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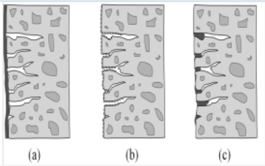

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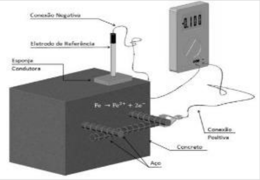

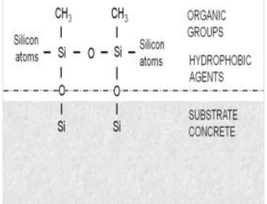

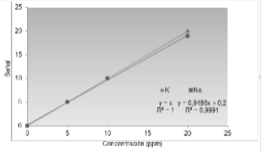

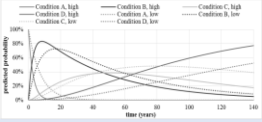

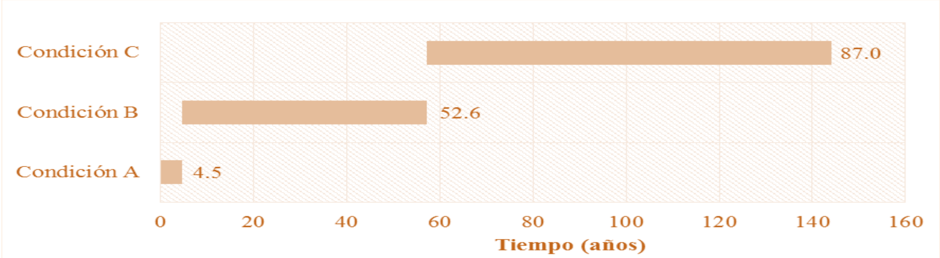

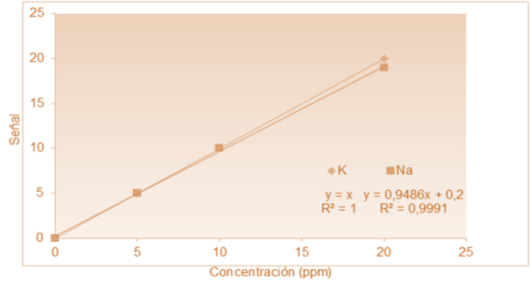

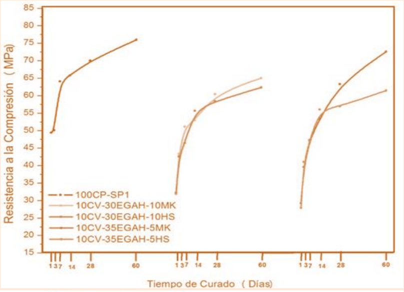

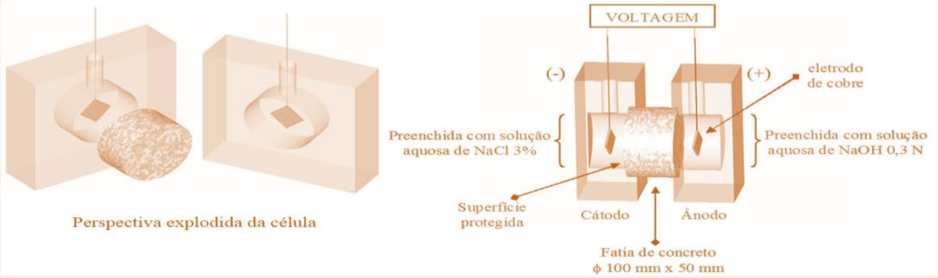

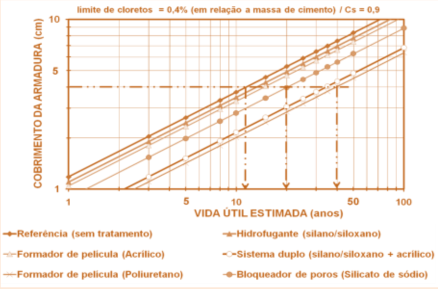

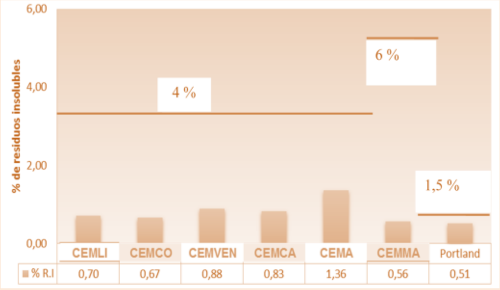

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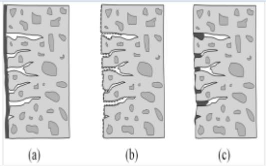

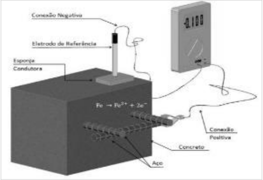

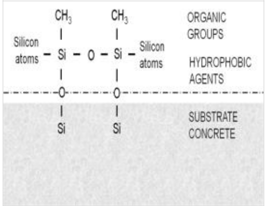

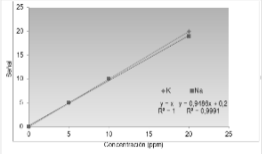

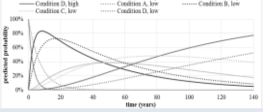

CONTENT

Review papers:

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RAV5N3, September - December 2015

Message from the Editor in Chief

LATIN AMERICAN MAGAZINE ON QUALITY CONTROL, PATHOLOGY AND CONSTRUCTION RECOVERY

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It is a proud and joyful moment for the ALCONPAT magazine team to see the third and last issue of our fifth year published.

The objective of the ALCONPAT (RA) magazine is the publication of case studies related to the topics of our association, quality control, pathology and construction recovery, motivating as well the presentation of basic or applied research that could be applied to case studies.

In this V5N3, we began with our article from **Portugal and the United Kingdom**. A. Silva and colleagues discuss useful life prediction models where information is extrapolated in order to predict the future behavior of the construction elements, anticipating the moment when intervention is required. This study also helps to understand the influence of exposure conditions on the evolution of the degradation of coatings.

In the second work, S.H., Lopes da Silva and his colleagues from **Brazil** discuss the combinations of cement types in order to obtain the one with the highest ability to protect the reinforcement of the concrete from corrosion induced by chlorides. For this, the hierarchical analysis was used, which helped in the selection of the type of cement.

In the third article, which comes from **Venezuela,** Humberto Bolognini and colleagues comment that in the last few years in Venezuela there has been a crisis on the demand, commercialization and production of cement, which is the primary construction material. This work presents the chemical and physical-mechanical characterizations done to the main commercial brands of cement with aggregates in the country, characterizing them according to: chemical composition, Blaine fineness, setting time and mechanical resistance to compression. The results show that these cements do not comply with the minimum requirements set by the Venezuelan standards for their use in the elaboration of structural concrete.

The fourth article comes from **Mexico,** Lauren Y. Gómez Zamorano and colleagues present a research work which focused on the evaluation of the effect that different replacement materials and two superplasticizer additives had on the development of the mechanical properties, phase formation and evolution of heat on hydration in Portland cement pastes replaced up to 60%. Based on the results it was confirmed that with the use of replacement materials, the quantity of calcium hydroxide was reduced due to the pozzolanic reaction and the resistance to compression was increased.

The fifth work of this issue was written by Marcelo Medeiros and his colleagues from **Brazil**. They analyzed the contributions of three protection methods for the surface of concrete on the efficiency of surface treatments to prevent the penetration of chloride ions. Some results indicated that concrete with a certain type of protection could increase the contamination time up to three times.

The sixth article is a review on the State of Art from **Mexico**, where Elia Alonso Guzmán and her colleagues discuss how the generation of solid residues of hydraulic concrete, considered waste, have turned into an environmental problem. The elaboration of recycled concrete faces the search of optimal designs in order to achieve the highest mechanical performance under static and dynamic requests. This work reviews the international advancements on this topic.

Each RA issue aims to balance the participation of topics concerning the social objectives of the International ALCONPAT.

We are grateful for the authors' collaboration on this issue, their resolve and effort to comply with the established quality and deadlines.

Each issue of the magazine will include the articles in the original language, and before the following issue the versions in other languages will be published. The official languages of the ALCONPAT magazine are English, Spanish and Portuguese.

The Editorial Board

Pedro Castro Borges
Editor in Chief

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Probabilistic analysis of the evolution of degradation of natural stone claddings applying Markov chains

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ABSTRACT

The service life prediction models intend to extrapolate the future behaviour of building elements, anticipating the instant at which an intervention is required. Markov chains can be used to assess the future condition of the construction components and are applied in this study to model the service life of stone claddings (directly adhered to the substrate), based on visual inspections of buildings in service conditions. The degradation of stone claddings is evaluated using a discrete scale with five condition levels. In this study the probability of transition from degradation conditions and the time spent in each of these conditions are evaluated. This study also allows a better understanding of the influence of the exposure conditions on the evolution of degradation of the claddings under analysis.

Keywords: Markov chains, Service life prediction, Stone claddings.

RESUMO

Os modelos de previsão de vida útil procuram extrapolar o comportamento futuro dos elementos construtivos, antevendo o momento a partir do qual é necessário intervir. As cadeias de Markov permitem avaliar a condição futura dos elementos da construção, sendo utilizadas no presente estudo, na modelação da previsão da vida útil de revestimentos pétreos (fixados directamente ao suporte), a partir de inspecções visuais de edifícios em serviço. A degradação dos revestimentos pétreos é classificada numa escala discreta composta por cinco níveis, sendo avaliada a probabilidade de transição entre condições de degradação e o tempo de permanência em cada uma dessas condições. O presente estudo permite ainda compreender a influência das condições de exposição na evolução da degradação deste tipo de revestimentos.

Palavras-chave: cadeias de Markov, Previsão da vida útil, Revestimentos pétreos.

RESUMEN

Los modelos de predicción de la vida útil intentan extrapolar el comportamiento futuro de los elementos de construcción, anticipando el punto en el que se requiere la intervención. Cadenas de Markov se pueden usar para evaluar la condición futura de los elementos de construcción y se utilizan en este estudio para modelar la vida útil de revestimientos pétreos, a partir de las inspecciones visuales de edificios en servicio. La degradación de los revestimientos pétreos se califica en una escala discreta de cinco niveles, y se evalúa la probabilidad de transición de condiciones de degradación. Este estudio también permite comprender la influencia de las condiciones de exposición en la evolución de la degradación de los revestimientos.

Palabras clave: Cadenas de Markov, Predicción de la vida útil, Revestimientos pétreos.

Corresponding author: Jorge de Brito

1. INTRODUCTION

The degradation is a complex and dynamic process, in which agents and degradation mechanisms act synergistically and are in constant permutation. The current and future state of buildings are associated with different degrees of uncertainty. To overcome this difficulty, sometimes it is necessary to use a stochastic approach in service life prediction (Frangopol et al., 2004). In general, this approach has a high complexity and is based on the premise that the deterioration is a process ruled by random variables (Moser, 2003). Thus, the degradation can be seen as a continuous loss of performance process, which evolves probabilistically over time. The degradation phenomena can also be described as the transition between consecutive states, characterized by different degradation levels (Basso et al., 2012). Markov chains are one of the methods that allows predicting (in a stochastic way) the future condition of the façade claddings. Markov chains simulate the evolution of the buildings degradation state, allowing defining the probability of the future performance of a construction element based only on their current performance, ignoring the history of deterioration and maintenance of the building, their age, and other parameters (Neves et al., 2006).

In this study, a model based on Markov chains is proposed to predict the service life of stone claddings, which allows estimating the probability distribution of each of the degradation conditions over time (as well as the average time of permanence in each degradation condition). Additionally, the influence of some characteristics of stone claddings is analysed, aiming to understand the influence of this characteristics in the claddings' degradation process. This methodology is central to the built environment maintenance, once it provides data for the most probable time for claddings' failure according to its characteristics, and the ages in which is extremely unlikely that the rupture of these elements occurs. Using this method it is then possible to comprise the notion of risk associated with the failure of claddings, thus enabling the definition of maintenance plans and warranty periods by insurance companies.

2. DEGRADATION OF STONE CLADDINGS

Markov chains are based on a set of discrete states that characterize the buildings' performance. There are various methods for evaluate the deterioration state of buildings and components that vary according to the hierarchical classification of building elements, the hierarchical classification of defects and the setting condition parameters associated with defects (Straub, 2003). Different authors (Balaras et al., 2005; Shohet et al., 1999) established classification systems or degradation scales to describe the visual and functional deterioration of the elements under analysis; usually, these systems include the classification of defects across a range of discrete variables that vary from the most favourable condition level (no visible degradation) to the most unfavourable situation (extensive degradation or loss of functionality). In this study, it is adopted a scale with five degradation levels, ranging between condition A - no visible degradation - and condition E - generalized degradation. This classification relays the degradation state of stone claddings, according to the physical and visual assessment of façades at the inspection time ("Table 1").

3. EXPERIMENTAL PROCEDURE

In this study, 203 natural stone claddings (directly adhered to the substrate) in-use conditions were inspected. The degradation condition of the claddings analysed is evaluated through visual inspections, assessing in situ the characteristics of the claddings, their condition (according to the scale described in “Table 1”, which gives to the claddings inspected a given level of degradation based on the area of stone affected by a given set of defects), their environmental exposure and maintenance conditions. The sample comprises buildings of the nineteenth and twentieth centuries, intended for different uses: housing, commerce and services. The sample was randomly selected; however, it is tried to get a coherent and representative sample of the type of natural stone present in the Portuguese claddings. Additionally, the sample presents a wide range of ages, in which the youngest building only has 1 year and the oldest building has 82 years, allowing a more precise evaluation of the claddings’ aging process. In this study, it is assumed that age is given by the period of time elapsing since the last generalized rehabilitation action to the inspection date (since an intervention in the cladding should restore the initial characteristics, thus restarting its degradation process). In the sample analysed, none of the case studies belongs to the most unfavourable degradation condition (condition E). “Figure 1” illustrates the different degradation conditions, characterized in “Table 1”.

Table 1. Proposed degradation levels for natural stone claddings

Physical and visual degradation	Degradation condition
No visible degradation	Condition A
Visual or surface degradation defects ≤ 15% Loss-of-integrity defects ≤ 20%	Condition B
Visual or surface degradation defects ≤ 30% Joint defects ≤ 30% Bond-to-substrate defects≤ 20% Loss-of-integrity defects ≤ 20%	Condition C
Visual or surface degradation defects > 30% Joint defects > 30% Bond-to-substrate defects > 20% Loss-of-integrity defects ≤ 20%	Condition D
Bond-to-substrate defects > 20% Loss-of-integrity defects > 20%	Condition E

Figure 1. Degradation conditions for stone claddings

4. PROBABILISTIC ANALYSIS OF DEGRADATION OF NATURAL STONE CLADDINGS OVER TIME

In this study, the optimization of the infinitesimal generator matrix **Q** is carried out using the function *fmincon* (constrained nonlinear optimization) available in MATLAB, which provides the transition between degradation states, depending on the original state and the transition rate between the current and future state. Based on the transition rates, the probability of transition between states of condition and the mean probability of permanence in these states can be computed using Chapman-Kolmogorov differential equation. For this, in this study, the active-set numerical algorithm present in *fmincon* is used (Kalbfleisch and Lawless, 1985). To increase the stability of the optimization algorithm, in this case the logarithm of the likelihood was maximized as shown in equation (1) (Fletcher and Powell, 1963; Carrington et al., 2005; Higham and Higham, 2005). The matrix **Q** obtained for stone claddings is given by equation (2).

$$\boldsymbol{Find\ \theta} \xrightarrow{\boldsymbol{maximize}} \log(L(\boldsymbol{Q})) = \sum_{k=1}^{n} \sum_{l=1}^{m} \log(P_{ij}^{\Delta t}) \qquad \textbf{(1)}$$

$$\mathbf{Q} = \begin{bmatrix} q_{\mathrm{A,B}} \\ q_{\mathrm{B,C}} \\ q_{\mathrm{C,D}} \end{bmatrix} = \begin{bmatrix} 0{,}2210 \\ 0{,}0190 \\ 0{,}0115 \end{bmatrix} \qquad \textbf{(2)}$$

Based on the estimation of the intensity matrix (**Q**), the mean time of duration in each degradation state can be determined (“Figure 2”). Transitions between condition states of stone claddings occur faster for less deteriorated claddings. This results is directly related with the definition of the degradation states. Certainly, the transition between degradation states is not made uniformly, since the condition states follow a scale that is also irregular. The degradation condition A (more favourable) corresponds to a stone cladding without visible deterioration and, therefore, for a stone cladding transit to the following condition it is only necessary that the cladding presents changes in its surface or stains. Therefore, it seems reasonable that the transition from condition A to the next condition occurs only after 4.5 years. The transition between levels associated with higher degradation states imply the presence of a larger number of defects and/or more hazardous defects, including simultaneous occurrence of defects and synergies between them.

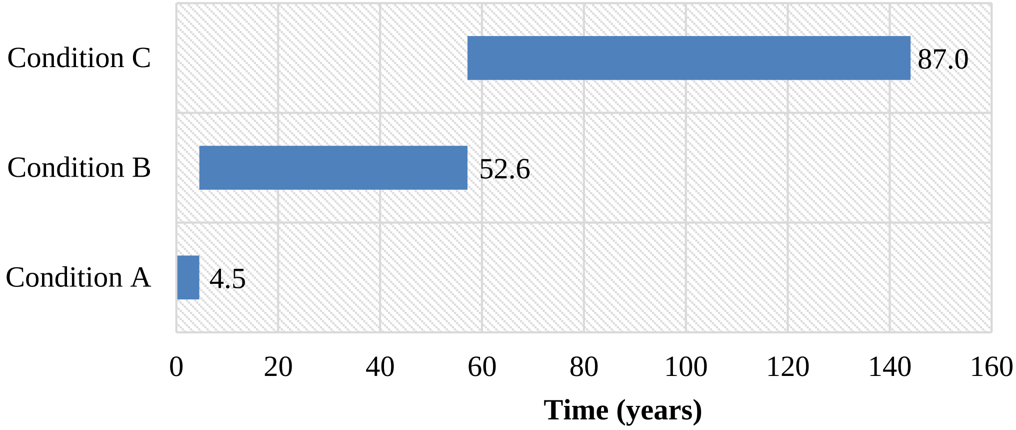

Figure 2. Mean time of permanence in each degradation state for stone claddings

The probabilistic distribution of the degradation condition of stone claddings over time is presented in “Figure 3”.

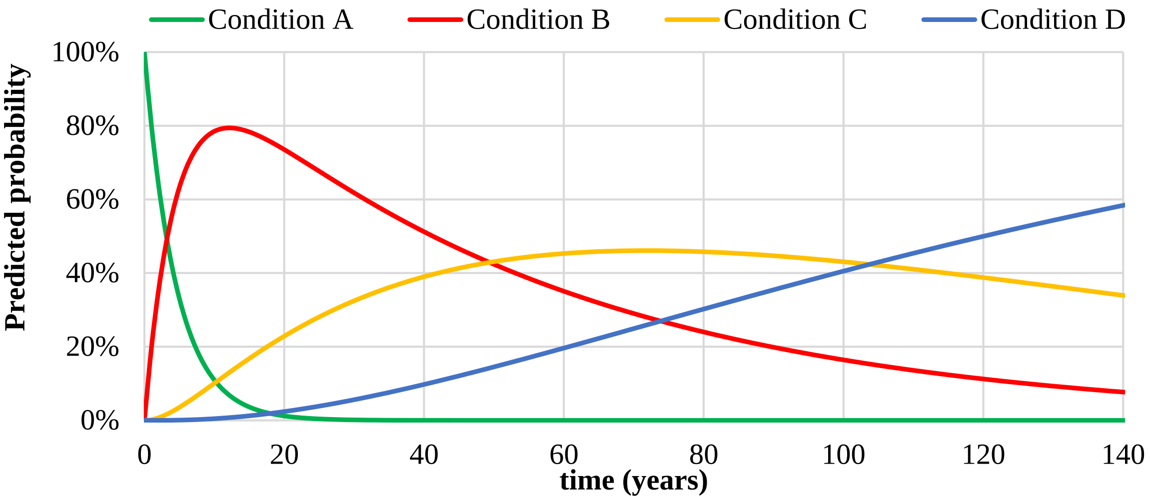

Figure 3. Probabilistic distribution of the degradation condition for stone claddings according to the age of the case studies

The probability of belonging to condition A decreases rapidly over time, being practically nil (lower than 2%) at year 8. The maximum probability (79.2%) of being in condition B is reached at age 12, decreasing after that. Regarding condition C, it is reached a peak of maximum probability of belonging to this condition between 71 and 73 years (with a probability of 46.1%). The probability of belonging to condition D increases over time: after being practically nil until year 41, it reaches 60% after year 145.

“Table 2” shows the probabilistic distribution of the degradation condition of stone claddings over time.

Table 2. Probability of belonging to a condition as a function of the age for stone claddings

Range in years	**Probability of belonging to a condition level**			
	Condition A	**Condition B**	**Condition C**	**Condition D**
[0:10]	41.81%	53.94%	4.11%	0.14%
]10:20]	3.95%	77.34%	17.32%	1.40%
]20:30]	0.43%	67.08%	28.42%	4.07%
]30:40]	0.05%	55.84%	36.29%	7.83%
]40:50]	0.00%	46.23%	41.42%	12.34%
]50:60]	0.00%	38.25%	44.44%	17.31%
]60:70]	0.00%	31.65%	45.82%	22.53%
]70:80]	0.00%	26.18%	45.98%	27.84%
]80:90]	0.00%	21.66%	45.23%	33.11%
]90:100]	0.00%	17.92%	43.83%	38.25%
]100:110]	0.00%	14.82%	41.97%	43.21%
]110:120]	0.00%	12.27%	39.81%	47.93%
]120:130]	0.00%	10.15%	37.47%	52.39%
]130:140]	0.00%	8.39%	35.04%	56.57%
]140:150]	0.00%	6.94%	32.58%	60.47%

At years 3 to 4 the probability of condition A is practically the same as that of condition B. After years 49 to 50 the probability of any case study of being in condition B is similar to that of being in condition C. Between years 103 and 104 the probability of belonging to condition C is similar to that of condition D. In these time intervals, there is a maximum probability of transition between one degradation condition to the next one.

To evaluate the efficiency of the model obtained using Markov chains, the number of expected and observed façades in each condition state is compared (“Table 3”). The percentage error obtained is relatively low, given the complexity of the phenomenon under analysis.

Table 3. Efficiency of the model obtained with Markov chains for stone claddings

Degradation condition	Observed	Predicted	Mean percentage error (%)
Condition A	9	12.096	34.40
Condition B	114	105.419	7.53
Condition C	57	63.959	12.21
Condition D	23	21.527	6.41

5. PROBABILISTIC ANALYSIS OF THE DEGRADATION OF STONE CLADDINGS ACCORDING TO THEIR CHARACTERISTICS

The characteristics of stone claddings significantly affect their durability. Therefore, various models using Markov chains are defined in order to analyse the probability of belonging to each degradation condition over time according to the characteristics analysed. Thus, the following variables are considered: (a) type of stone; (b) type of finishing; (c) size of stone plates; (d) exposure to damp; (e) and distance from the sea. The analysis of the results is performed in Section 6, being made some considerations regarding the durability of stone claddings according to their characteristics.

5.1 Type of stone

Koch and Siegesmund (2004) refers that the durability is an essential requirement to be considered when specifying the natural stones used as cladding material, especially in exterior claddings exposed to environmental degradation agents. Therefore it seems relevant to analyse the influence of the type of stone in the stone claddings’ degradation process. “Figure 4” presents the probabilistic distribution of the degradation condition over time for stone claddings according to the type of stone. Limestone claddings remains for the lowest period of time in condition A; for the other types of stone, the mean time of permanence in this condition is similar. At condition B, limestone claddings reach a maximum probability (85.2%) at 7 years of age; marble claddings reach this peak (73.7%) at 12 years and granite claddings at 18 years (P = 83.5%). Marble claddings reach a maximum probability (44.7%) of belonging to condition C after 55 to 56 years; limestone claddings reach this peak (52.5%) after 66 to 67 years and granite claddings after 105 to 108 years (P = 36.7%), i.e. considerably later. The highest probability of transition between conditions B and C occurs: between 37 and 38 years for limestone claddings; between 40 and 41 years for marble claddings; and between 106 and 108 years for granite claddings.

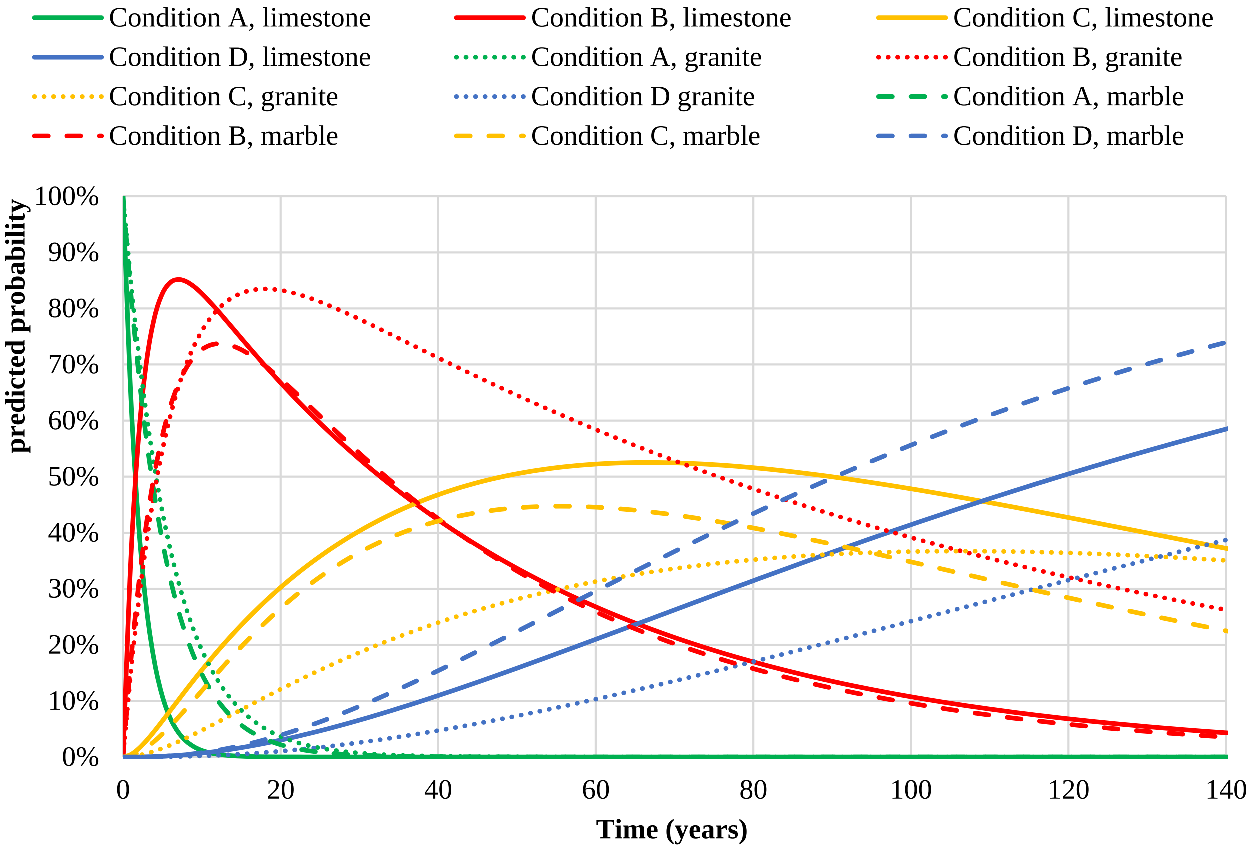

Figure 4. Probabilistic distribution of the degradation condition over time according to the type of stone

5.2 Size of stone plates

“Figure 5” presents the probabilistic distribution of the degradation condition over time according to the size of the stone plates. Stone claddings with large plates ($A \geq 0.4$ m^2) reach the maximum probability (71.1%) of belonging to condition B at 13 years of age and the maximum probability (44.6%) of belonging to condition C is reached at 53 to 54 years. These claddings have a maximum probability of transition between conditions B and C after 39 to 40 years and a maximum probability of transition between conditions C and D after 73 to 74 years. On the other hand, claddings with medium-size plates ($A < 0.4$ m^2) reach the maximum probability (83.2%) of belonging to condition B at 13 years of age and the maximum probability (43.8%) of belonging to condition C is reached at 86 to 88 years. For these claddings, the maximum probability of transition between conditions B and C occurs after 64 to 65 years and the maximum probability of transition between conditions C and D occurs after 121 to 122 years.

