

# *Physicochemical evaluation of portland cement produced in Brazil via X-ray fluorescence and mechanical strength*

## *Avaliação físico-química de cimentos portland produzidos no Brasil, via fluorescência por raios-X e resistência mecânica*

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### Abstract

Portland cement is the basic component of concrete. X-ray fluorescence spectroscopy is an established analytical technique used in cement plants throughout the world. A comparative study of the elemental constituents presents in Portland cements produced in Brazil was carried out via EDXRF analyses. The main elements identified and quantified in cement samples were Al, Ca, Fe, K, Si, S, Ti, Mn, Zn and Sr. The main components of cement are lime (CaO), silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), magnesia (MgO), alkalis (Na<sub>2</sub>O and K<sub>2</sub>O) and sulfates (SO<sub>3</sub>). The components C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF were calculated via Bogue's formula. Mortar with water, cement and sand was produced for each cement brand, and analyses were performed in order to evaluate the mechanical compressive strength. The bodies were broken after curing over the following timeframes: 1, 3, 7, 28 and 91 days. The results from mechanical tests were correlated with the components found in the different cement brands. Our results indicate that initial compressive strength can vary greatly from one brand to another and the values for the Bogue's potentials show large differences for C<sub>3</sub>S and C<sub>2</sub>S. It was showed by strength tests, how it is possible to predict the behavior of mortars made with these cements. Cements proved to be good for the manufacture of mortars and meet the Brazilian's specifications.

**Keywords:** EDXRF. Portland Cement. Mechanical resistance. Bogue's potential.

### Resumo

O cimento Portland é o componente básico do concreto. A espectroscopia de fluorescência de raios X é uma técnica analítica estabelecida usada em fábricas de cimento em todo o mundo. Um estudo comparativo dos constituintes elementares presentes em cimentos Portland produzidos no Brasil foi realizado através da análise via EDXRF. Os principais elementos identificados e quantificados nas amostras de cimento foram Al, Ca, Fe, K, Si, S, Ti, Mn, Zn e Sr. Os principais componentes do cimento são cal (CaO), sílica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), óxido de ferro (Fe<sub>2</sub>O<sub>3</sub>), magnésia (MgO), álcalis (Na<sub>2</sub>O e K<sub>2</sub>O) e sulfatos (SO<sub>3</sub>). Os componentes C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A e C<sub>4</sub>AF foram calculados pela fórmula de Bogue. Foram feitas argamassa com água, cimento e areia para cada marca de cimento e foram realizadas análises para avaliar a resistência à compressão mecânica. Os corpos foram quebrados após a cura nos seguintes prazos: 1, 3, 7, 28 e 91 dias. Os resultados dos ensaios mecânicos foram correlacionados com os componentes encontrados nas diferentes marcas de cimento. Nossos resultados indicam que a resistência à compressão inicial pode variar muito de uma marca para outra e os valores para os potenciais do Bogue mostram grandes diferenças para C<sub>3</sub>S e C<sub>2</sub>S. Foi demonstrado por testes de resistência como é possível prever o comportamento das argamassas feitas com esses cimentos. Os cimentos provaram ser bons para a fabricação de argamassas e atendem às especificações Brasileiras.

**Palavras-chave:** EDXRF. Cimento Portland. Resistência mecânica. Potencial de Bogue.

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## Introduction

Until the XIX century, little was known about the proper proportioning of the constituent materials of concrete and mortar. In 1828, in France, Louis J. Vicat (FERRARI, 1968) found experimentally that a certain cement/sand ratio led to the ultimate strength of mortars. Later, in 1824, the English builder Joseph Aspdin burned together calcareous clay and stones, turning them into a fine powder, leading him to realize that the mixture thus produced, following drying, became as hard as the stones used in construction. The mixture did not dissolve in water after hardening, and has been patented by the manufacturer in the same year as a concrete with the name Portland, thus being named due to presenting color and properties of durability and strength similar to those of the rocks of the British Island of Portland (KAEFER, 1998). Portland cement is defined as a hydraulic binder obtained by mixing Portland clinker, calcium sulfate and standard additions of lime, slag and pozzolan, finely ground. Portland cement mixed with water and other building materials such as sand, crushed stone, powder-stone, lime, and others, results in the concrete and mortars used in the construction of houses, buildings, bridges, dams etc. The characteristics and properties of concrete and mortar will depend on the quality and proportions of the materials they are made of. Among them, however, cement is the most active constituent, from a chemical point of view (ABCP, 2002). It can be said that cement is the main responsible for the transformation of the mixture of component materials of concrete and mortar into the desired final product. Combination of the different elements present in Portland cement with oxygen form the binary bodies known as components. The main components of cement are lime (CaO), silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), magnesia (MgO), alkalis (Na<sub>2</sub>O and K<sub>2</sub>O) and sulfates (SO<sub>3</sub>). The oxides TiO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> are found in small amounts and are generally not separately determined. The ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) reacts with aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) and lime (CaO) to form tetracalcium aluminoferrite (Ferrite C<sub>4</sub>AF or Ca<sub>4</sub>Al<sub>2</sub>Fe<sub>2</sub>O<sub>10</sub>). The remaining aluminum oxide reacts with lime to form tricalcium aluminates (C<sub>3</sub>A or Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>). The lime reacts with the silicate oxide (SiO<sub>2</sub>) to form two calcium silicate phases, the dicalcium silicate (Belite, C<sub>2</sub>S or Ca<sub>2</sub>SiO<sub>4</sub>) and tricalcium silicate (Alite, C<sub>3</sub>S or Ca<sub>3</sub>SiO<sub>5</sub>) (TAYLOR, 1990). The chemical analysis of cement is performed to verify that the product supplied complies with the requirements of standards and as a way to predict the results

