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# Critical Analysis on HPC with Very High Contents of Mineral Additions (Part I)
# Mix Proportion and Carbonation

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## Abstract

The increasing number of researches and concrete structures made with HPC containing high contents of cement substitution (above 50%, by mass) by mineral additions, has revealed apprehension among some researches on topics related to durability of these concretes, especially carbonation, due to parameters used in the mix proportions. According them, the low cement content combined with the great amount of mineral additions would induce increase in total water content that, in spite of the lower water/cementitious materials ratio, would carry higher carbonation, possible leaching and durability loss. This paper presents critical analysis concerning to these subjects, showing data of researches performed by the authors, compared with others published by the literature. It is demonstrated that lower cement content, higher total water per m³ of concrete, although entailing consequences to carbonation, preventive actions may overcome these inconveniences in order to limit possible side effects, inducing the attainment of durable concretes, in such mix proportion conditions. The addition of hydrated lime to the concrete mixtures in order to replace the alkaline reserve and the possibility of the cement paste lixiviation is also discussed.

***Keywords***: mix proportion, carbonation, mineral additions, high contents, calcium hydroxide

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## 1 Introduction

Cement substitution by very high mineral additions content has as scope the durability increment of concrete structures, less cement consumption, decreased economical cost and energy savings. In despite of the technical and economical advantages obtained by high pozzolan or slag content to structural concrete, literature shows that, among the possible side effects, carbonation increase is the first one, due to the lower alkaline reserve of those cementitious mixtures. To compensate the higher neutralization speed, one of the possible actions is to decrease the water/cementitious (w/cm) ratio in order to obtain a denser paste and, consequently, to obstruct the fluids percolation through the paste pores, especially of the $CO_2$ to retard the carbonation progression. Another way of retarding this behavior is to add calcium hydroxide from an external source, besides those resulted from the hydration reactions of the $C_3S$ and $C_2S$. Such addition replaces the alkaline reserve and decreases carbonation speed, however, it is necessary to know the influence of the additional lime upon the other concrete durability properties.

In these concrete types, the w/cm ratio decrease has consequences on the mixture proportion, inherent to the mineral addition reactivity and the content in the mixture, substituting cement. Mineral additions with lower reactivity such as fly-ash or granulated blast-furnace slag have lower efficiency than that of cement, that is, to obtain the same performance level of the axial compressive strength, higher quantity of addition than those of the cement substituted is required.

Therefore, the reduction of the w/cm ratio and the quantity increase of mineral addition in the mixtures carry increases in the paste volume that, generally, are partially compensated by lower volume of the added sand, with the purpose of maintaining the same mortar volume in the mixture proportion. As consequence of the higher quantity of cementitious materials in the mixture and the adoption of low w/cm ratio, the added total water quantity increase, even though more efficient superplasticizing admixtures are utilized.

According to author's experience for the local materials, to reach the axial compressive strength level of 50 MPa with cement substitution of 70%, or more, by mineral additions, cementitious materials content from 500 to 600 kg/m³ is required, with total water content from 160 to 180 l/m³. These figures, at first sight, show that, due to the higher fines and water quantity, connected to lower cement contents, it would be able alter the carbonation behavior so as to accelerate it.

On the other hand, the low alkaline reserve and greater carbonation speed has been the main reason why some standards or codes such as CEB-FIP [1] or ENV-206 [2] restrain the maximum content of pozzolanic additions or ground blast-furnace slag in structural concrete, due to the risk of the rebar depassivation in very short terms and the possibility of corrosion starting before the end of the structure useful life.

The carbonation advance is proportional to the total alkalinity available in the paste matrix, function of the cement chemical composition, of the CH and hydrated compounds content. Portland cement hydration presents greater alkaline reserve than those of cement with mineral additions, resulting in higher alkaline hydroxides concentration in the pore solution of the former, propitiating slower $CO_2$ diffusion because it needs to reduce the pH and react with the existing CH, to proceed penetrating and precipitating calcium carbonate. In the second cement type, although the mineral additions propitiate pores and grains refinement, it increases the capillary pores disconnection and decrease the permeability, preponderating the lower alkaline reserve effect, resulting faster carbonation front compared with Portland cement concretes (Isaia et al [3]).

Consequently, considering the authors' experience along the development of several research projects with high mineral addition content, the carbonation depth depends on the mineral addition type and quantity, being as higher as more reactive and elevated its content in the mixtures, factors related to the calcium hydroxide consumption. So, for concrete with mineral additions the carbonation is related to the effective cement content in the mixture, being as higher as lower this content because this behavior depends to the remaining CH in the pore solution available to react with the carbon dioxide.

In the literature some researchers, among them [4], [5], declare that the carbonation of HPC with high content of mineral additions and low w/cm ratios and reduced quantity of water per m³ of concrete, would not present durability problems because the carbonated depth would be low related to others concrete types. They affirm also that the addition of calcium hydroxide to the mixture as strategy to reduce carbonation would not be a correct approach because, eventually, the cementitious paste could be lixiviated. So, the use of high content of addition the HPC, combined with low Portland cement consumption and more elevated content of water per m³ of concrete would not result in more durable concrete at long term, mainly due to the higher shrinkage that would present.

