões de 1937 a 2020 no Brasil. Este trabalho faz parte de um projeto de pesquisa que visa elaborar um protocolo de datação para concretos brasileiros. A partir da revisão realizada, os autores observaram que a ausência de registros sistemáticos no setor da construção civil brasileira dificulta a tentativa de se fazer uma cronologia do desenvolvimento do concreto no país. Além disso, concluiu-se que o conhecimento da evolução do cimento Portland e dos aditivos químicos é uma informação relevante que pode auxiliar em processos de datação de concretos. Os dados de comparação confiáveis, posteriormente combinados com técnicas de caracterização microestrutural, podem servir de base para uma metodologia de datação eficaz.

Palavras-chave: cimento Portland, aditivos químicos no Brasil, indústria cimentícia, revisão, datação de concretos.

1 INTRODUCTION

The Laboratory of Civil Construction Materials in the Federal University of Ouro Preto recently received the following demand: to date a building that was under legal dispute. The records and documents regarding the exact year

of construction of this building were inconclusive and/or conflicting. Faced with this challenge, the authors decided to investigate if the dating would be possible through the building materials, more specifically, the concrete.

In addition to the case, knowledge about the age of a concrete structure allows for assessing material durability and determining repair procedures. It can also assist in restoration interventions and historic mapping of buildings. However, despite the relevance for both public and private sectors, no articles or systematic methods for this complex problem were found in the literature.

Carbonation depth has been studied to identify the approximate age of concrete cracks [1]. It is roughly precise as a comparative method (surface already carbonated along the years vs. recently exposed surface of the same concrete) [1]. However, in absolute terms, it has limitations, since the quality of the concrete mixing, pouring, and curing can strongly influence the carbonation depth [2], [3]. Additionally, this phenomenon can be influenced by the technology of chemical admixtures of its time.

The same can be said for chloride ion penetration. Different concrete structures with the same concrete mix proportion and age can have different penetration depths, depending on the curing and exposure conditions [4]. Thus, the age of construction of a concrete structure cannot be accurately associated with its durability parameters.

Regarding dating from the aggregates, most Brazilian aggregates originate from natural crushed rocks [5]. Normally, there are multiple quarries with different geological origins supplying the same city. Additionally, it is known that the mineral characteristics of a rock can vary slightly, even within the same deposit. Therefore, the aggregates' composition is also not a suitable approach for estimating the age of a concrete element.

On the other hand, given that the technological evolution of concrete reflects, above all, the development of Portland cement and the introduction of chemical admixtures to the matrices [6], knowledge on how these materials advance over the years can be useful in dating strategies. A database of the evolution of the use and composition of cement and admixtures in Brazil was not found in the literature and can assist researchers of various fields. In this sense, the present work seeks to create a collection of reliable data on the topic in Brazil. This study represents the initial step on the development of a methodology for dating Brazilian concretes.

1.1 Review Methodology

To gather the information on the evolution of these materials and their standards, a narrative literature review was conducted, focusing on the Brazilian construction industry. Since this work seeks to establish a critical historic overview, a systematic approach to the selection of sources was not adopted. The literature covers a wide variety of publication types (e.g., standards, books, reports, conference articles, news) and dates (1937-2020).

The review is divided into two parts. The first covers the development of Portland cement in Brazil, while the second covers the evolution of chemical admixtures in the country. On the Portland cement section, a concise historic background of the first Brazilian plants is presented, followed by the definition of the types currently sold in the market and their current consumption. Subsequently, the authors investigate how the Brazilian Portland cement standards have evolved along the past decades and trace parallels to the American and British ones. To conclude the study on the Portland cement, graphs show the changes in the proportion of clinker components along the last century. Afterwards, the advancements of the use of chemical admixtures and their standards in Brazil are discussed. Finally, the authors present their final remarks with the conclusions drawn from the investigations carried out.

2 A BRIEF HISTORY OF PORTLAND CEMENT

In 1824, Joseph Aspdin received a patent for a binder developed by burning limestone and clay. This fine powder received the name Portland cement due to its similarity, in colour and solidifying properties, to the limestone rocks of the British island of Portland. The product created by Aspdin back then had different mineralogy and properties from the Portland cement sold nowadays [7]-[9]. Some modifications performed by this English builder and his son, William Aspdin, in the second half of the 19th century, resulted in a product more similar to the modern material [6].

The well-known constituents of cement are tricalcium silicate ($3CaOSiO_2$ - C_3S), dicalcium silicate ($2CaOSiO_2$ - C_2S), tricalcium aluminate ($3CaOAl_2O_3$ - C_3A) and tetra-calcium aluminoferrite ($4CaOAl_2O_3Fe_2O_3$ - C_4AF). Additionally, other minerals can be formed in minor proportions, such as free lime (CaO), periclase (MgO) and various alkaline sulphates [10], [11]. According to studies carried out by Tennis and Bhatty [12], from 1950 to the present day, the chemical composition of the main constituents of this Portland cement remained essentially unchanged.

The first record of Portland cement production in Brazil dates from 1888, in a small industrial unit located in the state of São Paulo [13], [14]. This was the first attempt to manufacture hydraulic binders for civil construction purposes in the country [13]. Several isolated cement plants were developed in the following years [14]. However, only in 1933, with the consolidation of the Brazilian Portland Cement Company (Companhia Brasileira de Cimento Portland, in Portuguese), the country achieved a production capacity able to surpass the imports (226 thousand tons at the time), creating prospects for the opening of new plants [13]. In comparison, the first British cement association, the Associated Portland Cement Manufacturers Ltd, was founded in 1900 [15]. In the US, the Association of American Portland Cement Manufacturers (AAPCM) was created in 1902 (and renamed Portland Cement Association, PCA, in 1916) [16].