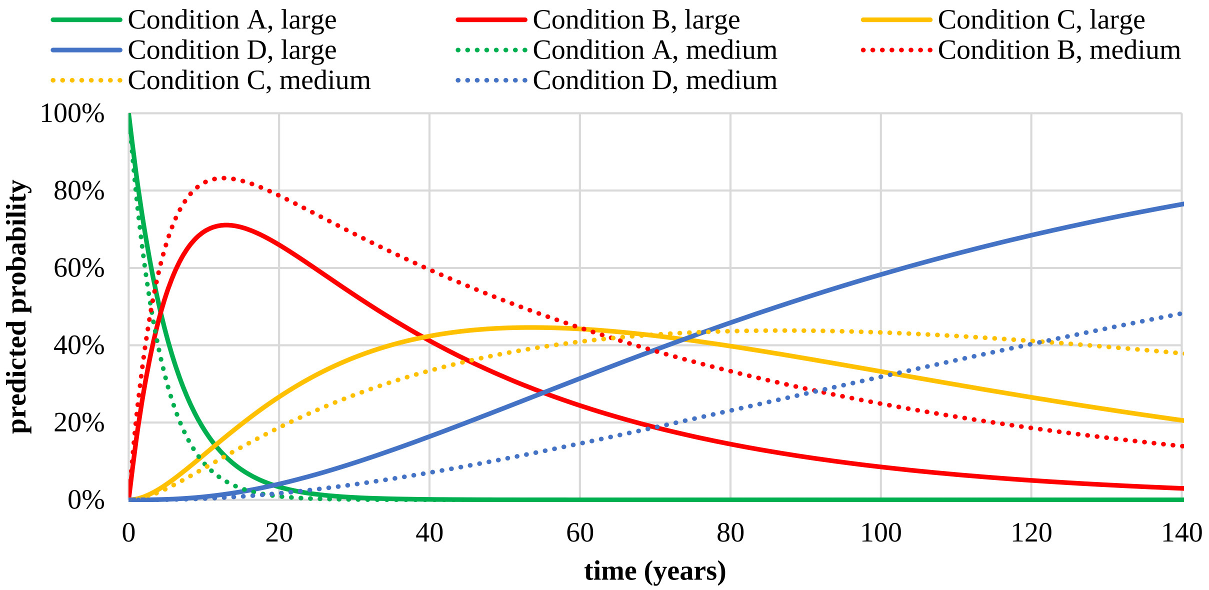

Figure 5. Probabilistic distribution of the degradation condition over time according to the size of stone plates

5.3 Exposure to damp

Figure 6 shows the probabilistic distribution of the degradation condition over time for stone claddings according to their exposure to damp. Regarding the definition of damp exposure conditions two categories are considered: (i) low exposure, for buildings located in urban context, located at more than 5 km from the sea and without influence of prevailing winds; (ii) buildings in coastal areas without protection of the combined action of wind and rain. Claddings highly exposed to damp remain less time in the most favourable condition (A). Claddings highly exposed reach the maximum probability (83.3%) of belonging to condition B at 8 years of age and of belonging to condition C (38.7%) at 51 to 52 years. Claddings less exposed reach the maximum probability (72.7%) of belonging to condition B after 17 years and the maximum probability (48.4%) of belonging to condition C after 80 years.

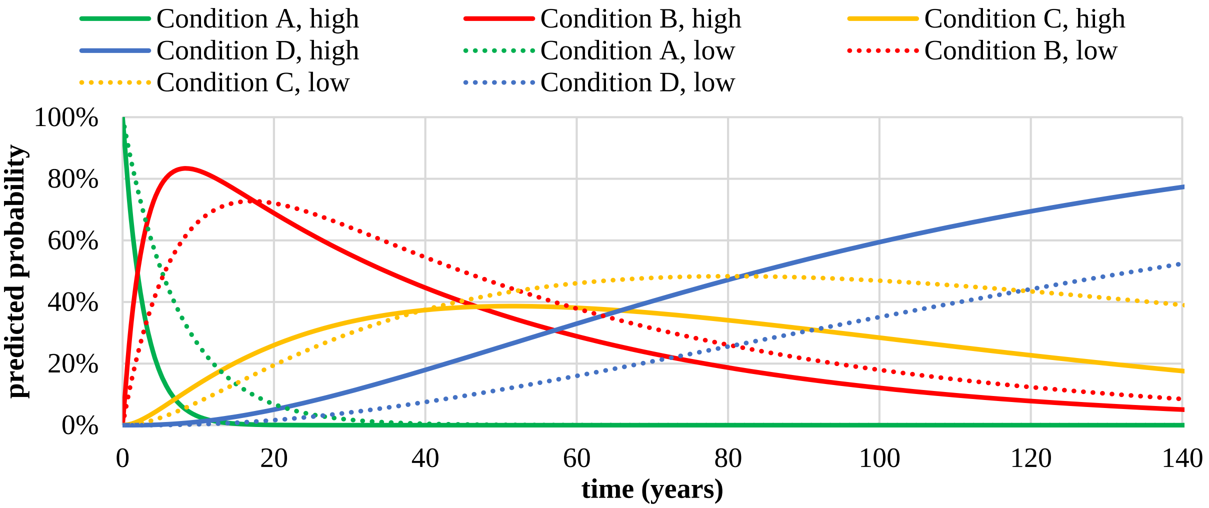

Figure 6. Probabilistic distribution of the degradation condition over time for stone claddings according to their exposure to damp

5.4 Distance from the sea

“Figure 7” presents the probabilistic distribution of the degradation condition over time for stone claddings according to their distance from the sea. The probability and mean time of permanence in condition A is similar for claddings located more than 5 km and less than 5 km. Claddings in coastal areas reach the maximum probability (71.7%) of belonging to condition B at 10 years of age and the maximum probability (43.1%) of belonging to condition C at 43 years. Claddings located more than 5 km away from the sea have a maximum probability (84.6%) of belonging to condition B after 80 years and a maximum probability (41.3%) of belonging to the condition C after 92 to 94 years.

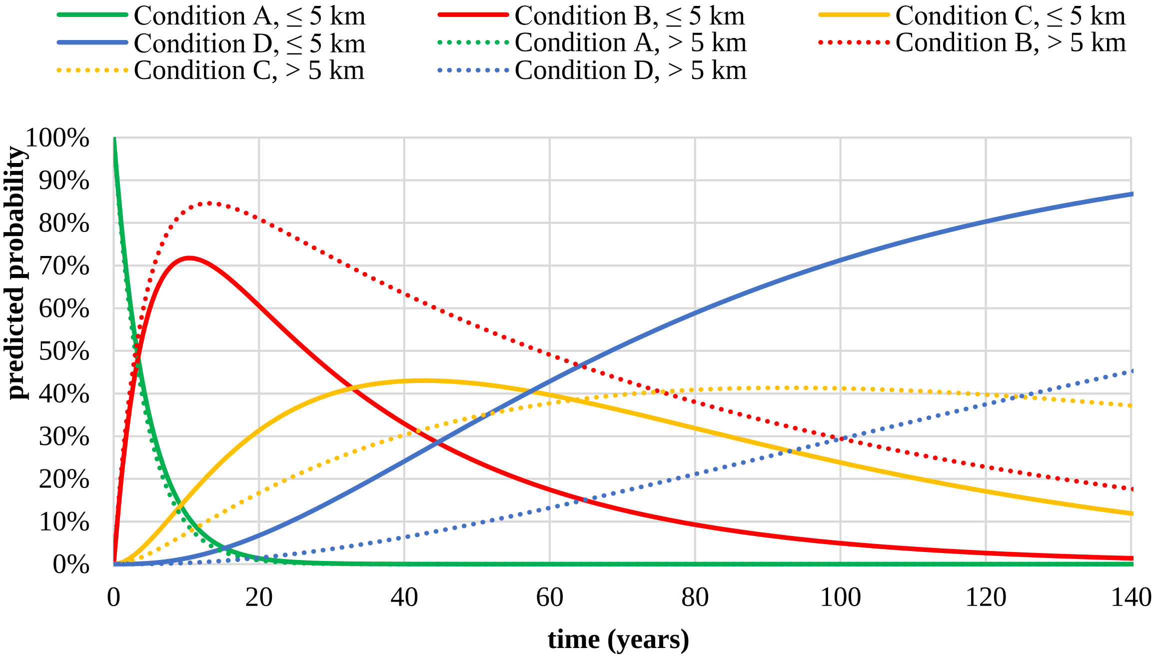

Figure 7. Probabilistic distribution of the degradation condition over time for stone claddings according to their distance from the sea

6. RESULTS DISCUSSION

“Table 4” shows the probability of belonging to a degradation condition as a function of the variables considered for stone claddings. The results obtained are coherent, make sense from a physical point of view and they lead to the following conclusions (valid for the sample analysed):

- Granite claddings have a 94.4% probability of belonging to the more favourable conditions of degradation (A and B), and no probability of belonging to condition D; marble claddings are those with lower probability of belonging to the most favourable conditions and greater probability of being in the most unfavourable degradation condition (E); these conclusions confirm the results obtained in previous studies, which indicates that granite claddings are the most durable, reaching the end of their service life later, followed by limestone claddings and marble claddings (the least durable);
- Claddings with medium-size plates have higher probability of belonging to more favourable conditions and a low probability of belonging to condition E; this suggests that larger plates reach the end of their service life sooner, especially when compared with

medium-size plates; this can be explained by the lower relative area of the joints in the bigger plates and consequent higher concentration of stresses due to the larger area of each plate and the greater stress needed to guarantee the adherence of the material (Silva et al., 2012);

- Claddings highly exposed to damp are more likely to belong to the highest degradation condition (P = 14.3% as opposed to coatings less exposed, with 9.2%); these claddings also present a higher probability (although in a small significant level) of belonging to the most favourable conditions (A and B);
- Claddings located more than 5 km away from the sea are more prone to belonging to degradation conditions A and B (P = 68.6% as opposed to 51.9% for coatings located less than 5 km away); claddings in coastal areas have a higher probability of belonging to the more serious condition of degradation (P = 26%, substantially higher than those away from the coast, with 2.5%).

Table 4. Probability of belonging to a condition as a function of the variables considered relevant for natural stone claddings

Variables		**Probability of belonging to a condition level**			
		Condition A	**Condition B**	**Condition C**	**Condition D**
Type of stone	Limestone	4.2%	45.8%	38.9%	11.1%
	Granite	5.6%	88.9%	5.6%	0%
	Marble	3.9%	42.9%	33.8%	19.5%
Size of stone plates	Large	1.4%	40.5%	33.8%	24.3%
	Medium	6.2%	65.1%	24.8%	3.9%
Exposure to damp	High	6.0%	60.7%	19.0%	14.3%
	Low	3.4%	52.9%	34.5%	9.2%
Distance from the sea	Less than 5 km	7.8%	44.2%	22.1%	26.0%
	> 5 km	2.5%	66.1%	28.9%	2.5%

The upper and lower limits of conditions C and D correspond respectively to the maximum allowable degradation level, considered in this study as being the end of service life of stone claddings. Therefore, the maximum probability of transition between conditions C and D marks the moment with the highest probability of stone claddings reaching the end of their service life. For the overall sample, the maximum probability of transition between conditions C and D occurs between 103 and 104 years. Regarding the type of stone, the highest probability of transition between conditions C and D occurs: at age 109 for limestone claddings; between 77 and 78 years for marble claddings; and between 131 and 132 years for granite claddings. The results reveals that granite claddings are the most durable, followed by limestone and marbles claddings. These results confirm the study by Schouenborg et al. (2007), who tested the mechanical resistance of the samples from 200 case studies (through laboratory tests and *in situ* analysis), obtaining similar conclusions. Claddings with medium-size plates transit between conditions C and D significantly later (between 121 and 122 years) than claddings with large plates (between 73 and 74 years). Concerning the exposure to damp, the transition between conditions C and D is more prone to occur between 65 and 66 years for claddings with high exposure and between 118 and 119 years to claddings with low exposure. These results confirm that claddings with high exposure tend to present higher degradation levels. Regarding the distance from the sea, for claddings in coastal areas, the transition between the conditions B and C has a higher probability of occurrence between 32 and 33 years, while the transition between conditions C and D is more likely to occur between

57 and 58 years. Claddings away from the coast (over 5 km) has a maximum probability of transition between conditions B and C between 75 and 76 years and the maximum probability of transition between conditions C and D occurs between 124 and 125 years. Thus revealing that claddings in coastal areas are more prone to possess more severe degradation indexes due to the exposure to winds that contain harmful marine salts that compromises the integrity of natural stone. The probabilistic distribution of degradation conditions over time can be seen as an assessment of risk of loss of performance due to degradation. Therefore, by establishing a threshold of acceptable risk, a stakeholder may estimate the need for re-pair based on the probabilistic analysis of a set of data. To illustrate this concept, one can consider that "high", "average" and "low" probabilities of a given condition correspond to "high", "average" and "low" risks associated to the consequences of the defects and the cost of repair and thus produce an indication of the urgency to maintenance and repair actions. Low risk (no actions required apart from monitoring) may correspond to P > 75% of belonging to either condition levels "A" or "B". High risk (need to extensive repair) may correspond to P > 25% of belonging to condition levels "D" and average risk may correspond to the intermediate states. The interpretation of the results, which depends on the assumptions made previously, leads to the following recommendations: i) monitor until year 20; ii) perform light maintenance actions before year 70; iii) consider their replacement after year 70, subject to on-site confirmation of their condition state.

7. CONCLUSION

In service life prediction models, it is relevant to know the rate of transition between degradation conditions, foreseeing the behaviour of the element under analysis and predicting the instant at which it will be unable to meet the requirements for which it was designed.

In this study, the future performance of stone claddings is predicted through the application of a Markov chain model, corresponding to a stochastic approach widely used to modelling the durability of buildings and its elements, which requires little information on its calibration. The proposed models are able to provide information regarding a complex phenomenon such as the claddings degradation, giving information on the synergy between the degradation agents (as in the case of environmental exposure conditions) and the degradation conditions. Additionally, this study provides information on the probabilistic distribution of the degradation condition for stone claddings over time (and according to their characteristics). Also, the knowledge of the average time of permanence in each degradation condition allows analysing the effects of degradation agents in the durability of stone claddings. This information is extremely useful to define (in a technically and rational manner) a set of maintenance strategies throughout the building's life cycle. When this type of information is available for different building components, it is possible to define common maintenance strategy for the different parts of the building. Stochastic models, such as Markov chains provides crucial information in the context of insurance policies, since they allow the assessment of the risk of failure of the claddings in order to evaluate the most probable time to failure of building elements according to their characteristics.

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Analytic Hierarchy Process to choose the cement type to protect reinforced concrete to corrosion caused by chloride ions attack

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ABSTRACT

This paper discuss cement types combinations to obtain the best one to protect against the steel reinforcement corrosion caused by chloride ions. In this case, it was used the method of Analytic Hierarchy Process (AHP), which is based on the definition of the main elements for making fast, reliable and objective decision. Three types of cement (CPII-Z-32: pozzolanic admixture, CPIII-40: blast furnace slag admixture and CPIV-32: pozzolanic admixture), two water/cement ratio (0,4 and 0,7) and two curing times (7 and 28 days), were analyzed trough results of five experiments. The application of AHP was effective to choose the type of cement, concluding that the CPIII-40 cement showed the best performance compared to the other cements.

Keywords: Analytical hierarchy process. Reinforced concrete. Steel corrosion.

RESUMO

Este trabalho discute combinações de tipos de cimento, buscando obter o de maior capacidade de proteger o concreto quanto à corrosão das armaduras sob ação de cloretos. Para isso, utilizou-se o método Análise Hierárquica (AHP), baseado na definição de elementos principais para uma tomada de decisão rápida, confiável e objetiva. Foram analisados três tipos de cimento (CPII-Z-32: com adição de pozolana, CPIII-40: com adição de escória e CPIV-32: com adição de pozolana), duas relações água/cimento (0,4 e 0,7) e dois tempos de cura (7 e 28 dias), através do resultado de cinco ensaios. A aplicação do AHP mostrou-se eficaz na escolha do tipo de cimento, gerando a constatação que o cimento CPIII-40 apresentou o melhor desempenho entre os cimentos avaliados.

Palavras-chave: Análise hierárquica. Concreto armado. Corrosão de armadura.

RESUMEN

Este trabajo discute combinaciones de tipos de cementos, buscando obtener el de mayor capacidad de proteger el concreto de la corrosión del acero de refuerzo bajo la acción del ion cloruro. Para esto, se utilizó el método de Análisis Jerárquico (AHP) basado en la definición de elementos principales para la toma de una decisión rápida, confiable y objetiva. Fueron analizados tres tipos de cemento (CPII-Z-32: con adición de puzolana, CPIII-40: con adición de escoria y CPIV32: con adición de puzolana), en dos relaciones agua/cemento (0.4 y 0.7) y dos edades de curado (7 y 28 días), a través del resultado de cinco ensayos. La aplicación del AHP evidenció ser eficaz para escoger el tipo de cemento, verificando que el cemento CPIII-40 presento el mejor desempeño entre los evaluados.

Palabras clave: Análisis Jerárquico, concreto reforzado, corrosión del acero de refuerzo.

Autor de correspondencia: Marcelo Medeiros

1. INTRODUCTION

Concrete consists in one of the main construction materials used in modern society, being the Portland cement the most appropriate construction material to those structures, overcoming also feasible alternatives as steel and wood. This is due to a combination of two materials that work to resist distinct efforts, concrete that has a good compressive strength and steel which resist tensile stresses, allowing a variety of applications.

Its intense use started from the 50s, however, until 70s it was believed that reinforced concrete was a material that does not deteriorate. Nevertheless, at this time, reinforced concrete structures began to show significant pathological manifestations, causing a concern about their durability (MEDEIROS, 2008).

Based on this, a lot of researches were accomplished with the aim to express the pathological manifestations incidence in reinforced concrete structures. Thus, Andrade (1997) established that 64% of pathological manifestations found in buildings at the state of Pernambuco were steel corrosion due to intense chloride ions attack.

Hence, the reinforced concrete structures deterioration due to steel corrosion represents one of the biggest problems of civil construction. That is because the repair cost is high, corresponding to 3,5% of the annual loss of Brazil's gross national product, occasioned by investments to prevent corrosion and to maintain or substitute structural elements damaged by corrosion (DOTTO, 2006).

Corrosion happens by an electrochemical mechanism that affords at least one oxidation reaction and one reduction reaction occurring simultaneously. Even so, there are three basic conditions for steel corrosion to occur: existence of an electrolyte; electrode potential difference and presence of oxygen (BARBOSA et al., 2012). According to Pereira et al. (2013), steel corrosion may be influenced by factors such as concrete properties, exposure time to aggressive agents, surface conditions of the steel bar, environmental characteristics around the structure, etc. Commonly concrete offers a protection against corrosion, due to a formation of a thin protective oxide layer on bars surface, because of the high material alkalinity. However, when the presence of chloride ions achieve a level of 0,4% of cement (in mass), the layer that once protected the reinforcement is destroyed and the steel becomes despassivated providing corrosion.

Therefore, researchers such as Page et al. (1986), Tessari (2001), Mather (2004), Sakr (2004) e Pereira (2011), studied about the influence of cement types and its admixtures in protecting against chloride ions attack. Based on those researchers, the admixtures of the different types of cement may contribute with benefits like capillary porosity and permeability reduction. Thus, with these benefits and their influences on steel corrosion, arose the assumption that the types of cement influence the protection against steel corrosion due to chloride ions.

Thereby, and using the data from Pereira's master dissertation (PEREIRA, 2011), this work presents a discussion, from Hierarchical Analysis, on choosing some cement types from Northeast region of Brazil, CPII-Z-32 (pozzolan Portland cement compound), CPIII-40 (blast furnace Portland cement) and CPIV-32 (pozzolanic Portland cement), regarding steel corrosion due to chloride ions.

2. INFLUENCE FACTORS ON CHLORIDE PENETRATION IN PORTLAND CEMENT COMPOSITE

Steel corrosion may occur by harmful chemical or electrochemical processes. In the case of reinforced concrete structural elements exposed to chloride ions attack, mainly on marine environments, it has been noticed frequent pathological manifestations like: cracking, spalling and severed of the concrete cover. Therefore, the cause of these manifestations is the loss of the steel bar section due to its corrosion, that on the other hand leads to the formation of expansive products inside concrete.

To avoid this corrosion process it is necessary that the concrete is in an alkaline environment provided by hydroxides. Hence, owing to a high alkalinity, there is a formation of a thin oxide layer on steel surface acting as a protective barrier. Thus, if there is a chloride contamination, steel corrosion may happen even with an alkaline concrete pH around 13.

As that kind of corrosion occurs in aqueous environment, the process is called as electrochemical, in other words, it implies that there is an oxide reaction and a reduction reaction, and circulation of ions through the electrolyte, being responsible for concrete deterioration (HELENE, 1993).

One of the main factors that influence corrosion is the pore structure of the concrete cover, and if it has a high absorption it must result to a more accelerated corrosion process. Thereby, the water ingress, dependent porosity variable, is of great significant because it controls the water, oxygen, CO_2 and chloride content inside concrete (CERVO, 2001). Therefore, it is important to evaluate the type of cement, the water/cement ratio (w/c) and cure conditions as influences to steel corrosion process due to chloride ions attack.

Cement chemical composition also has an influence on corrosion process due to chloride ions, because tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) combine with chloride forming chloroaluminate. The tricalcium aluminate has the ability to immobilize the chloride ions by forming an insoluble compound, the chloroaluminate and hidrated lime (PAGE et al., 1986). The work of Hoppe Filho et al. (2013), applying the X-ray diffraction technique also indicates the formation of chloroaluminate on concrete subjected to contact with a chloride ion aqueous solution.

It is important to emphasize that a mineral admixture, as pozzolans, on cement composition decreases porosity leaving concrete less susceptible to fluids percolation, and so, decreasing permeability. Besides, pozzolans have great ability to chloride retention, related to high levels of aluminates (CERVO, 2001).

As well as cement chemical composition, the w/c ratio directly influence shape, size and pores distribution being one of the factors that controls chloride penetration. That happens because a low w/c ratio decreases concrete porosity decreasing penetrability and diffusivity.

Hence, several surveys proposed studies about chloride ions related to different water/cement ratios. These studies proved that the lower w/c ratio the smaller chloride penetration (GASTALDINI *et al.*, 2010).

Another influence factor about diffusivity of chloride ions in Portland cement composite is the cure process, which also acts on pore structure formation on Portland cement paste. The longer cure time of concrete, the higher the resistance against aggressive agents ingress because of a better internal and superficial concrete cover conditions, occasioned by cement hydration.

3. EXPERIMENTAL PROGRAM

This paper consists of an application of a decision-making tool designated Analytic Hierarchy Process (AHP), that needs a data base to justify a given choice of a specific application. Hereafter, there are presented the conditions and assumptions of this paper, which focused on choosing the most suitable type of cement to execute a job inserted in a contaminated environment by chloride ions.

3.1. Data from the study used as data base to

The work used as data base do apply the AHP was developed by Pereira (2011) using the following variables:

- Water/cement ratio (2 levels – w/c = 0,4 e 0,7) – it was chosen two different w/c ratio to avoid the effect of this parameter in a significant way;
- Type of cement (3 levels - CPII-Z-32, CPIII-40 and CPIV-32) – This choice was based on each cement capacity to protect concrete in contaminated environments by chloride. The cement CPII-Z-32 and CPIV-32 are composed, respectively, of 12% and 43% of natural pozzolan from rocks, and the cement composition of CPIII-40 there is 67% of blast furnace slag;
- Cure process (2 levels – 7 and 28 days at a moist chamber) – It was chosen two cure periods at moist chamber in order to quantify how much important is to increase de cure period on Portland cement composites.

During the experimental program it was worried to maintain the same conditions of the specimens producing them in the same range of workability, varying in the interval of 260 mm and 300 mm. It was used cylindrical mortar specimens with dimensions of 50 mm, in diameter, and 100 mm, in high, to execute the complementary tests. For the accelerated corrosion test it was made prismatic specimens (60 x 80 x 25 mm) with two steel bars with 5 mm in diameter, 100 mm of length and 10 mm of cover.

After properly dried and cured in a laboratory environment for 15 days, the prismatic specimens were subjected to a corrosion test that consists of half cycles of partial drying and wetting in an aqueous solution with 5% of NaCl, for three months. The half cycles occurred for 5 days and the specimens stayed inside the storage, after 2 days they were submerged on the solution cited.

To execute the accelerated corrosion test it was needed the following equipment: a reference electrode, an electrical junction device, electric wires and a high impedance voltmeter. It was connected the positive pole to the steel bar and the negative pole to the reference electrode to measure the corrosion potential. In this way, the voltmeter indicates the potential difference intensity between the cells, representing a parameter to determine the occurrence of steel corrosion (PEREIRA, 2011).

It is necessary a conductive interface between the reference electrode and the steel bar to close the circuit, and it was made using a saturated sponge placed in electrical contact between the reference electrode and concrete surface. Picture 1 illustrates the configuration of the test for determining the corrosion potential (MEDEIROS et al., 2013).

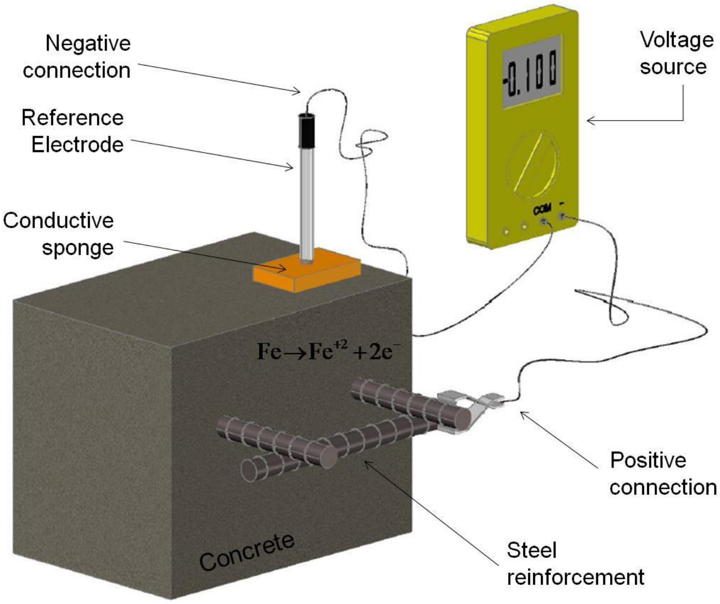

Figure 1. Circuit configuration for determining the corrosion potential (ROCHA, 2012; MEDEIROS et al., 2013)

The aim of the method is not quantify the corrosion of steel, since the corrosion rate is not determined by the procedure. According to Medeiros, Balbinot and Helene (2010), the potential for corrosion identifies part in the study sites where the thermodynamic conditions are favorable to the start of the corrosion process, although the armor does not show signs in the concrete surface that surrounds it.

For the assessment of the likelihood of corrosion was used the procedure recommended in the ASTM C 876 (2009) , and for relating the corrosion potential of the reference electrode copper/ copper sulphate (E_{corr}) of less than -350 mV , the probability corrosion is higher than 90%. In addition, for E_{corr} greater than -200 mV, the likelihood of corrosion is less than 10%.

In addition to the accelerated aging test was held the testing of immersion absorption (NBR 9778: 1987), wicking (NBR 9779: 1995) and compressive strength (NBR 7215: 1997) . The author's intention to conduct the testing was to assist in the understanding and interpretation of the main trial.

3.2. Analytic Hierarchy Process

Decision-making for complex problems requires treatment of simplified data, however systematic in order to get results fast, reliable and are inexpensive.

Taking into account factors of importance to the realization of a particular choice, Saaty developed in 1971 the technique of hierarchical analysis (*Analytic Hierarchy Process – AHP*). The AHP consists of a multi-criteria decision tool addressing factors that are organized in a hierarchical structure (SAATY, 1990).

