

# Carbonation resistance of high volume fly ash concrete

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**Abstract.** The cement industry is responsible for a large part of the global environmental problems: is the largest consumer of natural resources; the most responsible for the emission of greenhouse gases, including about 1.8 Gt of CO<sub>2</sub>; and requires huge amounts of energy, corresponding to between 12 and 15% of industrial energy use. The cement is also not used in the most appropriate manner, since 40% of the consumption of concrete is due to the renovation and repair of buildings, making concrete structures inefficient because its durability is relatively low. However, in the future, concrete can and should evolve in order to improve its eco-efficiency, with a smaller amount of cement in its composition, replacing it with high quantities of mineral additions, particularly fly ash. Nevertheless, current technology may not allow this type of concrete to be very efficient, because its long-term durability may be compromised. In fact, with increasing dosage of pozzolanic mineral additions, alkali paste components are consumed in the reaction leaving it vulnerable to concrete carbonation which may compromise the passivation layer needed for steel rebar protection against corrosion. This article explores a promising approach to mitigate this problem, which consists in the careful addition of hydrated lime in the concrete composition, highlighting the synergy of its components, significantly enhancing its carbonation resistance. It is proposed, therefore, to manufacture a concrete with high volume of fly ash, low cement content and high service life period: an efficient and sustainable concrete. In this context, an experimental campaign was developed with the aim of characterization of pastes behavior with high fly ash content, in particular with respect to its durability. The results will be presented and properly analyzed.

## Introduction

The corrosion of reinforcing steel embedded in concrete is one of the most serious forms of durability related problems, common in building structures [1-5]. Corrosion is the main vehicle for degradation of reinforced concrete structures and consequently negatively affects its lifetime [5-10]. Besides the damage caused to buildings, one must take into account and consider the additional economic costs of rehabilitation, and social and operational losses. If corrosion is not detected and treated, the concrete will be more exposed to aggressive agents, providing the appearance of more damage with consequent cyclic deterioration. In this circumstances its performance may be drastically reduced and, consequently, also its service lifetime [7]. Carbonation is precisely one of the most important sources of corrosion occurring in reinforcement steel of concrete structures [3, 5]. In a simplified form, that carbonation is a case of chemical attack in which the aggressive agents are the constituents of atmosphere gases, primarily carbon dioxide (CO<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S) [5, 11, 12]. These, usually diffuse in gaseous form into the pore solution of porous system, the cracks occurrence in the interfacial transition zone between cement paste and aggregate in concrete, neutralizing alkaline compounds, resulting in a decrease of pH to less than nine, thus widely destroying the passive protection layer and causing corrosion [4, 13-16] (Fig. 1).

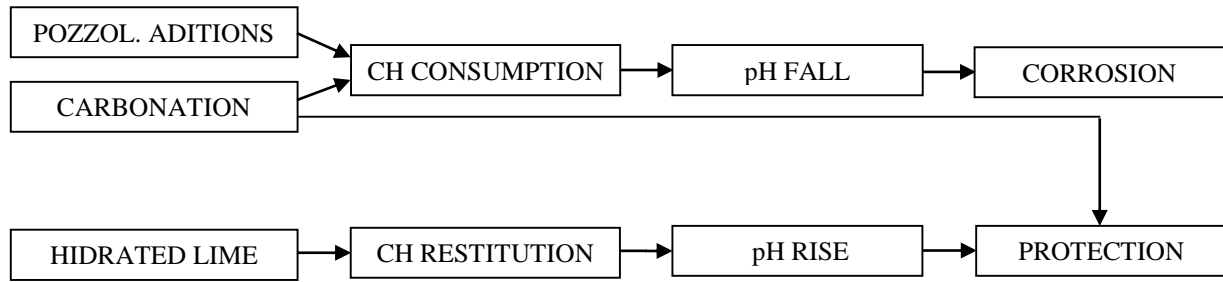


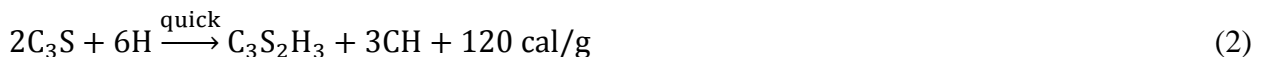
Fig. 1 – Carbonation in concrete containing high volumes of pozzolan addition