In 2019, according to the National Union of the Cement Industry (SNIC), the production of this binder reached 42 million tons [17]. In 2017, Brazil was the sixth largest cement producer in the world [18].

3 TYPES AND COMPOSITION OF BRAZILIAN PORTLAND CEMENT IN BRAZIL OVER THE DECADES

3.1 Standardisation in Brazil and comparison with American and British standards

The first batches of Brazilian-produced Portland cement had no mineral admixtures nor components other than clinker and plaster. This common type is now specified as CP I, where "CP" refers to "Cimento Portland" (Portland cement in Portuguese) and "I" marks the "ordinary" classification. The first Brazilian standard related to Portland cement was published in 1937 [19], approximately 33 years after the first American and British ones [20], [21]. Brazilian type CP I is equivalent to American ASTM type I and British BSI CEM I. The scientific and technological mastery of this product enabled the development of other types of cement in the following years.

One of the first new types was the high early strength Portland cement, specified nowadays in Brazil as CP V (equivalent to ASTM type III and BSI notations "-N" and "-R"). This type must reach a high mechanical resistance in the early ages, obtained from a higher C_3S content and by grinding the cement in finer particles, [6], [22]-[24]. In Brazil, its first standardisation dates from 1940.

Aiming to reduce the cost and energy consumption of the manufacturing process [25]-[27], the use of supplementary cementing materials (SCMs) to partially replace the clinker was gradually adopted worldwide. Granulated blast furnace slag was the initial solution, followed by pozzolanic materials [28]. The first cases of adoption of SCMs in the Brazilian cement industry date from 1952, while this practice was already regulated since 1946 in the USA (ASTM C250) and 1923 in the UK [20], [29].

The Portland Blast-Furnace slag cement (now CP III) was the first standardized cement with admixtures in Brazil (1966). It is equivalent to BSI type CEM III and ASTM binary blended cement type IS ("S" for slag), although the Brazilian type currently allows up to 10% limestone filler (which is not covered in BSI and ASTM binary blended cements).

The Portland-pozzolan cement (now CP IV) was the next blend to get its standard, in 1974. It is equivalent to BSI type CEM IV and ASTM binary blended cement type IP ("P" for pozzolan) but may also include up to 10% limestone filler. In 1991, the Brazilian Association of Technical Standards (ABNT) published the standard for Portland composite cements (CP II), whose composition is intermediate between ordinary Portland cement (CP I) and Portland cements with blast furnace slag and pozzolanic materials, CP III e CP IV.

The Portland-composite cement can be further divided in CP II – E (clinker + calcium sulphate partially replaced by blast furnace slag and limestone filler), CP II – Z (clinker + calcium sulphate partially replaced by pozzolanic materials and limestone filler) and CP II – F (clinker + calcium sulphate partially replaced by limestone filler). Brazilian types CP II – E and CP II – Z are equivalent to ASTM ternary blended cement (IT) but have no equivalent in the BSI standards, which do not include a cement type with high contents of slag + filler or pozzolan + filler. In turn, CP II – F is equivalent to ASTM limestone cement (IL) and, depending on the composition proportion and material quality, can be equivalent to BSI CEM II A-L, A-LL, B-L, or B-LL.

Until 2018, each type of cement had its specific ABNT standard. In that year, the standards were unified in NBR 16697, which, in line with its British and American counterparts, presents all the specifications and requirements for all types of cement. Table 1 summarises the latest Brazilian cement types and their equivalents in the US and UK. Due to its particularities, white cement is not included in the present study.

Table 1. Summary of current Brazilian cement types and their American and British equivalents [30]-[33].

Brazilian ABNT Type	Name	Composition (range of percentage by mass)				American ASTM equivalent	British BSI equivalent
		Clinker + calcium sulphate	Granulated blast furnace slag	pozzolanic materials	limestone filler		
CP I	Ordinary Portland cement	95-100		0-5		Type I	CEM I
CP I-S	Ordinary Portland cement with admixtures	90-94	0	0	6-10	Type I	CEM II A-L or A-LL[1]
CP II-E	Portland-composite cement with blast furnace slag	51-94	6-34	0	0-15	Type IT(Lα)(Sβ)[2]	-
CP II-Z	Portland-composite cement with pozzolanic materials	71-94	0	6-14	0-15	Type IT(Lα)(Pβ)[2]	-
CP II-F	Portland-composite cement with limestone filler	75-89	0	0	11-25	Type IL(α)[2]	CEM II A-L, A-LL, B-L, or B-LL
CP III	Portland blast-furnace slag cement	25-65	35-75	0	0-10	Type IS(α)[2,3]	CEM III A or B[3]
CP IV	Portland-pozzolan cement	45-85	0	15-50	0-10	Type IP(α)[2,3]	CEM IV A or B[3]
CP V	High early strength Portland cement	90-100	0	0	0-10	Type III	Notation "-N" or "-R" to the other types

[1] Brazilian CP I-S may contain 6-10% limestone filler, while British CEM II/A may contain 6-20%. Therefore, they are only equivalent when the cement comprises up to 10% limestone filler. [2] Where α and β are the replacement rate of the material. E.g. a) 20% slag (S) and 10% limestone filler (L) = Type IT(S20)(L10); b) 40% pozzolan (P) = IP(40). [3] Brazilian standards allow up to 10% limestone filler to binary blends CP III and CP IV since 2018, whereas their American and British counterparts do not. An American cement with both limestone filler and slag or pozzolan would be identified as a ternary blend. British BSI standard does allow up to 5% "minor additional constituents" but does not label them as limestone filler.