In order to discuss the opinion of these researchers, the present work conducts critical analysis on mix proportion of HPC with more elevated content of water per m³ of concrete, low w/cm ratio, very high mineral additions content, with the addition of calcium hydroxide to reduce the carbonation effects. It makes considerations by comparing results obtained by Concrete Studies and Researches Group (GEPECON) of UFSM with those of other investigators cited by literature. The presented arguments are based on the papers of Isaia and Gastaldini [6] and other published by GEPECON in recent years, related to this subject. The second part of this paper that will be published in sequence of this one, will deal with on mix proportion, shrinkage and durability aspects of these concrete mixtures with very low cement content.

Table 1 – Chemical composition of the cementitious materials and hydrated lime

| Chemical composition | Content in mass (%) | | | |
|---|---|---|---|---|
| | PC HES * | Fly-ash | Blast furnace slag | Hydrated lime |
| LOI | 2.99 | 1.16 | 0.00 | 26.12 |
| $SiO_2$ | 19.33 | 64.57 | 34.07 | 0.87 |
| $Al_2O_3$ | 4.74 | 27.27 | 12.94 | 0.37 |
| $Fe_2O_3$ | 3.01 | 2.21 | 10.55 | 0.16 |
| CaO | 63.39 | 1.51 | 41.05 | 73.07 |
| MgO | 1.79 | 0.76 | 8.28 | 0.37 |
| $SO_3$ | 3.07 | 0.06 | 1.15 | 0.17 |
| $Na_2O$ | 0.07 | 0.15 | 0.16 | 0.09 eq. |
| $K_2O$ | 0.85 | 1.50 | 0.55 | |

* High-early strength Portland cement

## 2 Materials and experimental program

This study takes part in the research project 'Hydrated Lime addition effects on structural concrete with high mineral additions content' developed by GEPECON. High early-strength portland cement from a national supplier; fly-ash from a regional power plant, ground for one hour; ground granulated blast-furnace slag from a national steel plant; packed calcium hydrated lime; Glenium 51 superplasticizer admixture; natural quartz sand with Dmax = 4.8 mm and diabasic crushed stone aggregate with Dmax = 19 mm were utilized. Tables 1 and 2 show cement and mineral-addition test results.

Eleven mixtures with 0.35, 0.45 and 0.55 w/cm ratio, being one of reference and six with substitution contents between 50% and 90% of fly-ahs and/or slag were cast. Hydrated lime was used as addition to the cementitious materials, in 15% (mixtures with ≤50% of mineral additions) and 18% (mixtures with >50% of mineral additions) contents, near to the ones of the CH replacement produced by the cement, to restore the alkaline reserve of the respective mineral addition mixture. The mixture proportions were accomplished for 60±15 mm slump, in equality of mortar volume. Table 3 shows the cementitious material contents used in the investigation and, Table 4, shows the material quantity per cubic meter of concrete, of all tested mixtures.

Table 2 – Physical characteristics of the cement and mineral additions

| Cementitious Materials | Specific mass ($kg/m^3$) | Blaine Specific area ($m^2/kg$) | BET Specific area ($m^2/kg$) |
|---|---|---|---|
| HES Portland cement | 3,150 | -- | 1800 |
| Fly-ash | 2,240 | -- | 350 |
| Blast-furnace slag | 2,900 | 470 | -- |
| Hydrated lime | 2,330 | 900 | -- |

Table 3 – Quantity (%) and designation of the mineral addition mixtures

| Materials | REF | FL | F | SL | S | FSL | FS |
|---|---|---|---|---|---|---|---|
| Cement | 100 | 50 | 50 | 30 | 30 | 10 | 10 |
| Fly-ash * | - | 50 | 50 | - | - | 20 | 20 |
| Slag * | - | - | - | 70 | 70 | 70 | 70 |
| Hydrated lime ** | - | 15 | - | 15 | - | 18 | - |

* cement substitution, by mass ** sand substitution, by mass
**Keys: F**=fly-ash **S**=blast-furnace slag **L**=hydrated lime

The following tests were conducted: a) compressive strength according Brazilian standard NBR 5738 [7]; b) carbonation depth in conditioned chamber in 10ox100 mm specimens, 24-hours cured in the moulds and until 7 days in humid chamber and, after this term placed in lab environment for 28 days, when were preconditioned according RILEM recommendation TC 116-PCD [8]. After that the specimens were then placed in the conditioned chamber at 23°C temperature and 65% relative humidity in 5% $CO_2$ atmosphere. The carbonation depths were measured by the RILEM CPC-18 [9] method after 4, 8 and 12 weeks of stay in the chamber, and then split by diametrical compression, receiving aspersion of phenolphthalein solution; c) remaining

