

## **CALCIUM HYDROXIDE CURING FOR ACCELERATED CARBONATION TESTING OF HIGH VOLUME FLY ASH CEMENTITIOUS BLENDS**

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**Abstract.** During wet curing, the alkali concrete compounds, such as calcium hydroxide, can be leached out to the curing solution, due to the pH gradient between concrete and curing solution. In the presence of high volume fly ash cementitious blends, there is a decrease in concrete pH that may further magnify the problem. In this context it was carried out a research in mortars with an original composition of high volume fly ash and calcium hydroxide. These were exposed to water curing and water saturated with calcium hydroxide curing. The results show that the introduction of calcium hydroxide in the curing solution, provides a slightly enhancement of carbonation resistance. Based on the obtained results, the incorporation of calcium hydroxide in the initial composition seems to be useful to develop extra strength to carbonation of high volume of fly ash concrete.

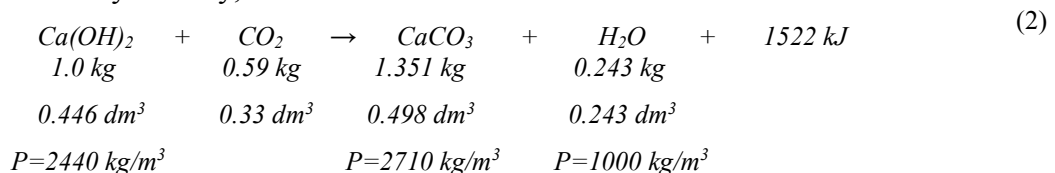
### **1 INTRODUCTION**

Lime is one of the oldest building materials [1], whose first known uses in mortar, date back to the Palaeolithic Age in the Fire Age [2]. Some of known ways of using lime refer to the Neolithic period: lime fragments were found in Nevalı Çori, in eastern Turkey, referring to 8.000-10.000 B.C.; the oldest mortar made with just lime are in Jericho, Palestine, dating

from 7.000 B.C.; the first uses of hydrated lime in the construction are in the city of Catal Huyuk, South Anatolia, Turkey, dated 6.000 B.C.; and knows the use of lime in stabilization of soils on construction of Shersi pyramid in Tibet, dated 5.000 BC [1-3]. Until the Nineteenth Century, the air lime was the most widely used material as a binder. Was replaced by hydraulic lime and later by the cement. Today, with less expression is used for rehabilitation of old buildings [1, 4]. More recently, mainly in the last decade, the use of hydrated lime with cement has also been declining due to increased use of superplasticizers [5]. Today, knowing that there are large environmental problems connected with the cement industry [6-8], we can use lime to take advantage of some of its properties, reducing the use of cement in the concrete at the same time we add added value on its properties [9].

In this study, we intend to make mortars with cement, high volume of fly ash and hydrated lime. Fly ash, when applied in high volume, have many environmental advantages, but tend to dramatically lower the mechanical and carbonation resistance. Furthermore it is intended to add to hydrated lime on initial mixture and in the curing solution.

Hydrated lime is a dry powder, too thin, obtained from quicklime, consisting essentially of calcium hydroxide, magnesium hydroxide, or both. It is a very versatile material with wide range of applications [3, 5, 9], such construction, treatment, water retainer, asphalt additives, disinfectant, chemical stabilization of soils, fertilizers, etc. Used in concretes and mortars, could increases the yield of the mixtures reducing cement consumption, increase mechanical strength, increase workability, liquids penetration resistance, elasticity, water retention or better surface finish [1, 3, 5, 9-11]. Besides, The lime provides increased mechanical strength due 3 mechanism [10]: carbonation, pozzolanic reactions, and increased solubility of the siliceous materials of the mixture. At least, another advantage may be found in the literature: carbonation reaction is in accordance with Eqn. (1) [4]. It can be seen that the resulting calcium carbonate product shows a mass superior to 21%. In addition, his volume increased 12% [4]. So, it is expected a reduction of voids [1, 4]. For these reasons, it is expected that the use of hydrated lime, increase the density of the matrix, the mechanical strength and durability. Finally, create a functional and sustainable material