In civil engineering, the potential of hierarchical analysis has been little explored, but it is possible to cite examples of studies using this tool as a decision making tool, such as: 1 - Marchezetti et al. (2011), in the treatment of household waste; 2 - Silva and Souza (2011), the check-gatherer solid waste compactor trucks; 3 - Lisboa e Waisman (2006) and Zayed et al. (2008), in decisions related to highway project area; 4 - Pan (2008), in the selection of bridge construction methods; 5 - Lai et al. (2008), the public works project; 6 – Pereira, Medeiros and Levy (2012), for selecting replacement percentage construction waste as aggregate in concrete dosage; 7 – Mattana et al. (2012), the choice of coating mortars; 8 – Pereira et al. (2014), the choice of adhesive mortars for use in floor system on floor.

The method AHP develops three main operations, which correspond to build a hierarchy of priorities analysis and consistency checks. The construction of the hierarchy is to tease out the component parts of the problem and organize them into levels. As for the priority analyzes carried out a comparison of the elements of each level based on the knowledge and experience of the decision maker. Finally, it is executed consistency checks to ensure consistency among comparisons (HO, 2008).

Thus, before you start implementing the AHP technique it is necessary to define the objective , which in this work is to choose a type of cement a water/cement ratio (w/c) and a time of healing , as previously specified , able to better protect the concrete for corrosion of the reinforcement under the action of chloride ions . So the alternative of choice for this work are shown in Table 1. We analyzed each situation seeking to obtain and compare the best type of cement for each w/c ratio and healing time.

Table 1. Combination of the types of cement for two levels of the w/c ratio and curing

Cement type	**w/c ratio**	**Curing time**
CP II-Z-32	0.4	07 days
CP II-Z-32	0.4	28 days
CP II-Z-32	0.7	07 days
CP II-Z-32	0.7	28 days
CP III-40	0.4	07 days
CP III-40	0.4	28 days
CP III-40	0.7	07 days
CP III-40	0.7	28 days
CP IV-32	0.4	07 days
CP IV-32	0.4	28 days
CP IV-32	0.7	07 days
CP IV-32	0.7	28 days

After the definition of choice, shown in Table 1, it has established the criteria to be considered in assessing the performance of alternatives. Pereira (2011) analyzed the results of three major trials being water absorption, compressive strength and accelerated corrosion, which are the primary level of the hierarchy. The water absorption test includes three other trials arranged on the secondary level of the hierarchy, and accelerated corrosion test also involves test data evolution of the corrosion potential, based on data obtained from the variation of mass of the specimens.

Figure 2 is a tree showing the hierarchical levels analyzed and considered criteria.

Table 3 shows the values of the first hierarchical level decision matrix indicating the weights of each parameter. As the water absorption and compressive strength tests was considered slightly less important than the accelerated corrosion test by comparing these with the last received values for standardizing the inverse of the data trend.

Table 3. Decision matrix of the first level of AHP

	Water absorption	Compressive strength	Accelerated corrosion	Line Total (Tl)	Relative importance
Water absorption	1.00	1.00	0.33	2.33	0.20
Compressive strength	1.00	1.00	0.33	2.33	0.20
Accelerated corrosion	3.00	3.00	1.00	7.00	0.60
General total (Gt)				11.67	1.00

In preparing the second hierarchical level decision matrix was decided to consider all the criteria considered as equally important. This practice was carried out because it is very difficult and subjective to assign different levels of importance for each of the three results of water absorption. In Table 4 are willing values of the decision matrix of the second hierarchical level.

Table 4. Decision matrix of the second level of AHP

	Immersion absorption	Capillary absorption height (cm)	Absorptivity (Kg/m²h$^{1/2}$)	Line Total (Tl)	Relative importance
Immersion absorption	1.00	1.00	1.00	3.00	0.3333
Capillary absorption height (cm)	1.00	1.00	1.00	3.00	0.3333
Absorptivity (Kg/m²h$^{1/2}$)	1.00	1.00	1.00	3.00	0.3333
General Total (Gt)				9.00	1.00

After developing matrices, decision with the weights of each criterion was calculated consistency AHP through the reasoned consistency test by Saaty (2000) and pointed out by (2002). Thus, we determined the ratio of consistency, it should be a value less than or equal to 0,1. In the case of this study, because of the calculation resulted in 0 (zero) for both developed arrays, being less than the limit. Thus, the AHP is mounted considered perfectly consistent.

In this work, all the data used in the comparison analysis of quantitative criteria are requisites, that is, we used the numerical values extracted from the results of tests performed by Pereira (2011), as follows in Table 5.

The test evolution of the corrosion potential was performed with 12 cycles of drying and wetting (in 5% NaCl solution) and total duration of 84 days. For the cement performance evaluation considered the average of all the results only of the phases of wetting, that the presence of water presents the most representative values in relation to the likelihood of corrosion.

Figure 2. Hierarchy tree with the criteria and levels of analysis

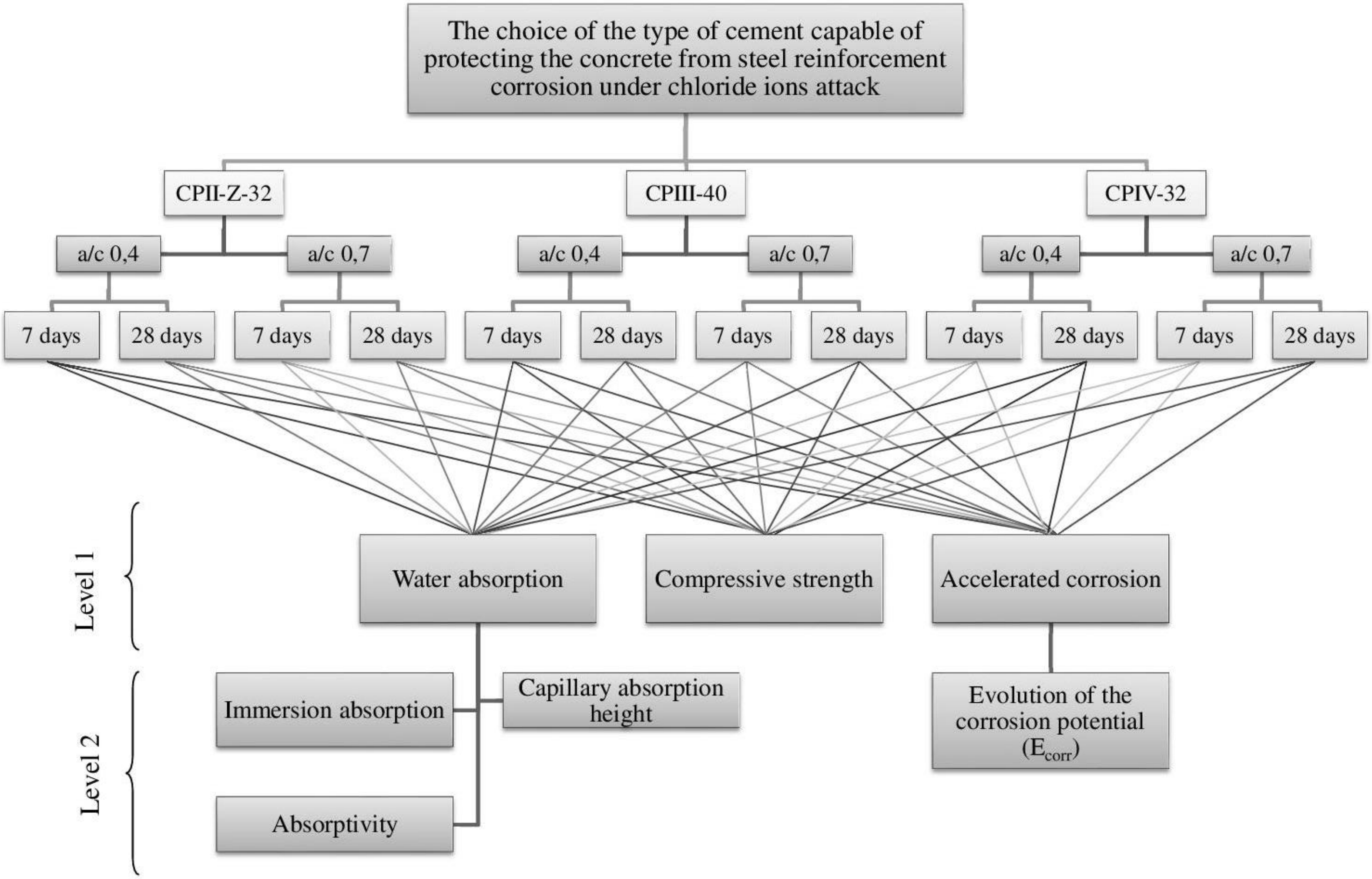

Table 5. General data for the preparation of AHP

Cement type	CPII				CPIII				CPIV			
Curing time	7 days		28 days		7 days		28 days		7 days		28 days	
w/c ratio	0.4	0.7	0.4	0.7	0.4	0.7	0.4	0.7	0.4	0.7	0.4	0.7
Height capillary rise (cm)	4.7	6.1	4.4	6.7	3.5	5.3	3.3	4.2	4.3	4.8	3.5	5.5
Absorptivity ($Kg/m^2h^{1/2}$)	1.27	1.93	1.14	1.87	0.97	1.37	0.89	1.24	1.26	1.72	0.98	1.48
Immersion absorption (%)	0.11	0.12	0.11	0.11	0.12	0.11	0.12	0.11	0.13	0.12	0.13	0.11
Compressive strength (MPa)	34.5	16.8	46.2	20.4	47.5	18.7	50.0	28.6	37.1	14.5	43.6	18.3
Corrosion potential (mV)	-387	-474	-379	-492	-406	-514	-339	-462	-460	-481	-434	-503

4. RESULTS - APPLICATION OF HIERARCHICAL ANALYSIS

With this research. using test data performed by Pereira (2011) and by the method of Analytic Hierarchy. sought to get the best type of cement (CPII-Z-32. CPIII-40 e CPIV-32) or corrosion reinforcement under the action of chloride ions . also considering two level w/c ratio (0.4 e 0.7) and two cure times (7 e 28 days). The results of the analysis were verified separately by combination of the selection elements. generating two analysis matrices comparing the types of cement with the 0.4 w/c ratio of to as much as 7 days cure for 28 days. and two arrays with types of cement 0.7 w/c ratio of and cure times of 7 days and 28 days.

To optimize space and objectify the results of this study. it was decided to present the details of the evaluation procedures only of the cement kinds decision matrix for w/c ratio of 0.4 to 7 days . which is described the item that follows. For other matrices. we chose to show only the final tables with the performance and final evaluation indexes. Therefore. it is clear to the reader how to get up in the final analysis by AHP.

4.1. Choice of cement to w/c ratio = 0.4 and curing time = 7 days

After meeting the criteria considered in AHP and establish the weighting factors for comparison of these properties. the appraiser must perform the normalization of data for performance verification. For the calculation divides the value of each item of the line by the larger value. so that all criteria exhibit the same magnitude of values between 0 and 1.

The values of the tests relating to water absorption and corrosion potential needed to be reversed. since the results were the smaller. the better the performance. When converting the data it is possible to standardize analysis by greater values getting coherence in the assessment. In Table 6 are standardized and normalized data of the water absorption test (immersion absorption and capillary absorptivity). the compressive strength and accelerated corrosion (potential corrosion).

Table 6. Modified and standard values used in the AHP

Data		Modified values			Normalized values		
		CP II	CP III	CP IV	CP II	CP III	CP IV
Criteria	immersion absorption (%)	9.09	8.33	7.69	1.00	0.92	0.85
	Altura ascensão capilar (cm)	0.21	0.29	0.23	0.74	1.00	0.81
	Absorptivity (Kg/m²h$^{1/2}$)	0.79	1.03	0.79	0.76	1.00	0.77
	Compressive strength	34.50	47.52	37.09	0.73	1.00	0.78
	Potential corrosion (mV)	0.00259	0.00246	0.00217	1.00	0.95	0.83

The normalized value of each item (Table 6) multiplied by the relative importance of each criterion (Table 4). and also by 100 (percentage). it was possible to achieve the performance levels. An example: Equation (1) describes the procedure for calculating the performance index of the immersion absorption criterion to the cement type CP II, w/c ratio 0.4 and 7 days.

$I_c = Vn_i \text{ x } P_c \text{ x } 100$ (1)
$I_c = 1.00 \text{ x } 0.3333 \text{ x } 100$
$I_c = 33.33$

Where.
I_c: performance index of the criterion
Vn_i: normalized value of the criterion
P_c: relative importance of the criterian

After that. we add up all the performance indices of comparison criteria corresponding to water absorption. The performance indices of the compressive strength criteria and evolution of the corrosion potential are not added for each criterion it is an isolated test. Table 7 shows the performance indices of the criteria.

Finally. the final evaluation is the sum of the performance index multiplied by the relative importance (Table 3) of each property analyzed. The calculation procedure for the final evaluation of the cement type CP II is exemplified by Equation (2).

$Af = \Sigma(I_p \text{ x } P_p)$ (2)
$Af = (83.62 \text{ x } 0.20) + (72.60 \text{ x } 0.20) + (100.00 \text{ x } 0.60)$
$Af = 91.24$

Where.
Af: Final Evaluation
I_p: Property Performance Index
P_p: Relative Importance of Property

Table 7. Performance index for cement types. w/c = 0.4 and 7 days of curing

Data analyzed		Performance index		
		CP II	CP III	CP IV
water absorption	Immersion absorption (%)	33.33	30.56	28.21
	Height capillary rise (cm)	24.82	33.33	27.13
	Sortivity (Kg/m²h$^{1/2}$)	25.46	33.33	25.66
	Performance index	83.62	97.22	81.00
Compressive strength	Compressive strength	72.60	100.00	78.05
	Performance index	72.60	100.00	78.05
Accelerated corrosion	Corrosion Potential (mV)	100.00	95.26	83.99
	Performance index	100.00	95.26	83.99

Table 8 shows the evaluation of each cement type. The best result among the combinations of cement types. w/c ratio and cure times presents the highest value in the final assessment.

Table 8. Final assessment for cement types. w/c = 0.4 and 7 days of curing

	water absorption	Compressive strength	Accelerated corrosion	Final Evaluation
Relative importance	0.20	0.20	0.60	
CP II	83.62	72.60	100.00	91.24
CP III	97.22	100.00	95.26	96.60
CP IV	81.00	78.05	83.99	82.21

For the case study. seeking the best cement type to protect the reinforced concrete to corrosion in chloride ion environment. to w/c equal to 0.4 and cure time of 7 days. the option that presented the best performance using the Analytic Hierarchy Process (AHP) was the cement type CPIII-40. followed by the CPII-Z-32 and CPIV-32.

4.2. Choice of cement to other combinations of w/c ratio and curing time

The calculation procedures stated above for the choice of the type of cement. with w/c ratio equal to 0.4 and 7 days of curing. were the same as those used for the other combinations of w/c ratio and curing time. Thus. in order to simplify the presentation of results in Tables 9. 10 and 11 are placed data from performance indicators and the final evaluation of other matrices analyzed.

Table 9. Final assessment for cement types. w/c = 0.4 and 28 days of curing

	water absorption	Compressive strength	Accelerated corrosion	Final Evaluation
Weight	0.20	0.20	0.60	
CP II	84.36	92.41	89.36	88.97
CP III	97.22	100.00	100.00	99.44
CP IV	89.91	87.21	78.09	82.28

Table 10. Final assessment for cement types. w/c = 0.7 and 7 days of curing

	water absorption	Compressive strength	Accelerated corrosion	Final Evaluation
Weight	0.20	0.20	0.60	
CP II	80.45	90.04	100.00	94.10
CP III	96.86	100.00	92.17	94.68
CP IV	90.44	77.68	98.35	92.63

Table 11. Final assessment for cement types. w/c = 0.7 and 28 days of curing

	Absorção água	Resistência a Compressão	Corrosão Acelerada	Avaliação final
Peso	0.20	0.20	0.60	
CP II	76.33	71.38	94.01	85.95
CP III	100.00	100.00	100.00	100.00
CP IV	86.72	64.03	91.84	85.25

Individually analyzing each test. it was found that the cement CPIII-40 stands out with respect to water absorption performing better as identified with w/c ratio equal to 0.4 with a cure time of 28 days. This result is due to the improvement of Portland cement composite microstructure caused by the extension of the curing period. In relation to the w/c ratio. it influences the amount of voids in mortar. that controls the porosity influencing the properties related to transport mechanisms in concrete (MENDES et al.. 2010).

Using Analytic Hierarchy Process (AHP). regarding the compressive strength it was confirmed which is expected: the compression strength tends to increase with decreasing the water/cement ratio (MEHTA e MONTEIRO. 2008).

It was noted that the CPIII-40 cement showed the highest compressive strength values because of the very high blast slag furnace quantity. Pereira (2011) showed that such cement has a greater fineness in relation to the other studied. which results in a higher reactivity of the cement.

Evaluating final results of accelerated corrosion tests is noticed again that in all matrices analyzed to choose the best cement type corresponded to CPIII-40. followed by the CPII-Z-32 and CPIV-32. This is in accordance with the statements of Tumidajski and Chan (1996). that concretes incorporating blast furnace slag. in partial replacement of Portland cement. are more efficient in preventing the penetration of chloride ions compared to concretes proportionated with ordinary cements.

Finally. it was found that for the samples made with CPIII-40. which was chosen in all matrices analyzed. water/cement ratio values resulted in relatively similar effects. and in favor of the concrete protection by chloride attack. For curing. prolonged time also improved the CPIII-40 in concrete protection.

This work was carried out taking as a database Pereira (2011) and it should be noted that the AHP application would be more complete if the database includes corrosion rate data and even another indication of rebar corrosion as occurrence of corrosion spots on the surface of the concrete. However. this study shows that AHP is an open system to include other parameters. which can enrich the result of choice.

5. CONCLUSIONS

Analytic Hierarchy Process (AHP) is a tool for decision making with advantages such as ease of application method and the possibility of modifying the factors in a choice by providing clear and objective results. The AHP allows the construction of hierarchies that consider multiple variables and acknowledge the comparison and evaluation criteria prioritizing the results.

The AHP application of this work helped to choose the type of cement capable to protecting the reinforced concrete by corrosion induced by chloride ion. also considering different water/cement ratio and curing times.

Evaluating the selection criteria through the water absorption tests. compressive strength and accelerated corrosion performed by Pereira (2011). it was found that the CPIII-40 cement showed the best performance in all combinations evaluated in this work. However. according to the curing time. the better performance of the chosen cement was 28 days. as expected due to the higher hydration degree.

It is important to note that the relative importance in the considered criteria were established by the authors and informed in Pereira (2011). And the intention of this work is to demonstrate the utility and application of the AHP. when it involves a decision-making among various possibilities and data combinations related to reinforced corrosion studies under chloride ion attack.

Thus. it can be concluded that the Analytic Hierarchy Process (AHP) was efficient for the systematization of choices and a new analysis of the results of Pereira (2011). The variables to be considered and their respective weights can be discussed in future work. aiming to improve the method developed in this work. One point of improvement to be suggested is considers the corrosion rate.

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Chemical and physical-mechanical characterizations of cement with the addition of limestone filer in Venezuela

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ABSTRACT

In recent years in Venezuela, there has been a crisis on demand, production and marketing of cement, primary building material. In this work the chemical and physical mechanical characterization made a Top Trademark blended cements in the country, characterizing them according to: chemical composition, Blaine fineness, setting time and compressive strength. The results show that these cements do not meet the minimum requirements established in the Venezuelan standard for use in the manufacture of structural concrete.

Keywords: Blended cement, Corrosion, Reinforced Concrete.

RESUMEN

En los últimos años en Venezuela, se ha presentado una crisis sobre la demanda, comercialización y producción del cemento, principal material de construcción. En este trabajo se presentará la caracterización química y físico- mecánica realizada a las principales marcas comerciales de cementos adicionados en el país, caracterizándolos de acuerdo a: composición química, finura Blaine, tiempo de fraguado y resistencia mecánica a compresión. Los resultados demuestran que estos cementos no cumplen con los requisitos mínimos establecidos en la norma venezolana para su uso en la elaboración de concreto estructural.

Palabras clave: Cemento Adicionado, Corrosión, Concreto Armado.

RESUMO

Nos últimos anos na Venezuela, tem-se apresentado uma crise sobre a demanda, comercialização e produção de cimento, um dos principais materiais de construção. Este artigo apresentará a caracterização química e físico-mecânica realizada nas principais marcas de cimentos com adições comercializados no país, caracterizando-os de acordo com a sua composição química, finura Blaine, tempo de pega e resistência à compressão. Os resultados demonstram que estes cimentos não cumprem com os requisitos mínimos estabelecidos na norma venezuelana para a sua aplicação na elaboração de concreto estrutural.

Palavras-chave: Cimento com adições, Corrosão, Concreto Armado.

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1. INTRODUCTION

Over the last few years, there has been a crisis regarding the demand, commercialization and production of cement, a basic construction material in Venezuela. This has led manufacturers to seek alternatives in order to meet this growing demand, consequently including in the commercial offering of this material cement aggregates. These aggregates are usually the Portland type with the addition of limestone, with a concentration varying between 15% and 30% based on the weight of the cement.

Even though the production of cement aggregates is a global phenomenon that aims, among other things, to reduce the environmental impact of the production of Portland cement and to decrease the emissions of CO_2 in the construction industry, the indiscriminate use of this product in Venezuela has been noted as the technical limitations of this cement have not been considered, mainly in regards to mechanical resistance and their reaction to corrosion of reinforced concrete. The latter is addressed in our hypothesis on the basis of the chemical composition of these cements, which prevents not only a lower alkaline reserve which would make them less resistant to the action of environmental agents, more specifically carbonation, but also their inability to guarantee the adequate mechanical resistance for the design of conventional mixtures.

Cement aggregates (or reinforced) are Portland cement clinker mixtures, calcium sulphate (plaster) and aggregates. These cements can be produced through the joint grinding of these components or through the mixing of grinded components (Salamanca 2000). Type CPCA 1 and CPCA 2 cement aggregates are formulated for their use in the production of concretes and mortars that need to improve their workability, water retention ability, appropriate resistance on use and greater durability (Salamanca 2000). According to the Venezuelan standard COVENIN (COVENIN 3134-2004/ASTM C-150), the CPCA 1 is that whose content of limestone or any other calcareous material is more than 15% and less than or equal to 30% of its total weight.

As mentioned before, it is important to know the nature and the physical-mechanical characteristics of these cements, as the achievement of the established characteristics for their use as structural concrete, one that is resistant and durable, will depend upon them. The problems that arise from the incorrect use of concretes elaborated with different types of cements without taking any precautions make it necessary to look into the materials to be used and the transformation products generated in the manufacturing of concretes.

Venezuelan law does not designate particular conditions for the characteristics of cements with limestone additions, and does not regulate the chemical requirements as it does with standardized Portland cement. For cement aggregates, the COVENIN 3134-04/ASTM C-150 standard establishes the physical, chemical and mechanical requirements to be followed, mandating the same physical-mechanical requirements that have been established for Portland cement type I and only three parameters for the the chemical requirements among which the following can be found: loss on ignition, insoluble residues and sulphur trioxide (SO_3). However, these components are not the only ones that guarantee the quality of the cement. For this reason, the existing chemical parameters in the current COVENIN 109-90/ASTM C-114 standard should be applied to the cement aggregates. This standard contemplates the test methods employed to perform chemical analyses of hydraulic cements, which are fundamental for the determination through the Bogue method of the main chemical components: alite, belite, tricalcium aluminate, and tetra-calcium aluminoferrite. Due to all of the aforementioned, it is necessary to determine the technical limitations of the use of these cements in the manufacturing of concrete for structural elements, which will undoubtedly contribute to the improvement of the durability of the buildings in the country. Thus, this work is oriented towards the determination of the chemical and physical-mechanical characteristics of the cement aggregates of the different companies that manufacture this material in Venezuela, that allow the estimation of their behavior as structural concrete.

2. EXPERIMENTAL PROCEDURE

The following materials were used: Portland cement type I, cement aggregates with limestone filer CPCA from six different companies in the country (identified as CEMA, CEMCA, CEMCO, CEMLI, CEMVEN and CEMMA), and standardized silica in compliance with the Venezuelan COVENIN 2503/ASTM C-778 standard. For the mixture design, the recommendation by the ACI 211 was used.

For the evaluation of the chemical and physical-mechanical properties, the validation criteria for cement aggregates described in the COVENIN 3134-04 (ASTM C-ASTM C-150) were used through the following tests: chemical analysis (COVENIN 109-90/ASTM C-114), Blaine fineness (COVENIN 487/ASTM C-204), setting time (COVENIN 493:1992/ASTM C-19) and resistance to compression (COVENIN 484:1993/ASTM C-109). In relation to the number of samples in each test, the amount established in each standard was used as a minimum.

For the chemical analysis of cement aggregates, the COVENIN 109-90/ASTM C-114 standard indicates that platinum crucibles should be used. One of the limitations of this work was the lack of availability of these crucibles; it was therefore decided to use conventional ceramic crucibles with a capacity of 15 cm^3 and 30 cm^3.

3. RESULTS AND DISCUSSION

3.1. Physical-mechanical characterization of CPCA cement aggregates:

The most relevant results of the physical-mechanical characterization done to six commercial brands of CPCA type cements manufactured in Venezuela are presented.

Six (6) samples for each type of cement were tested for fineness through the Blaine's permeability meter in regards to the fineness of standardized cement; results are shown in Table 1. This table shows that in all evaluated cases the determined fineness values of Portland cements with CPCA additions exceed the minimum normative value established (3000 cm^2/gr), which also indicates a larger specific surface for better hydration to the specific surface required for its hydration.

Table 1. Results of the fineness determination (specific surface) of the Portland cement with CPCA aggregates, normative value (minimum) of 300 cm^2/gr.

DETERMINATION OF BLAINE’S FINENESS (SPECIFIC SURFACE)	
CEMENT TYPE	**FINENESS**
CEMA	3534,06 cm^2/gr
CEMCA	3602,17 cm^2/gr
CEMCO	3093,08 cm^2/gr
CEMLI	3827,47 cm^2/gr
CEMVEN	3246,46 cm^2/gr
CEMMA	3588,06 cm^2/gr
PORTLAND I	3867,06 cm^2/gr

It is important to note that one of the last stages in the manufacturing of cement is the mixture of the grinded clinker with hydrated calcium sulphate. That said, as hydration begins on the surface of the cement grains, its superficial area constitutes the material of hydration. In this manner, the speed of hydration depends on the fineness of the cement particles; therefore, for a quick development of resistance, a high level of fineness is necessary. However, the grinding of cement particles in order to obtain more fineness represents a considerable expense. It is required for the cement to achieve the necessary resistance to different ages through the clinker quality and not through the fineness of the grinding.

It should also be noted that in Venezuela the usual cements are grinded to Blaine's fineness on the order of 2800 to 3500 cm^2/gr. When it exceeds 4000 cm^2/gr, and depending on the chemical composition of the cement, secondary problems may arise on the concrete, such as difficulty in the mixing of it and more retraction. These results are therefore considered acceptable due to the fact that the values obtained from the Portland cement with CPCA aggregates in the study exceed the minimum established by the COVENIN 3134:2004 standard, without reaching inadequate fineness values (>4000 cm^2/gr).

The average results of nine (9) samples of each type of tested cement obtained through the determination of the initial setting time and final setting time of the cement are shown in Table 2. As it is already known, the setting time is that in which a binder changes its initial plasticity to a stony state, making this a fundamental property for these types of materials, as it establishes the average time of workability and placement without affecting the development of its final properties. It can be observed in this table that for Portland cement with CPCA aggregates, in all evaluated cases, the values of minimum initial time determined do not achieve the standard value that has been established. This results in the non-compliance of this characteristic of the material, inferring potential difficulties in the manufacturing of concretes and mortars due to the low setting time that was determined. In contrast, the behavior of Portland cement type I showed results similar to what was expected.

Table 2. Results of the characterization of Portland cements with CPCA aggregates. Determination of setting time.