**Table 4 – Materials quantity per m$^3$ of concrete (kg/m$^3$)**

| Mixture | w/cm | PC | FA | GBFS | Lime | Sand | Admix. | Water |
|---|---|---|---|---|---|---|---|---|
| REF1 | 0.35 | 540 | | | | 605 | 0.5 | 189 |
| REF2 | 0.45 | 393 | | | | 753 | | 177 |
| REF3 | 0.55 | 309 | | | | 837 | | 107 |
| FL1 | 0.35 | 270 | 270 | | 81 | 514 | 19.5 | 170 |
| FL2 | 0.45 | 197 | 197 | | 59 | 686 | 8.5 | 168 |
| FL3 | 0.55 | 155 | 155 | | 46 | 784 | 4.6 | 165 |
| F1 | 0.35 | 270 | 270 | | | 514 | 5.1 | 184 |
| F2 | 0.45 | 197 | 197 | | | 686 | 2.4 | 176 |
| F3 | 0.55 | 155 | 155 | | | 784 | 1.6 | 168 |
| SL1 | 0.35 | 162 | | 378 | 81 | 578 | 8.6 | 180 |
| SL2 | 0.45 | 118 | | 275 | 59 | 733 | 5.9 | 171 |
| SL3 | 0.55 | 93 | | 216 | 46 | 822 | 3.1 | 167 |
| S1 | 0.35 | 162 | | 378 | | 578 | 2.7 | 186 |
| S2 | 0.45 | 118 | | 275 | | 733 | 1.6 | 175 |
| S3 | 0.55 | 93 | | 216 | | 822 | 1.2 | 169 |
| FSL1 | 0.35 | 54 | 108 | 378 | 97 | 541 | 16.6 | 172 |
| FSL2 | 0.45 | 39 | 78 | 275 | 71 | 708 | 7.1 | 170 |
| FSL3 | 0.55 | 31 | 61 | 216 | 56 | 802 | 3.4 | 167 |
| FS1 | 0.35 | 54 | 108 | 378 | | 541 | 2.7 | 186 |
| FS2 | 0.45 | 39 | 78 | 275 | | 708 | 0.8 | 176 |
| FS3 | 0.55 | 31 | 61 | 216 | | 802 | | 170 |

**Obs.:** Coarse aggregate quantity in all mixtures: 1,0153 kg/m

**Keys: w/cm** = water/cementitious materials; **PC** = Portland cement; **FA** = fly-ash; **GBFS** = granulated blast-furnace slag

calcium hydroxide content according Brazilian standard NBR 5748 [10].

The procedure of strength equality was adopted for results analysis. The 55 MPa strength level, at 91 days, was chosen to represent high-performance concrete. Table 5 shows the utilized material proportions for the cementitious materials, the carbonation coefficients and the remaining CH content for some selected mixtures. In this paper the following correlation was adopted for carbonation coefficient: 1 mm.week$^{-0,5}$ (accelerated test) = 1 mm.year$^{-0.5}$ (natural test), according [11]. The carbonation coefficient was calculated according the equation: $kc = x \cdot t^{-0.5}$, being x de carbonation depths, in mm, and t the time, in weeks (4, 8 and 12), of exposure in the climatic chamber. The linear regression between time and carbonation depth to calculate kc was adopted.

**Table 5 – Data and test results for 55 MPa at 91 days (Isaia and Gastaldini, (6))**

| Mix * | Mineral Additions % | w/cm | Total water consumption kg/m$^3$ | Cementitious materials consumption kg/m$^3$ | Cement content kg/m$^3$ | Carbonation Coefficient mm.week$^{-0.5}$ | Remaining CH % |
|---|---|---|---|---|---|---|---|
| Ref. | - | 0.46 | 188 | 397 | 397 | 1.13 | 5.24 |
| FL | 50 | 0.44 | 168 | 418 | 209 | 3.67 | 0.70 |
| F | 50 | 0.35 | 184 | 536 | 268 | 4.36 | 0.34 |
| SL | 70 | 0.37 | 178 | 503 | 151 | 0.97 | 1.90 |
| S | 70 | 0.29 | 186 | 627 | 188 | 0.53 | 0.71 |
| FSL | 20+70 | 0.32 | 174 | 570 | 57 | 1.42 | 0.26 |
| FS | 20+70 | 0.31 | 192 | 590 | 59 | 2.99 | 0.11 |

**Table 6 – Carbonation depths of a concrete block (Malhotra, (4), Bilodeau, Malhotra, (5))**

| Age: months | 31 | 41 | 50 | 57 | 90 | 156 |
|---|---|---|---|---|---|---|
| Age: years | 2.58 | 3.42 | 4.17 | 4.75 | 7.50 | 13.00 |
| Carbonation depths: mm | 4 | 4 | 7 | 7 | 8 | 11.5 |

Following-up, considerations will be realized on the use of hydrated lime to reduce the carbonation speed in high-performance concrete, associated with mixtures with low water/cementitious ratio and more elevated water content per m³. In sequence, will be discussed the role that the external hydrated lime addition associated to very high cementitious materials quantities are able to carry to long term concrete carbonation and durability, specially to its lixiviation.

## 3 Discussion

### 3.1 Carbonation depth versus carbonation coefficient

Some researches are of opinion that, for HPC, the use of low w/cm ratio and reduced quantity of water per m³ are sufficient factors to attain low carbonation. Others still utilize the carbonation depth only as measure parameter among different concretes to compare theirs performances, without caring about the speed of the carbonation front displacement. This approach may lead to conclusions not always valid or even erroneous.