## 2 EXPERIMENTAL PROGRAM

As a starting point for this research, it was considered the equivalent mortar composition of a self-compacting concrete with 500 kg/m<sup>3</sup> of cement (C), 731 kg/m<sup>3</sup> of aggregate (S) and water-binder ratio (W/B) of 0.25 [12]. Forty five mortar samples were produced by keeping previous that proportion for three distinct groups: cement (C); cement replaced by 50 and 70% of fly ash (FA) by mass of binder (B=C+FA); cement replaced by 50 and 70% fly ash by mass of binder plus hydrated lime (HL) as an aggregate replacement. Besides, three W/B ratio were performed: 0.25, 0.30 and 0.35. Superplasticizer (SP) was used in all mixtures, by 1.70% by mass of the binder. Details of these composition are in Table 1.



**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> ]	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	1252	214	1.7
	0.30	856	856	0	0	1141	257	1.7
	0.35	856	856	0	0	1029	300	1.7
II 50C+50FA	0.25	856	428	428	0	1151	214	1.7
	0.30	856	428	428	0	1040	257	1.7
	0.35	856	428	428	0	928	300	1.7
III 50C+50FA+2.5HL	0.25	856	257	599	21.4	1126	214	1.7
	0.30	856	257	599	21.4	1015	257	1.7
	0.35	856	257	599	21.4	903	300	1.7
IV 50C+50FA+5HL	0.25	856	257	599	42.8	1101	214	1.7
	0.30	856	257	599	42.8	990	257	1.7
	0.35	856	257	599	42.8	878	300	1.7
V 50C+50FA+10HL	0.25	856	257	599	85.6	1051	214	1.7
	0.30	856	257	599	85.6	940	257	1.7
	0.35	856	257	599	85.6	828	300	1.7
VI 50C+50FA+15HL	(0.25)	856	428	428	128	1002	214	1.7
	0.30	856	428	428	128	890	257	1.7
	0.35	856	428	428	128	779	300	1.7
VII 50C+50FA+20HL	(0.25)	856	257	599	171.2	952	214	1.7
	0.30	856	257	599	171.2	840	257	1.7
	0.35	856	257	599	171.2	728	300	1.7
VIII 50C+50FA+30HL	(0.25)	856	428	428	257	852	214	1.7
	0.30	856	428	428	257	740	257	1.7
	0.35	856	428	428	257	628	300	1.7
IX 30C+70FA	0.25	856	257	599	0	1111	214	1.7
	0.30	856	257	599	0	999	257	1.7
	0.35	856	257	599	0	887	300	1.7
X 30C+70FA+15HL	0.25	856	257	599	128	961	214	1.7
	0.30	856	257	599	128	850	257	1.7
	0.35	856	257	599	128	738	300	1.7
XI 30C+70FA+30HL	(0.25)	856	257	599	257	811	214	1.7
	0.30	856	257	599	257	700	257	1.7
	(0.35)	856	257	599	257	588	300	1.7

(W/B) was not possible to produce, due to its low workability

After mixing and prior to casting, was evaluated the workability by flow table test [13]. They were produced four samples with 40x40x160 mm<sup>3</sup> for each mixture. 24 hours after mixing, the samples were demoulded [14], and subjected to two kind of curing until 38 days of age: two samples in wet curing immersed in water (H); two samples in water saturated with calcium hydroxide curing (CH). After, these samples were subjected at 40 °C for 2 days in an oven. Then, all the samples were prepared for the carbonation test, and four opposing surfaces were sealed with paraffin and stored in a carbonation chamber with  $4 \pm 0.5\%$  CO<sub>2</sub>,  $55 \pm 5\%$  RH and  $20 \pm 2$  °C [15]. After 100 days of testing, they were measured the carbonation depth in two samples, one for each type of curing: a cross-sections were taken, to measure the carbonation depth, using thymolphthalein acid-base indicator. The faces broken were divided

into equidistant parts, so, the carbonation depth of each mixture, was the arithmetic average of 10 measured points.