The American cement classifications are based on the intended use or resulting property (e.g., Type II - when moderate sulphate resistance is desired, or Type IV - when a low heat of hydration is desired). On the other hand, the Brazilian and British naming systems mostly consider the type and content of mineral admixtures. The current Brazilian standard, NBR 16697, allows the application of the suffixes "RS" for sulphate resistance and "BC" for low heat of hydration to any cement type, given that it fulfils the prescribed specifications.

Both American and British standards require some form of identification of how much mineral admixture is added to the cement. The American ASTM prescribes a straightforward approach: the percentage of each admixture must be clearly stated (e.g. IT(S20)(L10) or IP(40)). British standards have different ratings for different replacement percentages. For example, blast furnace cement (CEM III) can be classified as "A" if 36-65% of its clinker + calcium sulphate is replaced by blast furnace slag; "B", for 66-80%; and "C" for 81-95%. Brazilian cement manufacturers are not required to display this information; they only use it to classify their cement in the broad ranges mentioned in Table 1.

Both ASTM and BSI allow blends with both slag and pozzolans, currently not allowed by Brazilian ABNT. Also, the British standard provides specifications on the type of pozzolanic addition, and the quality of the carbonaceous material used. The Brazilian standard does not require the manufacturer to specify whether only one or more than one type of pozzolan is used. There is also no mention of whether this is allowed.

While the British BSI standard allows any type of cement to have high initial strength, Brazilian ABNT and American ASTM standards restrict this characteristic to a specific type of cement. BSI also brings 2 classifications for high initial strength cement (according to performance limits), in addition to 1 classification for low initial strength cement, which does not happen for Brazilian and American cement types.

Finally, the American ASTM standards have the notation "-A" to indicate air-entrained cement. Since Brazil is a tropical country where temperatures rarely fall below 0ºC, the concretes are not commonly required to ensure freezing and thawing durability.

Nowadays, all Brazilian types of cement (except for High Early Strength) must present one out of three strength classes: 25, 32 or 40 [30]. These values represent the minimum 28-days compressive strength (in MPa) required from a standard 1:3 mortar cast in ϕ5×10 cm cylindrical specimens. High Early Strength Portland cement (CP V) must reach 14 MPa in 24 hours and 34 MPa in 7 days. Its strength class is called "ARI", standing for "*Alta Resistência Inicial*" (High Early Strength).

3.2 Portland cement consumption in Brazil

Figure 1 presents the evolution of consumption of Brazilian Portland cement types according to data from the National Union of the Cement Industry (SNIC), presented at statistical yearbooks published by the Brazilian Institute of Geography and Statistics (IBGE) [34].
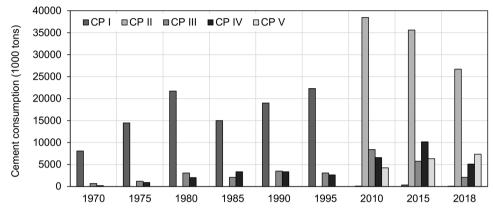

Figure 1. Brazilian consumption of Portland cement, by type. Note: the yearbooks of the 70s, 80s and 90s do not present values for CP V consumption, and there was no specification on the consumption of Portland cement in the years 2000 and 2005.

Ordinary Portland cement (CP I) was the most adopted in Brazilian constructions until 1995. From 1996 onwards, Portland-composite cement (CP II) takes its place as the favourite in the usual construction applications. The replacement of CP I by CP II is probably linked to the reduction of costs related to the use of SCMs, as will be later discussed. Nowadays, the commercial production of CP I is restricted to cement companies far from thermoelectric and steel industries, such as those in the Northern region of Brazil.

The graph also shows a significant increase in cement consumption (for all types) in the last decade, followed by a slight decrease in 2018 due to the economic recession in Brazil. CP III and CP IV have also been gaining space in the Brazilian market, attributed to the greater use of these types in concrete elements of large volume (such as dams and foundations), and in those that require greater durability. Finally, the increase in CP V consumption stands out in the past few years, probably related to the advance of precast concrete structures and the requirement for quicker formwork removal times, associated with the industrialisation of civil construction in the country.

3.3 Types of Portland cement in Brazil

3.3.1 Ordinary Portland cement (CP I and CP I-S)

The first cement type produced and sold in Brazil was the ordinary Portland cement (originally CP, now CP I), without any components other than clinker and calcium sulphate [28], [35]. Table 2 shows the evolution of the standardisation of CP I in Brazil. It is noteworthy that, from 1977 onwards, the addition of small amounts of SCMs to this type of cement was allowed, probably due to the cost, performance and environmental advantages achieved in CP III and CP IV, as will be seen in the next sections. In 1988, the CP I was broken down in three types (CPS, CPE, and CPZ), according to the mineral admixture added to it. In 1991 a new subtype for low levels of admixtures was established, the "ordinary Portland cement with admixture", CP I-S, and CP I returned as the type without any.

Table 2. Evolution of standardisation of the ordinary Portland cement (CP I and CP I-S) in Brazil, in terms of maximum clinker + calcium sulphate replacement in mass.