Nevertheless, the use of low w/cm ratio and reduced water content per m³ of concrete parameters are not always conditions to attain low carbonation. It is known that, with the introduction of high contents of mineral additions in the concrete mixtures, the lower cement contents allied to the pozzolanic reactions, reduce the CH content in the pore solution and, if its content reaches figures near its exhaustion (<0.5%), the carbonation speed will be higher and would be able to reach the rebar depassivation. Jepsen et al [12] say that if two concrete have different initial CH content, that one with the lower content will be more sensitive to carbonation, because its front will displace more rapidly. This signifies that the initial content of CH in concrete express a kind of potential carbonation. In the same direction, Thomas et al [13] declare that, although high fly-ash content in concrete is desirable for several applications, the existing code and standards limitations could not be sufficient to ensure long-range acceptable performance in some exposure conditions (mainly because of the carbonation risk).

Therefore, carbonation is a property that is not only related with low w/cm ratios or reduced water content per m³ of concrete but, also, with the alkaline reserve represented by the remaining CH content, in addition to other factors like cement type and content, mineral addition reactivity, etc. Depending on mineral addition type and content, the carbonation front will displace in the rebar direction, more or less rapidly according with the remaining CH quantity. In other words, what matters in the carbonation study is the rate (coefficient) in which neutralization occurs, in unit of time, and not only the depth measuring, in a given time. Consequently, the carbonation front displacement depends directly on the available calcium hydroxide, that is, the residual CH quantity in the pore solution that remains beyond the carbonation front.

To illustrate the above points of view, three case studies are presented. The first is a research project according to data showed by Malhotra [4] and Bilodeau and Malhotra [5]. Considering that both papers are parts of the same project, the results were unified in order to give more significance and increase the statistical correlation between time and carbonation depth. These ones were obtained from 102x203mm cores extracted from a 1.6x1.6x1.6m concrete block cured by 28 days and later under environmental conditions of 23ºC and 50% of relative humidity. The concrete mix proportion presented the following data: water = 95 l/m³, ASTM cement type I = 147 kg/m³, class F fly-ash = 187 kg/m³ (56%), total cementitious materials = 334 kg/m³, superplasticizer = 7.0 kg/m³ and w/cm ratio = 0.30. Table 6 shows the test ages and the measured carbonation depths.

At a first sight, it seems that the carbonation depth of 11.5mm at 13 years age, according Table 6, does not seem to be very high when this datum with absolute value is taken. However, it is observed that the carbonation advance from 4.75 to 7.5 years (2.75 years difference) was of only 1 mm, while that from 7.5 to 13 years (5.5

**Table 7 – Natural carbonation depths of mould specimens (Isaia et al (15))**

| Years | 0.5 | 1 | 2 | 4* |
|---|---|---|---|---|
| Carbonation depth: mm | 1.75 | 2.15 | 3.28 | 4.48 |

* Datum not presented in the paper

**Table 8 – Summary of the results of the three case studies**

| | Case Study 1 Malhotra (4), Bilodeau (5) | Case Study 2 * Isaia et al (15) | Case Study 3 * Isaia (16) |
|---|---|---|---|
| Water/cementitious ratio | 0.30 | 0.37 / ***0.34*** | 0.33 / ***0.32*** |
| Portland cement – kg/m$^3$ | 147 | 287 / ***539*** | 271 / ***570*** |
| Fly-ash – kg/m$^3$ - (%) | 187 – (56) | 287 – (50) | 271 – (50) |
| Cementitious materials – kg/m$^3$ | 334 | 574 / ***539*** | 542 / ***570*** |
| Water – kg/m$^3$ | 95 | 168 / ***178*** | 178 / ***171*** |
| Carbonation coeff. – mm. year$^{-0.5}$ | 3.68 | 2.18 / ***0*** | 4.5 / ***0.4*** |
| Remaining CH – % | n. a. | 2.1 / ***4.9*** | 1.9 / ***11.1*** |
| Estimated time (years) to reach 20mm depth | 30 | 84 | 20 |

* The figures in ***bold-italic*** represent data from the reference concrete, without pozzolan. The case study 3 figures were obtained from accelerated tests, on contrary of cases studies 1 and 2.

years difference) was of 3.5 mm, evidencing carbonation acceleration with time elapse. Thus, the mere comparative analysis of the carbonation depths, do not provide precise idea on long-term concrete behavior.

One of the most utilized models to relate the carbonation evolution with time is the square root, that is,

$$x = kc\ .\ t^{0.5} \qquad \textbf{(eq. 1)}$$

being *x* the carbonation depth, *kc* the carbonation coefficient and *t* the exposure time to $CO_2$. The straight line angular coefficient kc is the variation measure of the carbonation depth with time, being referred as the rate or carbonation coefficient. According the authors' experience the equation (1) has given good results even for high mineral additions contents, such the ones of this investigation. Applying the linear regression between the depths (in mm) and year$^{0.5}$ to the data given in Table 6, the following equation is obtained:

$$x = 3.68.\text{year}^{0.5} - 1.68 \qquad (r^2 = 92\%) \qquad \textbf{(eq. 2)}$$

To this concrete the carbonation coefficient is 3.68 mm.year$^{0.5}$, that is, for a 100 years age the carbonation depth would be 36.8mm. The Brazilian Standard NBR 6118 [14] denotes 20 mm minimum cover to reinforce concrete slabs in interiors. To the concrete former described with its respective carbonation coefficient, the 20 mm depth would be reached in time $t = (20/3.68)^2 = 30$ years, when would be removed the rebar passivation layer creating conditions to possible corrosion.