**Table 2:** materials characteristics

	<i>C</i> <i>I 42.5 R</i>		<i>FA</i> <i>Pego</i>		<i>HL</i> <i>Calcidrata</i>
<i>Chemical properties [%]</i>	[19]	<i>XRF</i>	<i>MEV</i>	<i>XRD</i>	<i>STA/XRD</i> [16]
SiO <sub>2</sub>	18.27	49.12	56.83	28.7 vitr.*	<0.4 [16]
Al <sub>2</sub> O <sub>3</sub>	4.75	27.30	28.59	22.1 vitr.*	<0.5 [16]
Fe <sub>2</sub> O <sub>3</sub>	3.23	8.19	6.86	4.8 vitr.*	<0.08 [16]
CaO	63.94	2.36	1.80		
CaO free	1.39				
MgO	1.31	1.42			<0.85 [16]
SO <sub>3</sub>	3.05	1.30			
K <sub>2</sub> O	0.57	3.34	1.97		
Na <sub>2</sub> O		0.99	1.78		
TiO <sub>2</sub>		2.32			
Cl <sup>-</sup>	0.09				
Other				15.4 vitr.*	
Carbon			3.65		
Loss on ignition	2.72	3.97			
Insoluble residue	0.74				
<i>Physical properties</i>					
D10 (laser an.) [%]	1.33		1.53		1.36
D50 (laser an.) [%]	9.30		8.55		3.80
D90 (laser an.) [%]	24.16		20.19		7.73
Sp. gravity [kg/m <sup>3</sup> ]	3100	2420			2240
Blaine [cm <sup>2</sup> /g]	4315				
<i>Mineralogical properties [%]</i>					
Quartz				18.4	
Mullite				7.2	
Hematite				3.4	
Total crystalline phase *				29.0	
Total glassy phase				71.0	
Portlandite					75.8
Calcite					22.6
* vitreous phase by Rietveld method					

The materials used were: cement type I 42.5R from the Outão production center of Secil; fly ash from Portuguese Pego thermoelectric power plant, hydrated lime type class 1, grade A, type 1, from Calcidrata [16]; superplasticizer based on modified polycarboxylic, reference BASF Glenium Sky 617; river rolled sand 0/4 mm. The particles of materials were analysed by laser analysis which, whose results are reflected in Table 1 (physical properties). It was

observed that the cement and fly ash had a similar particle size and hydrated lime was the thinner material. Fly ash were analysed with x-ray diffraction (XRD) and x-ray fluorescence spectroscopy (XRF). Besides, the identification and quantification of reactive phase was carried out by Rietveld method. Simultaneous thermal analysis were also carried out for the hydrated lime, to confirm the lime purity. A scanning electron microscope Hitachi SU1510 (SEM) was used for evaluation fly ash and hydrated lime. It was found that: fly ash were cenospheres particles, some trapped within in carbon clusters. The hydrated lime consists mainly small particles, slightly clustered, without visible impurities (Figure 1). These trials were analysed according a previous study [17] and are reflected in the Table 2.

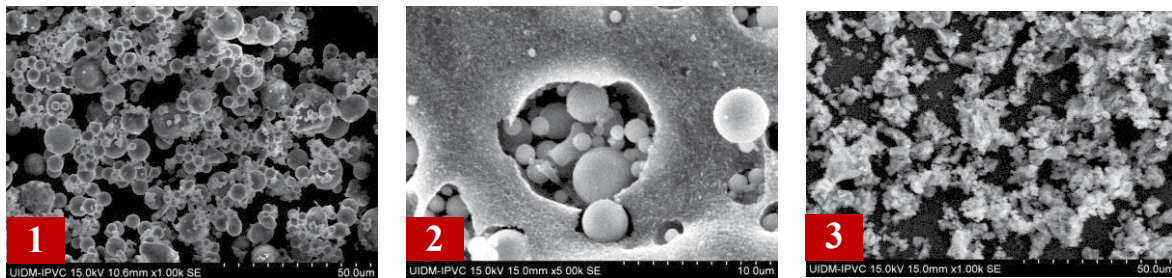


Figure 1: SEM images- 1-FA (x 1.0k); 2-FA (x 5.0k); 3-HL (x 1.0k)