Standard	Year	Allowed content of mineral admixtures for CP I	Allowed content of mineral admixtures for CP I-S	Strength classes
EB-1 (originally) NBR 5732	1937	0%	-	25
EB-1 (originally) NBR 5732	1973	0%	-	25 32 40
NBR 5732	1977	0 to 10% blast furnace slag	-	25 32
		0%		40
NBR 5732	1988	0 to 5% limestone filler (CPS)	-	25 32 40
		0% to 10% blast furnace slag (CPE)		
		0% to 10% pozzolanic materials (CPZ)		
NBR 5732	1991	0%	0% to 5% blast furnace slag or pozzolanic materials or limestone filler	25 32 40
NBR 16697	2018	0% to 5% blast furnace slag or pozzolanic materials or limestone filler	6 to 10% limestone filler	25 32 40

3.3.2 Portland Blast-Furnace slag cement (CP III)

Granulated blast furnace slag, a by-product of the conversion of iron ore into pig iron, is comprised mainly by CaO, SiO_2 and Al_2O_3 [36], and consists of a vitreous material with cementing properties [37], [38].

In Brazil, the addition of blast furnace slag to Portland cement began in 1952, with the Tupi company, in the city of Volta Redonda (state of Rio de Janeiro), using the residues from the National Steel Company (Companhia Siderúrgica Nacional – CSN) [39]. In 2017, Brazil was the ninth-largest steel producer in the world, manufacturing 34.4 million tons of the metal, and generating 8.8 million tons of blast furnace slag in the process [40]. Table 3 shows the evolution of the standardisation of CP III in Brazil.

Table 3. Evolution of standardisation of the Portland Blast-Furnace slag cement (CP III) in Brazil, in terms of maximum clinker + calcium sulphate replacement in mass.

Standard	Year	Allowed content of mineral admixtures for CP III	Strength classes
EB-208 (originally) NBR 5735	1966	25% to 65% blast furnace slag	25
NBR 5735	1974	25% to 65% blast furnace slag	25 32
NBR 5735	1987	35% to 70% blast furnace slag	25 32 40
		0% to 5% limestone filler	
NBR 5735	1991	35% to 70% blast furnace slag	25 32 40
		0% to 5% limestone filler	
NBR 16697	2018	35% to 75% blast furnace slag	25 32 40
		0% to 10% limestone filler	

In the 1960s, there was only one strength class for Portland blast furnace cement, 25. Classes 32 and 40 came in the 70s and 80s, respectively. Technological advances in the cement manufacturing process, such as the increase of grain fineness and changes in C_3S content, led to greater mechanical strength [22]-[24], [6].

The increasing trend in the replacement of clinker + calcium sulphate by blast furnace slag continued from the 1980s onwards. Several factors are favourable to this adoption. First, the increased use of SCMs promotes a reduction in CO_2 emissions, energy costs and consumption of natural resources. Secondly, the incorporation of slag into cement production also contributes to a more suitable destination for these residues. These scenarios also reduce the costs and environmental impacts of both steel and cement companies. Finally, there are major technological advantages in increasing the replacement of clinker by SCMs in cement-based composites, such as the reduction of the heat of hydration, lower permeability, and greater durability [41], [36], [38].

With all these advantages, coupled with the increase in cement consumption in recent years, in 2009 the steelmaker CSN inaugurated its own cement plant [42]. With the supply of blast furnace slag reduced, as the main supplier in the

Southeastern Region now consumes most of its production, some Brazilian cement companies started to import their slag from foreign steelmakers. Others began to invest in pozzolanic materials [14].

3.3.3 Portland-pozzolan cement (CP IV)

Pozzolans are SCMs that by themselves possess little or no cementing capacity, but finely divided and in presence of moisture chemically react with calcium hydroxide ($Ca(OH)_2$ or CH), forming calcium silicate hydrates (C-S-H) [11]. The reaction between the pozzolan and CH is called pozzolanic activity, and the resulting C-S-H increases the strength and decreases the permeability of the matrix.

In Brazil, the addition of pozzolanic materials to Portland cement began only in 1969 by Indústrias Reunidas Francisco Matarazzo, with the use of fly ash from the Charqueadas thermoelectric plant [39]. Table 4 shows the evolution of the standardisation of CP IV in Brazil. There has been an increase in the maximum allowed content of pozzolanic additions to cement over the years. This increase is also related to the environmental, economic, and technological factors previously mentioned for the blast furnace slag.

Table 4. Evolution of standardisation of Portland-pozzolan cement (CP IV) in Brazil, in terms of maximum clinker + calcium sulphate replacement in mass.

Standard	Year	Allowed content of mineral admixtures for CP IV	Strength classes
EB-758 (originally)	1974	10% to 40% pozzolanic materials	25
NBR 5735 (later)		10% to 30% pozzolanic materials	32
NBR 5736	1986	15% to 40% pozzolanic materials	25 32
NBR 5736	1991	15% to 50% pozzolanic materials	25 32
		0% to 5% limestone filler	
NBR 16697	2018	15% to 50% pozzolanic materials	25 32 40
		0% to 10% limestone filler	

The pozzolanic materials most used by the cement industries are silica fume, fly ash, volcanic ash, rice husk ash, and metakaolin [43]-[45]. In Brazil, given the size of the country, the type of pozzolana adopted varies with the availability of each region. In the Southern Region, for example, fly ash is widely used, obtained from the thermoelectric plants of the area. In the Northeastern region, calcined clays are the most common pozzolans adopted [28].