that will be obtained, when it is used in various locations for the construction industry. Various methods are used to analyze the chemical composition of cement, and among them we could mention the wet chemistry and atomic absorption spectroscopy, however, the technique of analysis by X-ray fluorescence (XRF) is arguably the most widely used one nowadays, due its accuracy and simplicity. XRF and its variants (Energy Dispersive X-ray Fluorescence – EDXRF and Total Reflection X-ray Fluorescence – TXRF) have been used for elemental analysis, in various areas of knowledge (WEST *et al.*, 2016; VIEIRA *et al.*, 2018; MOLARI *et al.*, 2019). The U.S.A.'s cement industry was the first to use the XRF technique back in 1953. In 1966, Uchida, Tominagu and Imamura (1966) in Japan used the XRF technique for determination of the light elements Al, Si, and Mg as a way of controlling the quality of cement and raw materials used in its production. Abelmann and Smallbone (1967) used the XRF analysis in the cement produced in California and rated the presence of Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> compounds. In 1976, Cooper, Wheeler and Bartell (1976) used the technique of EDXRF to make multielemental analysis of Portland cement having the following compounds quantified with high precision: Na<sub>2</sub>O, SrO, Mn<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, SO<sub>3</sub>, MgO, K<sub>2</sub>O, CaO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>. Bahjat and Latif (2001) analyzed Iraqi cement samples also using XRF. Elbagermia, Alajtala and Alkerzab (2014) used EDXRF to analyze four brands of Portland cement produced and available in the Libyan market. In the research effort entertained herein, the analytical technique EDXRF was used to analyze the elemental composition of twelve brands of Portland cement produced in Brazil. Knowing the basic composition of cement, it was used the analytical method proposed by Bogue (1947) to obtain the main components present in the cement, i.e., C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF. In plants in which the production process parameters and the proportion of smaller elements are maintained approximately constant, the potential of calculation can be quite helpful and sufficient (GOBBO, 2003). Tests were carried out comprising mechanical compressive strength, for each brand of Portland cement used in the present study, at 1, 3, 7, 28 and 91 days of cure, in order to correlate the compressive strength with the percentage of each component (C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF) present in the cement. To our knowledge, no studies have been reported yet in the literature regarding major component analyses of Portland cement produced and available in the Brazilian market, and its relation with the mechanical strength of the cement.

## Materials and Methods

### Sample collection

Twelve samples of Portland cement type CP-II were used in this study. Each cement sample was prepared using four different lots of cement, which were thoroughly mixed, hence producing the final (homogeneous, representative) sample used in all tests. Each final cement sample was sealed and labeled with the sample number, brand and type of cement, as shown in Table 1.

**Table 1** – Samples of Portland cement used in this study.

Sample nº	Cement type	Brand
1	CP-II-E-32 <sup>a</sup>	ATU
2	CP-II-E-32 <sup>a</sup>	BCA
3	CP-II-F-32 <sup>b</sup>	CSU
4	CP-II-E-32 <sup>a</sup>	DNA
5	CP-II-E-32 <sup>a</sup>	EUA
6	CP-II-Z-32 <sup>c</sup>	FRI
7	CP-II-E-32RS <sup>d</sup>	GNA
8	CP-II-E-32 <sup>a</sup>	HCA
9	CP-II-Z-32 <sup>c</sup>	IVO
10	CP-II-E-32 <sup>a</sup>	JHO
11	CP-II-E-32 <sup>a</sup>	KRI
12	CP-II-E-32 <sup>a</sup>	LVO

<sup>a</sup> Portland cement with addition of slag.