### 3 RESULTS

#### 3.1 Workability

The flow test results varied between 134 to 345 mm, although some blends presented no valid results: segregation or no workability (Figure 2). It was found that the introduction of fly ash increases the workability, as it increases the volume of incorporation (II and IX). With 70% FA, this increase was very high, which led to the segregation of the mixture com  $w/b=0.35$  (IX-c). This is consistent with as expected, since the fly ash are finer than the cement, spherical and without gaps. Otherwise, the introduction of hydrated lime, continually reduced the workability and prevented the execution of some mixtures (VI-a, VII-a-VIII-a, XI-a-b).

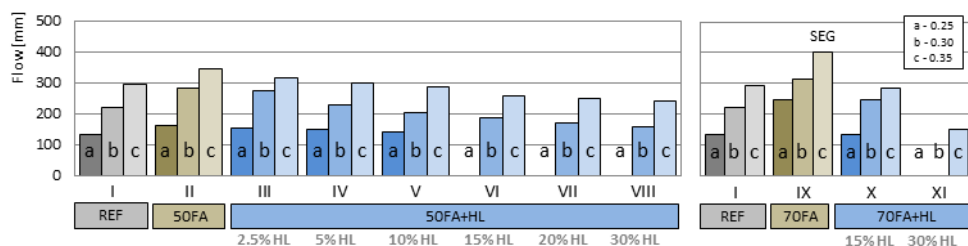


Figure 2: flow test

#### 3.2 Carbonation depth

The 100 days carbonation depth, for water curing samples is shown in Figure 3.

Carbonation depth was very high when the fly ash was used and it is further with the incorporation of more volume of this addition (II and IX). This is because the fly ash consume the calcium hydroxide released during the cement. It was observed that the hydrated lime may be able correct this problem, mainly with lower w/b ratio. In fact, it was found that the best results were between 2.5 to 10% hydrated lime additions. First, it was noted that increasing alkalinity is not enough by itself to reduce carbonation depth. On the other hand, addition further hydrated lime, may not find enough fly ash vitreous phase to react with calcium hydroxide. The worst results with higher w/b ratio may be due to the increased porosity of the matrix or leaching.

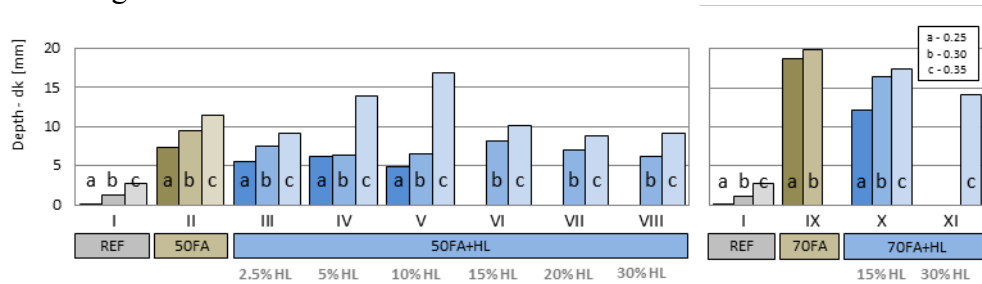


Figure 3: 100 days carbonation depth – water curing

To analyse the difference of the curing type, the relative carbonation depth ratio was calculated according Eqn. (2).

$$ratio = \frac{calcium\ hydroxide_{depth} - water_{depth}}{water_{depth}} \quad (2)$$

The Figure 4 shows the result of this ratio. It was noted that in general, the calcium hydroxide curing improve carbonation resistance. Most of the samples, had lower depths of carbonation. However, it was also observes that in mixtures with just fly ash, the results were modest (II-a,b and IX-a,b) or worse (II-c). This could mean that the calcium hydroxide curing does not offer great advantages for this type of mixtures. Moreover, the best results for mixing with hydrated lime, can be justified by the reduction in the alkali gradient between the samples and the curing solution, avoiding leaching compounds.