3.3.4 Portland-composite cement (CP II-E, CP-II Z and CP II-F)

Composite cement was the last one to be standardised. The three types of composite cement (CP II-E, CP II-Z and CP II-F) may have limestone fillers, with CP II-E and CP II-Z also presenting intermediate levels of blast furnace slag and pozzolanic materials, respectively. Table 5 shows the evolution of the standardisation of CP II in Brazil.

Table 5. Evolution of standardisation of Portland-composite cement (CP II) in Brazil, in terms of maximum clinker + calcium sulphate replacement in mass.

Standard	Year	Allowed content of mineral admixtures for CP II-E	Allowed content of mineral admixtures for CP II-Z	Allowed content of mineral admixtures for CP II-F	Strength classes
NBR 11578	1991	6% to 34% blast furnace slag	6% to 14% pozzolanic materials	6% a 10% limestone filler	25 32 40
		filler0% to 10% limestone	limestone 0% to 10% filler		
NBR 16697	2018	6% to 34% blast furnace slag	6% to 14% pozzolanic materials	11% a 25% limestone filler	25 32 40
		0% to 15% limestone filler	0% to 15% limestone filler		

Note that Brazilian standards only allow the use of "carbonate materials" as fillers, not referring to other types of inert minerals. The limestone filler is obtained from ground limestone rocks. Up to certain limits, this mineral admixture is known to increase concrete workability in the fresh state, as the fine particles act as a lubricant [46], [47]. In the hardened state, the fillers promote filling of voids and dispersion of grains [48], leading to enhanced mechanical strength

and lower porosity [46], [47]. Due to these technical advantages and its relatively low cost, the maximum allowed addition of limestone filler in Brazilian cement has been increased over the decades.

3.3.5 High Early Strength Portland Cement (CP V)

High Early Strength Portland cement (CP V) was first regulated in 1940, only 3 years after CP I. The mastery of Portland cement composition, grinding processes and hydration reactions enabled the development of CP I to a binder capable of producing matrices with high resistance already in early ages. Although its standardisation is relatively old, only in the past decade the CP V has gained space in the Brazilian market, due to the growth of the precast industries, the introduction of cast-in-place concrete wall systems, and the pressure for increasingly early removal of concrete formworks in conventional structures [28]. Table 6 shows the evolution of the standardisation of CP V in Brazil.

Table 6. Evolution of standardisation of the High Early Strength Portland cement (CP V) in Brazil, in terms of maximum clinker + calcium sulphate replacement in mass.

Standard	Year	Allowed content of mineral admixtures for CP V	Minimum strength (MPa)		
			1 day	3 days	7 days
EB-2 (originally) NBR 5733 (later)	1940	0% to 1% of any material	11	22	31
NBR 5733	1974	0%	11	22	31
NBR 5733	1991	0 to 5% limestone filler	14	24	34
NBR 16697	2018	0 to 10% limestone filler	14	24	34

As of the 1991 regulations, an increase in the mechanical strength is required at all ages. This demand is obtained through an enhanced grinding process and an increase in the clinker's C_3S content, which accelerate the hydration reactions at early ages [2]-[5]. It is also noticeable that, related to the reduction in costs and environmental impacts, the 2018 version allows a greater amount of limestone filler addition to this type of cement.

3.4 Evolution of clinker components

Since the development of Portland cement, its most demanded properties are the speed and intensity of mechanical strength gain [6]. To this purpose, the proportion of cement constituents and the fineness of the grains have been changing over the years [2]-[5].

This development was made possible thanks to studies on cement chemistry and advances in micro and nanometric characterisation techniques [7]-[9]. These analyses allowed, above all, the better understanding of the hydration mechanisms of the Portland cement components [8], [10]-[12] and their interactions with other materials [13]-[15]. The improvement in the quality of the cement was also possible due to the evolution of kiln designs, which ensured a greater control of production and an increase in clinker uniformity [16], [17].

Figure 2 shows trends in the levels of constituents of Portland cements produced worldwide over time. Brazilian cement technology followed the same trends. The graphs were constructed from a series of data collected in books and scientific articles, shown in the Appendix.

The increase in the average C_3S content by about 100% and the reduction in the average C_2S content by approximately 66% are related to rapid strength gain of the concretes, a characteristic increasingly demanded by the construction industry [3], [4], [8]. Although the C-S-H produced by the hydration of C_3S and C_2S have similar structure, the hydration of C_3S occurs much earlier, contributing to almost half of the mechanical strength at 28 days [8].

These results agree with the literature. Gonnerman and Lerch [2] studied concrete samples collected between 1904 and 1950 and observed an increase in the specific surface of the grains and the C_3S content. More recently, Tennis and Bhatty [18] analysed cement samples from 1950 to 2004 and reached the same conclusions.

One of the consequences of the increase in the C_3S proportion and grain fineness is an increase in the heat released during hydration reactions. In this sense, the reduction of the average C_3A content by about 31% can be justified by the search for lower heat release, since C_3A is one of the components that most contribute to the exothermic nature of the hydration process [8], [19]. The only main constituent that remained roughly unaltered over the years was the C_4AF phase, possibly due to its low impact on the mechanical and rheological properties and in the hydration kinetics.
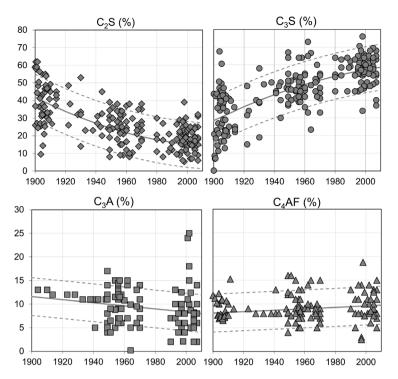
Figure 2. Variation in the proportion of the main components of Portland cements over the years in Brazil and worldwide.