The second case study is a paper by Isaia et al [15] that presents comparative study between concrete with mineral additions in natural and accelerated carbonation. For the 50% fly-ash mixture, content very close to the preceding study, the materials quantities were the following: cement = 287 kg/m$^3$, fly-ash = 287 kg/m$^3$ (total cementitious materials = 574 kg/m$^3$), water = 168 l/m$^3$, w/cm = 0.37, CH remaining content (91 days) = 2.1%. The natural carbonation was accomplished in 100x200mm specimens 7 days-cured followed by laboratory environmental curing. This paper shows the carbonation depths measured until 2 years age. Table 7 shows the data obtained including the last reading taken in 4 years (not presented in the paper of [15]).

For this concrete the carbonation coefficient is 2.18mm. year$^{-0.5}$, that is, for 20 mm cover the carbonation will reach the rebar in $(20/2.18)^2 = 84$ years. According to table 8, the reference concrete of the same investigation, without mineral additions, with w/cm ratio = 0.34, cement = 539 kg/m$^3$, water = 178 l/m$^3$ and CH = 4.9% (2.3 times higher than the 50% fly-ash concrete) presented null carbonation until 4 years of age. Notice that the decisive factor for the lower carbonation of the reference mixture is the higher calcium hydroxide content in the pore solution.

The third case study (Isaia, [16]), according to Table 8, presents the following data for the 50% fly-ash mixture: cement = 271 kg/m$^3$, fly-ash = 271 kg/m$^3$, total cementitious materials = 542 kg/m$^3$, water = 178 l/m$^3$, w/cm = 0.33, remaining CH content = 1.9%. Accelerated carbonation test was conducted in a climatic chamber with 10% of $CO_2$, 23ºC and 75% of relative humidity, in 100x200 mm mould specimens. The calculated carbonation coefficient was 4.5 mm.year$^{-0.5}$, that is, 45 mm depth in 100 years. For 20 mm cover, the carbonation front will reach to the rebar in $(20/4.5)^2 = 20$ years. The reference concrete with w/cm = 0.32 presented carbonation coefficient of 0.4 mm.year$^{-0.5}$ and 11,1% of remaining CH (5.8 times more than the fly-ash mixture content). It is observed that the reference mixture presented carbonation coefficient (4.5/0.4) = 11 times lower, for an increase of (11.1/1.9) = 6 times of the remaining CH. Table 8 resumes the results of the three case studies.

The analysis of Table 8 reveals that, to obtain low carbonation rate it is not necessary that the concrete have much reduced w/cm ratio or low water content per m³ of concrete. Comparing cases studies 1 and 2 it is observed that the second one has (168-95) = 73 l/m³ (+77%) in excess of water than the first one, although the carbonation coefficient of this be 41% lower, with w/cm 23% higher in relation to the first one.

Comparing case studies 1 and 3, the latter presents (178-95) = 83 l/m³ (+87%) in excess of water, w/cm ratio 10% higher and carbonation coefficient 22% more elevated. For the case study 3, conducted with accelerated carbonation in climatic chamber with 10% of $CO_2$, it must be considered that these test conditions are more aggressive than the natural carbonation, inducing generally to higher values due to the higher employed carbonation rates. According to Massazza [17] and Goñi et al [18], the accelerated carbonation modifies the $CO_2$ concentration in the pore solution increasing the reactions speed, becoming difficult the correlation generalization with the natural carbonation tests. This reason explain why the case study 3 presented kc higher than case 1, evidencing the care that must be taken when results between different test conditions are compared, such as accelerated and natural carbonation tests. In any case, Table 8 demonstrates that it is not mandatory to employ reduced total water per m³ to obtain low carbonation values.

## *3.2 Carbonation versus w/cm ratio*

As seen, there are two ways to reduce the HPC carbonation coefficient: a) to decrease the w/cm ratio to restrain the $CO_2$ flow in the capillary pores and, b) increase the remaining CH content in the pores to reduce the speed of the carbonation front displacement. There must be a balance between these two parameters for HPC with very high mineral additions content. In fact, Isaia et al [15] show that for the 70 MPa strength level, the mixtures with high rice husk ash content (50%) presented w/cm ratio = 0.41, higher than to those with fly-ash, w/cm = 0.30. However, for the first ones, the carbonation rates were higher in the accelerated tests showing that the CH content decrease in the more reactive pozzolanic mixtures, rice husk ash, prevailed upon the w/cm ratios decrease. This result shows that analyzing carbonation only from the w/cm ratio point of view, can lead to false appraisals because what predominates in the carbonation advance, in these cases, mainly when the mineral addition is very reactive, is the CH balance in the interstitial pores, after the pozzolanic reactions.

The preceding statement shows that when high mineral additions content are utilized in concrete, mainly of those more reactive, when low carbonation coefficients are desired, w/cm ratio decrease alone is not sufficient because of the remaining CH rate in the pores is low, near exhaustion, because of its consumption by pozzolanic reactions.