<sup>b</sup> Portland cement with addition of fillers.

<sup>c</sup> Portland cement with addition of pozzolan.

<sup>d</sup> Portland cement with addition of slag and resistant to sulfates.

**Source:** The authors.

Table 1 shows the characteristics of the 12 cement brands used in this study, being CP the universal acronym for Portland cement, the numeral indicates the type of cement (I, II, III, IV or V), the letter indicates the type of addition (E = dross, Z = pozzolan, F = filer) and the last numeral provides the minimum resistance expected after 28 days of curing of mortar or concrete, respectively. The 12 brands of Portland cement used in this study were produced by Brazilian companies and duly available on the market, and were randomly chosen in the region of Sorocaba city, state of São Paulo, Brazil.

### X-ray Fluorescence analysis

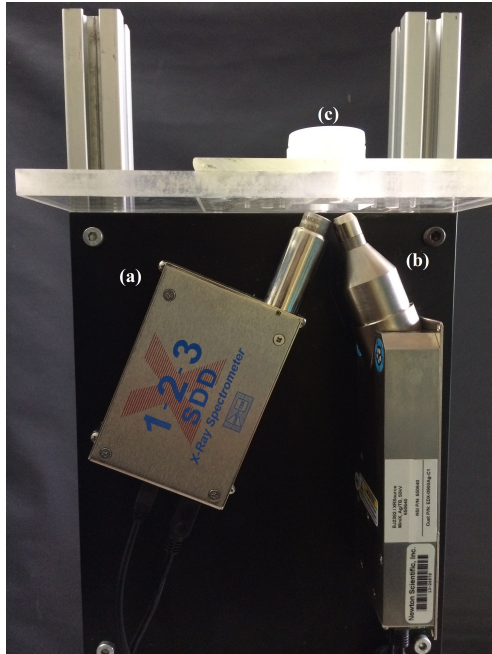
The XRF consists in the emission of characteristic X-rays from a material that has been excited via bombardment with either X-rays or gamma rays. Because each element has a unique set of atomic energy levels,

it emits a unique set of X-rays, which are characteristic of such element. Hence, the presence of characteristic X-rays directly indicates the presence of a given element. Moreover, the intensity of an X-ray line depends on the number of corresponding atoms which were excited, allowing the identification and quantification of the chemical elements present in a sample. After collecting all cement samples, they were transported to the Applied Nuclear Physics Laboratory at the University of Sorocaba (LAFINAU) for carrying out the EDXRF analyses.

The EDXRF technique was chosen to be used in this research work due to several key advantages over other analytical techniques, viz. (a) it requires no sample preparation; (b) it is a very fast analytical technique (although sensitivity improves with measurement timeframes); and (c) it is the analytical technique of choice used by the cement industry to analyze the elemental composition of cement. EDXRF can provide analytical results with an accuracy of a few parts per million ( $\mu\text{g/g}$ ) and can be used to quantify chemical elements present in a formulation as long as they have an atomic number between that of element magnesium ( $Z=12$ ) and that of element fermium ( $Z=100$ ). The results were analyzed both qualitatively and quantitatively. The XRF analysis was performed in powder cement, by placing it into a sample holder, without compression. The sample holder was made of polypropylene, a polymer composed of carbon and hydrogen atoms ( $(\text{C}_3\text{H}_6)_n$ ) which, when excited, produce no characteristic X-rays of sufficient energy to be detected by the fluorescence system, hence not interfering with the results of the elemental analysis. For each cement sample (brand), fluorescence measurements were performed in quadruplicate and, as a result, it was considered the mean value and its associated standard deviation. The experimental setup used in this research effort is shown in Figure 1. It included: (a) an Amptek (Bedford, Massachusetts, USA) 25 mm<sup>2</sup> SDD X-ray detector with a resolution of 128 eV at the Mn-K $\alpha$  line; (b) mini X-ray tube with an Ag anode, manufactured by Amptek (Bedford, Massachusetts, USA) and set up to work at 30 kV and 10  $\mu\text{A}$ .

All measurements were carried out using atmospheric air, and the measuring time was set at 300s (live time) for each sample. A collimator with an aperture of 1 mm was used in the exit of the X-ray source. The XRF system was calibrated using a certified sample of Portland cement FLX-CRM 106 provided by Fluxana (FLUXANA<sup>®</sup> GmbH & Co. KG).

**Figure 1** – Image of the X-ray fluorescence setup utilized in the XRF analyses. (a) X-ray detection system, (b) X-ray source and (c) sample holder.



