

Effect of Carbonation in Mortars with Different Types of Metakaolin and Curing Procedures

Helena Carasek, Mônica E. Jungblut, Paulo M. Passos and Oswaldo Cascudo

PPG-GECON, Universidade Federal de Goiás-UFG, Av. Universitária, nº 1488, 74605-220-Goiânia, Brazil, hcarasek@ufg.br; monicaengel.j@hotmail.com; paulompengc@gmail.com and ocascudo@ufg.br

Abstract. *This study aimed to evaluate the influence of different types of metakaolin and curing conditions on mortars depth of carbonation. To do so, prismatic mortar specimens were produced by using three different 1:2 mix proportions (binder: sand): a reference mix proportion (without mineral addition) and two mixes with partial replacement of the cement by metakaolin, in the content of 10% by mass of cement. Two types of metakaolin with different characteristics were used in order to verify their capacity of changing the mortar microstructure and the pore solution, modifying this way the carbonation behavior of these materials. Three curing conditions for the test specimens were defined: no wet curing and wet curing (by immersion in water) for 3, 9 and 28 days. After the accelerated carbonation procedure in a CO₂ chamber (in an atmosphere of 10% of CO₂), with a relative humidity of 70% and a temperature of 20°C, for a period of 7 days, the carbonation depth was measured by using pH-indicators based on phenolphthalein and thymolphthalein. The results indicated influence of the type of curing in the carbonated depth and the significant interaction between curing and the type of metakaolin. When wet curing was not performed, the carbonation was more intense in the reference mortar. The effect of curing in the mortars with metakaolin was much less significant compared to that in the reference mortar. A global discussion about carbonation behavior of metakaolin modified mortars will be performed, based on the characteristics of the metakaolins.*

Keywords: Carbonation, Durability, Metakaolin, Curing Procedures, Mortar.

1 Introduction

The durability of structures fits into an important context for building performance, as well as sustainability and economy.

Among the phenomena responsible for the deterioration of reinforced concrete, there is the reinforcement steel corrosion due to carbonation or chloride attack. This pathological manifestation causes the most damage due to the technical difficulty of long-term recovery and to the cost involved (Castro *et al.*, 2008). Carbonation is a natural phenomenon that occurs by the chemical reaction between carbon dioxide, presents in the atmosphere, with cement hydration products, thus reducing the concrete pH. As a result of the phenomenon, the depassivation of reinforcement steel occurs, facilitating the onset of corrosion.

In this context, mineral additions play an important role in the improvement of concrete and mortars properties, regarding mechanical resistance and durability, since its use in concrete improves the interfacial transition zone, densifies the cement paste, refining pores and reducing their interconnectivity. On the other hand, when considering carbonation, additions can lead to a negative effect, namely: a reduction in the carbonation resistance of the concrete, due to the reduction of the "alkaline reserve" of the cementitious system. This effect is influenced by the type and content of mineral addition used, as well as by the water/binder ratio and curing

conditions (Cascudo; Carasek, 2011).

Several authors have studied the effect of mineral additions on durability parameters, such as porosity, permeability, carbonation, chloride attack and others (Hossain *et al.*, 2016; Papadakis, 2000; Lim; Mondal, 2015). Some authors report that the replacement of cement by metakaolin increases the carbonation depth (Meddah *et al.*, 2018; Fikhailenko *et al.*, 2018), whereas other researchers have observed smaller depths (Duan *et al.*, 2012, 2013; Rossignolo; Oliveira, 2006). So, there are still divergences in relation to the behavior of concrete or mortar modified with metakaolin, with regard to its performance against carbonation.

Thus, this work aims to analyze the influence of different metakaolins and curing conditions in the accelerated carbonation of mortars, trying to understand this behavior from the point of view of the characteristics of metakaolin. In addition, it was sought to analyze the relationship between the measurements of carbonated depth using two pH indicators: phenolphthalein and thymolphthalein based solutions.

2 Experimental

2.1 Materials



The mortars were produced with a washed riverbed quartz sand, with a fineness module of 1.65 and a maximum size of particles of 1.18 mm. The cement used was a Brazilian-type CP II F-40 portland cement, with a specific surface area of 4120 cm²/g and chemical characteristics according to Table 1. A polycarboxylic ether based superplasticizer admixture (density of 1.09 g/cm³ and solids content of 30%), water from public supply network, and two metakaolins derived from different deposits (Table 2) completed the constituent materials of the produced mortars. Brazilian-type CP II F – 40 is a portland cement similar to European CEM II/A-L 42,5 R (NF EN 197-1: 2012), being composed of 75-89% of clinker and calcium sulfate, and 11-25% in mass of limestone filler, according to the Brazilian standard NBR 16697: 2018.