It is known that carbonation depends on two processes: the physical, governed by the pore structure that controls the $CO_2$ diffusion and the chemical, consequence of the reaction between the $CO_2$ and existing CH in the pore solution. For a given environmental condition and pores structure, this latter reaction depends of the available CH content and, consequently, more rapidly the carbonation will occur. Table 8 demonstrates this point of view because all reference concrete, without mineral additions, with w/cm ratios between 0.32 and 0.34 presented negligible carbonation coefficient, while the remaining CH content was 2.3 times for case 2 and 5.8 times higher in case 3, in relation to the respective concrete with 50% of fly-ash.

Other implication derived from w/cm ratio reduction and related with the pore structure is the lower existing space to form C-S-H (lower combined water content and higher non-hydrated cement content) and, consequently, lower CH quantity in the pore solution. Chaussadent et al [19] explain these mechanisms: *"SEM examinations and EDX analysis show that, for an equivalent degree of hydration, the calcium hydroxide amount increases and that the CaO/$SiO_2$ ratio of the C-S-H decreases as the W/C increases (p. 523)… The analysis of the results shows that W/C has a significant influence on the cement hydration and on the hardened cement paste structure. Moreover, some compounds like calcium hydroxide, which play an important role in the durability of cementitious materials and in particular with respect to the carbonation, are distributed differently according to the W/C (p. 528)…It can be also considered that the age of the cement paste has practically no influence but that the lower the W/C, the higher the value of 'calcium hydroxide surface area'. This surface area is, for example, 10 times larger for W/C decreasing from 0.60 to 0.25. This result would mean that material with low W/C could be carbonated faster. Actually, some other parameters must be taken into account, such as cementitious material permeability to carbon dioxide, accessibility of the carbon dioxide to calcium hydroxide and presence of other carbonatable compounds (p. 529)".*

It is known also that carbonation modifies the paste pore structure. Distler et al [20] investigated the pore structure development for cement mixtures with 60% of slag, 20% of fly-ash, (20+20)% of slag and fly-ash and 40% of natural fly-ash. They conclude that: *"Carbonation in turn also affects the porosity and pore structure of the paste, and for cement with a high clinker content the pore volume accessible to mercury penetration is reduced … For 4 different cements, that also the distribution of the pore sizes in this range is affected and, for some system (*cementing materials – NA*), coarser pores develop on carbonation, even though the total volume intruded may reduce. These coarser pores may increase the perviousness (*permeability – NA*) of the paste… For cements with high clinker content a reduction in pore volume as well as in the size of pores had been observed due to the deposition of calcium carbonates, whereas cement with low clinker content exhibited a coarsening of the pore structure (p.434)".*

The last two citations allow to conclude that:

- the lower the w/cm ratio, the lower the combined water and CH content;
- in the case of cement substitution by high mineral additions content (50% or more) due to the lower cement content, the remaining CH content is even lower;

Table 9 – Results of the mixtures with fly-ash and reference for w/cm = 0.35 (Isaia and Gastaldini (6))

| | 50% FA Mix F (without lime) | 50% FA Mix FL (with lime) | Reference |
|---|---|---|---|
| w/cm ratio | 0.35 | 0.35 | 0.35 |
| Portland cement – kg/m³ | 270 | 270 | 540 |
| Fly-ash – kg/m³ | 270 | 270 | - |
| Cementitious materials – kg/m³ | 540 | 540 | 540 |
| Water – kg/m³ | 184 | 170 | 189 |
| Carbonation coefficient – mm.year$^{-0.5}$ | 3.95 | 1.39 | 0.10 |
| Remaining calcium hydroxide – % | 0.47 | 0.34 | 3.0 |
| Estimated time (years) to reach 20mm depth | 26 | 207 | 40,000 |

- the lower the w/cm ratio, the higher is the calcium hydroxide surface area and, simultaneously with the lower content of this in the cementitious paste, may result in higher carbonation rate;
- the concrete carbonation with low clinker content shows coarser pore structure what increase the permeability of the cover layer;
- the latter processes show that decreasing the w/cm ratio to overcome carbonation is not always an adequate measure. In fact, the physical action of porosity decrease is accompanied by chemical action of CH reduction and specific surface increase of this, factors that lead to an increase in the carbonation rate;
- in order that the w/cm ratio decrease to be effective on carbonation, it is necessary to examine other parameters as a whole such as type, quantity and fineness of the mineral addition as well as the mix proportion, desired level for the compressive strength, cover layer thickness, specified useful life, etc.;
- the w/cm ratio decrease has a limit given by the characteristics of the component materials of the mixture, in order not to increase too much the cementitious materials content in the paste and/or the superplasticizer content to supply the desired or specified workability for a given application. The admixture content is relevant because it is one of the most expensive components of the mixture and, according to its quantity, may invalidate the low cost advantage and sustainability of the cement substitution by high content of mineral additions.

## 3.3 Hydrate lime addition

### 3.3.1 Carbonation effects

For sustainability reasons, the present guideline is introduce in structural concrete the higher possible quantity of mineral additions in order to decrease the cement consumption, the consumed energy, the emanation of pollutant gases and, overall, the cost reduction (Isaia and Gastaldini [21]). To reach this objective and solve the inherent problem to carbonation of these mixtures with very low Portland cement content, the better and cheaper solution is to introduce external calcium hydroxide to these mixtures to replace the non-formed CH by the cement that was substituted by the mineral additions. With this strategy, the alkaline reserve of the cementitious paste is increased and the carbonation front progress is delayed.