DETERMINATION OF SETTING TIME				
Cement	**Initial Time (min)**	**Final Time (min)**	**Normative Value**	
			Minimum Initial Time (min)	**Maximum Final Time (min)**
CEMA	30	255	45	480
CEMCA	30	165	45	480
CEMCO	40	180	45	480
CEMLI	40	165	45	480
CEMVEN	15	240	45	480
CEMMA	15	240	45	480
PORTLAND I	90	290	45	480

Even though the characteristics already mentioned reflect that the evaluated cement presents discrepancies with the normative values to be met, the quality of cement in building practices is measured based on its resistance to compression once it has set and hardened, this mechanical characteristic being the main evaluation factor of the binder. Therefore, this property was evaluated on the cements that were studied, putting together 18 cubic test tubes with cement mortar (cement to be evaluated and standardized silica sand) with sides of 50.8 mm for each type of cement and each age of assay (7 and 28 days).

Table 3 presents the results obtained from each test, obtaining results that confirm the non-compliance of the normative values for the evaluated cements.

Table 3. Resistance to compression of Portland cement with CPCA aggregates, 7 and 28 days.

RESISTANCE TO COMPRESSION OF CPCA CEMENT AGGREGATES (kg/cm^2)							
Cement Days	**CEMAN**	**CEMCA**	**CEMCO**	**CEMLI**	**CEMVE**	**CEMMA**	**PORTLAND I**
7 days (Average)	117,73	149,06	46,29	93,06	127,75	132,89	296,63
Deviation	+/- 4,50	+/- 4,00	+/- 7,76	+/- 3,88	+/- 4,83	+/- 3,43	+/- 3,21
28 days (Average)	145,12	213,45	178,45	176,87	216,85	157,77	394,08
Deviation	+/- 5,03	+/- 4,07	+/- 4,83	+/- 3,76	+/- 4,14	+/- 4,73	+/- 4,03

When observing the results, it is evident that the lowest average tested resistance for the test age (7 days) came from the CEMCO cement with a value of 46,29 kg/cm^2, while the highest came from the CEMCA cement with a value of 149,06 kg/cm^2. However, none of the evaluated cements reached the 170 kg/cm^2, the value recommended by the COVENIN 3134:2004/ASTM C-150 standard for Portland cement with CPCA1 aggregates. A similar behavior was noticed when evaluating the resistance to compression at 28 days where none of the evaluated cements achieved the normative value of 280 kg/cm^2; these were all surpassed by control Portland cement type I. This undoubtedly compromises their performance as structural concrete. Starting from the premise that the material does not possess the minimum conditions, its evolution should not be able to achieve the expected values. This is why it was considered to characterize them chemically in order to determine the components that are contributing to their failure to meet high compression resistance.

3.2. Chemical characterization of the main and secondary components of CPCA cement aggregates.

3.2.1 Main components of cement aggregates

Silicon Dioxide (SiO_2).- Double calcination of the sample was done during this test, and the residue therefrom was used in the determination of the group of ammonium hydroxide. Figure 1 shows the average of the results that were obtained.

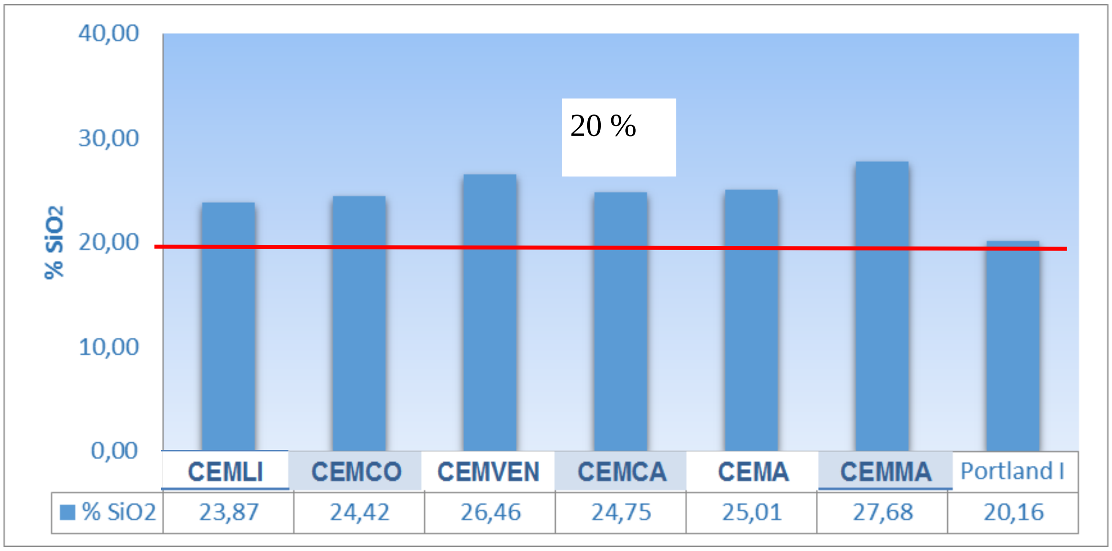

Figure 1. Percentage of SiO_2 in the different evaluated cements.

The obtained values indicate that Portland cement had a value of 20.16% and all the other samples possessed more than the 20% of silicon dioxide, the minimum established parameter in the COVENIN 28-93/ASTM C-150 standard for Portland cement type II; the standard does not specify the content of this component for Portland I. All values are set within a range between 20% and 30%, with the lowest percentage being Portland cement type I.

Aluminum Oxide (Al_2O_3).- In this determination, as indicated by the COVENIN 109-90/ASTM C-114 standard, the quantity of ferric oxide is subtracted from the value obtained by the ammonium hydroxide study. All studies complied with the variation parameter allowed by the standard to ensure the reliability of the study. The total % results of Al_2O_3 are shown in Figure 2.

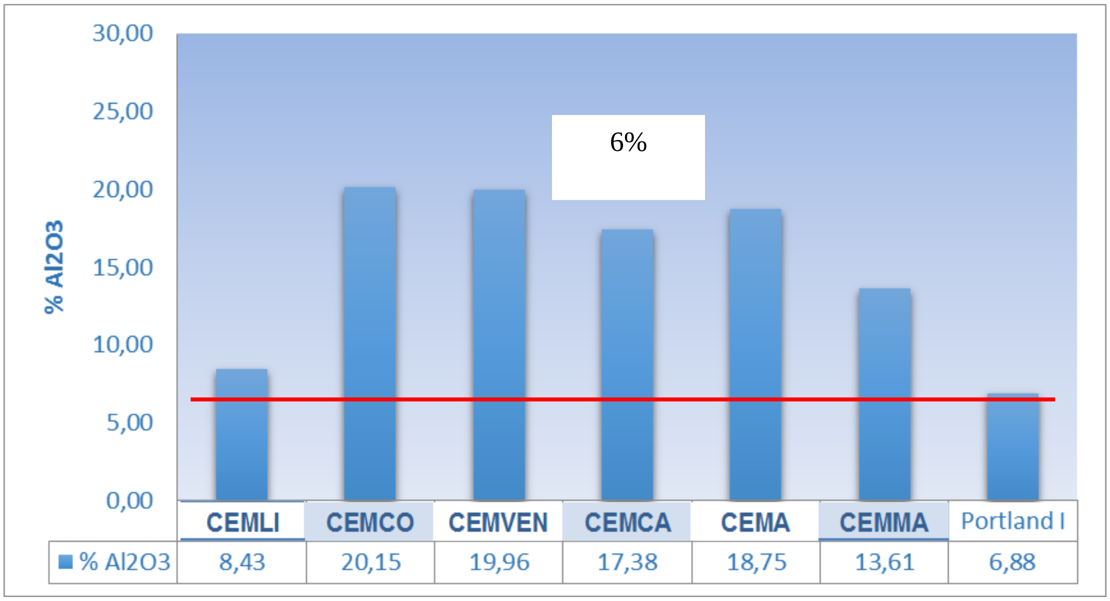

Figure 2. Percentage of Al_2O_3 in the different evaluated cements.

The results obtained indicate that all samples are above the value accepted by the standard for Portland cements type II, which should be less than 6%. The Portland type I and CEMLI samples are the closest to this value with 6.8% and 8.3%, respectively. On the other hand, CEMCO and

CEMVEN possess the highest percentage of Al_2O_3 (20.15% and 19.96%, respectively). Porrero (2004) mentions that the values for this parameter of Portland cement are between 3.5% and 8%, parameter which the cement aggregates exceed.

Ferric Oxide (Fe_2O_3).- The percentages of ferric oxide for each of the samples are detailed in Figure 3.

All analyzed samples are below the maximum value stipulated in the COVENIN 28-93/ASTM C-150 standard, the CEMA cement sample representing the highest percentage of ferric oxide with 5.10% and the CEMLI cement sample representing the lowest percentage of this component with 3.18%.

Calcium Oxide (CaO).

The results of the test were adjusted to a difference of 0.2 between the duplicates allowed by the COVENIN 109-90 standard. Figure 4 shows the results obtained of the % of calcium oxide.

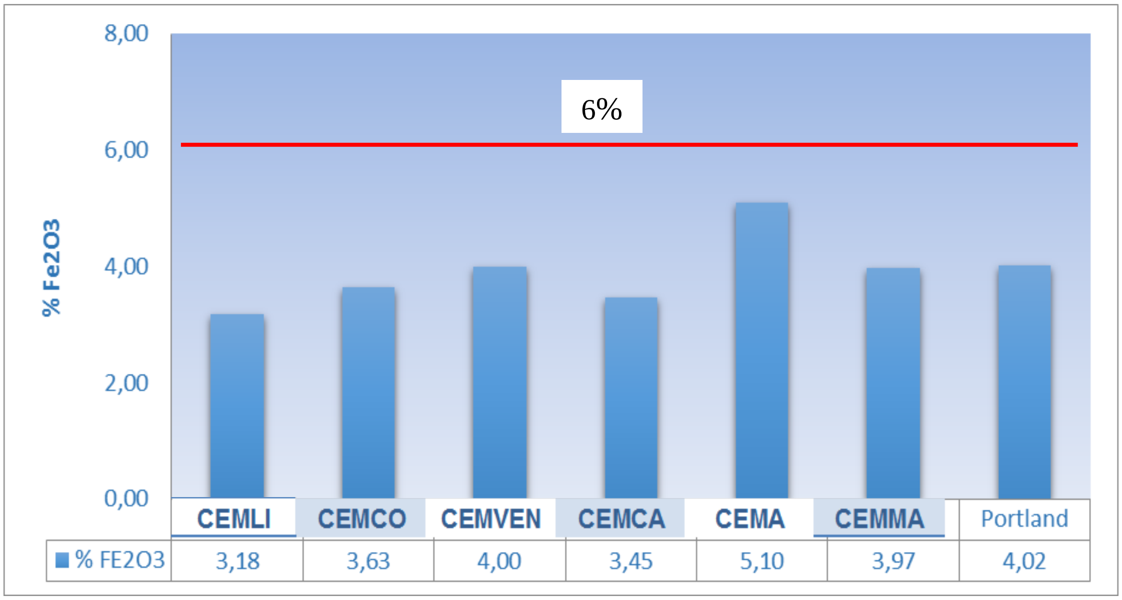

Figure 3. Percentage of Fe_2O_3 in the different cements evaluated.

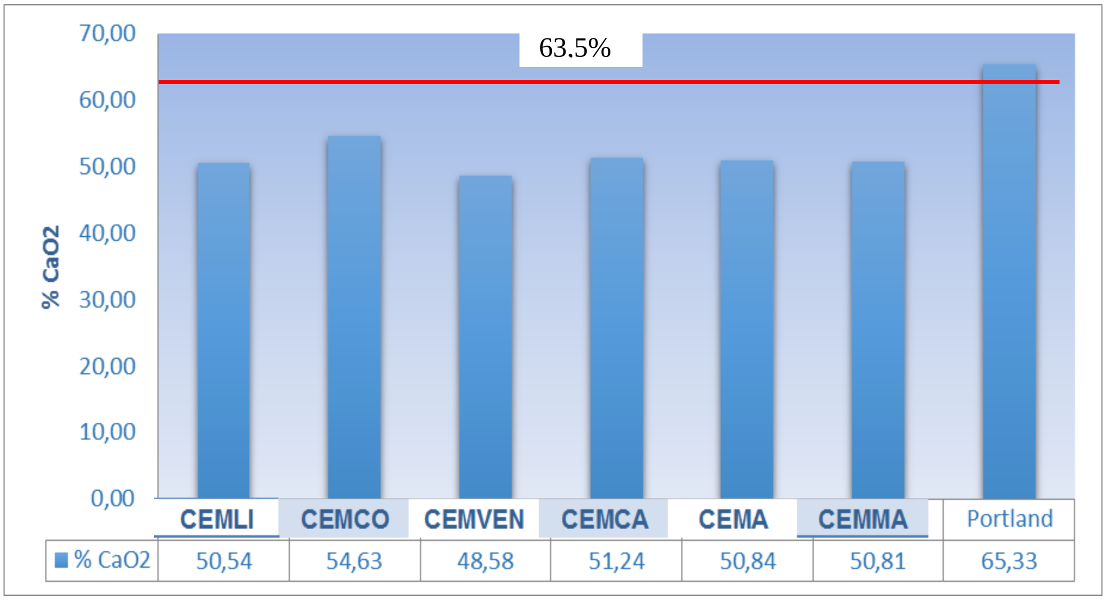

Figure 4. Percentage of CaO in the different cements evaluated.

This test does not possess a standardized value for comparison purposes. However, Porrero (2004) indicates values between 60% and 67% for Portland cement type I of excellent quality, with the evaluated cement aggregates below these values, with percentages between 48.58% and 54.63%.

Magnesium Oxide (MgO).- This test is done with the filtrates from the determination of calcium oxide, obtaining the values that are shown in Figure 5.

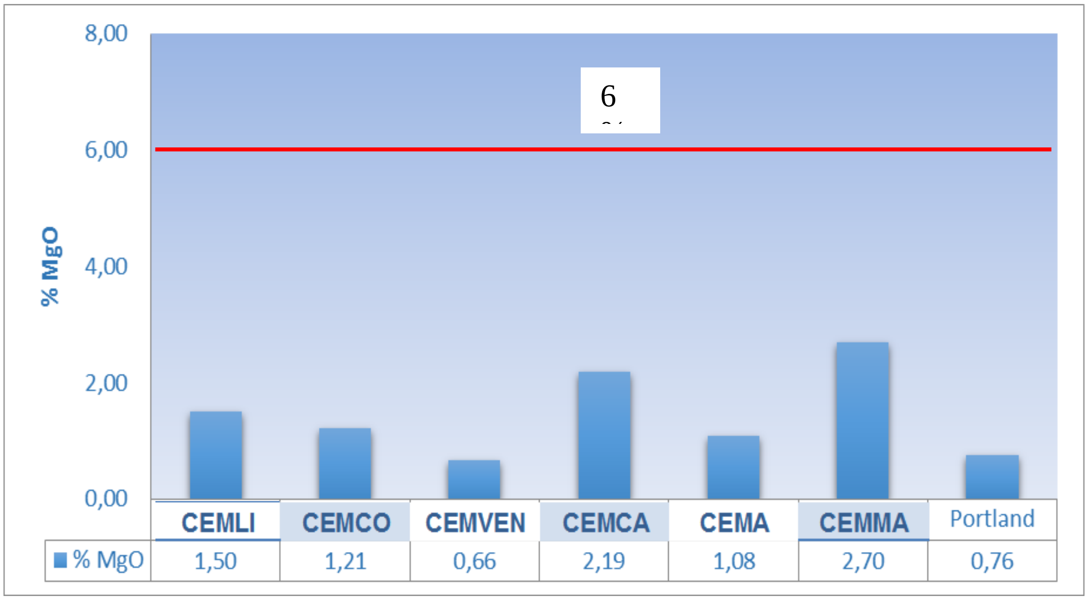

Figure 5. Percentage of MgO in the different cements evaluated.

All the values are below the limit (6%) stipulated in the COVENIN 109-90/ASTM C-114 standard. It can be observed that the percentages of magnesium oxide are comprised between 0.66% for the CEMVEN sample and 2.70% for the CENMA sample.

Sulphur Trioxide (SO_3).- The results obtained for the duplicated values can be observed in Figure 6.

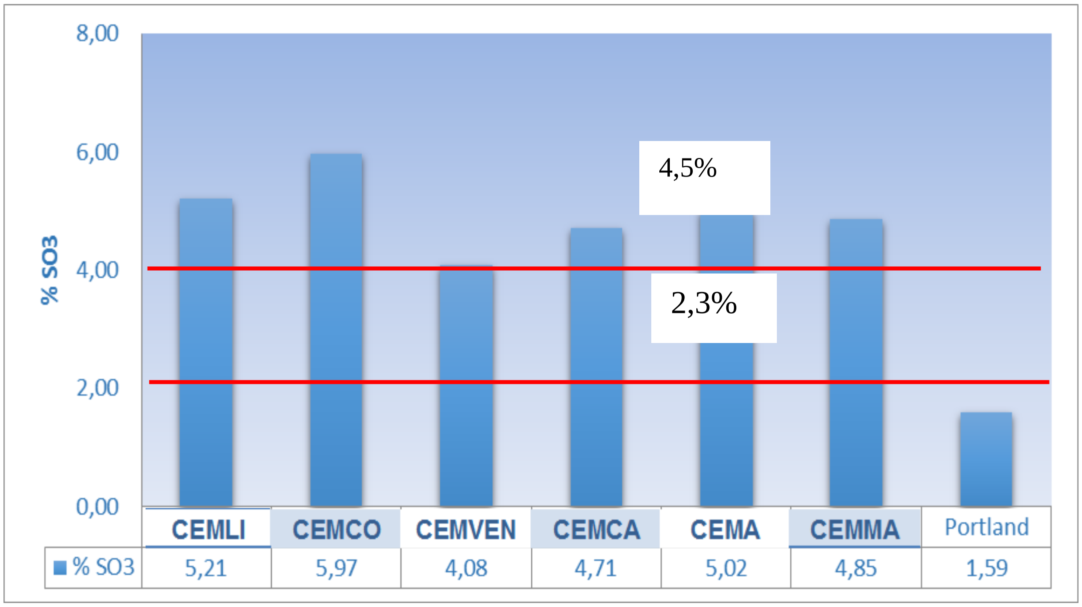

Figure 6. Percentage of SO_3 in the different cements evaluated.

The minimum chemical requirements established in the COVENIN 28-93 standard dictate that the percentage of sulphur trioxide present in the Portland cement is not higher than a range between 2.3% and 4.5%. Figure 6 shows that only CEMVEN (4.08%) and Portland (1.59%) comply with this standard, as the rest of the samples contain higher quantities comprised between the range of 4.85% and 5.97%.

3.2.2 Special Tests

Loss on ignition of the cement.- This test represented one of the simplest as it only needed the sample to be burned at 950°C and then calculated the difference in weight.

Figure 7 shows the percentages of loss on ignition obtained during the test.

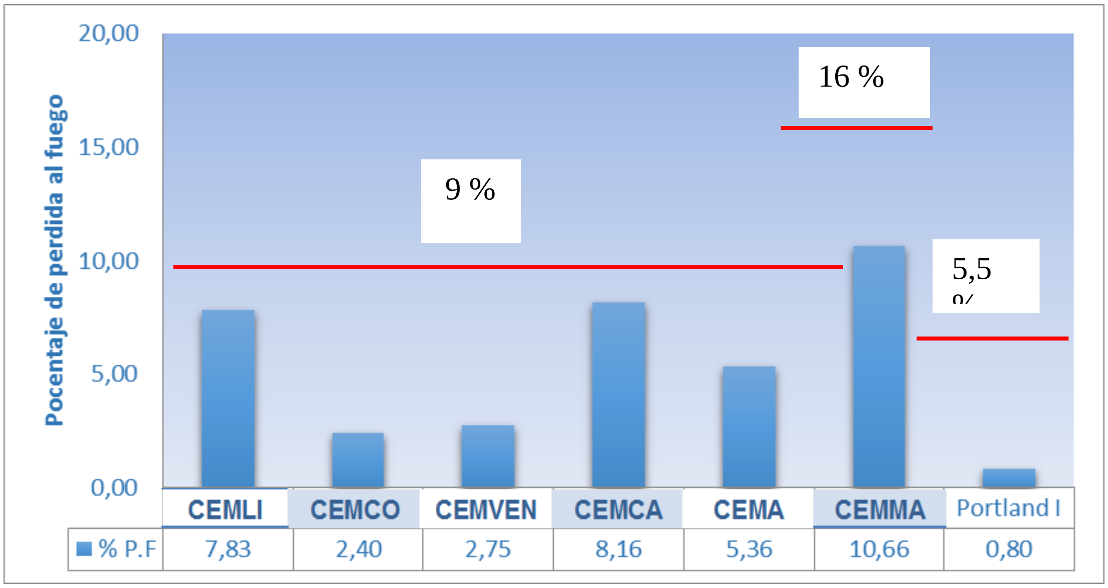

Figure 7. Loss on ignition percentage of the different cements evaluated.

All the samples analyzed comply with the parameters established by the COVENIN standard. The loss on ignition values should be less than 9% for CPCA1, less than 16% for CPCA2 and less than 5.5% for Portland cement type I. The CEMLI and CEMCA cements with 7.83% and 8.16% respectively present the highest percentages of loss on ignition in comparison with the other samples.

3.2.3 Secondary Components

Sodium Oxide (Na_2O) and Potassium Oxide (K_2O).- For the determination of this component, a dilution 1:10 was done on all samples so that the reading could be accepted on the calibration line of the flame photometer. The calibration curve for the determination is shown in Figure 8.

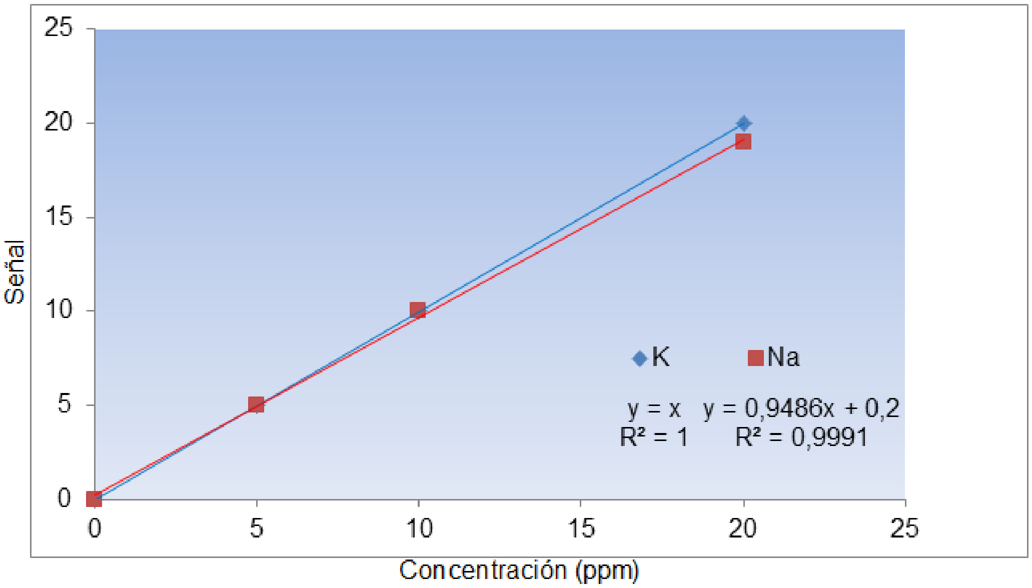

Figure 8. Calibration curve for the determination of Na and K in the different cements evaluated.

As it can be observed in Figure 8, both Na and K show an excellent linearity index. The results obtained (Table 4) for the value limits of the duplicates indicate that all concentrations of Na are below the maximum deviation allowed, which is 0.03%. In the case of K, 72% of the results are below 0.03% which is the accepted value. Only CEMCO and CENMA do not comply with a percentage of 0.04%; however, they do not duplicate the accepted limit and therefore comply with the standard.

Table 4. Results obtained in the determination of Na_2O and K_2O in the different cements evaluated.

Sample	σ*Na	σ*K	N.C 109-90**	%Na_2O***	%K_2O***
CEMLI	0,00	0,02	0,03	**0,11**	**0,38**
CEMCO	0,00	0,04	0,03	**0,11**	**0,31**
CEMVEN	0,00	0,00	0,03	**0,17**	**0,67**
CEMCA	0,01	0,02	0,03	**0,12**	**0,36**
CEMA	0,00	0,00	0,03	**0,11**	**0,67**

CEMMA	0.01	0,04	0,03	**0,12**	**0,45**
Portland I	0,00	0,00	0,03	**0,16**	**0,51**

* Standard deviation among duplicates ** COVENIN 109-90/ASTM C-114 standard *** Arithmetic measure of the %

Table 4 also indicates that the highest % of Na_2O comes from CEMVEN cement with 0.17% and the lowest from CEMLI, CEMCO and CEMA with 0.11%. On the other hand, Portland cement has a percentage of 0.16% of Na_2O which is in the aforementioned range. The highest % of K_2O comes from CEMVEN and CEMA cements with 0.67% and the lowest from CEMCO with 0.31%. Meanwhile Portland cement has a 0.52% of K_2O, which is within the aforementioned range.

3.2.4 Insoluble Residue (I.R.)

In this case study, more than 70% of the duplicate tests comply with the parameter established by the COVENIN 109-90/ASTM C-114 since the variation of these tests is not higher than 0.1%; only the CEMAN and Portland samples presented higher percentages of 0.12% and 0.15%, respectively. Figure 9 shows these results.

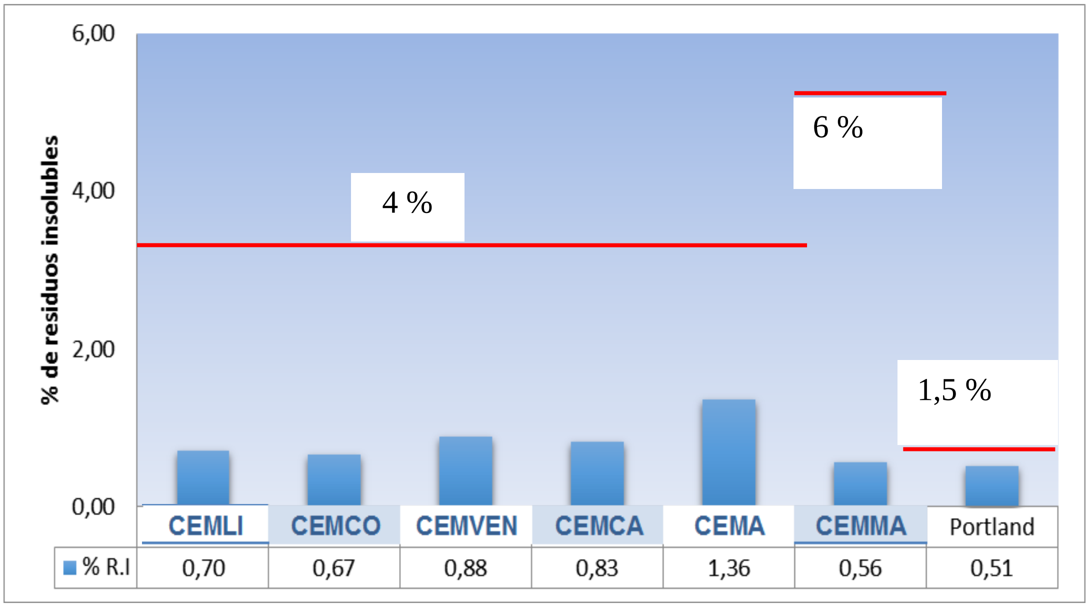

Figure 9. Percentage of insoluble residues in the different cements evaluated.

Based on the results obtained, it can be observed that all samples comply with the parameters established by the COVENIN standard regarding insoluble residues for cements, with percentages lower than 4% for CPCA1, lower than 6% for CPCA2 and lower than 1.5% for Portland type I . Among the data it can be noted that in the majority of cases the insoluble residue % of the samples is below 1%, with the exception of CEMAN which slightly surpasses 1%. If all samples were to be compared in regards to the COVENIN 3134-04/ASTM C-150 standard for Portland cement, they would also comply with this parameter.

Table 5 shows all the results of the chemical characterization of the different cements evaluated. As already mentioned, it can be observed that the concentrations of some of these components are outside the specifications of the COVENIN standard.