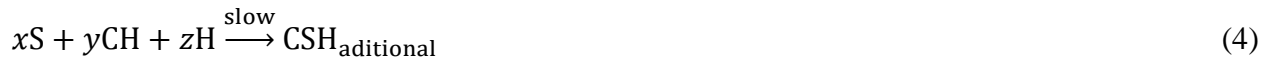
The primary alkaline compounds presented in the hydrated paste susceptible to react with carbon dioxide are the hydroxides of potassium, sodium and calcium (CH), being the last one the most important (Eq. 1). Therefore, this pathology is more susceptible in urban and industrial areas or places with high concentrations of carbon dioxide [17]. The main reaction of concrete carbonation can be expressed by Eq. 1, concerning calcium hydroxide (CH) from cement hydration, environment carbon dioxide ( $\bar{C}$ ) and resulting calcium carbonate ( $C\bar{C}$ ), described in their abbreviated forms.



However, the susceptibility to attack by external agents is also related to the quality of the concrete [18] and the concrete of the modern era may be more vulnerable than traditional one. The composition of the concrete has been suffering many technological advances, mainly since the first half of the twentieth century. One of the most important issues was its ability to incorporate mineral additions such as industrial by-products as cement replacement [19]. The production growing of certain mineral additions like fly ash, creates a problem of processing, storage and control of the environment, which call for more than a decade, finding an effective solution for their use [20]. Once concrete is the second most consumed material by man, exceeded only by water [19, 21, 22], it is, naturally, an attractive vehicle to incorporate high volumes of industrial by-products with technical, economic and environmental advantages [13, 19, 22-24], being a paradigm of sustainable development of the cement and concrete industry [25]. Nowadays, conventional concrete can be made with 20-40% of additions. Being even possible in very specific situations reach to 70% [26]. However, when using high volumes of pozzolanic additions as cement replacement, the phenomenon of carbonation is aggravated [27], and can jeopardize the advantages of using high volumes of mineral additions.

In the cement hydration, the first two hydrate compounds are tricalcium silicate (alite) and dicalcium silicate (belite) (Eq. 2 and 3): these compounds react with water to form calcium silicate hydrates (C-S-H) and portlandite (CH). The mechanical strength of the concrete is mainly due to the C-S-H. Derivatives of alite are responsible for early age strengths, and derivatives of belite for long term resistances [28]. CH represents about 20 to 25% of the volume of solids of the hydrated cement paste, does not participate in strength, has a negative influence on the chemical resistance attack [29], although conferring the necessary concrete alkalinity [21, 30]. In the presence of pozzolanic additions the consumption of CH in its pozzolanic reaction (Eq. 4) cause a decrease on the alkalinity of concrete. Thus, the susceptibility to carbonation increases [11] (Fig. 1) which in turn accelerates CH consumption, further worsening the process.





In this paper one proposes to add artificially the alkalinity which will be consumed by fly ash and by carbonation, incorporating commercial available hydrated lime (CH) in the initial composition. This technique appears to provide two advantages: more reagent for the production of pozzolanic reaction with additional silicates (increased strength and durability) and also higher alkalinity to maintain the passivation layer of steel rebars and provide additional protection against carbonation attack (Fig. 1).

## Experimental program

The experimental program has focused on the study of the mortar compositions presented in Table 1. The adopted reference mixture mix-design was determined in order to be equivalent to the mortar (particles less than 5 mm) contained in a self-compacting high performance concrete, made with 500 kg/m<sup>3</sup> of binder, 731 kg/m<sup>3</sup> of aggregate and water-binder ratio (W/B) of 0.25 [31].

For each concrete mixture three mortar mixes were performed with three different W/B and with 1.7% of superplasticizer (SP) (of the mass of the binder). The total mass of the binder (B) refers to the sum of the masses of the cement (C), fly ash (FA) and metakaolin (MTK). For mix-design purposes, hydrated lime (HL) was tacked into account as an aggregate, along with the sand (S).

After mixing, 40x40x160 mm<sup>3</sup> specimens were prepared for testing the accelerated carbonation of all compositions. After mixing and prior to casting workability was evaluated through flow table test [32]. The samples were kept in saturated lime water for curing during 38 days [33]. Subsequently, in the greenhouse, the specimens were subjected to an environment at 40 °C temperature for two days. Later, two opposite sides and the tops of the two specimens were sealed with paraffin, in order to put them in the climate carbonation chamber with 4 ± 0.5% CO<sub>2</sub>, 55 ± 5% RH and 20 ± 2 °C. The specimens remained in the carbonation chamber for 100 days, thereafter were broken and sprayed with thymolphthalein indicator (Fig. 2 (left)). Prismatic specimens of 40x40x160 mm<sup>3</sup> were also produced for capillary water absorption test, carried out in accordance with EN 1015-18 [33] and cubic samples with 50 mm edge for water absorption by immersion test (marked with \* in Table 1), carried out according with the specification LNEC E394 [34].