Source: The authors.

Additionally, Amptek's ADMCA software for data acquisition and control of the signal processor and Amptek's XRS-FP™ software for spectrum processing and quantitative analysis were utilized. The software used in the data analysis (XRS-FP™) has a calibration tool, in which it is possible to read a standard sample (FLX-CRM 106) and knowing the results of the concentration of elementary constituents present in the standard, it is possible to correct the values obtained, making them equal to those provided by the report of the standard used. With this, a good calibration is obtained, which was used for the quantitative analysis of all samples used in this study. With this experimental apparatus, it was possible to detect and quantify various chemical elements with atomic number from element magnesium upwards. The measured spectra were analyzed with the XRS-FP™ package provided by Amptek Inc., taking into account escape peaks, sum peaks and representing the background with a polynomial function.

#### Mechanical strength test

For each cement brand, 20 specimens were prepared employing cement, water, and sand (coarse, medium and fine Normal Brazilian sand, mixed in the same ratio), which were used in the mechanical compression tests, performed in quadruplicate, with 01, 03, 07, 28 and 91 days, thus amounting 240 test specimens. The mortar for

the molding of the test specimens using the different cement brands was made following the trait given by the Brazilian NBR 7215 (ABNT, 1996), with one part of cement to three parts of sand and water:cement ratio of 0.48. The sample holder for the specimens had the following dimensions: 50 mm of diameter by 100 mm of high. The launch of the mortar specimens was performed in four layers of mold. With the aid of a metal rod (16 mm in diameter), 30 punches were applied by grout layer. After 24 hours from the start of molding, the specimens were demolded and identified. The four specimens to be broken, one day old, were taken to the mechanical press and the others were placed in containers for wet curing in water saturated with lime, until the break date. The press used in the compression tests was from Bovenau (model P10 ST, city of Rio do Sul, SC, Brazil), working with a pressure up to 10 tons.

#### Bogue's potential

According to Bogue (1947), the main components present in the cement, i.e.,  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$  can be obtained using the equation (1) for  $C_3S$ , equation (2) for  $C_2S$ , equation (3) for  $C_3A$  and equation (4) for  $C_4AF$ :

$$C_3S = 4.07(CaO) - 7.6024(SiO_2) - 6.7187(Al_2O_3) - 1.4297(Fe_2O_3) \quad (1)$$

$$C_2S = 8.6024(SiO_2) + 1.0785(Fe_2O_3) + 5.0683(Al_2O_3) - 3.0710(CaO) \quad (2)$$

$$C_3A = 2.6504(Al_2O_3) - 1.6920(Fe_2O_3) \quad (3)$$

$$C_4AF = 3.0432(Fe_2O_3). \quad (4)$$

This method has, however, several limitations due to its intrinsic distance from the characteristics observed in commercial clinkers and takes into account a clinkering temperature near 1500 °C, a perfect combination of the oxides, the existence of balance between  $C_3S$ ,  $C_2S$  and liquid phase and that this state is maintained during cooling. The study restricts the clinker contents to the compounds  $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$  in pure form, and disregards the existence of minor elements ( $P_2O_5$ ,  $TiO_2$ ,  $MgO$ ,  $K_2O$ ,  $Na_2O$  and others) that may make up amounts from about 8% to 9% of the clinker as well as the presence of alkali sulfates. In addition, errors that can be committed in the calculation of the potential composition depend on the inherent precision of the results from elemental chemical analysis (MARCIANO JUNIOR; ZAMPIERI;

CENTURIONE, 1987). The Bogue's potential calculations should thus be used as a first approximation, since the chemical equilibrium conditions, which invariably underlies prospective calculations, are not commonly obtained in industrial clinkers. Despite all of the potential limitations of these calculations, simplicity and speed are their main advantages.

## Results and Discussion

Figure 2 shows the typical spectrum of the cement of one of the brands used in this research effort. The major chemical elements found are pinpointed in Figure 2.

Essentially, the same elements were detected in all XRF spectra of Portland cements. The main elements detected and quantified were Al, Ca, Fe, K, Si, S, Ti, Mn, Zn and Sr. By knowing the elemental concentrations of the different constituents present in the cement, one was able to determine the stoichiometric amounts of the compounds, as displayed in Table 2 and Table 3.