It is important to note the high and low contents of aluminum oxide and calcium oxide, respectively, in the majority of the evaluated cements, which in the proportions obtained generate certain limitations for the manufacturing of structural concrete, particularly regarding the resistance to compression, which in all cases was always inferior to the one obtained with Portland I cement. The low rates of CaO do not allow the formation of C_3S and C_2S in sufficient amounts to be able to generate a resistance to compression that is equal or as high as the one obtained with Portland I.

Table 5. Chemical characteristics of the CPCA1 and CPCA2 cement aggregates

Sample	**SiO_2**	**Al_2O_3**	**$F_{e2}O_3$**	**CaO**	**MgO**	**SO_3**	**P.F**	**K_2O**	**Na_2O**	**R.I**
CEMLI	23,87	8,43	3,18	50,54	1,50	5,21	7,83	0,38	0,11	0,70
CEMCO	24,42	20,15	3,63	54,63	1,21	5,97	2,40	0,31	0,11	0,67
CEMVEN	26,46	19,96	4,00	48,58	0,66	4,08	2,75	0,67	0,17	0,88
CEMCA	24,75	17,38	3,45	51,24	2,19	4,71	8,16	0,36	0,12	0,83
CEMA	25,01	18,75	5,10	50,84	1,08	5,02	5,36	0,67	0,11	1,36
CEMMA	27,68	13,61	3,97	50,81	2,70	4,85	10,66	0,45	0,12	0,56
Portland I	20,16	6,88	4,02	65,33	0,76	1,59	0,80	0,51	0,16	0,51

In addition, the high content of Al_2O_3 is related to the low setting time determined for the different types of cement aggregates due to the potential formation of high contents of C3A, which would also increase the susceptibility to sulphate attacks which is very important in constructions in marine environments.

Finally, it is important to note that it seems contradictory for the norms to demand from these cement aggregates physical-mechanical requirements similar to those of Portland I cement when their chemical composition is significantly different as shown in the results of this work.

4. CONCLUSIONS

1. Type CPCA cement aggregates manufactured in Venezuela and evaluated in this research do not comply with the minimum requirements established in the Venezuelan standard for their use in the elaboration of structural concrete.
2. The use of these cements in the elaboration of structural concretes could degenerate in premature pathological manifestations.
3. The contents of aluminum oxide, calcium oxide and sulphur trioxide of the cement aggregates are outside of the specifications.
4. The percentages of additions used in the manufacturing of these cements directly affect their properties.
5. The results obtained regarding the determination of Al_2O_3 could be related to the results of the setting time.

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Study on the hydration of Portland cement paste replaced with blast furnace slag, fly ash, and metakaolin: effect on the usage of two superplasticizer additives

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ABSTRACT

This research was focused on assessing the impact that different replacement materials and two superplasticizers on the development of the mechanical properties, phases formation and heat evolution of portland cement pastes, with replacement levels up to 60%. For this purpose, fly ash, ground granulated blast furnace slag, metakaolin and silica fume were used. The mixtures were manufactured with a water/solid of 0.4, 0.3% of superplasticizer and cured up to 60 days. Results showed that with the use of replacement materials, the calcium hydroxide content was reduced, due to the pozzolanic reaction, and the compressive strength was increased.
Keywords: Reactivity, Supplementary cementitious materials.

RESUMEN

Este trabajo de investigación se enfocó en la evaluación del efecto que tienen diferentes materiales de reemplazo y dos aditivos superplastificantes en el desarrollo de las propiedades mecánicas, formación de fases y en la evolución del calor de hidratación de pastas de cemento portland reemplazadas hasta un 60%. Para esto se empleó ceniza volante, escoria granulada de alto horno, metacaolín y humo de sílice. Las mezclas fueron fabricadas con una relación agua/sólidos de 0.4, 0.3% de aditivo superplastificante e hidratadas durante 60 días. En base a los resultados se confirmó que con el uso de materiales de reemplazo, se redujo la cantidad de hidróxido de calcio, debido a la reacción puzolánica y se incrementó la resistencia a la compresión.
Palabras clave: Reactividad, Materiales cementosos suplementarios.

RESUMO

Esta pesquisa teve como objetivo a avaliação do efeito de diferentes adições e de dois aditivos superplastificantes no desenvolvimento das propriedades mecânicas, formação de fases e na evolução do calor de hidratação de pastas de cimento com substituição de até 60%. Para tanto foi empregada cinza volante, escória granulada de alto forno, metacaulim e sílica ativa. Os traços foram elaborados com uma relação água/sólidos de 0,4, com 0,3% de aditivo superplastificante e curadas durante 60 dias. Com base nos resultados obtidos, confirmou-se que com o uso de adições, a quantidade de hidróxido de cálcio foi reduzida, devido à reação pozolânica e elevou-se a resistência à compressão.
Palavras chave: Reatividade, Materiais cimentícios complementares.

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1. INTRODUCTION

Currently, a great part of scientific and technological investigation is focused towards sustainable development. This involves the development of new materials characterized as eco-friendly, reducing the environmental impact of the processes involved in their acquisition, transport, production, implementation, and recycling. One of the industrial sectors most concerned with reducing this impact is construction, in particular the cement industry. The production process for cement requires a great quantity of thermic and electrical energy; furthermore, the process demands a large quantity of non-renewable raw materials, such as the use of limestone, clays and fossil fuels necessary for the production of clinker. This process emits large quantities of CO_2 (827 kg CO_2/t of clinker) and other gasses (such as SO_2 and NOx) that cause harmful environmental impact and which contribute to global warming. The production of Portland cement (CP) emits 5 to 8% of the global CO_2 [Cembureau (2014); Damtoft et al. (2008); Schneider et al. (2011)]; thus, the increase in the demand for cement and the environmental impact the elaboration process carries with it have made it necessary to opt for alternative materials and technologies. In recent years, supplementary cementitious materials (MCS) such as blast furnace slag from the steel-making process (EGAH), fly ash (CV) from the burning of coal in power plants, as well as natural or artificial pozzolans, and limestone are used for the production of compound cements. It is possible to implement different types of materials that partially replace Portland cement; however, the effect that each one has individually on the hydration process of the cement is still being researched and the effects that two or more constituents have on the reactions is still under constant investigation [Juenger and Siddique (2015)]. The replacement level, the chemical composition, the amorphous fraction, the pozzolanic or hydraulic activity, the size of the particulates, and the morphology of each material are some of the variables to be taken into account when designing compound cement pastes with more than one replacement material [Juenger and Siddique (2015)]. It is important to note that the development of the mechanical properties of compound cement pastes is directly related to the effect of the replacement materials in the hydration process of the cement pastes. For a compound cement, the hydration mechanism involves the participation of various species in the reaction in a solid state. Additionally in binary cements, Bentz et al. (2011) found that the MCS, in addition to altering the distribution of the particles of the cementitious material, also increase degassing. Yun et al. (2013) found that for mortars with 60% EGAH, the mechanical properties increased with the amorphous fraction of the same. Sharfuddin et al. (2008) reported that the addition of silica fume (HS) reduced the permeability of the concrete due to the reduction in porosity and the density of the matrix caused by the pozzolanic reaction. However, the combined use of CV and HS caused greater porosity in the cementing matrix, probably caused by the rapid reaction of the HS. In this manner, the HS must be maintained at a maximum of 10% weight of the cementing material. The concurrent addition of HS and EGAH reduced the resistance of the concrete. Furthermore, according to Ali et al. (2014), the type of additives modified the morphology of the ettringite and therefore the reaction heat. Ping et al. (2013) analyzed the content of calcium hydroxide (CH) in cements with 40% CV and 20% EGAH, reporting a 65% decrease when compared to pure CP due to the pozzolanic and hydraulic reactions. Schöler et al. (2015) concluded that the types of hydrates observed in the systems with a 50% substitution of MCS are similar to those formed in pure CP, with a reduction in the quantity of CH and an increase in the C-S-H and the AFm phases. However, if the CV has a relatively small amorphous fraction, its reactivity will diminish and thus the quantity of products formed and the compression strength. It is worth highlighting that the authors mention additions of up to 30% CV do not significantly reduce compression strength. Janotka et al. (2010) investigated the effect of different types of MK in the mechanical properties of partially replaced pastes and reported that by increasing the replacement level of MK, the compression strength of the cement pastes decreased. Snelson et al. (2008) utilized MK and CV as replacement materials for CP in order to investigate the effect in the progress of released heat. The hydration process of the CP pastes replaced with CV changed with the level of replacement, given that an increase in the CP replacement level decreased the hydration heat. The replacement materials such as CV, MK, and HS, better the performance of the CP pastes, mortars and cements, but tend to reduce the workability of the mixtures. The most common reason is that the fine particles of the replacement materials have a greater surface area and therefore the amount of water to create a mixture increases. Various authors [Mansour et al. (2010); Esteves et al. (2010)] have shown that by adding HS, CV, and MK the required water increased, thus, in order to better the workability, they employed chemical superplasticizers (SP) additives.

This article contributes investigation on the development of sustainable technologies and materials for the construction sector, with the assessment of the behavior of supplementary materials in cement paste and the analysis of the results, with the purpose of contributing parameters that make it feasible to partially replace Portland cement. It is worth mentioning that this article contributes in an important manner to the understanding of the effect of various materials on the kinetic hydration of cement, which currently is under investigation by various groups around the world.

2. MATERIALS AND METHODS

The starting materials used were: (a) Portland cement obtained from CEMEX Mexico; (b) granulated blast furnace slag (from AHMSA, with 97% amorphous fraction); (c) type F fly ash (Comisión Federal de Electricidad (Federal Electricity Commission) – Mexico); (d) metakaolin (obtained through the calcination of kaolin mineral at 700ºC, with a particle size of less than 75 microns); (e) silica fumes (decondensed through mechanical grinding); and, (f) two polycarboxylate-ether based superplasticizer additives. The chemical composition and surface area are shown in Table 1. The DRX patterns for the raw material are shown in Figure 1. Initially, the materials were homogenized into powder over the course of 5 minutes so that the particles would have a homogeneous distribution; subsequently, a quarter of water with additive was added. When the first agglomerates formed, they were mixed at the second velocity and the rest of the water was added slowly over the course of 3 minutes. After having obtained an adequate workability, the mixture was left to mix for one more minute and then poured into the molds. Afterwards, in order to let out the air that was generated during the mixing of the materials, the cubic 5cm molds were vibrated for a minute and were subsequently set up at 25ºC with 100% humidity during the hardening and treatment. After 24 hours, the test pieces were taken out of the molds and placed in a saturated solution of calcium hydroxide (with the purpose of avoiding lixiviation) for the treatment process at 1, 3, 7, 14, 28, and 60 days. Different systems of cement pastes were prepared, pure and substituted with 10% fly ash, different levels of granulated blast furnace slag of 25% to 45%, with metakaolin being used from 5 to 15%, and 5% and 10% silica fumes being used. The mixtures were manufactured with an a/s ratio of 0.4 and 0.3% of superplasticizer additive.

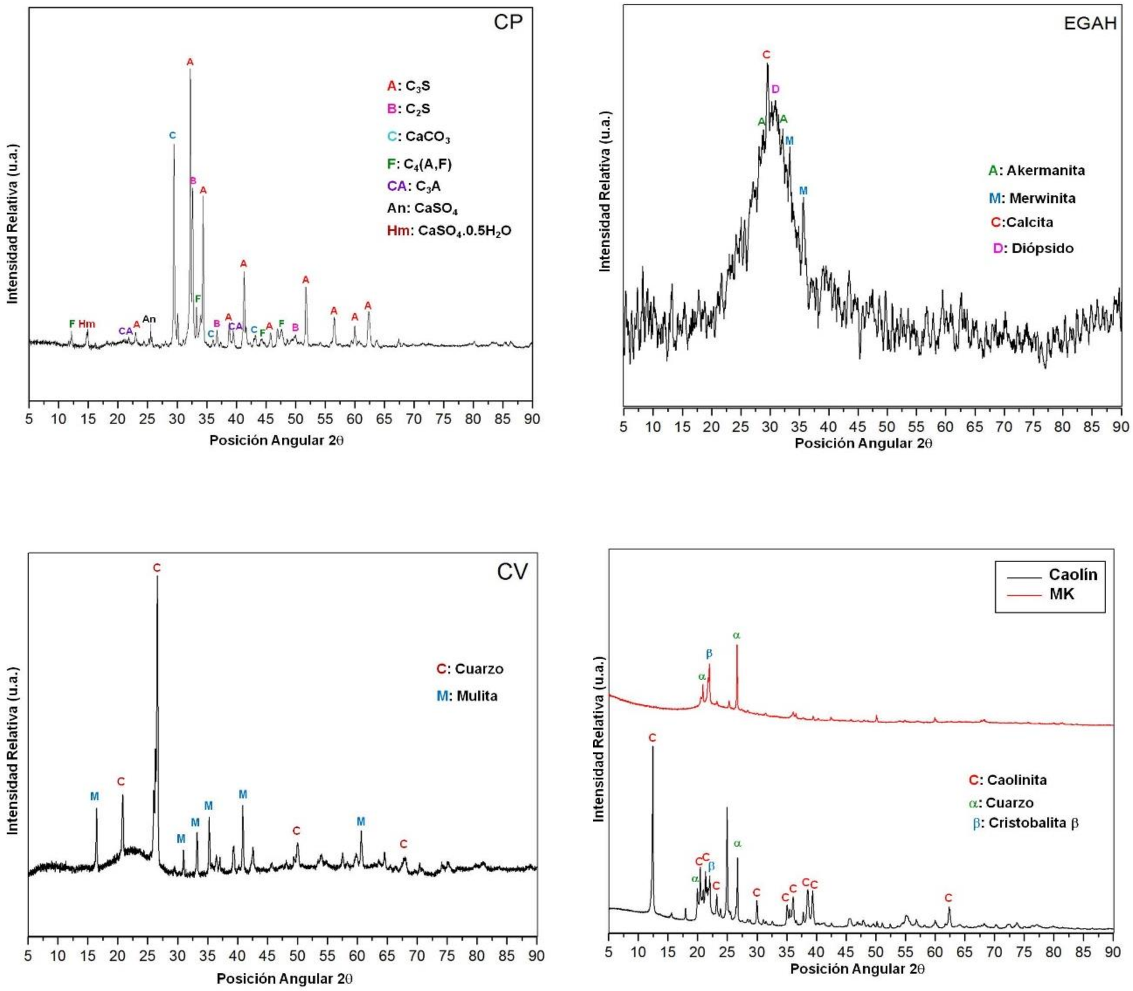

Figure 1. Raw material X-ray diffraction patterns

Table 1. Elemental composition in percentage of oxides of the starting materials and surface area (BET) of the materials used

	CP	EGAH	CV	MK
SiO_2	18.69	38.01	61.17	56.97
Al_2O_3	4.73	9.98	25.14	35.46
Fe_2O_3	2.17	1.85	4.56	1.02
CaO	63.46	34.32	2.42	1.45
MgO	1.78	10.04	0.85	0.03
SO_3	4.21	2.18	0.18	1.01
Na_2O	0.27	0.49	0.27	0.13
K_2O	0.67	0.58	1.41	0.54
TiO_2	0.21	1.21	0.99	1.08
P_2O_5	0.13	0.00	0.00	0.20
Mn_2O_3	0.07	1.03	0.01	0.00
LOI	3.73	0.34	3.02	2.17
Total	100.12	100.13	100.02	100.06
BET* (m^2/kg)	511	491	432	573

* Surface area

The samples were characterized through their compression strength (RC); subsequently, solid fractions of the samples were submerged in acetone and dried in a vacuum at 50ºC for 24 hours, with the purpose of stopping the hydration reactions and analyzing them through X-ray diffraction (DRX) and isothermal calorimetry through conduction (CIC).

3. RESULTS AND DISCUSSION

3.1. Compression strength.

Figure 2 shows the results of all the systems analyzed in this study. In Figure 2A, it can be observed that the use of additives SP1 and SP2 bettered the development of the RC for all treatment time periods, resulting in a RC at 1 and 60 days of approximately 49 and 76 MPa for the system manufactured with SP1 and of 44 and 76 MPa for the paste with SP2. The polycarboxylate-based superplasticizers are efficiently absorbed on the surface of the CP particles causing a highly observed dispersion in the functional ether groups, providing as a result an increase in workability and compression strength. The CP paste manufactured with the SP1 additive showed slightly higher resistances than that made with SP2. This result is possibly due to the presence of the functional ether group that appears in the FTIR spectrum of the SP1 additive. Winnefeld et al. (2007) reported a compression strength between 38.1 to 54.6 MPa at 7 days into the treatment, indicating that at early stages the RC increases with the increase of longitude and density of the lateral chain of the functional ether groups of the superplasticizer. Figure 2B shows the results of the RC developed by the binary systems, where it is observed that at 60 days, 10CV pastes with SP1 and SP2 developed a compression strength above the binary systems of 45EGAH and 15 MK. Golapan (1993), Isaia et al. (2003), and Slanicka S (1999) have reported that the RC increase of cement paste partially replaced with CV is due to the size and morphology of the fly ash particles. Small and spherical particles fill the gaps and produce a dense matrix, further increasing the pozzolanic activity of the material which causes an increase in the RC. It is worth mentioning that this pozzolanic activity is not immediate, rather it can take up to 3 to 7 days; thus, improvement in the RC is seen at intermediate treatment stages. This effect is also seen in cement pastes with 10 and 15% CV [Gutteridge et al. (1990)]. The 15MK pastes with both additives showed superior RC to CP and other binary systems at a period of 1 day of treatment. This behavior is attributed to the fine size of MK. It has been published [Mansour et al. (2010); Caldarone et al. (1994); Wild et al. (1996)] that the use of MK contributes to the development of mechanical resistances at early stages due to the fine particle size that densifies the microstructure of the pastes, and due to its strong pozzolanic activity. Khatib et al. (1996) analyzed the development of resistances for cement pastes replaced with 10% MK at different points in time during the treatment and obtained the maximum RC at 14 days, which indicated that the pozzolanic activity of MK reaches its maximum reaction point in this timeframe. It has also been reported [Mansour et al. (2010)] that in order to disperse the MK in a cement paste the use of superplasticizers is needed, which improves the workability, rheology and mechanical properties of the pastes. The CP paste replaced with MK using SP2 showed superior RC, approximately 10% when compared to 15MK paste with SP1. The factors that could have affected this behavior were the a/s ratio, the SP quality and the dispersion effect caused by the additive.

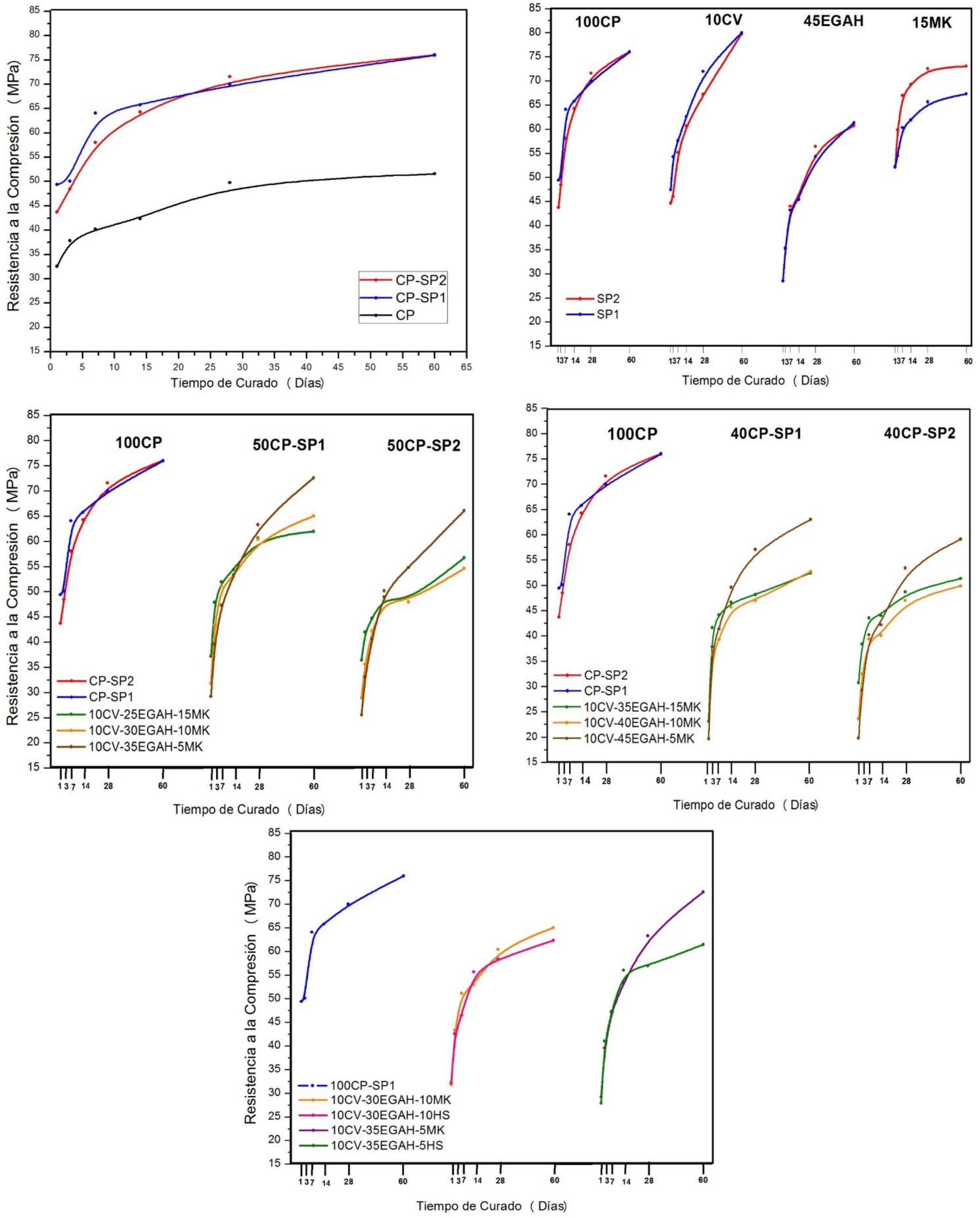

Figure 2. Compression strength of the systems with SP1 and SP2 additives: A) CP pastes, B) Binary systems, C) CP pastes 50% replaced with CV, EGAH and MK, D) CP pastes 60% replaced with EGAH, CV and MK, E) CP pastes 50% replaced with CV, EGAH, MK and its HS comparative using SP1 additive.

The development of the RC for the 45EGAH binary systems, at 1 and 60 days of treatment, was found to be below the RC of 100CP pastes and 10CV and 15MK systems; this behavior was attributed to the fact that under these conditions the a/s ratio, level of EGAH replacement and SP dosage, the fluidity of the paste of the 45EGAH binary systems was increased causing an excess of water in the mixture and consequently a change in the hydration process and on the mechanical properties of the system.

The results for the RC tests in the quaternary cements with both superplasticizers are shown in Figures 2 C and D. It is understood that the 10CV-25EGAH-15MK system was the one that developed the greatest RC at 1 day of treatment (approximately 37 and 36 MPa for both SP). However, these resistances were found to be below the RC of CP pastes at the same stage of treatment. The 10CV-35EGAH-5MK paste for the two superplasticizer additives developed the best RC at 60 days of treatment, being greater for SP1 (73 MPa). This behavior was related to the one presented by the binary systems with 10CV and 15Mk, given that the effect of the pozzolanic activity of MK in the early development of RC was evident. On the other hand, the pozzolanic activity of the CV and the larger ratio of EGAH benefitted the development of RC at 60 days of treatment. Furthermore, it can be observed that the pastes with SP1 developed RC above those manufactured with SP2. The factors that could have had an impact on this behavior were the a/s ratio, the dosage of the superplasticizer, and the dispersion caused by the additives. On the other hand, the development of RC in the CP pastes replaced 60% with CV, EGAH, and MK show a similar tendency to the RC results of the CP pastes with 50% replacement; however, the RC development at early stages was smaller. Moreover, the 10CV-35EGAH-15MK with both additives developed a better RC at 1 day of treatment in comparison with the 10CV-45EGAH-5MK paste, which showed the best RC at 60 days of treatment. Due to the fact that the 10CV-35EGAH-5MK paste manufactured with SP1 showed the highest RC values at 60 days of treatment, the effect of replacing the 5% MK for 5% HS was compared. In addition, there was consideration to study the same effect on the 10CV-30EGAH-10MK paste.

The tendency of the results in Figure 2E indicates that pastes 10CV-30EGAH-10MK and 10CV-35EGAH-5MK showed a greater RC than the pastes with 10CV-30EGAH-10HS and 10CV-35EGAH-5HS at 60 days of treatment, with the resistance being greater in the pastes where MK (~73MPa) was used. Roy (2001) indicated that HS only increases resistance at early stages, while RC at later stages decreases with the increase of CV replacement. However, in this investigation, the CV replacement was maintained at a set point. Furthermore, the best resistances were in the pastes with a greater replacement of EGAH and a treatment time of 60 days, which corresponds to the study presented by Gesoglu et al. (2003), who concluded that the addition of 30% EGAH and 10% HS betters the RC at 28 days of treatment.

3.2. X-ray Diffraction.

Representative samples of the cement pastes replaced at 50% and 60%, manufactured with the two SP and treated for 28 days, were analyzed, observing the following phases:

✦ - Portlandite (CH). **C** - Calcite ($CaCO_3$), α - Quartz (α-SiO_2), ★ - Alite (C_3S), ▲ Ettringite ($Ca_6Al_2(SO_4)_3\,(OH)_{12}.26H_2O$), **S** - Stratlingite ($Ca_2Al_2SiO_7.8H_2O$,), $\boldsymbol{\beta}$ - Belite (Ca_2SiO_4- C_2S,),
● - Hydrotalcite ($(Mg_{0.667}Al_{0.33})(OH)_2(CO_3)_{0.167}(H_2O)_{0.5}$).

In Figure 3A, the results of the DRX analysis for the CP paste manufactured with SP1 (CP-SP1) are shown and in Figure 3B those manufactured with SP2 (CP-SP2) at 28 days of hydration, where it was possible to observe that for both the portlandite (CH) reflection characteristics were shown in an angular position 2θ of 18.08° and 34.3°. Also in the CP-SP1 system, ettringite was identified with characteristic reflections in angular positions 2θ of 9.147°, 23° and 51.784°. The ettringite is directly related to the quantity of C_3A and the availability of SO_4^{2-} ions in the liquid phase (Meredith et al., 2004). A study on the effect of the polycarboxylate-based superplasticizer additives in the hydration process of C_3A showed that the molecules of the superplasticizer additive are preferably absorbed in the surface of the C_3A phase [Plank et al. (2006)]. However, during initial hydration of the C_3A, the molecules of the superplasticizer additive can form complex organometallics by interlocking between the layers of the hydrated phases of the C_3A. The interlocking of the polycarboxylate molecules is not a desired process, as it decreases the dispersion effect of the cement particles. Plank et al. (2010) carried out a study on the interlocking mechanism of polycarboxylate between the layers of hydrated C_3A phases and the function of the sulfate ions present in the cement. They reported that a high concentration of sulfate ions in the aqueous solution favors the interlocking mechanism of the sulfate ions between the layers of the hydrated C_3A phases giving rise to the formation of AF_t and AF_m. phases.

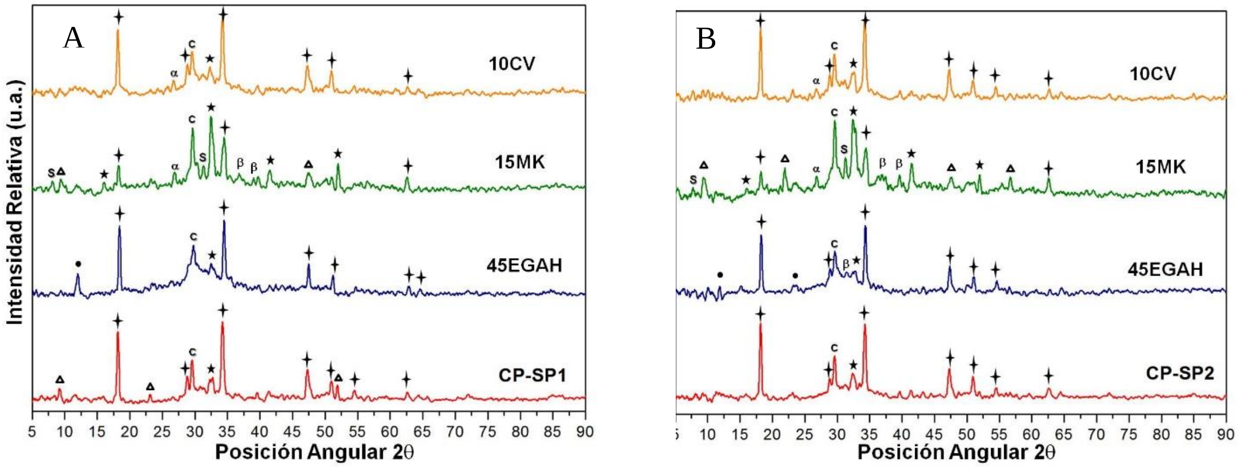

Figure 3. Diffraction pattern of the binary systems at 28 days of treatment, manufactured with (A) SP1 additive, and (B) SP2 additive.