Hydrated lime is already utilized as an activator in the cement-slag mixtures to accelerate concrete strength. Mira, Papadakis and Tsimas [22] presented a paper that studied the addition effect of the hydrated lime to improve the mechanical properties and concrete durability. They studied different types of cement, such as Portland, pozzolanic cement and Portland cement with 20% of fly-ash addition. The authors conclude that: *"The lime putty addition in concrete improves the compressive strength development when pozzolanic materials are used in parallel (p.687)… When lime putty is added in concrete that contains pozzolanic materials, a significant improvement in durability is observed. A denser structure is created, which is responsible for the lower degree of concrete carbonation and corrosion of reinforcement due to chloride attack. Thus, an extended concrete service life is expected. The above results are positive for the usage of hydrated lime as an admixture in concrete, when pozzolanic materials are also incorporated in the concrete mixture (p.689)".*

The paper by Isaia and Gastaldini [6] presents experience similar to that of the above authors. Table 1 shows, for the 55 MPa strength level, the 70% slag mixture with 15% of lime (SL, w/cm = 0.37) showed kc = 0.97 mm.year$^{-0.5}$ and the 70% slag one with 18% of lime (FSL, w/cm = 0.32), kc = 1.42 mm.year$^{-0.5}$. The carbonation coefficients were 16% and 53% lower for the mixtures with lime (SL and FSL), in relation to that without lime (F and S). These two mixtures with lime presented the lower carbonation coefficients as well as the lowest cement consumption, respectively, 151 and 57 kg/m³.

To compare the data of the above research with the case studies of the Table 8, Table 9 shows the mixtures with

50% of fly-ash, with and without lime and the reference concrete, for w/cm = 0.35, value very close to that presented in those studies. These data are not presented in that paper because the discussion was on 55 MPa equality compressive strength and not on w/cm ratio equality.

The mixture F with 50% of fly-ash without lime presented kc = 3.95 mm.year$^{-0.5}$ and, with lime, kc = 1.39 mm.year$^{-0.5}$, representing drop of 2.8 times in the carbonation rate. Comparing with the case study 1 (Malhotra [4]; Bilodeau and Malhotra [5] whose concretes exhibited w/cm = 0.30, water = 95 l/m³ (-94%) and kc = 3.68m.year$^{-0.5}$ (-7%) and 30 years to reach 20 mm depth; with the 50% fly-ash mixture without lime, this one presented w/cm ratio 17% higher, 89 l/m³ (+94%) more of water and kc only 7% higher and time to reach 20mm depth of 26 year (13% higher).

With the addition of 15% of hydrated lime, in substitution to sand in the mixture proportion, the FL mixture with 50% of fly-ash, with the same ratio of w/cm = 0.35, the carbonation coefficient decreased to 1.39 mm.year$^{-0.5}$, that is, 2.65 times below of the case study 1, with time of 207 years (6.9 times higher) to reach the same 20 mm depth. These figures justify the hydrate lime addition to concrete because such decrease of the carbonation rate would not be possible only by the w/cm ratio decrease. One of the reasons that explain such behavior of the lime action is not only the increasing of the remaining CH content but, also, the increase of the compressive strength, for the same w/cm ratio. For the 50% fly-ash mixture, at the age of 91 days, the compressive strength was 59.1 MPa, while for the same mixture with hydrated lime was 78.6 MPa, a 19.5% increase.

For the reference concrete Table 9 shows that, practically for the same parameters of the mixtures with and without lime of the 50% fly-ash mixture, the carbonation coefficient was only 0.10 mm.year$^{-0.5}$ and CH content = 3.0%. This last number show that the increase of 3.0/0.47 = 6.4 times in the alkaline reserve in relation to the fly-ash mixture without lime, increased the time of 40,000/26 = 1538 times so that the carbonation reached the 20 mm depth.

On the other hand, Table 9 still shows that the 50% fly-ash mixture with 15% of lime presented 0.34% of remaining CH while the mixture without lime was more elevated, that is, 0.47%. This shows that CH contents below 0.5% in the interstitial pore solution are already considered as exhaustion and that, the extra lime addition, by external source, increases the CH consumption for the neutralization reactions and, as a consequence, decreases the speed of the carbonation displacement.

Thus, in view of the data and arguments presented above, the hydrated lime addition to concrete has undeniable advantages, confirming studies by Mira et al [16]. In fact, it is demonstrated that only the w/cm ratio decrease and the water unit content per m³ are not sufficient conditions, that is, by means of physical effects, to minimize the carbonation effects. For attainment of low carbonation coefficients, when great quantities of mineral additions are utilized, besides the latter condition, it is necessary also to increase the remaining CH content through external lime source, with the purpose of delaying the carbonation front displacement.