These tests were conducted on carbonated and on non-carbonated samples. So, half of these samples was also subjected to climate carbonation chamber for 100 days and the other half remained immersed in CH saturated water. Samples for capillary water absorption test were prepared for climate chamber covering with paraffin all sides except the fracture zone, the one that will be in contact with CO<sub>2</sub> (Fig. 2 (right)).

Fig. 2 – Specimens sealing with paraffin. Evaluation of carbonation (left) and capillarity (right)

The cement used was a CEM I 42.5R one (Outão, Secil), the aggregate was a commercial available river rolled sand 0/4 mm, and next-generation superplasticizer based on modified polycarboxylic ether chain was also used. Considering the importance of characterization of fly ash, a trial of X-ray diffraction (XRD) with a Bruker D8 Advance (Fig. 4) and X-ray fluorescence spectroscopy (XRF) was carried out with a ray equipment Philips X 'Unique II, in order to identify and quantify the reactive phase by Rietveld method. An electronic scanning microscope Hitachi SU1510 (SEM) was also used to evaluate the quality of fly ash, verifying that they are mainly composed by cenospheres particles, some of them (in a small percentage) trapped in carbon clusters (Fig. 3). In order to characterize the potential of CH contained in the hydrated lime and the amount of calcium carbonate present, simultaneous thermal analysis (STA, Netzsch 402 EP, heating rate of 10 °C /min) was adopted (Fig. 5), and simultaneously with the help of XRD analysis to determine the calcium carbonate crystallization process. The material characteristics are described in Table 2.

Table 1 – Tested compositions

Designation	W/B	Materials							
		B [kg/m <sup>3</sup> ]	C [kg/m <sup>3</sup> ]	FA [kg/m <sup>3</sup> ]	MTK [kg/m <sup>3</sup> ]	HL [kg/m <sup>3</sup> ]	S [kg/m <sup>3</sup> ]	W [kg/m <sup>3</sup> ]	SP [%L]
I 100C *	0.25	856	856	0	0	0	1252	214	1.70
	0.30	856	856	0	0	0	1141	257	1.70
	0.35	856	856	0	0	0	1029	300	1.70
II 50C+50FA *	0.25	856	428	428	0	0	1151	214	1.70
	0.30	856	428	428	0	0	1040	257	1.70
	0.35	856	428	428	0	0	928	300	1.70
III 50C+50FA+2.5HL	0.25	856	257	599	0	21.4	1126	214	1.70
	0.30	856	257	599	0	21.4	1015	257	1.70
	0.35	856	257	599	0	21.4	903	300	1.70
IV 50C+50FA+5HL	0.25	856	257	599	0	42.8	1101	214	1.70
	0.30	856	257	599	0	42.8	990	257	1.70
	0.35	856	257	599	0	42.8	878	300	1.70
V 50C+50FA+10HL	0.25	856	257	599	0	85.6	1051	214	1.70
	0.30	856	257	599	0	85.6	940	257	1.70
	0.35	856	257	599	0	85.6	828	300	1.70
VI 50C+50FA+15HL *	0.25	856	428	428	0	128	1002	214	1.70
	0.30	856	428	428	0	128	890	257	1.70
	0.35	856	428	428	0	128	779	300	1.70
VII 50C+50FA+20HL	0.25	856	257	599	0	171.2	952	214	1.70
	0.30	856	257	599	0	171.2	840	257	1.70
	0.35	856	257	599	0	171.2	728	300	1.70
VIII 50C+50FA+30HL *	0.25	856	428	428	0	257	852	214	1.70
	0.30	856	428	428	0	257	740	257	1.70
	0.35	856	428	428	0	257	628	300	1.70
IX 30C+70FA *	0.25	856	257	599	0	0	1111	214	1.70
	0.30	856	257	599	0	0	999	257	1.70
	0.35	856	257	599	0	0	887	300	1.70
X 30C+70FA+15HL *	0.25	856	257	599	0	128	961	214	1.70
	0.30	856	257	599	0	128	850	257	1.70
	0.35	856	257	599	0	128	738	300	1.70
XI 30C+70FA+30HL *	0.25	856	257	599	0	257	811	214	1.70
	0.30	856	257	599	0	257	700	257	1.70
	0.35	856	257	599	0	257	588	300	1.70
XII 50C+40FA+10MTK	0.25	856	428	342	86	0	1156	214	1.70
	0.30	856	428	342	86	0	1044	257	1.70
	0.35	856	428	342	86	0	933	300	1.70
XIII 40C+55FA+5MTK	0.25	856	342	471	43	0	1133	214	1.70
XIV 40C+50FA+10MTK	0.25	856	342	428	86	0	1136	214	1.70
	0.30	856	342	428	86	0	1024	257	1.70
	0.35	856	342	428	86	0	912	300	1.70
XV 50C+40FA+10MTK+10HL	0.25	856	428	342	86	85.6	1056	214	1.70
	0.30	856	428	342	86	85.6	944	257	1.70
	0.35	856	428	342	86	85.6	833	300	1.70