Figure 3 also shows the DRX patterns for the binary systems 10CV, 15MK, and 45EGAH manufactured with additives SP1 and SP2. In this figure one can observe that the 15MK paste showed a greater pozzolanic activity due to the reflection intensity of the CH at 34.3º from an angular position 2θ decreasing in a larger proportion with regard to the other pastes; this was associated with a greater CH consumption. It was also possible to identify the stratlingite-$Ca_2Al_2SiO_7.8H_2O$ (angular position 2θ at 7.045º and 31.08º), phase from the AF_m phase family, a characteristic of the hydration products of cement pastes replaced with MK (Janotka et al., 2010) and the hydration of EGAH (Martinez Alvarado, 2009). The ettringite phase was also identified, whose intensity was slightly greater in the 15MK paste with SP2 additive. The formation of ettringite is evidently due to the preferential reaction of the MK aluminates with the SO_4^{2-} ions of CP [Talero, (2005)]. In the same patterns, the presence of C_3S and β-C_2S was also observed, indicating the incomplete reaction of the phases of Portland cement, at least up to the first 28 days of treatment. Another of the identified phases was hydrotalcite (angular position 2θ at 11.81º), which was observed in the 45EGAH pastes with both additives. The reflective intensity of the characteristic peak of this phase was slightly greater in the 45EGAH paste with additive SP1. The formation of this phase is attributed to the hydration of EGAH through the activation caused by the presence of CH. Haha et al. (2011) reported that for an alkaline activated slag, hydrotalcite is observed intermingled with the C-S-H and MgO that contained the slag as one of the products of the reaction.

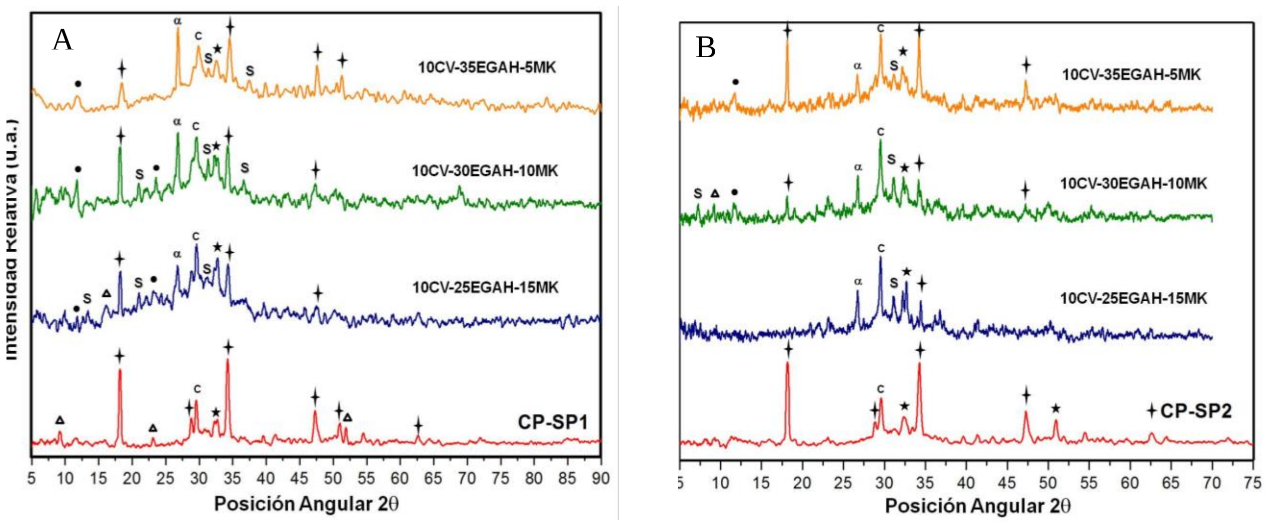

Figure 4. Diffraction pattern for the CP pastes replaced 50% with CV, EGAH, and MK using additive a) SP1 and b) SP2 at 28 days of treatment.

Figure 4A shows the diffraction patterns of the CP pastes and the CP pastes replaced 50% with CV, MK, and EGAH and manufactured with SP1 at 28 days of treatment. Based on the results, it is possible to consider a high consumption of calcium hydroxide caused by the pozzolanic reaction of CV and MK and by the hydration of the EGAH. Crystalline phases were also identified, which are characteristics of the hydration products of MK and EGAH, such as stratlingite and hydrotalcite, respectively. Furthermore, the analysis of the CP pastes replaced with CV, MK, and EGAH indicated that paste 10CV-35EGAH-5MK showed reflections characteristic of stratlingite (angular position 2θ at 11.65º and 34.88º) and hydrotalcite, and in paste 10CV-30EGAH-10MK only stratlingite was present. Based on these results, it is possible to consider that with a replacement level of 15% MK in the Portland cement pastes replaced with CV, EGAH and MK, the formation of stratlingite is favored due to the pozzolanic activity of MK at early stages. It is also suggested that the formation of hydrotalcite is due to the activation of EGAH with CH and is favored at 28 days of treatment in the system with greater EGAH replacement.

Figure 4B shows the diffraction patterns for CP pastes and CP pastes with 50% replacement with CV, MK, and EGAH manufactured with SP2 at 28 days of treatment. According to the analysis of this information, SP2 had a slightly different effect in the hydration process of these cement pastes when compared to SP1. Whereas in the diffraction patterns of the CP pastes, reflections characteristic of weak intensity ettringite were identified, which was not observed in the CP paste manufactured with SP2. In pastes 10CV-25EGAH-15K, 10CV-30EGAH-10MK, and 10CV-35EGAH-5MK, the reflections characteristic of stratlingite were identified, but not those for ettringite and hydrotalcite. These results suggest that the SP2 was preferably absorbed in the C_3A phase and the reaction of the sulfate, calcium, and aluminum ions in the aqueous solution promote the formation of ettringite during the initial hydration. Moreover, the interaction of the SP2 polycarboxylate molecules with the amorphous silica-alumina fraction favors the formation of stratlingite during the initial hydration of the cement pastes. In pastes 10CV-30EGAH-1OMK and 10CV-35EGAH-15MK, the presence of hydrotalcite was observed. According to these results, the SP2 additive favors the formation of the stratlingite phase and a greater consumption of CH in the pastes with a larger MK content at 28 days of treatment.

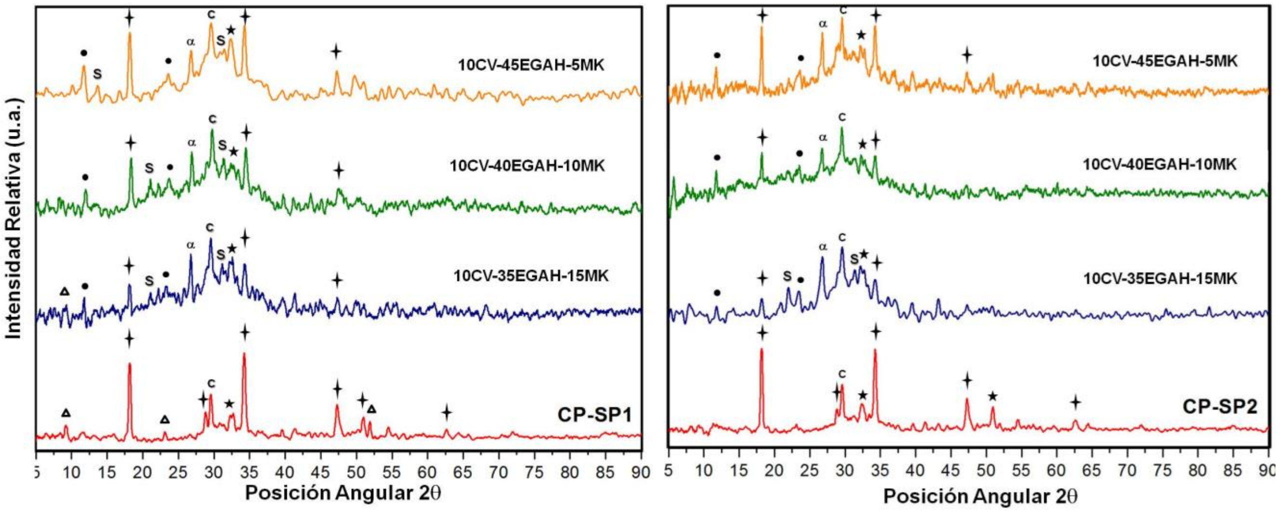

Figure 5. Diffraction pattern for the CP pastes 60% replaced with CV, EGAH, and MK, using additive a) SP1 and b) SP2 at 28 days of treatment

Figure 5 shows the diffraction patterns of the CP pastes 60% replaced with CV, EGAH, and MK at 28 days of treatment. In general, the tendency of the X-ray diffraction results for the system with 60% CV, EGAH, and MK manufactured with SP1 can be described as follows: The reflective intensity of the peak characteristic of the CH phase in an angular position 2θ at 34.3° decreased in greater proportion in pastes 10CV-35EGAH-15MK and 10CV-40EGAH-10MK at 1 and 28 days of treatment, which contained a greater percentage of MK replacement, demonstrating the strong pozzolanic activity of MK. Stratlingite, ettringite, and hydrotalcite were identified at 1 and 28 days of treatment. Stratlingite showed a weaker intensity in paste 10CV-45EGAH-5MK. By using the SP1 additive and comparing the results of 50 and 60% replacement, the presence of the hydrotalcite phase could be observed in the latter. Carrying out the same comparison, but for pastes with SP2, it can be observed that ettringite was not identified at 28 days of treatment and no stratlingite reflections were present in pastes 10CV-40EGAH-10MK and 10CV-45EGAH-5MK at 28 days of treatment.

3.3. Conduction Isothermal Calorimetry

Initially, superplasticizer additives were tested in the CP pastes. Subsequently, based on the replacement percentage and the RC results, systems 10CV-35EGAH-5MK and 10CV-45EGAH-5MK were selected and manufactured with both additives. According to the RC results, the pastes with SP1 additive developed the best RC, therefore another paste was selected for this additive, paste 10CV-30EGAH-10MK. Finally, a comparison between the effects of adding HS instead of MK in the pastes manufactured with the SP1 additive was carried out. Figure 6 shows the results of the isothermal calorimetry analysis of the CP pastes with and without additives at 25°C.

It can observed that the main peak of the evolution curve of the hydration heat of the CP paste without additives, due to the hydration of the C_3S, corresponded to 9 hours of hydration time. By comparing this curve with those obtained for the CP with both additives, it is possible to observe a displacement of the same at the main hydration peak, which corresponded to 11 hours, showing a delay in the hydration process. It has been reported that the superplasticizer additives delay the hydration of silicates (especially C_3S). Lothenbach et al. (2007) found that the polycarboxylate based superplasticizers delay the dissolution of C_3S, and therefore the formation of portlandite and C-S-H. Furthermore, a difference was observed in the start of the acceleration period between the CP pastes without additives and those that contained SP1 and SP2. The initial hydration time for the acceleration period for the CP pastes was 2.5 hours, whereas for pastes with SP1 it was 4 hours and for those with SP2 3 hours. This difference was attributed to the fact that the introduction period in the presence of both additives was longer, providing more time for the hydration reaction of C_3S in order to form C-S-H. It is also observed that the progression of the hydration heat (J/Kg-h) and the release of total heat (Q/Kg) of the CP paste with SP2 was greater than that of the CP paste without additive and that with SP1. The acceleration period due to the nucleation and growth of the C-S-H gel and CH for the pastes with SP2 was more exothermic.

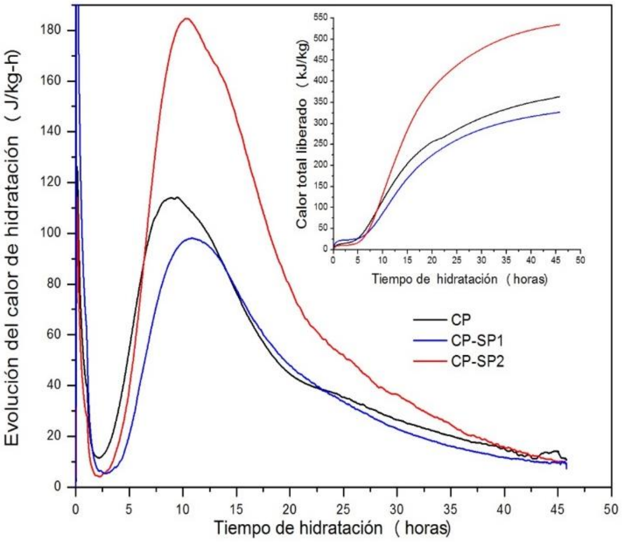

Figure 6. Progression curves for hydration heat and total heat released from the CP pastes without additives and those with additives SP1 and SP2.

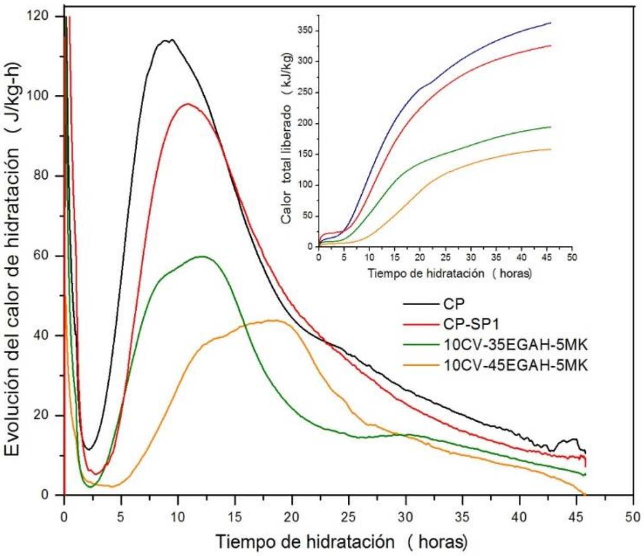

Figure 7. Progression curves for hydration heat and total heat released from the CP pastes without additives, with SP1, and pastes replaced with CV, EGAH, and MK manufactured with additive SP1.

From these results it is possible to infer that the superplasticizer additives change the hydration mechanism of the CP pastes; however, each additive also showed a different behavior in pure cement. In this way, additive SP1 prolonged the induction period, which can be related to the dispersion effect caused by the observed aversion to the presence of the ether functional groups of the polycarboxylate-ether based superplasticizers, associated with the presence of the vinyl ether functional group shown by SP1. Additive SP2 caused the induction period to be shorter than that of the CP paste with SP1, which can be attributed to the lesser absorption of the polycarboxylate molecules on the surface of the cement particles. The SP2 additive showed *two additional absorption bands characteristic of carboxylate salts*. It has been reported that high density and a long lateral chain polycarboxylate-based superplasticizer additives decrease the delay of the induction period due to the polymer molecules being absorbed in a smaller ratio in the cement particle. It is possible that the rapid progression of the hydration heat during the acceleration period of the hydration process of the CP paste with SP2 is related to the low absorption of the polymer molecules on the surface of the cement particles, due to a larger spread of Ca^+ ions and water from the liquid phase to the solid phase, which could have generated more sites of nucleation and growth of the C-S-H gel. Mollah et al. (2000) proposed three different mechanisms in order to explain the retardant effect of the polycarboxylate-based superplasticizers on the hydration of the cement, of which it is possible to associate the effect of SP1 and SP2 to two of them: (a) the molecules of the superplasticizer are absorbed on the surface of the cement particle and hinder the spread of water and calcium ions on the cement-solution interphase; however, the absorption in C_3S is less than in C_3A; (b) the spreading action of the superplasticizer changes the growth kinetic and morphology of the hydrated phases. According to the DRX results, one of the hydration products formed in the CP paste with SP1 at 28 days of treatment was ettringite; this phase could have been formed during the induction period, due to the fact that the absorption of the polycarboxylate-ether molecules of SP1 reduced the spread of Ca^+ ions and water from the liquid phase to the hydrated calcium silicate phase, and it is possible that the hydrated calcium aluminate phase and the SO42- ions of the aqueous solution were favored.

Figure 7 compares the progression curves of the hydration heat for pastes 10CV-35EGAH-5MK and 10CV-45EGAH-5MK manufactured with SP1. The progression of the hydration heat for pastes 10CV-35EGAH-5MK and 10CV-45EGAH-5MK was less than that for the CP pastes without additives and those with SP1. It has been reported [Langan et al. (2002); Snelson et al. (2008)] that the progression of the hydration heat of cement pastes with EGAH, CV, and MK was less than that of the CP paste and are related to the higher water requirement of the pozzolanic materials and to the lesser availability of Ca^+ ions for the growth of CH and C-S-H.

Another difference of the pastes 10CV-35EGAH-5MK and 10CV-45EGAH-5MK with regard to the CP paste is the formation of an additional peak in the hydration heat progression curve during the acceleration period. Talero and Rahhal (2009) reported a third peak in the hydration heat progression curves of the CP pastes replaced with 20% MK, to which they associated the pozzolanic activity of $Al_2O_3^{r-}$ of MK. Escalante (1996) also reported the appearance of a third peak in the hydration heat progression curve due to the contribution of the EGAH to the hydration process at temperatures of 10 to 60ºC. It is also possible to relate this increase in progression of the hydration heat with the formation of hydration products such as stratlingite and hydrotalcite, favored by the activation of the EGAH the formation of hydrotalcite was favored, whereas the pozzolanic activity of MK favored the formation of stratlingite and based on the RC results, it was also higher for paste 10CV-35EGAH-5M manufactured with SP1.

The delay in the hydration process of pastes 10CV-35EGAH-5MK and 10CV-45EGAH-5MK with regard to the CP pastes without additives and those with SP1, can be due to a slow dissolution of the C_3S for the production of C-S-H and CH. However, this effect was more significant for the paste 10CV-45EGAH-5MK, given that its main peak was observed at 12.5 hours, in comparison with the paste 10CV-35EGAH-5MK that occurred at 8 hours. This difference is likely due to the greater EGAH content and the retardant effect of the CV. According to Hwang and Shen (1991), the increase in the quantity of EGAH reduces the hydration heat produced by C_3S and C_3A. Langan et al. (2002) found that during the first minutes of hydration for CP pastes with 10 and 20% CV, the ion concentration in the solution for the first couple of hours decreases, which is why the nucleation and growth of the C-S-H- and CH is delayed.

The results of the isothermal calorimetry at 25ºC for pastes 10CV-35EGAH-5MK and 10CV-45EGAH-5MK with SP2 as an additive are shown in Figure 8. The progress of the hydration heat for these pastes was less (60 and 50 J/Kg-h, respectively) than that of the CP pastes with SP1 (190 J/Kg-h) and without it (115 J/Kg-h), due to the aforementioned. These curves also showed a third peak due to the MK pozzolanic activity and the hydration of the EGAH. Furthermore, the delay of the hydration process during the induction period was less for these systems, which can be related to the lesser absorption of the SP2 molecules on the surface of the cement particles.

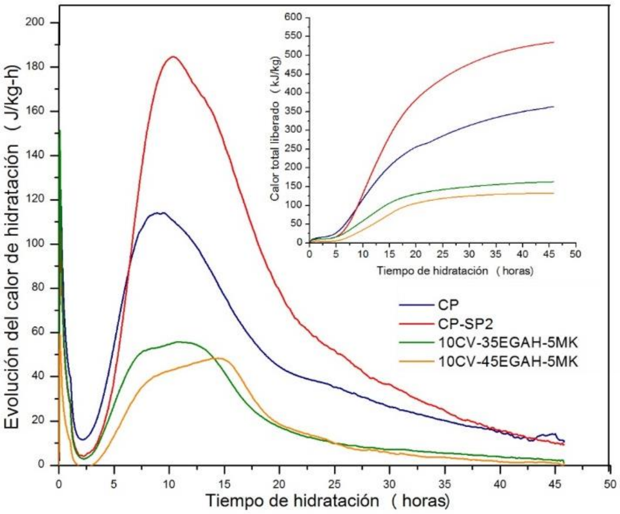

Figure 8. Progression curves for hydration heat and total heat released by the CP paste without additives, with SP2, and pastes replaced with CV, EGAH, and MK manufactured with SP2

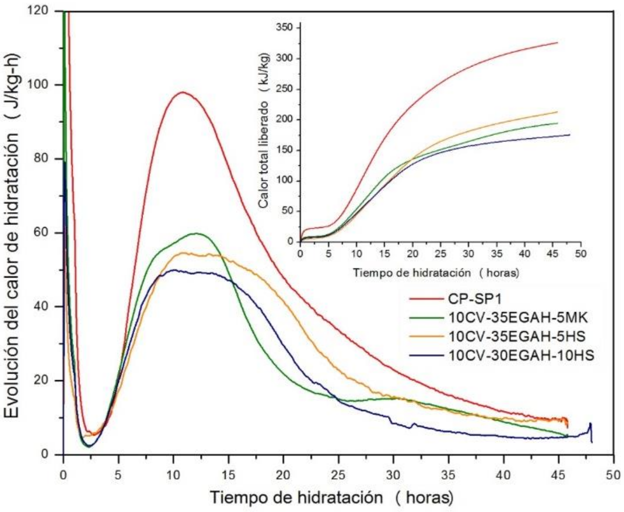

Figure 9. Progression curves for hydration heat and total heat released heat by the CP paste with SP1 and the pastes replaced with CV, EGAH, MK, and HS manufactured with SP1.

The results of the isothermal calorimetry analysis for the CP paste with SP1 are shown in Figure 9, comparing the behavior of an additional system manufactured with 5 and 10% HS. It can be observed that the hydration reactions of pastes 10CV-35EGAH-5HS and 10CV-30EGAH-10HS develop less hydration heat than paste 10CV-35EGAH-5MKS. This relates to the RC results in the presence of MK it generated the best values at early stages. The decrease in the hydration heat can be due to: (1) the precipitation of the reaction products in the CP pastes with MK was less exothermal than in the CP pastes, and (2) due to the smaller quantity of cement utilized it is possible for there to be a smaller quantity of hydration products formed in the initial stages [Janotka et al. (2010)]. The total heat released by the paste 10CV-30EGAH-5HS was greater than that of the paste 10CV-35EGAH-5MK, and it can be associated to the fact that during the hydration of paste 10CV-30EGAH-5HS the deceleration period was prolonged favoring the hydration process of the CP and that both the pozzolanic reaction of the CV and HS as well as the activation of the EGAH were more exothermal.

4. CONCLUSIONS

- The addition of 10% CV improved the development of RC in the binary system. The optimal replacement level of EGAH in pastes that also contained CV and MK was 35% and 45%. This replacement percentage favored the development of RC at stages of 60 days of treatment, being greater in the system with 10CV-35EGAH-5MK. Additive SP1 favored the development of RC of cement paste 10CV-35EGAH-5MK compound system. Additive SP2 favored the development of RC of the binary system of CP paste replaced with 15% MK.
- The pozzolanic activity of MK was favored in cement pastes with a greater level of MK replacement at 1 day of treatment, which favored the development of RC.
- The hydration process of the EGAH led to the formation of hydrotalcite, being favored in pastes with a greater EGAH replacement. The hydration of MK and the pozzolanic reaction with the CH of the hydration

of the CP favored the formation of stratlingite in CP pastes with 15% MK and in CP pastes replaced with CV, EGAH, and MK.

- In the hydration heat curve of the CP pastes, the superplasticizer additives delayed the nucleation and growth of the C-S-H- gel. In the hydration heat curve of the CP pastes, SP2 increased the release of heat of the main peak, being a more exothermal process. Additive SP1 bettered the hydration process of the systems with CV, EGAH and MK, with high EGAH and low MK replacements, showing greater hydration heat in the main peak of the hydration heat progression curve. The heat released by the hydration of the EGAH in system 10CV-35EGAH-5MK modified the hydration heat progression curve of the CP, showing an additional peak, which was prolonged at a greater EGAH replacement level. This implied a more exothermal hydration process for the paste with SP1. The hydration heat due to the pozzolanic activity of MK was superior to that shown by the HS, given that the main peak of the hydration curve of system 10CV-35EGAH-5MK was above that of the system 10CV-35GAH-5HS.
- In general, the use of high quantities of pozzolanic and hydraulic materials in the formation of the systems presented here produces an increase in the mechanical properties of the systems, as well as in the hydration reactions, bettering the compression strength.

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Concrete with treated surface and exposed to chlorides solution: thickness of equivalent coatings

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ABSTRACT

The main purpose of the experimental tests was to obtain the chloride diffusion coefficient and generate a chloride ingress prediction for surface treated concrete that could be valid during the initiation stage and transport by ions diffusion. The prediction was based on non steady-state conditions and some of the results indicated that a concrete with this type of protection can extend the chloride ingress up to three times. Data showed in this work indicated the equivalent cover of the surface treatment, ranging between 0.3 and 3.4 cm, showing large variations in results among the surface treatment materiais tested.
Keywords: Reinforced concrete, Marine environment, Chloride migration, Service life.

RESUMO

O objetivo principal dos testes foi obter o coeficiente de difusão de cloretos e gerar uma previsão de ingresso de cloretos em concretos com e sem superfície tratada, válida para o período de iniciação da corrosão de armaduras e penetração por difusão de íons. A previsão foi baseada no estado não estacionário e alguns resultados indicam que um concreto com esse tipo de proteção pode aumentar o tempo de contaminação em até três vezes. Também foram apresentados dados de cobrimento equivalente dos materiais de proteção indicando que os utilizados neste experimento variaram entre 0,3 e 3,4 cm, ou seja, apresentou grande variação de resultados entre os materiais de proteção testados.
Palavras chaves: Concreto armado, Ambiente marinho, Migração de cloretos, Vida útil.

RESUMEN

El principal objetivo de las pruebas era obtener el coeficiente de difusión y generar un cloruro de cloruro de entrada en previsión de hormigón con y sin superficie tratada, válido para el período de inicio de la corrosión de penetración de armadura y la difusión de iones. El pronóstico se basa en el estado inestable y algunos resultados indican que un hormigón con este tipo de protección puede aumentar el tiempo de contaminación hasta tres veces. Revestimientos equivalentes también presentados de protección de datos indica que los materiales utilizados en este experimento oscilaron entre 0,3 y 3,4 cm, es decir, los resultados mostraron una gran variación entre la protección de materiales probados.
Palabras clave: Concreto armado, Ambiente marino, Migración de cloruros, Vida útil.

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1. INTRODUCTION

The use of superficial protection for concrete is a possible way of increasing the service life of reinforced concrete structures exposed to marine environments. This type of protection inhibits the penetration of aggressive agents by diffusion and capillary absorption.

The surface protection materials for concrete can be classified into three groups: Pore liners (make the concrete water-repellent), pore blockers (react with some of the soluble concrete constituents and form insoluble products) and coatings (form continuous film on the concrete surface). Fig. 1 illustrates these three groups of superficial protection.

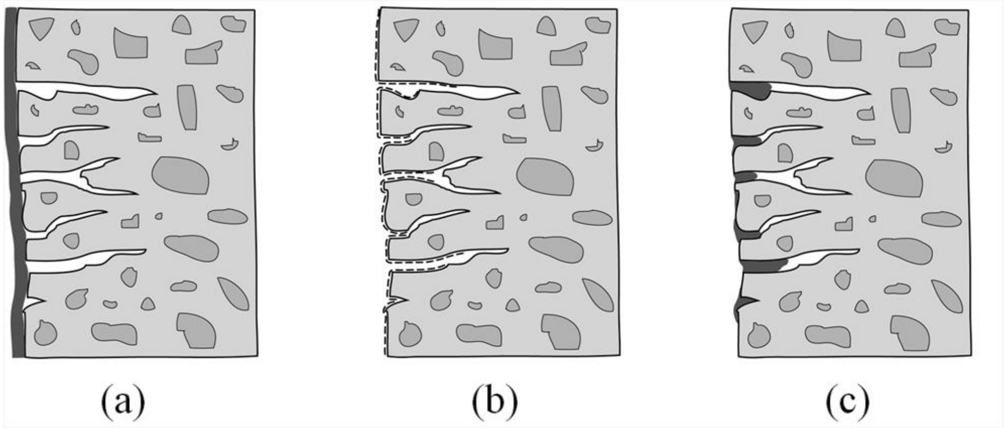

Figure 1. Groups of surface treatments: (a) coatings and sealers, physical barrier (b) pore liners, water repellent (c) pore blockers (adapted from Keer, 1992).