Table 1. Chemical characterization of cement (C) and metakaolins (J1 and J2).

	Chemical (%)									
	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	MgO	SO ₃	Loss Ignit.	Free CaO	Insoluble Residues	Alkali Content
C	4.24	18.48	2.63	61.02	4.33	2.76	4.99	0.78	1.10	0.66
J1	37.1	52.7	2.3	0.1	1.0	---	2.7	---	---	1.5
J2	39.5	47.6	5.3	0.1	0.3	---	4.7	---	---	0.5

The two metakaolins showed different chemical compositions. J1 has higher SiO₂ content and the reddish coloration of metakaolin J2 is explained by the higher iron oxide content in this material. Regarding fineness, J2 is 30% finer than J1. Despite these differences, the two metakaolins studied showed very similar pozzolanic activity (modified Chapelle - NF P18-513: 2012).

Table 2. Metakaolins' complementary characterization.

Metakaolin	Aspect/Colour	Specific gravity (g/cm ³)	BET Fineness (m ² /g)	Chapelle (mg CaOH ₂ / g)
J1		2.58	22.13	1037
J2		2.60	28.71	1075

2.2 Preparation of Specimens and Test Methods

Three different mortars were produced, one as reference and the other two with 10% replacement of cement by metakaolin J1 or J2, in mass. The mortars were produced with a 1:2 mixture (binder:sand, in mass), since this is a mix proportion commonly used in the mortar fraction of various concrete mix designs (1:2:3-binder:sand:gravel). The consistency index was maintained in 320±20 mm (according to ASTM C230: 2014). After mixing, two mortar specimens were cast, under controlled conditions, in prismatic dimensions of 40x40x160 mm (ASTM C349: 2018). The mortars' composition and identification are shown in Table 3.

Table 3. Mortars' identification and composition (kg/kg).

Identification	Cement	Metakaolin	Sand	Water/Binder	Superplasticizer Admixture
A - R	1.0	0,0			0
A - J1	0.9	0.1 (J1)	2	0.55	0.022
A - J2		0.1 (J2)			0.037

After 24 hours of molding, the specimens were demolded and subjected to four different curing conditions: no wet curing and curing by immersion in lime saturated water for 3, 9 and 28 days. For the specimens without wet curing, they were packed in PVC plastic after demolding and stored in a laboratory until the tests performing. For those specimens cured for 3 and 9 days, they were air-dried for about two hours (after the curing period) and then packed by means of PVC plastic until they reached the testing age of 28 days, in order to prevent natural carbonation.

At 28 days of age, the accelerated carbonation test (7 days) was started. Before the start of carbonation, the specimens were preconditioned with humidity (70±5%) and temperature (20±1°C) controlled (no CO₂), according to standard ISO 1920-12 (2015). It was used one CO₂ incubator, model 6034-1, Caron brand, with temperature of (20±1)°C, relative humidity of (70±5)% and CO₂ content of 10%. The carbonation depth was measured by spraying the pH indicators (thymolphthalein and phenolphthalein-based solutions) and using a digital calliper with an accuracy of 0.01 mm, as shown in Figure 1. Each specimen was sliced two times, resulting in a four-sided measurement of 40 x 40 mm, a specimen. In 2 faces the phenolphthalein was applied, and in the other two it was the thymolphthalein. On each side 4

measures were taken (in the central region on each side), which implies that the mean results of carbonation depth were obtained using 16 individual measures.

The compressive strength test (ASTM C349:2018) was performed with the mortars subjected to wet curing for 28 days.

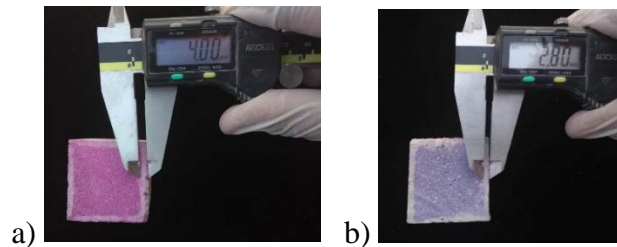


Figure 1. Measurement of carbonated depth using a) phenolphthalein and b) thymolphthalein.

For result analysis, the data was treated with Dixon statistic test (ASTM E178: 2016) in order to remove spurious values, and then analyzed using variances analysis (ANOVA) to identify the study's significant variables. In addition, multiple comparisons of means were performed by the Duncan test.