By comparing the values produced in this research work for the four major compounds, i.e., CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and F<sub>2</sub>O<sub>3</sub>, with the reference values, it appears that for CaO, on average, the values are smaller than the reference, except for JHO, GNA, HCA and CSU cements, getting the values within the expected range. For SiO<sub>2</sub> all cements were within the expected range, with the exception of JHO cement that was slightly above. For F<sub>2</sub>O<sub>3</sub> all cements were within the expected range, with the exception of EUA cement that was slightly above. LVO cement had the highest value of SO<sub>3</sub> and JHO the lowest SO<sub>3</sub> content. For Al<sub>2</sub>O<sub>3</sub> all cements were within the expected range. By knowing the values for the several compounds, the values of C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF were calculated as proposed by Bogue (1947). Table 4 shows the results from the calculation of the Bogue's potentials.

The concentration of each compound (C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF) present in the cement, will dictate the physicochemical behavior of the cement, when used for making either mortar or concrete. According to Mindess, Young and Darwin (2003), the mechanical strength of concrete and mortar is related both to the healing time and the concentration of each compound, as shown in Figure 3.

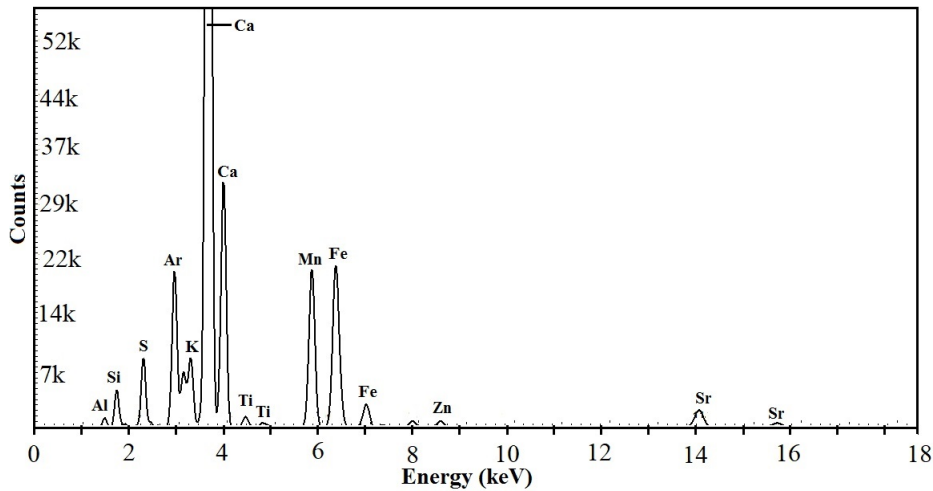
Knowledge of the concentration of these compounds is important because they interfere with various parameters, such as: (a) the hydration rate, (b) the cement grip, (c) heat release, and (d) mechanical strength in early and final ages of mortar made from these cements. The main features that each of these compounds imprint to mortars are: (a) C<sub>3</sub>S hydration begins within a few hours, has an average heat release and is responsible for mechanical strength at early ages, (b) C<sub>2</sub>S hydration occurs slowly, presents a low heat release and is responsible for the mechanical strength at older ages, (c) C<sub>3</sub>A produces extremely rapid hydration, crystallizing in a few minutes, presenting a high heat release, but does not increase the mechanical strength in later ages, and (d) C<sub>4</sub>A also produces rapid hydration, but not as intense as the C<sub>3</sub>A, presents a medium heat detachment, also being responsible for resistance at early ages.

As the cements analyzed in this research work presented a wide variation between the compounds C<sub>3</sub>S and C<sub>2</sub>S, as shown in Figure 4, having one quantity the inverse behavior of the other, for the cement brands showed in the abscissa of Figure 4, and knowing that the C<sub>3</sub>S compound is largely responsible for the mechanical strength of concrete and/or mortar in the early days of cure, one assembled the testing of mechanical compressive strength (F<sub>ck</sub>) with specimens made with these mortar cements, to study these relations.

These specimens were thus subjected to mechanical compression tests at 1, 3, 7, 28 and 91 days of curing. The results of compressive strength tests are shown in Figure 5. As expected, the mechanical strength increases with curing time, with all the samples reaching the minimum strength of 32 MPa after 28 days of curing. The highest and lowest mechanical strength after 28 days of curing were presented by the CSU and GNA cements, respectively. Looking at Figure 4, we find that the cement brand BCA is the one with the lowest value for C<sub>3</sub>S and the CSU greatest. As C<sub>3</sub>S compound is responsible for the mechanical strength in the early days of curing, it is expected that there is a correspondence between C<sub>3</sub>S and mechanical strength at early ages.