1.1 Coatings and sealers:

Coatings and sealers present the advantage of providing a physical barrier on the concrete surface, which isolates it from the aggressive agents of the external environment. These coatings require a homogeneous and smooth substrate with pores of 0.1 mm width at most. This means that they are capable of covering a 0.1 mm wide crack. However, the film breaks if the concrete structure cracks after painting. Moreover, coatings do not allow the concrete to dry if it is wet. This can cause the deterioration of the film, causing the formation of bubbles due to the vapor pressure of the internal humidity. From the architectural point of view, this group of surface treatment modifies the aesthetics of the structure adding brightness or color to the concrete surface, which is sometimes desired (Helene, 2000).

This group of surface treatment (coating and sealers) has been intensely studied in the last fifteen years. Delucchi et al. (1998) studied the importance of the parameters E (modulus of the material) and η (viscosity) in the crack-bridging ability of the coating. Seneviratne et al. (2000), using mechanical thermal analysis, suggested that the most successful coating is able to maintain its elastomeric properties over the required period of exposure and over a wide range of operational temperatures. Uemoto et al. (2001) showed a correlation between the paint pigment volume content and water permeability. Al-Zahrani et al. (2002) showed that the accelerated corrosion performance of the four coating systems studied correlates well with the performance results obtained from the physical properties, in particular, water absorption, water permeability, and chloride penetration. Medeiros and Helene (2009) suggested that the determination of the chloride diffusion coefficient allows a quantitative comparison of the protection systems and, therefore, needs to be made possible in migration tests. This kind of protection is probably the most used by the construction industry and that would be the reason why they are widely studied.

1.2 Water repellent:

Water repellents or hydrophobic agents always result from silicon resins that are chemically bound to the concrete base. Currently, the most commonly used are silanes, siloxanes oligomerics and a mixture of these two components (Medeiros; Helene, 2008).

Chemically, silanes are formed of small molecules that have one silicon atom and siloxanes are short chains of a few silicon atoms in which the molecules have alkoxy groups (organics) connected to the silicon atom. Silanes and siloxanes react with the silicate of the concrete, forming a stable bonding (Vries and Polder, 1997) (Fig. 2). Medeiros *et al.* (2009) showed that the penetration of the hydrophobic agent is better in finished faces than in formwork faces, due to the higher permeability of the second. Jacob; Hermann (1998), Batista (1998) and Moriconi et al. (2002) presented an ample review on surface hydrophobic agents. The use of hydrophobic agents in the construction industry is increasing at an interesting rate and they have been reasonably studied. However, there are some items that are still being studied, such as the influence of the water penetration mechanism (capillary suction and permeability) in the efficacy of the hydrophobic treatment (Medeiros; Helene, 2008).

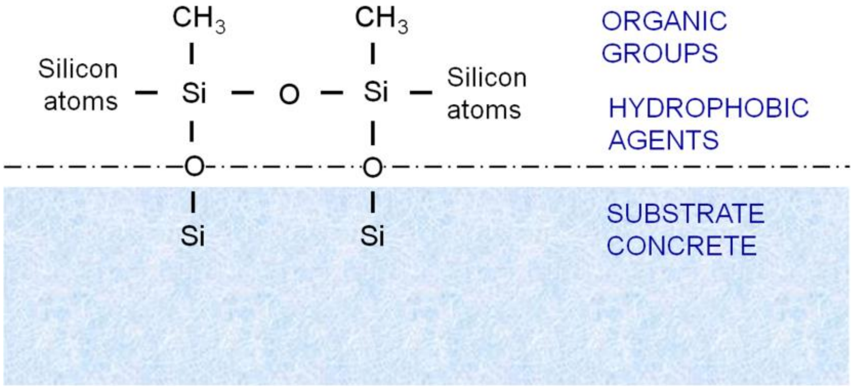

Figure 2. Chemical bond of the hydrophobic agent with concrete (adapted from Vries and Polder, 1997).

1.3 Pore blockers

Pore Blockers, such as sodium silicate, are used in the cement industry for some applications. For example, as slag cement activator; as treatments of vegetal fibers used for cement reinforcement, as surface treatment for concrete and as hardening/densifying of surface concrete floors (Mehta, Monteiro, 2008; Brough, Atkinson, 2002; Jones, 2002; Toledo *et al.*, 2003; Melo Neto, 2009).

Although this group of treatment has been known for several years, little technical and scientific information about this subject has been published. On the other hand, many products of this type are commercialized and indicated for the protection of concrete surfaces. Thompson et al. (1997) explained the 3 theories on how silicates act to improve the performance of concretes:

- SiO_2 precipitating in the pores.
- Silicates forming an expansive gel similar to that formed in alkali silicate reactions that fills the pores in the concrete by swelling.
- Silicates reacting with excess calcium present in the near surface region of the concrete to form relatively insoluble calcium-silicate hydrates.

The latter theory is currently the most accepted. In this way, theoretically, the pore blockers are products composed by silicate, which penetrate the superficial pores of the concrete and react with portlandite forming C-S-H. Sodium silicate is the mostly used silicate applied in this way.

According to Thompson et al. (1997), Eq. 1 represents what happens when the sodium silicate solution penetrates the pores of the concrete.

$$Na_2SiO_3 + yH_2O + xCa(OH)_2 \longrightarrow xCaO \cdot SiO_2 \cdot yH_2O + 2NaOH \qquad (1)$$

In this way, this treatment forms a less porous layer in the concrete surface modifying the water penetration into the concrete.

This treatment requires that sodium silicate reacts with portlandite [$Ca(OH)_2$]. Therefore, it is easy to understand that, in carbonated concrete, the reaction above fails to occur. This is why in the superficial layer the $Ca(OH)_2$ already reacted with CO_2 and originated $CaCO_3$. In this case, it is necessary to make an impregnation with hydroxyl ions before the application of sodium silicate. This explains why Kagi and Ren (1995) affirmed that a significant reduction in the permeability of concrete due to silicate solution impregnation can only be achieved if the concrete is very fresh and repeated impregnations are carried out to fill all the concrete capillaries. Another contribution of Kagi and Ren (1995) is related with water vapour permeability of the substrate which is not significantly affected by silicates because they only cover capillary walls without blocking them fully. Ibrahim et al. (1997) focused their work on measuring the time taken for reinforced concrete specimens coated with sodium silicate to crack by corrosion and concluded that the results were similar to that of the uncoated concrete specimens. However, their results are not in accordance to those of Thompson et al. (1997) regarding water absorption. It is important to emphasize that Ibrahim et al. (1997) do not inform the concentration of sodium silicate solution used in their study. The use of a low concentration may have influenced their results. Thompson et al. (1997) compared some concentrations of sodium silicate solutions and the value around 26% presented greater efficiency.

It is important to emphasize that the pore blocker should be applied after the structure is in service. This is after it has taken all the projected loads and cracks and microcracks have been produced. However, environmental effects can cause more cracks. If there are cracks (large enough to be visible) before the application of the silicates, it is necessary to repair them prior the treatment application. If the cracks (large enough to be visible) appear after the silicates treatment, they need to be repaired immediately because the low porosity layer formed by the treatment is ruptured. This is one of the main problems of the surface treatment (Pore liners, pore blockers and coatings): they do not absorb the deformation of the concrete of substrate. This means that the formed protection layer breaks if the concrete cracks, causing the prompt imperfection of the protection system.

It is important to remember that, independently of the crack width, the remaining superficial pores will still be smaller than if they do not have the pore blocker on the surface. Then, the environment attack will be isolated to the cracked area and the other areas will keep being protected.

In general, it can be said that more information is needed about the protection capacity of silicates applied on surfaces of reinforced concrete. On the other hand, the use of these types of concrete protection is wide and their application is contributing to many of the several concerns about service life prediction since they can be applied as preventive or corrective methods. The service life approach has significantly changed during the last years (Castro-Borges, Helene, 2007) and this is mainly due to the recent introduction of more quantitative parameters than a few years ago. These parameters include new concepts such as serviceability, functionality, security, reliability and durability.

Part of this work focuses on some additional contributions to the study of concrete surface treatments in the sense that they can constitute a useful tool in the field of protection of new reinforced concrete structures. However, based on the real concerns promoted by their application, the main purpose of this paper is to indicate a way to estimate the influence of concrete surface treatments in the service life of a reinforced concrete structure exposed to chloride contamination. This type of results presentation was made possible with the use of the diffusion theory developed by Fick.

2. EXPERIMENTAL PROCEDURES

2.1 Substrate concrete

The substrate concrete was produced with a Brazilian Portland cement designated CPII E-32, which is equivalent to ASTM C 595 (Slag-modified Portland cement). This cement has blast furnace slag admixture and is one of the most widely used cements in the state of São Paulo, Brazil. The chemical composition and physical properties of the cement are listed in Table 1. Coarse aggregate was a dense, crushed granitic stone. Fine aggregate was natural siliceous sand.

Table 1. Chemical compositions and physical properties of cement CP II E-32 (ASTM C 595).

(a) Chemical compositions (%)

Cement	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Free lime	Total alkalies as Na_2O_e*
CPII-E 32	22.80	6.75	2.45	56.40	3.20	1.83	0.12	0.61	0.44	0.52

* $Na_2O_e = Na_2O + 0.658\ K_2O$

(b) Physical properties

Cement	Specific gravity (23 ºC)	Fineness		Setting time		Compressive strength of mortar (MPa)		
	(kg/dm^3)	Residue on sieve of 75μm (%)	Blaine's specific surface area (m^2/kg)	Inicial set (h:min)	Final set (h:min)	3 days	7 days	28 days
CPII-E 32	3.02	3.6	395	3:40	5:30	15.9	24.0	37.5

The mix proportions details are summarized in Table 2. After mixing, a vibrating table was used to ensure appropriate compaction. The curing adopted was conditioning the specimens in wet chamber with relative humidity of 100 % and 24oC temperature for 91 days. This curing period was chosen to produce a high hydration level and eliminate the influence of an additional curing that could occur in the specimens exposed to water. This could especially affect the control series.

Table 2. Mix proportions of concrete.

Cement:aggregates	w/c ratio	Cement (kg/m^3)	Fine aggregate (kg/m^3)	Coarse aggregate (kg/m^3)	Water content (kg/m^3)	Plastic density (kg/m^3)	Compressive strength (MPa)
1 : 4.5	0.52	358	644.4	966.6	179.0	2155	32

2.2 Surface protection materials

The surface treatment systems investigated in this study are presented in Table 3. Table 4 shows the curing type, number of coatings and the manufacturer's recommended consumption rate for each surface treatment material.

Table 3. Characteristic of surface treated systems.

Product	Density (g/cm^3)	Viscosity CPs (temperature = 20 °C)	Setting time (h)
Silane/siloxane	1.0	10	2 - 6
Acrylic	0.9	45	1
Polyurethane	0.95	32	8
Sodium silicate	1.3	20	2
Silane/siloxane + Acrylic	---	---	---

Table 4. Curing type and manufactures recommended rate.

Product	Consumption rate (g/m^2/coating)	Number of coatings	Cure type
Silane/siloxane dispersed in water	300	1	Water loss + reaction
Acrylic dispersed in solvent	150	2	Drying
Polyurethane	180	2	Reaction
Sodium silicate	200	2	Reaction
Silane/siloxane + Acrylic	---	---	---

2.3 Estimation of chloride diffusion coefficients

The method used to estimate the chloride diffusion coefficient followed the procedure described by Luping and Nilsson (1992), which involves measuring the depth of color change of a freshly broken concrete surface in the direction of the chloride flow using 0.1 M $AgNO_3$ aqueous solution (Andrade *et al.*, 1999) and in the application of Eq. (2) in a migration test. fixed chlorides are ignored and it is possible to release a portion of the fixed chlorides among the Since the method is based on the depth of penetration of free chlorides, it should be noted that the time, becoming free. Thus, the method may produce inaccurate results. However, this practice was implemented due the ease of testing and because the free chlorides are the ones that effectively influence the steel depassivation.

$$D = \frac{RT}{zFE} \frac{x_d - a x_d^b}{t} \tag{2}$$

Where: D is the diffusion coefficient (cm^2/s), R is the gas constant (J/molK), T is the temperature (K), z is the valency of the ion, F is the Faraday constant (J/Vmol), E is the field density (V/m), xd is the penetration depth (m), t is the test time (s), a and b are test constants. For chloride ion z = -1 and, when E = -600 V/m and T = 298 K, then, a = 1.061 and b = 0.589. The model used is based on Fick's second law because the test is developed in a non-steady state condition.

Slices of 50 mm in thickness were obtained by sawing the mid-portion of the cylindrical specimen (10 cm diameter and 20 cm length). 3 concrete slices of each case were used in this test and these slices were extracted from the same specimen, as suggested previously (Medeiros et al., 2009). Then, the slices were kept in an oven at 60 ^{o}C until obtaining constant mass. Then, the surface protection materials were applied on one of the circular surfaces of specimens. Seven days after the application of protection, the specimens were saturated using the procedure of ASTM C 1202/12. The manufacturer guidelines for the amount of material per unit of area were followed in all cases.

The 50 mm thick slice was placed between two acrylic cells. One cell was filled with a 0.3 N NaOH solution and the other with a 3.0% NaCl solution. The cells were connected to a 30 V power source and maintained for 30 h. The schematic presentation of the accelerated chloride migration test cell is illustrated in Fig. 3.

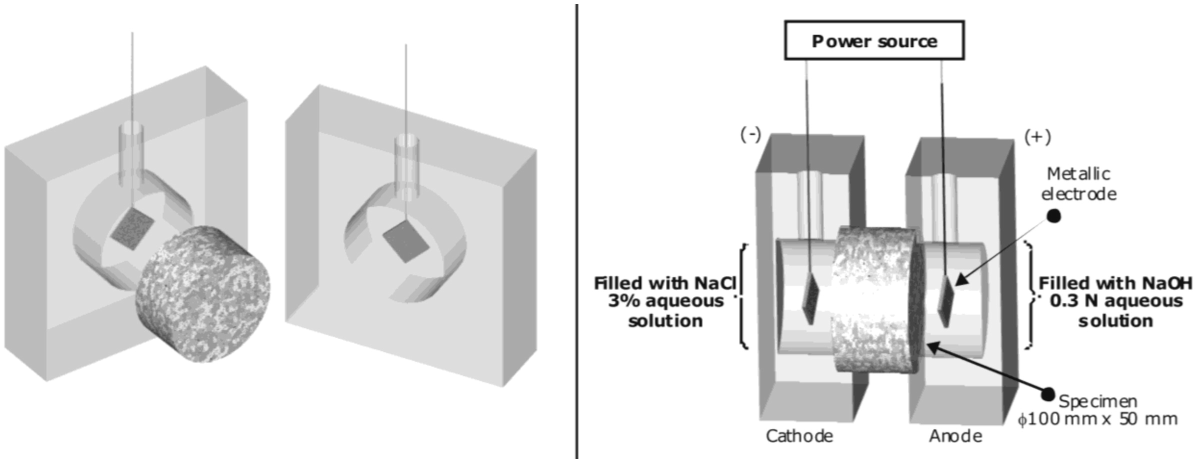

Figure 3. Experimental arrangement of chloride migration test cell.

Next, the slices were broken, and the depth of chloride penetration was determined as illustrated in Fig. 4. Andrade *et al.* (2000), comparing methods for determining the chloride diffusion coefficient in non-steady state using the accelerated chloride migration test, indicated that the Luping and Nilsson (1992) procedure presents better reproducibility of results, thus justifying the test method here presented.

Figure 4. Colorimetric method being applied.

3. RESULTS

Fig. 5 presents the results of chloride diffusion coefficient determined by the method proposed by Luping and Nilsson (1992). In this experiment, the concrete is saturated; therefore, the ion movement caused by absorption and permeability does not exist. Thus, the values of chloride diffusion coefficient presented in Fig. 5 are for saturated concrete.

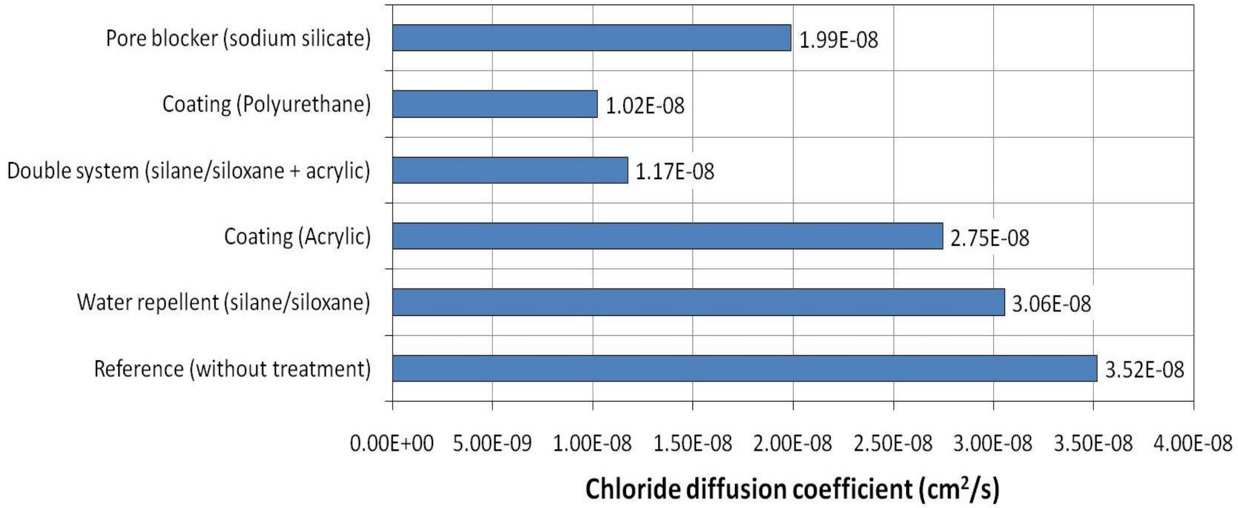

Figure 5. Chloride diffusion coefficients in treated and untreated concrete systems.

Generally, the chloride diffusion coefficient for the treated concrete surfaces was clearly reduced. This reduction increases the structure service life when exposed to a marine environment. However, there is a large difference in efficiency depending on the treatment used.

It is important to emphasize that, except for the polyurethane coating, the double system (water repellent + acrylic coating) is far more advantageous as compared to the single systems due to the double barrier formed in this category of protection. When the chloride ion passes the acrylic topcoat layer, there is still the silane/siloxane treatment, which has some capacity to inhibit the chloride ion penetration inside the concrete.

Concerning the operation, the quality coatings and sealers are more efficient because they act as a separation layer of the concrete with the external environment, like the polyurethane shown in Figure 5. On the other hand, the open pore systems such as silicates and water repellent tend to have lower protection capability when accompanied by low quality films such as of acrylic used in this study.

Table 5 shows the reduction rate of the chloride diffusion coefficients to each treatment. The double system reduced the chloride diffusion coefficient by 67%. The polyurethane coating was the most efficient protection, reducing the chloride diffusion coefficient by 71%. It is important to note that this result may not be universally regarded, since the efficiency of the treatment depends not only on the type of resin that composes it. This is in accordance with Vipulanandan and Liu (2005), which stated that for a specific type of resin, the effectiveness to reduce the penetration of chlorides can be highly different.

The silane/siloxane reduced the chloride diffusion coefficient by 13%, indicating that this material does not greatly influence chloride penetration. However, it is important to emphasize that according to Medeiros and Helene (2009) and Medeiros and Helene (2008), hydrophobic agents significantly reduce water penetration, which is the main mechanism of protection of this treatment.

Thus, when a water repellent is specified, the focus is to reduce the capillary suction, which may carry water contaminated with chlorides into the concrete. Then, the chloride penetration and the chloride migration tests on saturated concrete do not test or simulate the strength of activity of this product, although the hydrophobic agent has presented 13% of reduction in chloride diffusion coefficient. Medeiros *et al.* (2015) showed in their work, the use of goniometry technique for testing the hydrophobic capacity to increase the contact angle of water with the treated substrate, reducing the affinity for water.

Table 5. Reduction rate to each protection system.

Protection system	**Chloride diffusion reduction rate (%)**
Water repellent (silane/siloxane)	13
Coating (Acrylic)	22
Double system (silane/siloxane + acrylic)	67
Coating (Polyurethane)	71
Pore blocker (sodium silicate)	43

4. DISCUSSION

Service life prediction is one of the areas that need greater advancements. Currently, many models developed in this area exist; however, their validation still needs to be studied and disseminated.

In this work, a service life prediction based on the second Fick's law of diffusion is presented. The method proposed in this work allows correlating service life with concrete cover, which can be a useful tool to design reinforced concrete structures. It is important to verify that this is an application based exclusively on the chloride diffusion phenomenon. Its extrapolation to other penetration mechanisms such as absorption, convection, or a mixture of these must be careful. It is necessary to conduct more research on these phenomena to develop a way of making these considerations. However, the application proposed in this work is valid because it allows a quantitative comparison between different materials and supplies service life estimations, although the model still needs improvements.

The method originates from Fick's second law (Equation 3), which development is shown in Equations 3 to 5.

$$\frac{C_{Cl} - C_0}{C_S - C_0} = 1 - erf\left(\frac{e_{Cl}}{2\sqrt{Def_{Cl}\ t}}\right) \tag{3}$$

Where: C_{Cl} is the chloride concentration in depth e_{Cl} and time t (%); C_S is the surface chloride concentration, admitted as a constant (%); C_0 is the initial chloride concentration into the concrete structural component; D_{Cl} is the chloride diffusion coefficient (cm^2/s); t = is the service life (seconds); erf (z) is the Gauss error function; e_{Cl} = is the depth where the chloride concentration reached the threshold for reinforcement depassivation (cm).

Helene (2000) presents Eq. 3 and Eq. 4 based on the second Fick' law. These equations were used in this work to analyze diffusion coefficients results, allowing the construction of a plot that correlates the chloride penetration depth with the reinforced concrete structure service life (Fig. 6).

$$z=\frac{e_{Cl}}{2\sqrt{D_{Cl}\ t}} \qquad \Rightarrow \qquad e_{Cl}=2z\sqrt{D_{Cl}\,t} \tag{4}$$

Including z in Equation 3 and isolating erf (z), results in Equation 5.

$$erf\,(z)=1-\frac{C_{Cl}-C_0}{C_S-C_0} \tag{5}$$

In the construction of Figure 6 it was considered $C_0 = 0$, ie, the concrete had no chloride at the time of molding.

Setting a value for C_S and considering C_{Cl} equal to the critical limit for depassivation of reinforcement corrosion caused by chloride attack, one obtains the Gauss error function [erf (z)]. Referring tables that relate erf (z) with z, the value of z is obtained. Substituting this value of z and chlorides diffusion coefficient in Equation 4, it is obtained an equation that relates the depth at which the limit value (for depassivation of reinforcement) is reached to the time required for this to occur. This was the reasoning for the preparation of Figure 6.

It is important to emphasize that the service life predictions presented in this work are only valid in the conditions below.

- The reinforced concrete structure is at the beginning of its service life (starting from the initiation period);
- The fastest degradation agent is chloride attack;
- No accidental external factors have affected the properties of the concrete cover;
- The chloride threshold level for the steel depassivation is 0.4% relative to cement mass, and was chosen because it is specified in some important technical documents (Bulletin 152, 1992; BS 8110-1, 1997; EN 206- Part 1, 2007).

It is important to emphasize the fact that the diffusion coefficient has been obtained by a migration process (by applying a potential difference) in non-steady state. Therefore, it is quite different from the actual transport of chloride in the concrete, which restricts its direct application in a lifetime prediction model. However, the comparation of the results of this experiment is possible and consistent.

Despite the variation cycles of the concentration of chloride in the concrete surface (De Coss et al., 1998), a restriction of this study was the fixing of the surface chloride concentration (Cs) equal to 0.9%, which was reported by Helene (1993) as suitable for concrete between 20 and 30 MPa, water/cement ratio between 0.48 and 0.68 and cement consumption between 280 and 400 kg/m3, a condition that the concrete used in the experiment of this article falls.

Another simplification of the method is to only consider the diffusion process in chlorides penetration forecast. Thus the forecasts made are more suitable for an underwater concrete than in structures subjected to conditions close to the sea.

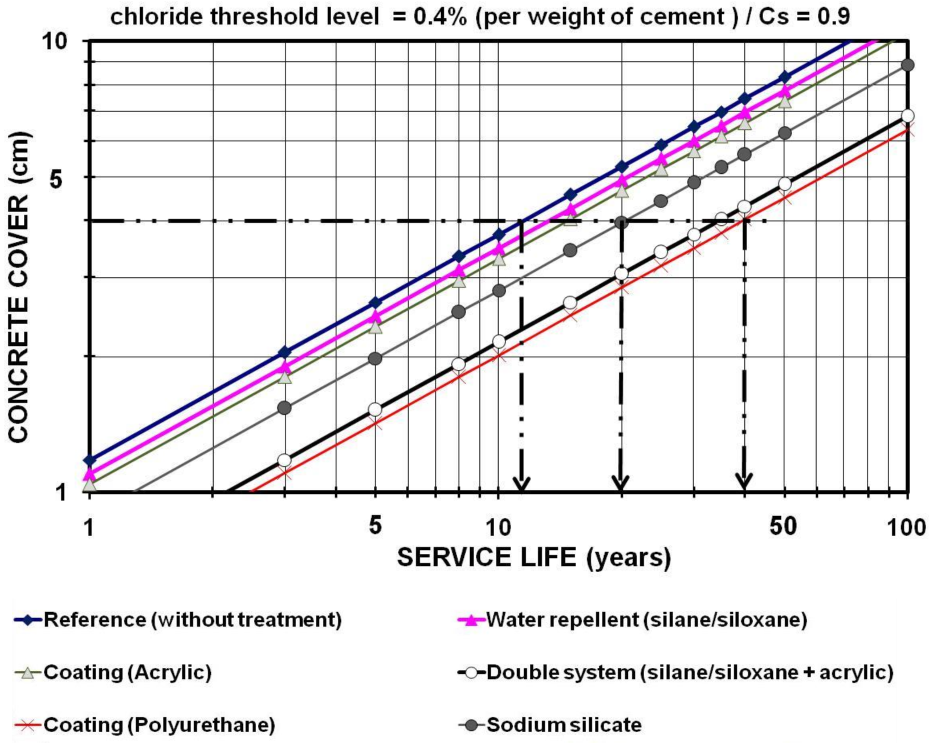

Figure 6. Relation between estimated service life and concrete cover related to chloride penetration (depth where 0.4% by weight of cement was reached).

In Fig. 6, it is clear that for concrete cover equal to 4 cm, the service life of the untreated reinforced concrete structure is about 12 years and can reach 40 years depending on the treatment system applied on the surface of the concrete (extends the service life in more than three times). It is important to emphasize that the polyurethane coating and the double system presented greater efficiency than the other treatments tested in this work.

It is important to report that Castellotti and Andrade emphasize that several life prediction models were analyzed in different workshops within the RILEM TC 178-TMC and that many uncertainties remain, which prevents, in the current state of the art of making accurate predictions in the long term based on short-term experiments (Castellote, Andrade, 2006). A few years have passed since 2006, however, it is considered that such uncertainties still exist. Thus, the life time predictions in this work should not be interpreted as precise and absolute values, because the methodology has approximations as in any life prediction model.

A good way to think in terms of surface protection was proposed in Medeiros and Helene (2009), where protection is represented in equivalent coatings, consisting of how many cm of concrete cover is the same as a coating of a particular protection system. That is, if a concrete is protected with surface protection that has an equivalent coating of X cm, that means that the concrete has X cm of covering, since the protection system has its performance properties maintained over time, which in practice is achieved by providing the periodic maintenance and renovation of surface protection. For example: if the concrete is protected with acrylic film, it is like the covering was increased by 5 mm.