4 TYPES OF CHEMICAL ADMIXTURES IN BRAZIL OVER THE DECADES

4.1 Use of admixtures in Brazilian concretes

The advances in concrete performance were promoted not only by modifications on the proportion of cement constituents and the increase in grain fineness, but also by the improvement of construction technologies and the emergence of chemical admixtures [5]. There are today over 20 commercial types of admixtures, which are capable of interfering with hydration kinetics, the amount of hydration products formed and the intermolecular attraction forces between cement grains [20].

Mehta and Monteiro [11] indicate that about 80 to 90% of the concrete produced in developed countries has at least one chemical admixture. In Brazil, there are no data on the use of admixtures, and there is no national syndicate or association of admixture manufacturers. It is believed that the percentage of concretes with admixtures is significantly lower, due to the predominance of self-built homes in the country [21], and the lack of technological control of concrete production in most construction sites [22]. However, in general lines, the concrete practices in the country have usually followed international trends.

Mehta and Burrows [24] point out that the industrial growth from 1950 onwards boosted the development of pumped concretes and the consolidation of immersion (or needle) vibrators. According to the authors, these factors triggered the need for more fluid concretes, which, before the advent of plasticizer admixtures in the 1960s, were only attained by increasing the water content.

The first plasticizer admixtures, developed in Japan in the 1960s [23], were introduced to the Brazilian market in the same decade [24]. Initially, they were mostly adopted by consumers with a high-level technical background, such as concrete plants.

In that same decade, the first superplasticizers based on sulfonated naphthalene-formaldehyde condensate were being formulated [24]. The dissemination of these admixtures reduced the water/cement ratio and improved the workability of fresh concrete. Due to these factors, these products have led to more resistant and less permeable concretes worldwide [25], [26]. In Brazil, these mixtures were introduced only in the mid-1970s [27].

This successful use of superplasticizers, coupled with labour shortages and construction time savings, encouraged the development of self-compacting concretes (SCC) in the 1980s in Japan [28]. According to Faria [49], SCC arrived in Brazil in the 1990s. The increase in productivity allowed this type of material to be used in the Brazilian precast

concrete industries [30]. There are no official data on the subject, but Costa and Cabral [31] state that the SCC in vertical constructions is still little used in Brazil, mainly due to the higher initial cost of the material.

The 1980s were also marked by the development of polycarboxylate-based superplasticizer admixtures by Japanese chemical industries [32], [33]. This new generation, which was popularized in Brazil and worldwide in the 1990s, promoted the development of high- and ultra-high-strength concretes [24].

There are no reports of when the set retarding admixtures started to be commercialised in the Brazilian market, however, it is assumed that their use has intensified since the consolidation of concrete plants in the country in the 1960s [34]. This type of admixture is especially important in hot climates, allowing a longer period for concrete mixing and pouring [24].

Ultimately, no records were found in the Brazilian literature regarding the beginning of the adoption of the other types of admixtures in the country. There was also no data on their production volume and when the first chemical industries were established. Records of when these admixtures were first introduced in the Brazilian concretes can lead to valuable clues as to the age of a concrete element. By identifying the chemical component of the admixture in the cement matrix, the age of the structure can be traced over a narrow range of years. The authors have ongoing initiatives seeking to recognize the type of admixture used in samples taken from hardened concrete.

4.2 Standardisation in Brazil and comparison with American and British standards

In Brazil, chemical admixtures for Portland cement concrete are currently specified by NBR 11768, whose first version was published in 1987 (originally EB-1763). In comparison, the first standards for admixtures in the US were published in 1977 (ASTM C 260) and 1979 (ASTM C 494); and, in the UK, 1974 (BS 5075-1, now BS EN 934-2).

NBR 11768 prescribes the required conditions related to homogeneity, colour, specific gravity, pH, solid residues content, and chlorides content; and determines the tests to be carried out on the concretes with admixtures. It also specifies that the mass of admixtures added during the concrete mixing should not exceed 5% in relation to the mass of Portland cement. The standard currently allows this amount to be exceeded in some specific applications, such as admixtures for shotcrete and shrinkage compensators.

In Brazil, there are no standards for admixtures for cement-based composites other than concrete (e.g., mortars and grouts). Table 7 shows the different types of standardised admixtures in the country and their equivalents in the US and UK.

Table 7. Types of chemical admixtures standardized in Brazil according to NBR 11768, and their American and British equivalents [35]-[38].