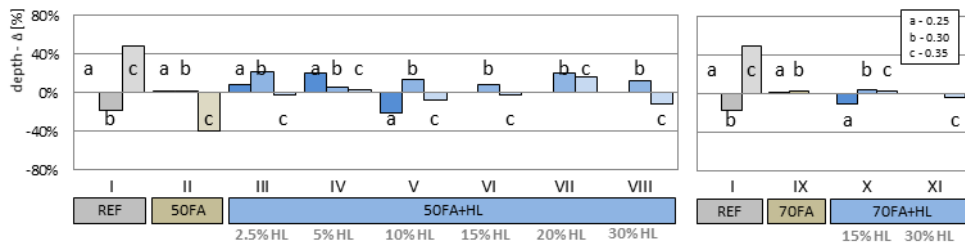


Figure 4: 100 days calcium hydroxide - water – depth curing ratio

### 3.3 Compressive strength

The 100 days carbonation compressive strength is shown in Figure 5. As expected, the binary mixtures with cement and fly ash, had less strength (II and IX). This is mainly due to the lower amount of available cement. The addition of hydrated lime had better results than the binary mixtures, mainly from 2.5 to 10% and low w/b ratio (III, IV and V). In fact, a consistent result with the carbonation depth. This may indicate that the best results in both resistance and carbonation was mainly due to an improvement in the matrix porosity. So, the alkalinity provided by lime, may not have had such a significant role.

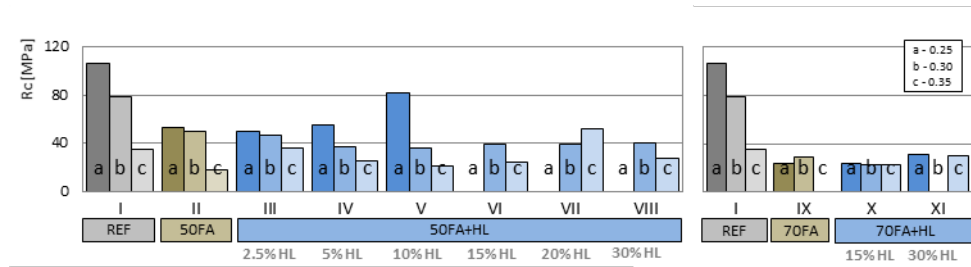


Figure 5: 100 days carbonation compressive strength

It also analysed the influence of calcium hydroxide curing according Eqn. (2). Through the Figure 6, it was suggested that the results were generally worse for calcium hydroxide curing samples. This result was different from the carbonation test. One hypothesis is that, the cure into calcium hydroxide may slow the rate of binder hydration. Other explanation, it occurred an increased porosity (reduces strength) at the same time as the alkalinity increases (decreases carbonation depth).

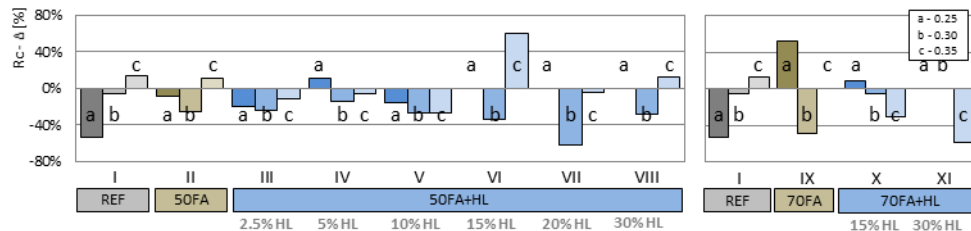


Figure 6: 100 days calcium hydroxide - water - Rc curing ratio

## 4 CONCLUSIONS

The results suggest that the use of high volumes of ash greatly reduces the strength and carbonation durability. The use of hydrated lime within the concrete composition may be a tool to mitigate these problems. The results suggest that for better results, the hydrated lime should be added until 10% binder. Also, such mixtures must be designed for low w/b ratio concretes or mortars. The curing results showed that the use of hydrated lime in the solution of curing, can increase carbonation durability, but the strength further worsens.

Additional studies will be needed to analyse the concrete microstructure changes, study the reaction products and his different characteristics.

## 5 ACKNOWLEDGEMENTS

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