Figure 7 shows the equivalent length for each treatment. These data are related to the specific substrate used in this study.

This kind of thinking may be the way to support the application of surface protection systems in conditions where the reinforced concrete structure is already conclued and thick coatings are lowers than the specified by the standards. This can happen, for example, in the case of structures built with low quality control and in cases of structures built but not completed for reasons such as the failure of the contractor.

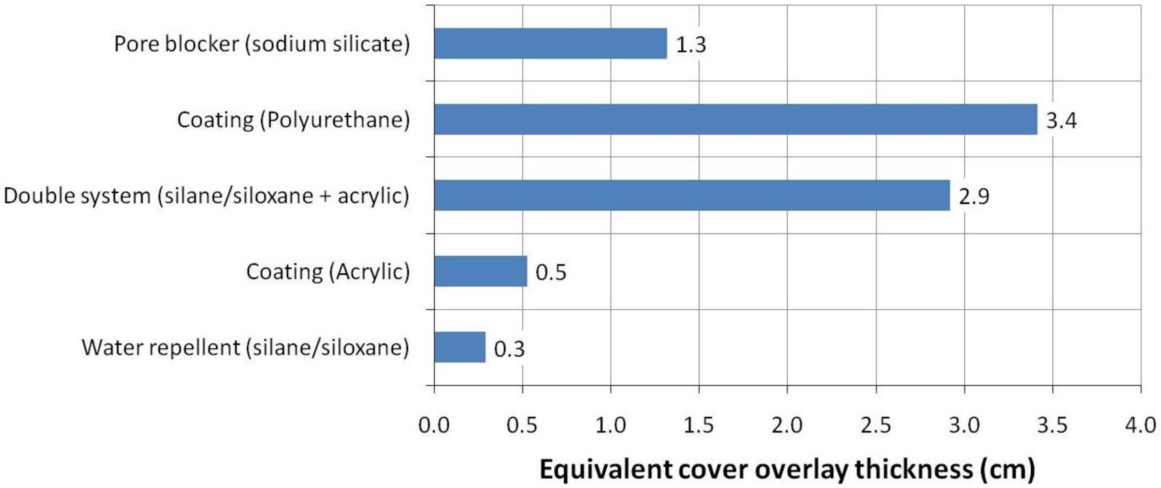

Figure 7: Equivalent cover overlay thickness of each treatment system related to the concrete substrate - Cs = 0.9% (chloride diffusion coefficient by the method of Luping and Nilsson, 1992).

5. CONCLUSIONS

The conclusions expressed here apply to the characteristics of this work and materials. Any extrapolation to other materials or circumstances must be carefully conducted.

A service life prediction for the corrosion initiation stage of concrete with surface treatments was obtained through the well-known Fick´s second law and will be valid only at the mentioned initiation stage.

The chloride contamination in a reinforced concrete structure exposed to a marine environment is one of the most challenging forms of degradation to amend. The ingress of these ions in concrete occurs by chloride diffusion or penetration of contaminated water. From the research presented herein, the following conclusions can be derived:

- The concrete surface protection can be an efficient means of inhibiting chloride penetration in concrete. Consequently, protection systems must be used to increase the service life of reinforced concrete in environments influenced by salt spray, such as buildings in coastal cities/towns.
- The results indicated that the most efficient protection system could reduce the chloride diffusion coefficient of concrete by 71%.
- It is important to emphasize that the results indicated that the use of a high efficiency protection system could extend the service life of a reinforced structure by more than three times. However, this level of increase in service life is related to the test conditions adopted in this work.
- Graphs (like Fig. 6) that relate service life with depth where the chloride concentration reached the threshold for reinforcement depassivation are the most efficacious means of presenting results of chloride diffusion coefficients.

- The results of this article indicate that the water repellent surface protection reduced by 13% the penetration of chloride into the concrete. However, it is important to note that this treatment showed the least ability to reduce the chloride diffusion coefficient.
- Polyurethane coating and double protection system are the surface treatments that showed the best efficiency in reducing the penetration of chlorides (71% and 67% reduction of chlorides diffusion coefficient, respectively).

This work proposes an interesting way to interpret chloride diffusion coefficient results. The possibility of making service life predictions, easiness of interpretation and correlation between concrete cover and service life are the advantages of this method. In this way, this interpretation procedure can become an important tool to predict the service life of reinforced concrete structures. However, it is important to observe that this is an application based exclusively on the chloride diffusion phenomenon. How to consider these other phenomena still is unknown.

Another positive aspect of the work is the conversion of the protective capacity of the surface protection to the equivalent coatings on concrete substrate. This type of approach allows to infer the equivalent thickness that the surface treatment gives to the coating. However, it is important to emphasize that this type of conversion is only valid if the surface protection material maintains its protective properties throughout the lifetime of the structure and this only occurs if the system is being renewed periodically.

6. ACKNOWLEDGEMENTS

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Recycled concrete: a review

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RESUMO

A geração de resíduos sólidos de concreto, considerados como entulho, está se tornando um problema ambiental. Este material de construção é composto principalmente por cimento Portland (CP), mas um dos problemas é a sua alta temperatura de fabricação, que gera poluentes. O uso de agregados triturados originados da demolição do concreto é aproveitável para a elaboração de Concreto Reciclado, um material que pode diminuir custos, diminuir a contaminação e tornar a edificação mais econômica. Porém, a elaboração de concreto reciclado enfrenta a busca por traços otimizados para se alcançar um maior desempenho mecânico sob solicitações estáticas e dinâmicas. Este artigo faz uma revisão dos avanços internacionais sobre este assunto.

Palavras Chave: Concreto reciclado, Resíduos sólidos, Cimento Portland, Agregados.

ABSTRACT

The generation of solid residues of hydraulic concrete, also considered waste, is turning into an environmental problem. The construction material primarily manufactured is Portland cement, but one of the main problems is its high manufacturing temperature which generates pollutants. The use of grinded aggregates that come from the demolition of hydraulic concrete is used to generate recycled hydraulic concrete, a material that could lessen costs, decrease pollution and cheapen construction. Nevertheless, the elaboration of recycled concrete faces the search for optimal designs in order to achieve the highest mechanical performance under static and dynamic requests. This work reviews international advancements in this field.

Keywords: Recycled concrete, Solid residues, Portland cement, Aggregates.

RESUMEN

La generación de residuos sólidos de concreto hidráulico, considerados como desecho, está convirtiéndose en un problema medioambiental. El material de construcción mayormente fabricado es el cemento Portland (CP), pero un problema es su alta temperatura de fabricación, que genera contaminantes. El uso de agregados triturados provenientes de demolición de concreto hidráulico se aprovecha para generar Concreto Hidráulico Reciclado, un material que puede abatir costos, disminuir la contaminación y abaratar la edificación. Sin embargo, la elaboración de concreto reciclado se enfrenta a la búsqueda de diseños óptimos para lograr el mayor desempeño mecánico bajo solicitaciones estáticas y dinámicas. En este trabajo se hace una revisión de los avances internacionales en esta temática.

Palabras Clave: Concreto reciclado, Residuos sólidos, Cemento Portland, Agregados

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1. INTRODUCTION

Among many other fields, environmental preservation is an area of civil engineering that could be supported by the use of recycled concrete, which: minimizes the discharge of solid residues that pollute the environment, reuses materials that are considered waste and that do not have a significant cost, and innovates material design to achieve the maximum mechanical performance under static and dynamic requests that allows for health improvement of those who use buildings constructed with these materials. Recycled concrete also preserves the environment as it prevents pollution from solid residues, decreases the emissions of COx into the air that we breathe and prevents the unnecessary extractions from quarries of geological materials preserving landscape architecture and the endemic flora and fauna.

Each profession is morally obligated and responsible to contribute to the best of its ability to the improvement and preservation of the environment. Recycling concrete is therefore an important research topic in order to prevent global warming. Its design, elaboration, durability, performance, economy and viability are researched.

The employment of recycled construction materials dates back to the 1940's as Europe had excessive amounts of debris due to bombardments. This debris was used as quarries for building reconstruction with successful results. The countries most affected were the United Kingdom and Germany. The publications of that time, mainly British, German and Russian, informed of the use of debris for the construction of new civil work. Much of the debris comprised ceramic material (bricks, ceramic from sanitary services), natural stone material, plastics and rubbers (Hoffmann et al., 2012; Kulakowski et al., 2012) and hydraulic concrete, which later used aggregates such as slags, ashes, and silica fumes (González-Fonteboa et al., 2009). Hydraulic concrete arrived to the United States at the end of the 21st century (Torres et al., 2014), and subsequently the United States began further investigation on recycled concrete as well. The first report of recycled concrete was done in the former Union of Soviet Socialist Republics by P. Gluzhge in 1946, shortly after the Second World War.

Following Gluzghe's research, the first studies carried out in the United States recommended the use of recycled hydraulic concrete from road infrastructures or rigid pavement, and in a secondary manner the use of recycled concrete from buildings such as homes. This research mentioned that these infrastructures and buildings could be contaminated with sulphur products since plaster was used for wall coverings (anhydrous or semi-hydrated calcium sulfate). The new concrete could be attacked by sulfates and this damages the steel reinforcement soaked in the hydraulic concrete. The recycled hydraulic concrete was mainly used in asphalt mixtures used for concretes, replacing the stone aggregates, the problem of which was the lack of electric affinity with asphalt materials (Harek et al., 1971; Buck, 1972). For a long time, the idea prevailed that natural acid stone materials (silica base: ignimbrites, dacite, andesite, plagioclases, orthoclase, quartz, cristobalite, tridymite, etc.) presented negative superficial electrical charges, while the basic or alkaline stone materials (ferromagnesian: basalts) presented positive superficial electrical charges. In recent research, it has been stated that all natural stone aggregates (volcanic and shredded: sandstone, granite, marble, dacite, andesite, rhyolite, limestone, dolomites, quartz, basalt) have negative electrical charges (Rodríguez Talavera et al., 2001).

Keeping in mind the aforementioned, it is extremely important to know if there will be affinity in the manufacture of asphalt mixtures with anionic or cationic emulsions. Recycled concrete was also elaborated with tyre residues as is done with asphaltic pavements (Kardos et al., 2015). The intensity of the aggregate's surface charge, combined with the intensity of the charge of the emulsion agent, could strongly influence the break speed, particularly in the case of cationic emulsions. The calcium and magnesium ions present on the surface of the aggregate could react with, and destabilize, certain anionic emulsions, accelerating the break speed of the emulsion (Carrasco, 2004). This superficial electric affinity problem does not happen with recycled hydraulic concretes with ceramic matrixes.

2. BACKGROUND

In order to recycle solid waste materials, such as garbage and residues in the case of demolished or collapsed concrete, reusable for the elaboration of new concrete mixtures, the following objectives must be accomplished: a) the reuse of solid waste, decreasing the amount of residues or waste that harm the environment and consequently humans as well, for example the problem with leachates; b) the design, innovation and elaboration of new ecofriendly construction materials; c) the conservation of natural minerals from quarries, which reverts back to the protection, non-exploitation and preservation of the natural habitat of native flora and fauna, conservation of the landscape architecture and geoparks, since mineral resources are non-renewable; and, d) decrease atmospheric pollution by providing a material, the production of which causes emissions of CO and CO2, a new purpose. The production of volcanic stone aggregates being extrusive igneous rocks, such as the regional ones from Michoacán, Mexico, implies that they are the product of volcanic events and the magmatic ejections are a source of oxidized sulfur, SOx. The volcanic activity constitutes an important source of SOx emissions to the atmosphere, being the main source of sulfur in the stratosphere (Amigo Ramos, 2000; López et al., 2015; Ruggieri, 2012). The CO and CO2 compounds are materials that due to photosynthesis can turn into O2; however, there is not a process that will absorb sulfur compounds and turn them into oxygen.

The manufacture of CP produces approximately the same weight in carbon compounds released into the atmosphere, such as CO and CO2; so, the recycling of concrete also reduces the carbon footprint in the atmosphere. Latin America does not stand out for its great contribution to global contamination.

In 2002, the main source of greenhouse gas emissions in Mexico was the energy sector, responsible for approximately 70% of emissions. Other industrial processes, such as the production of cement, glass, steel, paper, food and beverages, among others, contributed with approximately 9% of the total emissions of greenhouse gases in the country (Climatic Change, 2009). 40% of carbon dioxide produced by a typical family comes from the motor vehicles that run on fossil fuel and from the construction of houses (https://www.veoverde.com/2014/01/llegaron-las-viviendas-sustentables-a-mexico/).

Concrete is one of the most manufactured and used materials in the world for the construction of civil and military works, but it is also a generator of large volumes of solid residues associated with demolition and waste processes (Valdés et al., 2011). In order to reduce the climatic change and environmental production, the signing of the Kyoto protocol was pursued; it was negotiated in 1997 and enforced in 2005. The protocol intended for 37 developed countries to reduce their greenhouse gas emissions to 5% by 2012, with respect to their emission levels in 1990. Mexico did not sign as it was not considered a developed country.

The protocol has resulted in developed countries initiating policies focused on the reduction of such volumes of pollutants released into the atmosphere (Alonso et al., 2007) through its reuse, decrease or recycling (Debieb & Kenai, 2008; Rolón et al., 2007; Valdés et al., 2009).

Studies conducted in the European Union (Etxeberria et al., 2007; Vázquez et al., 2004; http://ficem.org/publicaciones-CSI/DOCUMENTO-CSI-RECICLAJE-DEL-CONCRETO/RECICLAJE-D-CONCRETO_1.pdf; Jianzhuang et al., 2012;

http://www.concretosreciclados.com.mx/; http://www.veoverde.com/2013/11/concretos-reciclados-otra-apuesta-mexicana-por-el-ambiente/) have been able to establish that the production of construction residues rose to around 900 million tons/year, as is shown in the summary of Table 1. Research done in Spain, Germany, France and England, all countries that lack an abundance of quarries with natural mineral stone aggregates, has been able to determine the viability of the reuse of hydraulic concrete from construction as granular material, even more so if there exists a lack of these materials. Their aim is toward those materials that require fewer fossil fuels for their manufacture, transport and recycling, which would reduce the necessary energy for their reuse.

It can be observed that in regards to the quantity or per capita recycling, Australia stands out with the highest amount, 25.78 ton/inhabitant. Regarding the amount of recycled concrete with respect to a country's territory, theoretically, the bigger the territory the more construction is done and therefore more residues would be present. However, Taiwan stands out with 1862.15 tons per km2 of territory, having the highest index of the abstract. Several countries do not have an accurate record yet.

Much has been said about the earthquakes that struck countries such as Turkey, Afghanistan, and Nepal, but there are no records in the indexed literature of the quantities used of recycled concrete, without forgetting that these countries still maintain the tradition of having ceramic and/or adobe walls, with large elasticity modules for the absorption of dynamic energies.

The global production of hydraulic concrete is estimated to be around 25 billion tons per annum.

Due to environmental contamination and climatic change, it is important to initiate the creation of collective conscience in lesser developed countries in order to reduce the extraction of stone materials from natural environments, as well as to reduce the accelerated depletion of aggregate reserves that originate both from river streams and quarries (Rhakshvir & Barai, 2006; Montoya et al., 2005). The demand of natural resources and the lack of raw materials are important; consequently, the need to preserve and protect the environment from an ecological imbalance makes the technique of recycled concrete (Oikonomou, 2005) an important activity in construction (Aguilar et al., 2005).

Previous research has demonstrated that the physical and mechanical properties of recycled hydraulic concrete, comprised by recycled aggregates in its matrix, could guarantee resistance and mechanical performance (Topcu, 1997; Topcu & Sengel, 2004; Topcu & Guncan, 1995). Studies derived from specific applications in civil works show that on several occasions concrete residue is neither enough nor efficiently employed. This concrete residue could also be employed to produce pre-manufactured elements of concrete, such as blocks, insulating materials, lightened materials, and panels.

For successful recycling, several variables should be considered in the design of new concrete mixtures: the percentage of recycled material, the percentage of recycled coarse ore, the percentage of fine material, the water/cement relation, the density of recycled material, the use of thinners, shrinkage (workability), mechanical resistance, and homogeneity (Chang et al., 2011). The microstructure study of recycled concrete presents new challenges as the interfacial zone (ITZ) has two zones difficult to identify according to the age/hydration (Kong et al., 2010; Li et al., 2012): old and modern rapid-setting concrete, with different compositions, porosities, densities, age, resistivity, hydration and hardness.

Table 1. Abstract of recycled concrete. 1. Millions of tons of recycled concrete (CSI Recycling Concrete Full Report, 2007); 2. Country territory in km^2; 3. Inhabitants in millions; 4. Relation of the recycled concrete in millions of tons per capita; and, 5. Relation of tons of recycled concrete produced per km^2 of territory.

Country	**1**	**2**	**3**	**4**	**5**
Germany	120.00	357,121	80	1.5	336.02
Argentina	5.50	2 780 400	43	0.13	1.99
Australia	550.00	7,692,024	21.5	25.58	71.50
Austria	22.00	83,371	8.3	2.65	266.88
Belgium	14.00	30,510	10.4	1.36	458.87
Brazil	50.00	8,500,000	200	0.25	5.88
China	200.00	9,600,000	1,300	0.15	20.83
Colombia	13.00	1,141,748	47.4	0.27	11.38
Costa Rica	0.50	51,100	5	0.10	9.78
Denmark	5.00	43,098	5.6	0.89	116.01
United States	335.00	9,826,675	316	1.06	34.09
Spain	39.00	504,645	47.1	0.83	77.28
Finland	1.60	337,030	5.4	0.3	4.74
France	25.00	675,417	66	0.38	37.01
Holland	26.00	41,526	16.8	1.55	626.11
Ireland	17.00	84,421	6.2	2.74	201.37
Israel	7.50	22 145	8.6	0.87	3.39
Italy	40.00	301,338	59.4	0.67	132.74
Japan	77.00	377,835	126.7	0.61	203.79
Luxembourg	2.70	2,586	0.54	5	1044.08
Mexico	30.00	1,964,375	119	0.25	15.27
Portugal	4.00	92,391	10.6	0.38	43.29
United Kingdom	70.00	243,610	63.2	1.11	287.34
Czech Republic	9.00	78,866	10.5	0.86	114.12
Switzerland	7.00	41,290	7.9	0.89	169.53
Sweden	1.20	449,964	9.6	0.13	2.67
Taiwan	67.00	35,980	23.1	2.9	1862.15
Thailand	10.00	513,115	65.5	0.15	19.49
Worldwide	900.00	150,386,640	7000	0.13	5.98

The reduction method for the size of the hardened hydraulic concrete in order to obtain gravel could result in loss by pulverization, aggregate sizes ≤ ¼ of an inch (6.4 mm), porous areas with their corresponding forms, sizes and distribution in the pores of the matrixes, which increase the superficial area increasing the demand of CP in the new mixture (Koeu et al., 2011; Gómez-Soberon, 2012). This is an undesirable morphology in the grinded particles where the dimensions regarding the X, Y and Z axes are very different among themselves, producing elongated or semicircular shapes (Eguchi et al., 2007). In order to avoid that the aggregates in the concrete present problems such as the ones described, the product of the grinding, fine and thick, should be characterized to make optimal concrete designs; some countries already have a code for recycled stones (Martín-Morales et al., 2011). Another parameter to be considered is the percentage of natural stones that could be replaced by recycled material (Etxeberria et al., 2007), the use of cement per m^3 of hydraulic concrete and the mechanical resistance are functions of this percentage (Marie & Quiasrawi, 2012). Some mixtures only replace thick aggregates with recycled material, while others only replace fine aggregates with recycled material (Evangelista & Brito, 2007; Raoa et al., 2007). The quality and properties of the aggregates depend on the mother rock or concrete from which they originate, the stronger the resistance of the primary concrete the stronger the resistance of the recycled aggregates that come from the original concrete (Kou et al., 2012). However, there is also the possibility that the primary concretes come from different origins. Other mixture designs use both types of recycled aggregates, some authors work with specific percentages of each aggregate (Mas et al., 2012). The variations are designed and elaborated taking the mechanical design properties into consideration, which are sought in recycled concrete (Padmini et al., 2009; Tabsh & Abdelfatah, 2009).

The use of CP depends on the design method, the security factor, the material type, the seismic coefficient, the soil quality, and the construction use. There are no universally recognized methods to design mortars or concretes with aggregates from recycled concrete, but mortars have been successfully manufactured with recycled material (Abbas et al., 2009).

The design of concrete mixtures started at the end of the 19th century and beginning of the 20th century with Dr. Duffus Abrams (Abrams, 1918). Until the end of the 20th century, hydraulic concrete was designed based on the mechanical resistance to compression, which is the index property of the concrete; however, that concept changed at the beginning of the 21st century. Due to concrete performance, its useful life, and the need for less maintenance, the design of concrete mixtures takes into consideration durability criteria (Kwan et al., 2012; López Celis et al., 2006), identifying resistance and the speed of ultrasonic pulse as quantifiable parameters.

Concrete mixtures with recycled material are evaluated from the viewpoints of mechanical performance, physical performance, durability (Casuccio et al., 2008), forms of failure (Liu et al., 2011), fluidity, workability and shrinkage (Guneyisi, 2010), age and hydration of the cement (Katz, 2003), and the degree of compaction that could be achieved with vibratory methods or with special self-compacting cements (Kou et al., 2009).

Mechanical performance is usually evaluated by destructive testing with simple compression (Xiaoa et al., 2005) if there are cubic or cylindrical specimens. However, if there are only splinters with approximate dimensions of 10.0 cm, the Point Load Method can be used for those samples that have not been carved, simple tension and indirect tension, bending or modulus of rupture. The modulus of rupture is the index value for the design of hardened pavements (Lye et al., 2016). The evaluation of the recycled concrete is also done with the use of test methods that are not destructive and that do not require material preparation. They can be repeated and do not cause damage to the material; the electrical resistivity and speed of ultrasonic pulse are the most common (Park et al., 2005). In order to improve hydraulic concrete mixtures, security factors and reduction of the A/C relations are used with a prolonged curing period through immersion or sprinkling (Fonseca et al., 2011). Another way to influence modification of the properties of recycled concretes is through the use of additives and aggregates or cement replacements with materials that have pozzolanic activity. Alkaline activated concretes can be manufactured with aggregates from the recycling of hydraulic concrete (Kathirvel et al., 2016)

3. PRESENTLY

The most meticulous problem nowadays relates to greenhouse gas emissions and the actions taken to reduce them.

Work is being done to come up with proposals that help with the reduction of emissions and residues to the atmosphere.

The development of concrete manufacturing using stones (rocks) from the recycling of concrete generally has been sufficient in order to produce a new material with mechanical performance and durability that complies with international standards. Perhaps the main disadvantage is the porosity of the thick and fine aggregates produced by grinding, which has been solved by taking into consideration the following elements for new mixture designs. Firstly, the reduction of the water/cement relation should favor the durability and help obtain the sufficient mechanical resistance. Its resolution is done using thinners, super-thinners or water-reducing admixtures (aggregates indicated in ASTM C-494) that obtain workable and fluid mixtures. Secondly, the use of agro-industrial waste that presents pozzolanic activity, aluminosilicate-rich, that “fills” the gaps in the hardened paste (recrystallization in the pores densifying the matrix), calcium oxalates such as weddellite and whewellite have demonstrated that they perform the same role as additives to concrete (Torres et al., 2010; Torres et al., 2010 bis; Del Valle et al., 2015). The hydrated and hardened concrete, even the containers of recycled concrete demolished in 2011 and constructed in the 60’s that remained outdoors during the rainy season formed new links among them, solidifying and making it had to break them by hand. The use of residues with pozzolanic activity also indirectly solves the accumulation of the other solid residues that pollute and take up space, the use of aluminosilicate-rich aggregates that increase the mechanical performance of the new mixtures, mixtures that increase the protection of the reinforcement steel soaked in them when densifying, reducing the attack by carbonation in concretes and thus also the corrosion in steel. Other ways of preventing corrosion in reinforcement steel in concretes is the use of stainless steel, which financially does not seem affordable, but significantly decreases the maintenance costs and increasing durability (Pérez Quiroz et al., 2014). The results of the physical and mechanical properties obtained from the additions, replacements and aggregates used in new mixtures of hydraulic concrete and mortar with cement bases and line, in a fresh and hardened state, show the veracity of these statements (Martínez et al., 2015; Bernabé, 2015 & 2012; Jacobo, 2014; Guzmán, 2014; Villicaña, 2014; Arreola, 2013; Zalapa, 2013; Contreras, 2013; Figueroa, 2013; Campos, 2013; Flores, 2013; Arguello, 2012; Gómez Zamorano et al., 2004; Moreno et al., 2004). And thirdly, the addition of chemical pozzolanic products of industrial purity level that can be activated at friendly temperatures, geopolymer materials (Rubio et al., 2014 Patent; Rojas, 2013; Medina, 2011) or alkaline activated materials are needed.

Currently, multiple solid residues are being experimented on as aggregates, which could have organic origins such as fibers, husks and seeds; additions that are residues from other industrial processes such as the ash from cane bagasse, mineral carbon ash, ashes from the elaboration of artisanal ceramic materials done with clays, metallurgical and steel production slags are being considered as well.

4. DISCUSSION

Table 1 shows that Australia is the country that recycles the largest quantity of tons per capita, while Taiwan is the country that recycles the most tons of concrete territory-wise. In the same table that lists the information on 28 countries, Mexico ranks in eleventh place indicating that we are far from using all our demolished concrete, but the effort made is important and sustainable, and shared by the community.

The use of recycled concrete is more common in Europe, maybe due to the lack of natural mineral aggregates. In Latin America, specifically Mexico, there is a continuous search for a sustained use of the materials considered solid waste that allow a response to environmental preservation, as well as to the search and innovation of additives, methods, techniques and processes that improve the mechanical processes of recycled concrete.

Another point to be mentioned is the sustained and continuous work done in the new design of hydraulic concrete by durability indexes, to prolong the useful life of the concrete structures, leading to the reduction of the demolition of the hydraulic concrete.

The reuse of solid residues has also conducted discoveries of properties that have allowed their addition to the mixtures of concrete/mortar, modifying some of their properties in favor of durability.

5. REMARKS

The use of recycled material prevents the accumulation of collapsed or demolished concrete that need to be removed or transported to dumping grounds of solid residues, with the corresponding fuel expense for its transportation. The accumulation of these solid residues has also caused changes in landscape architecture by modifying the morphology of the surface or topography of the reception zone of the demolished material.

The use of aggregates that originate from recycling allows a decrease in the amount of pollution emissions into the atmosphere.

The recycled material allows avoiding the overexploitation of quarries, preserving the landscape architecture and promoting specialized geological tourism which helps in the preservation of the endemic biota, diminishing the environmental impact of the extractions and the fail forms due to the slipping of material banks close to the population centers, as well as recharges to groundwater reserves.

6. CONCLUSIONS

Recycled concrete can solve the problem of lack of stone aggregates as well as protect their quarries. It clarifies if aggregates do not comply with current standards, such as the case of volcanic foam or pumicita. The use of aggregates that originate from recycled concrete also allow for these to be placed saturated in the mixtures and thus initiate the internal curing of the new mixtures of recycled concrete.

Stone aggregate obtained as a result of the demolition of concrete may not have ideal conditions, but there is also the fact that several locally existing natural mineral stone aggregates do not comply with existing recommendations in the current construction standards. Contractors, engineers and architects look for ways to make the most of recycled concrete achieving significant mechanical performances.

There is still much to be studied on recycled aggregate, but it is possible to obtain performances of 350 MPa in recycled concretes if the stones are measured correctly, the A/C relations are reduced, and if additives that modify the rheology of the fresh mixtures for their placement and simultaneously help to achieve the resistance are added.

Simultaneous to the design and elaboration of recycled concrete, the possibilities of the additions of other materials that modify the properties of the concretes elaborated likewise should be explored, achieving successful and economic conditions.

In the interest of preventing carbon emissions, stopping construction would mean putting a stop to the increase of infrastructure and the convenience of a country's inhabitants, but by not doing anything we appear to be accomplices. Therefore, alternatives are being sought for the production of construction materials that are the result of the use of materials that have turned into waste, residues and industrial garbage. This engages us in the search of modifying alternatives for the properties of new materials.

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