Brazilian ABNT Type	Chemical admixture	Characteristics	American ASTM Equivalent	British BSI Equivalent
PN	Water-reducing	First-generation plasticizer, based on lignosulfonates.	A[1]	Water reducing/ plasticizing[1]
SP-I N	High-range water-reducing Type I	Second-generation superplasticizer, based on condensates of formaldehyde sulfonates.	F[1]	High range water reducing/ superplasticizing[1]
SP-II N	High-range water-reducing Tipo II	Third generation superplasticizer, based on polycarboxylate.		
IA	Air-entraining	Incorporates uniformly distributed micropores of air during the mixing of the concrete, which remain in the hardened state.	Air-Entraining[2]	Air entraining
AP	Set Accelerating	Decreases the transition time from the plastic to the rigid state of the concrete.	C	Set accelerating
AR	Strength accelerator	Increases the rate of development of the initial strength of the concrete, with or without affecting setting time.	-[3]	Hardening accelerating
PP	Set Retarding	Increases the transition time from the plastic to the rigid state of the concrete.	B	Set retarding
PR	Water-reducing and Set Retarding	Combines the effects of a plasticizer (main function) and the effects of a retarder (secondary function)	D[1]	Set retarding/ water reducing/ plasticizing[1]
SP-I R or SP-II R	High-range water-reducing and Set Retarding	Combines the effects of type I or II superplasticizer (main function) and the effects of a retarder (secondary function).	G[1]	Set retarding/ high range water reducing/ superplasticizing[1]

Table 7. Continued…

Brazilian ABNT Type	Chemical admixture	Characteristics	American ASTM Equivalent	British BSI Equivalent
PA	Water-reducing and Set Accelerating	Combines the effects of a plasticizer (main function) and the effects of an accelerator (secondary function)	E[1]	Set accelerating/ water reducing/ plasticizing[1]
SP-I A or SP-II A	High-range water-reducing and Set Accelerating	Combines the effects of type I or II superplasticizer (main function) and the effects of an accelerator (secondary function).	-	-
MV-RT	Water retainer viscosity modifier	Retains water inside the concrete reducing the bleeding effect	-[3]	Water retaining
MV-AS	Anti-washout viscosity modifier	Reduces segregation of fluid or self-compacting concretes and allows the pouring of submerged concretes	-[3]	Viscosity modifying[4]

[1] Brazilian standard differentiates Water-reducing from High-range water-reducing admixtures according to the chemical composition. ASTM and BSI prescribe that the former should be able to reduce at least 5% of mixing water, and the latter at least 12%. [2] ASTM C494 does not have a specific letter/classification for Air-entraining admixtures, which are separately regulated by ASTM C260. [3] While ASTM C494 covers admixture types A to G, it does present provisions for a Type S, adopted when specific performance characteristics are required. [4] Brazilian standard specifies the Anti-washout viscosity modifier for self-compacting and submerged concretes, while BSI only mentions that it is "incorporated in concrete to limit segregation by improving cohesion".

Although the first Brazilian standards on chemical admixtures for concrete date from the late 1980s, there were reports of the use of plasticizers and set retarders decades before them, as seen in the previous section. The first standards launched in Brazil were EB-1763 (in 1987), with the specifications and requirements for various types, and EB-1842 (in 1987), specific for superplasticizers. In 1992, these standards were merged into NBR 11768.

The standards prior to 2011 did not establish maximum limits for the content of admixtures in concrete. Furthermore, they did not prescribe the specific requirements that the admixtures should meet, meaning that there was no standardised technological control of cement-based composites with admixtures at that time.

In 2019, the NBR 11768 was completely remodelled. It was split into three parts, where Part 1 refers to the classification and requirements, and Part 2 and 3 aggregate the specific tests for the various admixtures. While the 1992 standard classified the admixtures in 9 different types, and the 2011 version, 11 types, the 2019 standard brought 16 classifications (9 of them entirely new). Table 8 summarises the main differences observed throughout the years (note: the specified requirements are non-exclusive – only the most relevant ones were shown).

Table 8. Evolution of concrete admixture standards in Brazil and their main requirements

1992 (4 pages)		2011 (25 pages)		2019 (33 pages)	
Type	Description[1]	Type	Description[2]	Type	Description[4]
P	Plasticiser	PN	Water-reducing/Plasticiser	RA1	Water-reducing type 1
	· Minimum 6% water reduction[3].		· Minimum 6% water reduction[3].		· Minimum 8% water reduction[3].
	· No references to chemical composition.		· First-generation plasticizer, based on lignosulfonates.		· No references to chemical composition.
SP	Superplasticiser	SP-I N	High-range water-reducing Type I	RA2	Water-reducing type 2
	· Minimum 12% water reduction[3].		· Minimum 12% water reduction[3].		· Minimum 15% water reduction[3].
	· No references to chemical composition.		· Second-generation superplasticizer, based on condensates of formaldehyde sulfonates.		· No references to chemical composition.
		SP-II N	High-range water-reducing Tipo II		
			· Minimum 20% water reduction[3].		
			· Third generation superplasticizer, based on polycarboxylate.		
A	Set Accelerating and Strength accelerator	AP	Set Accelerating	AP	Set Accelerating
	· Minimum initial set time: -1:00h[3]		· Minimum initial set time: -0:30h[3]		· Setting time of test mortar must be smaller than the reference mortar (no value specified)
	· Minimum final set time: -1:00h[3]		· No requirements regarding minimum final set time.	APP	Set Accelerating for shotcrete