Figure 6 shows the trend line for the mechanical compression strength at 1, 3, 7, 28 and 91 days of curing, suggesting that really there is a correlation between the mechanical strength with the increase of C<sub>3</sub>S values. For early ages, the compressive strength is higher for cements that have greater amounts of C<sub>3</sub>S, as expected. The trend lines for 1, 3, 7, 28 and 91 days of compressive strength (F<sub>ck</sub>) as a function of C<sub>3</sub>S values presented by cements

**Figure 2** – Typical EDXRF spectrum of Portland cement. The YY axis represents the number of characteristic X-ray counts that reached the detector, while the XX axis represents the energy of the characteristic X-rays.



Source: The authors.

**Table 2** – Stoichiometric values obtained for compounds from the elemental analysis performed via EDXRF.

Cement	Compounds				
	Al <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	K <sub>2</sub> O (%)	SiO <sub>2</sub> (%)
Ref. values <sup>a</sup>	3.02-6.29	59.83-64.50	1.61-4.20	0.17-0.59	14.41-23.22
ATU	5.2±0.4	55.5±0.2	2.90±0.04	0.60±0.02	23.5±0.7
BCA	5.8±0.4	61.0±0.2	2.28±0.03	0.57±0.02	24.6±0.7
CSU	5.4±0.4	60.9±0.2	2.79±0.03	0.61±0.02	23.4±0.7
DNA	5.4±0.3	58.3±0.2	2.45±0.03	0.81±0.03	20.9±0.6
EUA	5.5±0.4	59.4±0.2	2.47±0.03	0.79±0.03	22.2±0.7
FRI	5.4±0.4	59.1±0.2	2.96±0.04	1.01±0.03	21.6±0.7
GNA	5.7±0.4	54.6±0.2	4.48±0.05	0.61±0.02	18.7±0.6
HCA	5.4±0.4	59.0±0.2	3.14±0.04	0.72±0.02	20.8±0.6
IVO	5.5±0.4	57.5±0.2	2.37±0.03	1.16±0.03	19.8±0.6
JHO	5.7±0.4	60.5±0.2	2.26±0.03	0.91±0.03	20.1±0.6
KRI	5.1±0.4	53.9±0.2	2.37±0.03	0.91±0.03	15.8±0.5
LVO	5.2±0.4	62.5±0.2	3.12±0.04	0.69±0.02	18.4±0.6

<sup>a</sup>Franco Junior (1999).

Source: The authors.

used in this study, show that the slope presented by fitting specimens with 7 days of cure is positive and greatest when we compare with others

$$Fck_{1day} = 0.085C_3S + 11.025, R^2 = 0.1917;$$

$$Fck_{3day} = 0.1177C_3S + 18.386, R^2 = 0.3814;$$

$$Fck_{7day} = 0.1365C_3S + 23.33, R^2 = 0.3838;$$

$$Fck_{28day} = 0.0621C_3S + 35.162, R^2 = 0.1136;$$

$$Fck_{91day} = 0.1111C_3S + 38.903, R^2 = 0.3055,$$

indicating that the larger the value of C<sub>3</sub>S, the greater the

strength obtained in the first days of curing. One calculated the Pearson correlation coefficient (STANTON, 2001) (values between -1 and 1 indicate minimum and maximum correlation, respectively, with zero value indicating no linear correlation) between the variable C<sub>3</sub>S and the compressive strength for 1, 3, 7, 28 and 91 days of curing, resulting for the correlation coefficient the following values: 0.44, 0.62, 0.62, 0.34 and 0.55, respectively. The Pearson's coefficient indicates that the correlation is maximum for compressive strength at 3 and 7 days of cure, in full agreement with the theoretical prevision for the expected behavior for C<sub>3</sub>S, as shown in Figure 6.

**Table 3** – Stoichiometric values obtained for compounds from the elemental analysis performed via EDXRF.

Cement	Compounds				
	SO <sub>3</sub> (%)	TiO <sub>2</sub> (%)	Mn <sub>2</sub> O <sub>3</sub> (%)	ZnO (%)	SrO (%)
Ref. values <sup>a</sup>	1.72-7.07	0.18-0.32	0.04-0.28	0.01-0.03	0.04-0.32
ATU	3.07±0.08	0.30±0.02	0.63±0.03	0.020±0.009	0.20±0.01
BCA	2.3±0.7	0.41±0.02	0.38±0.02	0.010±0.009	0.25±0.01
CSU	2.9±0.7	0.41±0.02	0.33±0.02	0.010±0.009	0.10±0.01
DNA	3.31±0.08	0.39±0.02	1.30±0.05	0.010±0.009	0.14±0.01
EUA	3.17±0.08	0.39±0.02	1.10±0.05	0.010±0.009	0.15±0.01
FRI	3.62±0.09	0.28±0.02	0.19±0.01	0.010±0.009	0.34±0.01
GNA	3.43±0.08	0.35±0.02	0.22±0.01	0.010±0.009	0.34±0.01
HCA	2.92±0.07	0.29±0.02	0.63±0.03	0.010±0.009	0.26±0.01
IVO	4.3±0.1	0.36±0.02	2.4±0.1	0.010±0.009	0.11±0.01
JHO	2.60±0.07	0.33±0.02	0.35±0.02	0.010±0.009	0.17±0.01
KRI	3.85±0.09	0.36±0.02	2.09±0.09	0.010±0.009	0.11±0.01
LVO	2.50±0.07	0.29±0.02	0.09±0.01	0.010±0.009	0.23±0.01