### 3.3.2 Lixiviation effects

Leaching is a degradation process of the cementitious paste compounds, especially the calcium hydroxide, because it is the more soluble one, by means of the aggressive substances attack, mainly acid solutions with pH lower to 6.5. Among the more usual substances that may attack concrete there is the carbonic acid, whose actions is describe by Neville [23]: *"A $CO_2$ concentration from 30 ppm to 60 ppm results in severe attack and, greater than 60 ppm, very severe attack. The attack progresses to a speed proportional to the square root of time, since the aggressive substance must pass through the residual layer of remaining low solubility products after the dissolution of $Ca(OH)_2$ ... Not all $CO_2$ is aggressive since part of it is necessary for forming and stabilizing calcium bicarbonate in the solution (p. 504) … The use of composed cements, like granulated blast-furnace slag, pozzolans and, especially silica fume, it is beneficial for the reduction of the entrance of aggressive substances. The action of the pozzolans fixes $Ca(OH)_2$, which is usually the most vulnerable product of the cement hydration, with respect to the attack by acids. However, the performance of the concrete depends more on its quality that on the type of cement used. The resistance of the concrete to chemical attack is increased when dried before the exposure, but after an appropriate cure. Thus, a thin layer of calcium carbonate is formed (produced by the reaction of $CO_2$ with lime) obstructing the pores and reducing the permeability in the surface region (p 505)".*

This citation shows that lixiviation is a process similar to that of carbonation, with respect to its effects and, that this may decrease its deleterious action by reducing the mobility of the ions from the outside towards the inside due to the external carbonated layer. It is observed that the attack of these aggressive substances, especially pure or carbonated water, depends on the permeability to fluids of the covering layer of the concrete and, also, on the quantity of soluble alkalis contained in the cementitious paste although silicates can also be decomposed when the attack is very severe.

Some codes (NBR 6118 [14], CEB-FIP [1]) recommend the use of low w/cm ratio, generally, lower than 0.45 when the concrete is exposed to aggressive acid environments or, even, which are used, with preference, cements with blast-furnace slag or with pozzolans, and not common Portland cement, in order to reduce the calcium hydroxide content in the pore solution. In Table 1 it is observed that the w/cm ratios for the level of strength of 55 MPa, the mixtures with hydrated lime presented values between 0.44 for the FL mixture and 0.32 for the FSL, while the reference mixture was 0.46. All the mixtures with high contents of mineral additions had w/mc ratio below 0.45, complying with the requirements demanded by the codes for impermeable concrete and, then, less propitious for the diffusion of aggressive fluids by the covering layer.

Table 1 reveals also, for the 55 MPa strength level, the mixture with most elevated CH content is that of slag with addition of lime (CH = 1.90%), 2.8 times lower than the reference concrete (CH = 5.24%). These numbers attest that the reference concrete, with higher w/cm ratio (0.46) and CH content almost 3 times higher, is more susceptible to lixiviation that the concretes with 50% fly-ash, 70% slag or with tertiary mixtures of 90% slag and fly-ash and plus the addition of hydrated lime. The FL and FSL mixtures with CH content of 0.70% and 0.26%, respectively, possess alkaline reserve close to exhaustion presenting, therefore, lesser tendency to lixiviation than the mixture without the addition of lime.

Therefore, in HPC with very elevated contents of mineral additions (above 50%), especially pozzolanic ones, the application of external hydrated lime in sufficient contents in order to replace the alkaline reserve only due to the cement that was substituted by the mineral addition, besides not being harmful to the performance of the resistance and durability of the concrete, also results in lower lixiviation probability.

## 4 Conclusion

In this paper arguments and comparisons between research developed by the UFSM Concrete Studies and Researches Group (GEPECON) and other investigators related by the literature were presented. Regarding the consequences of very high mineral additions content on the carbonation of HPC, the following main conclusions related with mixture proportion and addition of hydrated lime are presented.

a) The comparison of the carbonation test results only by means of the carbonated depth, can lead to erroneous conclusion when it is desired compare the HPC durability with focus on the structure useful life;
b) In general, only the w/cm reduction it is not sufficient physical condition to obtain low HPC carbonation with very high mineral addition contents (close to the CH exhaustion);
c) to maintain the carbonation in low rates it is necessary, besides the latter condition and, also, the pore structure, to increase the remaining calcium hydroxide content, by means of internal or external sources, to delay the carbonation front displacement;
d) Care must be taken in comparison of the carbonation coefficients determined by means of accelerated and natural tests because in the firsts the higher $CO_2$ concentration can lead to the increase of the neutralization rate;
e) The hydrated lime addition as external source to reduce the carbonation coefficient improve the physical, mechanical and, in general, durability properties of concrete. Respect to durability issues, according Table 1, the mixtures with lime presented CH content from 2.8 to 20.2 times lower than the reference concrete what induces the reasoning that these mixtures with very high mineral addition content with lime are more durable respect to the former ones This conclusion is related to the scope of the investigation and can not be extrapolated to other durability variables, such as alkali-aggregate reactions or sulfate attack. Tests for these variables must be accomplished in order to obtain specific results;
f) Case study of research realized by GEPECON of UFSM shows that the addition of 15% of hydrated lime reduced the carbonation coefficient from 16% to 53%, in relation to the concrete without lime;
g) The alkaline reserve increment by lime addition does not contribute to possible leaching because this is consumed by pozzolanic and carbonation reactions, resulting in lower remaining CH content to the reference concrete, without lime addition.

The statements abovementioned show that, in HPC with very elevated contents of mineral additions (above 50%), especially pozzolanic ones, the use of external hydrated lime in sufficient contents in order to replace the alkaline reserve due to the cement that was substituted by the mineral addition, besides not being harmful to the strength performance and durability of the concrete, related to the investigation scope, also results in lower carbonation and lixiviation probability.

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