Table 8. Continued…

1992 (4 pages)		2011 (25 pages)		2019 (33 pages)	
Type	**Description[1]**	**Type**	**Description[2]**	**Type**	**Description[4]**
					· Initial setting of cement paste: $\leq$ 0:10h[3]
					· Final setting of cement paste: $\leq$ 1:00h[3]
			Strength accelerator		Strength accelerator
		AR	· Minimum strength increase in 24h: +120%[3]	AR	· Minimum strength increase in 24h: 120%[3]
			· No requirements regarding setting time (may or may not alter)		· Maximum initial set time: 120%[3]
R	Set Retarding	RP	Set Retarding		-
	· Minimum initial set time: + 1:00h[3]		· Minimum initial set time: + 1:30h[3]		
PA	Plasticiser and Set Accelerating	PA	Water-reducing and Set Accelerating	RA1-A	Water-reducing type 1 and Set Accelerating
	· Combined requirements		· Combined requirements		· Minimum 8% water reduction[3].
					· Minimum initial set time: - 0:30h[3]
SPA	Superplasticiser and Set Accelerating	SP-I A or SP-II A	High-range water-reducing and Set Accelerating	RA2-A	Water-reducing type 2 and Set Accelerating
	· Combined requirements		· Combined requirements		· Minimum 15% water reduction[3].
					· Minimum initial set time: - 0:30h[3]
PR	Plasticiser and Set Retarding	PR	Water-reducing and Set Retarding	RA1-R	Water-reducing type 1 and Set Retarding
	· Combined requirements		· Combined requirements		· Minimum 8% water reduction[3].
					· Minimum initial set time: +2:00h[3]
SPR	Superplasticiser and Set Retarding	SP-I R or SP-II R	High-range water-reducing and Set Retarding	RA2-R	Water-reducing type 2 and Set Retarding
	· Combined requirements		· Combined requirements		· Minimum 15% water reduction[3].
					· Minimum initial set time: +1:30h[3]
IAR	Air-entraining	IA	Air-entraining	IA	Air-entraining
	· Maximum bleeding: 2%		· Minimum air-entrainment: +2.5%[3]		· Minimum air-entrainment: +2.5%[3]
	No references to air entrainment potential.		Total air-entrainment content: 4 to 6%		Total air-entrainment content: 4 to 6%
				IA-L	Air-entraining for lightweight concretes
					· No requirements specified[5]
-		-		CH	Hydration controller
					· Slump > 10mm[3]
					· No setting time or heat of hydration requirements specified.
-		-		CR	Shrinkage compensating
					· Shrinkage at 28 days: $\leq$ 95%[3]
					· Final setting time: $\leq$ 1:30h[3]
					· Other physical and chemical requirements.
-		-		RR	Shrinkage reducing
					· Shrinkage at 28 days: $\leq$ 95%[3]
					· Final setting time: $\leq$ 2:00h[3]
					· No other physical and chemical requirements specified.

Table 8. Continued…

1992 (4 pages)		2011 (25 pages)		2019 (33 pages)	
Type	**Description[1]**	**Type**	**Description[2]**	**Type**	**Description[4]**
-		-		RC	Corrosion-inhibiting
					· No requirements specified[5]
-		-		MV-RT	Water retainer viscosity modifier
					· Bleeding $< 15\%$
					· No workability requirements specified.
-		-		MV-AS	Anti-washout viscosity modifier
					· No requirements specified[5]
-		-		RAC	Capillary absorption reducer
					· No requirements specified[5]
-		-		RP	Permeability reducer
					· No requirements specified[5]
-		-		CVP	Admixtures for vibro-pressed concrete
					· No requirements specified[5]

[1] In the 1992 standard, excluding air-entraining admixtures (IAR), all others, when intended for concretes without entrained air, must not incorporate an air content greater than 3%. [2] In the 2011 standard, excluding air-entraining admixtures (IA), all others, when intended for concretes without entrained air, must not incorporate an air content greater than 2%. [3] In relation to reference concrete. [4] In the 2019 standard, admixtures CH, AR, CR, and MV-RT were required to promote less than 2% air-entrainment in relation to reference concrete; AP, 4%; and RR, 1%. No air-entrainment requirements were specified for the other types. [5] These admixture types were defined, but no requirements were presented regarding any property other than the general requirements for all admixtures (homogeneity, colour, density, solid content, pH, and water-soluble chlorides).

5 FINAL REMARKS

The present bibliographic review made clear that there are no systematic records in the civil construction sector in Brazil, motivating the authors to develop a chronology of the standards related to cement and admixtures in the country. The National Union of the Cement Industry (SNIC) itself only published annual reports from 2001 to 2013. No national statistics were found on the sale or use of chemical admixtures. In this scenario, this work sought to contribute to the creation of a literary collection about Portland cement and chemical admixtures in Brazil.

It is undeniable that Brazil is mainly an importer of concrete-related technologies, even though its construction sector heavily relies on this material. The changes that occurred in the Brazilian types of cement over the decades, motivated mainly by industrial and urban growth, followed international trends with a certain delay. This delay, originally on the order of decades, has been gradually reducing in recent years. This reducing trend relates to the acceleration of the rate of technology transfer worldwide, a consequence of the globalisation of the economy, and was observed both concerning the adoption of new technologies and the evolution of the standards for the studied materials. Brazilian standards generally follow closely their American and British counterparts.

The literature review showed that knowledge about the evolution of Portland cement and chemical admixtures is relevant information that can assist in the dating process of Brazilian concretes. On one hand, although periodic changes in the maximum limits of the compositions do occur, manufacturers do not disclose the content of admixtures effectively employed in each cement type. Additionally, alterations in the standards and in the main components of the clinker are gradual and occur over decades. On the other hand, in specific time windows, significant changes can be identified, such as the introduction of a new type of cement or chemical admixture [39]. In this sense, the combination of the historical basis developed in the present work with microstructural characterisation techniques may lay the basis for an effective dating methodology of Brazilian concretes.

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APPENDIX

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