<sup>a</sup>Franco Junior (1999).

Source: The authors.

**Table 4** – Mineral composition of cement samples obtained by Bogue's calculation.

Cement	C <sub>3</sub> S (%)	C <sub>2</sub> S (%)	C <sub>3</sub> A (%)	C <sub>4</sub> AF (%)	Sum (%)
ATU	8±6	61±7	9±1	9.0±0.1	87±9
BCA	19±6	56±7	11±1	6.95±0.09	94±9
CSU	30±6	44±7	10±1	8.5±0.1	92±9
DNA	31±6	37±6	10±1	7.81±0.09	86±9
EUA	32±6	41±7	10±1	8.4±0.1	92±9
FRI	35±6	35±7	9±1	9.0±0.1	89±9
GNA	36±5	26±6	7±1	13.6±0.1	83±8
HCA	41±6	28±6	9±1	9.5±0.1	88±8
IVO	43±6	24±6	10±1	7.22±0.09	85±8
IVO	43±6	24±6	10±1	7.22±0.09	85±8
JHO	52±6	18±6	11±1	6.86±0.09	88±8
KRI	62±5	-2±5	9±1	7.22±0.09	77±7
LVO	75±5	-4±6	14±1	9.5±0.1	95±8

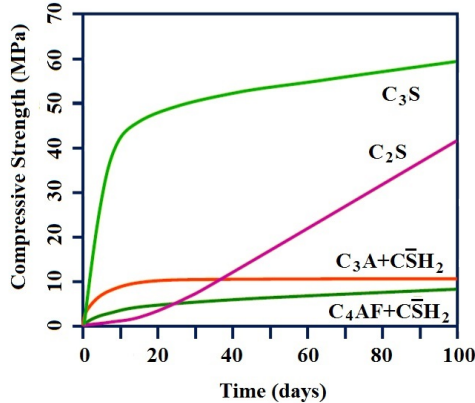
Source: The authors.

According to Marciano Junior, Zampieri and Centurione (1987), values of Pearson's coefficient between 0.10 and 0.29 may be considered weak; scores between 0.30 and 0.49 can be regarded as mean; and values between 0.50 and 1 may be interpreted as strong. Thus, we can consider that the variable C<sub>3</sub>S has a strong correlation with the mechanical compressive strength in the first curing ages. When we add the values of C<sub>3</sub>S with C<sub>2</sub>S, we find only a small change in this sum, i.e., (69.4±4.4)%, thus explaining why all cements analyzed acquire identical mechanical resistance to compression, at advanced ages,

as shown in Figure 5, since C<sub>2</sub>S is responsible for the mechanical strength at old ages and C<sub>3</sub>S at early ages. The compounds C<sub>3</sub>A and C<sub>4</sub>AF interfere less in mechanical strength compared with compounds C<sub>3</sub>S and C<sub>2</sub>S, with a small contribution of C<sub>3</sub>A increasing strength at early ages. For all cement samples analyzed, C<sub>3</sub>A and C<sub>4</sub>AF values varied only (9.7±1.2)% and (8.6±1.8)%, respectively. However, compounds C<sub>3</sub>A and C<sub>4</sub>AF are important because they serve as a reservoir for the removal of some deleterious ions like Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> that cause rusting of steel-reinforced concrete (TAYLOR, 1990).

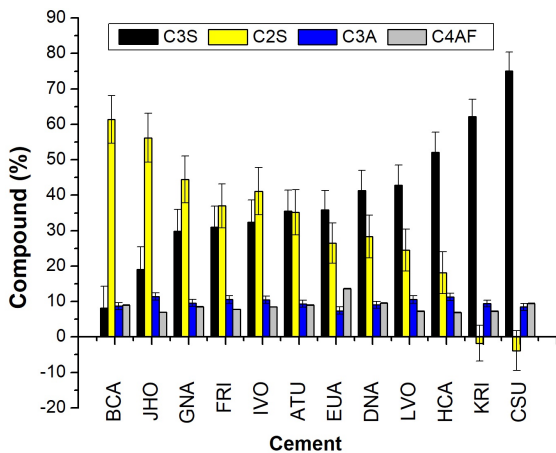
Chlorine element appeared in our analysis only as a trace element. In the case of the elements sodium and magnesium, one could not detect them with the experimental setup used. Regarding phosphorus element, although possibly present, was not detected.