Fig. 3 – SEM fly ash images

Fig. 4 – XRD fly ash spectrum

Fig. 5 – STA hydrated lime results

Table 2 - Materials characteristics

	C	FA		HL	MTK	
<i>Chemical properties [%]</i>	[35]	<i>XRF</i>	<i>MEV</i>	<i>XRD</i>	<i>STA/XRD</i> [36]	[37, 38]
SiO <sub>2</sub>	18.27	49.12	56.83	28.7 vitreous*	< 0.4 [36]	47.0
Al <sub>2</sub> O <sub>3</sub>	4.75	27.30	28.59	22.1 vitreous*	< 0.5 [36]	37.1
Fe <sub>2</sub> O <sub>3</sub>	3.23	8.19	6.86	4.8 vitreous*	< 0.08 [36]	1.3
CaO	63.94	2.36	1.80			0.1
CaO free	1.39					
MgO	1.31	1.42			< 0.85 [36]	0.15
SO <sub>3</sub>	3.05	1.30				
K <sub>2</sub> O	0.57	3.34	1.97			2
Na <sub>2</sub> O		0.99	1.78			0.2
TiO <sub>2</sub>		2.32				0.3
Cl <sup>-</sup>	0.09					
Other				15.4 vitreous*		
Carbon			3.65			
Loss on ignition	2.72	3.97				12.75
Insoluble residue	0.74					
<i>Physical properties</i>						
<i>Specific gravity</i> [kg/m <sup>3</sup> ]	3100		2420		< 0.08 [36]	2590
Blaine [cm <sup>2</sup> /g]	4315					
<i>Mineralogical properties [%]</i>						
Quartz				18.41		
Mullite				7.18		
Hematite				3.41		
Total crystalline phase *				29.00		
Total glassy phase				71.00		
Portlandite					75.8	
Calcite					22.6	
* Rietveld method						

The analysis of Fig. 4 and Table 2, show that the major crystalline phases of the fly ash are quartz, mullite and hematite. Apart these phases we can see that there is a significant amount of glassy phase which is estimated around 71% (28.7 + 22.1 + 15.4 + 4.8), with a carbon content of 3.65%, indicating a reasonable reactivity of the used fly ash. Due the fly ash fineness it is also expected some important influence of filler effect [27]. The observation of Fig. 5 for the hydrated lime showed the presence of some free water identified in the initial temperatures (peak A), the decomposition of portlandite between 410 and 620 °C (peak B) and the decomposition of calcium carbonate between 620 °C and 965 °C (peak C).

## Analysis of results

### Workability

The flow test obtained results are presents in Fig. 7. According to this figure analysis, some mixes didn't show adequate workability or present segregation (IX-c) and were therefore rejected. It became apparent that the addition of fly ash increases the workability while the addition of lime decreases it. This workability loss is such that it was impossible to manufacture a mixture of 50% fly ash with

15% hydrated lime (composition VI-a). This is indicative that higher quantities of hydrated lime addition can improve the workability problems occurrence.

Fig. 6: Flow-test results

### **Electrical resistivity**

The electrical resistivity was determined and the obtained results are presented in Fig. 7. Each result corresponds to the average value for measurements in 4 major faces of the specimens 40x40x160 mm<sup>3</sup>. One resistivity meter at 38 mm spacing between probes was used. According to the results (Fig. 7), the use of additions increased the electrical resistivity, especially in mixtures containing metakaolin and in the ternary mixtures made with 50% fly ash and lime in moderate amounts (up to 10% inclusive). This might be due to the greater compactness of the mixtures in the presence of the additions which may result in a greater difficulty of the aggressive agent to diffuse, thereby increasing its durability when compared with the reference, produced without any addition.