**Figure 3** – Theoretical contribution of each compound to the compressive strength as a function of cure’s time. The compound  $C\bar{S}H_2$  represents the gypsum added to cement.



Source: Adapted from Mindless, Young and Darwin (2003).

**Figure 4** – Concentration of compounds C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF present in the cements tested.

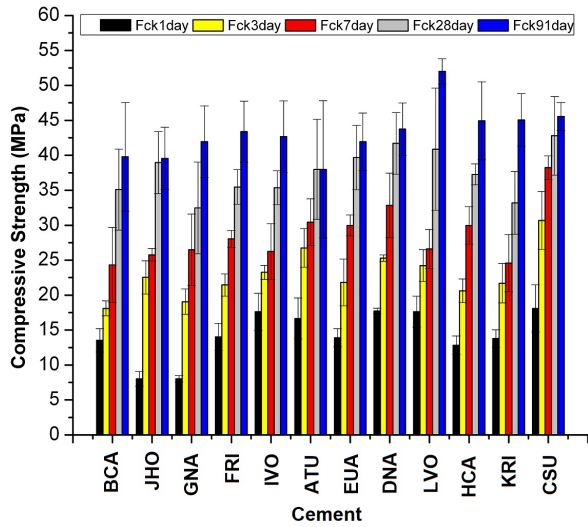


Source: The authors.

## Conclusions

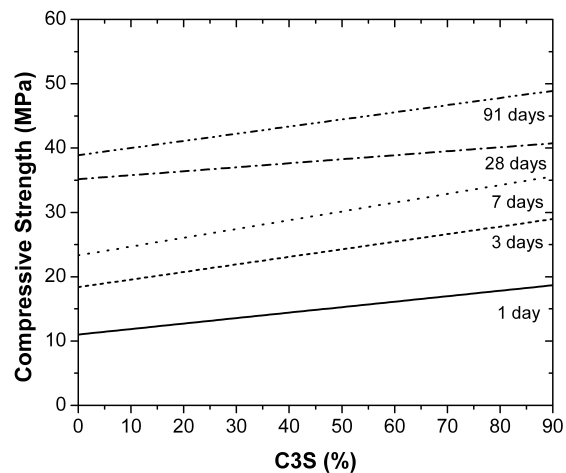
The EDXRF technique for cement analysis proved to be very effective because it is simple, fast and accurate. The analysis of cement by the EDXRF technique showed that there are physical and chemical differences in cements produced in Brazil by different manufactures. We found that initial compressive strength can vary greatly from one cement brand to another and, therefore, depending of the intended application, one brand of cement can be more effective than other, so the importance of the

**Figure 5** – Results from mechanical compressive strength of the various cement samples at 1, 3, 7, 28 and 91 days of curing.



Source: The authors.

**Figure 6** – Linear fittings of the compressive strength obtained after rupture of mortar with 1, 3, 7, 28 and 91 days of curing, as a function of C<sub>3</sub>S values, for the different cements studied.



Source: The authors.

physicochemical analysis presented in this work. For most of the compounds present in the cements analyzed in this study, our results indicate that they are within the reference range, with discrepancies smaller than 10%. The values for the Bogue’s potentials show large differences for C<sub>3</sub>S and C<sub>2</sub>S. The mechanical compressive strength tests showed that there is a strong correlation between the mechanical strength of mortars made with these cements, with the value of C<sub>3</sub>S’s potential, that is, the greater the value of C<sub>3</sub>S the greater the compressive strength in first days of curing. LVO cement had the highest value of SO<sub>3</sub> and JHO the least SO<sub>3</sub> content and, according to Taylor (TAYLOR, 1990). The lower the SO<sub>3</sub> value the better. For any cement



production plant, one of the most important parameters related to the quality of the final product is the knowledge of the chemical composition and cement phase. By knowing the main compounds present in the cement, we showed by strength tests, how it is possible to predict the behavior of mortars made with these cements. There is a strong correlation between the variable  $C_3S$  and compressive strength in the first curing ages. Finally, we conclude that all cements proved to be good for the manufacture of mortars or concretes and met the specifications of Brazilian regulations.

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