Fig. 7: Electrical resistivity results at 40 days

### **Carbonation**

The obtained results presented in Fig. 8 shown that the depth of carbonation was higher in mixtures containing mineral additions, especially fly ash. This may result as a consequence of the consumption of CH in the pozzolanic reaction. Generally, the incorporation of hydrated lime leads to lower carbonation depths. This effect was more pronounced up to moderate amounts (up to 10%) of CH and low W/B ratio. This may be due to the fact that the vitreous silica of the fly ash could not react with all the available lime, so that the surplus of lime even though it contributes to the maintenance of the pH did not contribute to the production of additional CHS and consequent densification of the matrix.

The carbonation results shown that the use of metakaolin together with fly ash was not so effective, probably because they consumed even more CH or because the increased density of the matrix due to the use of metakaolin was not enough to avoid the diffusion of CO<sub>2</sub>.

Fig. 8: Carbonation depth

### **Water absorption by immersion and by capillarity**

The water absorption by immersion test results allowed evaluating the open porosity and are presented in Fig. 9. The test of water absorption by capillary action made allowed the possibility to quantify the coefficient of capillary absorption, determined using the of least squares method, considering only the results obtained at 10 and 90 minutes of testing (Fig. 10). This index refers to the ratio between the mass of water absorbed per unit area as a function of square root of time.

As can be seen, both the open porosity and capillary absorption coefficient increased with the use of additions. The use of additions changes the pores dimension and its quantity and may lead to an increase of the micropores and a decrease of the macropores [11], which may explain the increase in the coefficient of capillary absorption. Furthermore, the presence of a large amount of fines particles, without pozzolanic reactivity, could also increase the coefficient of capillary absorption [39], which is congruent with the apparent low reactivity of the used fly ash. The total porosity tends to increase with the additions, because the main responsibility for the reduction of the voids of the matrix comes from the cement hydration [27]. The hydrated lime and fly ash will probably have more responsibility in the pores refining.

Fig. 9: Water absorption by immersion (open porosity)

Fig. 10: Water absorption by capillarity

In the carbonated specimens (with or without additions) the open porosity was lower, having an inverse pattern in the coefficient of capillary absorption. Since the density of calcium carbonate is higher than the CH, can give an increase in the solid phase, which according Younsi [13] can go from 3 to 19%. On the other hand, if there is no space in the matrix to accommodate this increase, this may lead to microcracking [40], which could explain the increased coefficient of capillary absorption. The increase of micropores also can consistently explain the increase in the capillary coefficient absorption with the carbonation because there are higher pores amount and with smaller radius.

The kinetics of capillary absorption over time is expressed in Fig. 11. For compositions (I, II, VIII, IX and XI) it was characterized by a large difference between the non-carbonated and the carbonated specimens. These last ones showed higher values. One exception was detected for composition with 50% fly ash and 15% of lime (VI) whose difference was very slight (Fig. 11). This may be due to a more compact array supplied for the lime, thereby restricting the creation of carbonation products. Knowing that the capillary absorption coefficient can be strongly influenced by fracture zones, especially at the interfacial transition zone [39], the healing process in this zone by carbonation, mainly in the presence of available portlandite, could also explain this result: the increased capillary absorption coefficient due to the decrease of the radius of the pores but, at the same time, there has been an increased formation of additional C-S-H which blocked the capillary network.

Fig. 11: Kinetics of capillary absorption over time

## Conclusion

The incorporation of hydrated lime can be a promising tool with potential to develop strength to carbonation of concrete with high volume of fly ash and therefore assure the production of eco-efficient and durable concrete. Although the chemical composition is similar to the CH resulting from cement hydration, the “artificial” incorporation of commercially available CH changes the reaction kinetics, mainly because a large amount of reagents is present from the beginning of the reaction and not throughout its maturity (Eq. 2 to 4). The best results was obtained for lowers amounts of hydrated lime, up to 10%. This small amount may be related to the quality of the fly ash, particularly the amount of its amorphous silica content. Another possible explanation could be given for the best synergy achieved because large amounts of CH allow the pH increase, maintain active the passivation layer of steel bars reinforcement and provide corrosion protection. On the other hand, if the concentration of CH added in the beginning of the mixing is too high, this excessive presence can be harmful, since the portlandite not converted into additional C-S-H will be subject to deleterious effects [29]. Future work should develop a methodology that allows associating the amount and type of fly ash with an optimal amount of hydrated lime to add at the beginning of the mixture process. Further studies should focus on concrete mixtures of high performance ( $W/B \leq 0.40$ ), with a high volume of additions, but with a maximum amount of binder up to  $350 \text{ kg/m}^3$ .

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