3 Results and Discussion

3.1 Compressive Strength

Table 4 presents the results of mortars' compressive strength. It can be noted that the metakaolin mortars achieved higher strengths compared to the reference mortar; in addition, there was no significant difference in strength between A-J1 and A-J2.

Table 4. Compressive Strength at 28 days of age.

Mortar	A - R	A - J1	A - J2
Compressive Strength - mean (MPa)	34	43	42
Standard Deviation (MPa)	10.4	5.0	2.7

3.2 Carbonation

The results of mortars' carbonation depth, for different curing situations, are presented in Figure 2. The carbonation depth is reduced with wet curing, showing the importance of performing curing in order to increase the durability of reinforced concrete. Comparing carbonation depths of mortars submitted to wet curing for 28 days and mortars not submitted to wet curing, it is possible to observe a reduction in carbonation up to 70% for A-R, and 45 % for A-J1 and A-J2.

The increase of wet curing time from 3 to 28 days reflected in a less pronounced depth reduction, about 50%, 25% and 30% for mortars A-R, A-J1 and A-J2, respectively. It is interesting to note that the type of curing exerts a greater influence on the reference mortar than on the metakaolin mortars (A-J1 and A-J2). It was found that concretes modified with metakaolin without the application of any curing procedure show superior carbonation resistance compared to reference concretes. From the literature, it is known that mineral additions such as blast furnace slag and fly ash require wet curing for a long time to consolidate

the pozzolanic reactions (Sulapha *et al.*, 2003), and that superpozzolans such as silica fume, nanosilica and metakaolin are generally not sensitive to wet curing (Couto *et al.*, 2003). This was verified in the present work for metakaolin and the main argument on the issue is based on the physical transformation capacity of the cement paste by the action of pozzolan, which reduces porosity and refines pores, thus increasing the volume of micropores capable of retaining water in its capillary structure (Duan *et al.*, 2013). In these cases, it can be said that self-healing occurs due to changes in the material's microstructure.

The analysis of variance - ANOVA (Table 4) confirms the statement that the type of curing exerts a strong influence on the carbonation depth, while type of mortar did not present significant effect on the results of this research.

Table 4. Carbonation depth ANOVA.

Effect	SQ	GL	MQ	F _{calc}	F _{tab}	Result (5% significance)
Model	652.73	11	59.34	78.5	1.8	Significant
Residual Error	278.02	368	0.76			
Total	930.75	379				
Type of curing	574.50	3	191.5	253.5	2.6	Significant
Mix design	2.80	2	1.40	1.9	3.0	Not Significant
Type of curing x Mix design	64.14	6	10.69	14.2	2.1	Significant
Residual Error	278.02	368	0.755			
Coefficient of Determination (R²) = 0.70				Coefficient of Correlation (R) = 0.84		

The multiple comparison of means (Figure 2), where dashed lines indicate separation into different groups, shows that the mortars with metakaolin present a tendency to be similar regarding the carbonation for all the curing conditions. The behavior similarity of mortars A-J1 and A-J2 can be explained by the fact that the metakaolins presented similar reactivity (Chapelle - Tab. 2), confirmed by the compressive strength results (Tab. 4), despite the chemical, coloring and fineness differences of the two pozzolans. When comparing the metakaolin mortars with the reference mortar (A-R), a distinct behavior is observed. In intermediate curing, the three mortars show same pattern from the statistical point of view.

However, when no wet curing is performed, the reference mortar presents a higher carbonation depth than the mortars with metakaolin. When wet curing is performed for 28 days, this behavior is reversed; this explains the significant interaction between Type of curing x Mix design found in ANOVA (Tab. 4). The approximately 50% increase in carbonation depth for A-J1 and A-J2 regarding A-R, in the wet curing for 28 days situation, can be explained by the hydration process and the pozzolanic reactions, in which the increased time of wet curing allowed better conditions for the hydration and pozzolanic reactions to occur, improving mortars' microstructure, but with pozzolanic reactions there is also reduction in alkaline reserve of mortars with mineral additions (Thomas; Matthews, 1992; Cascudo; Carasek, 2011). In contrast, the shorter depth for A-J1 and A-J2 without wet curing, regarding A-R, can be explained by the greater influence of curing on reference mortar, in addition to the filler and pozzolanic effects of mineral additions, which refined the mortars' porosity and microstructure (Duan *et al.*, 2013), as previously discussed.

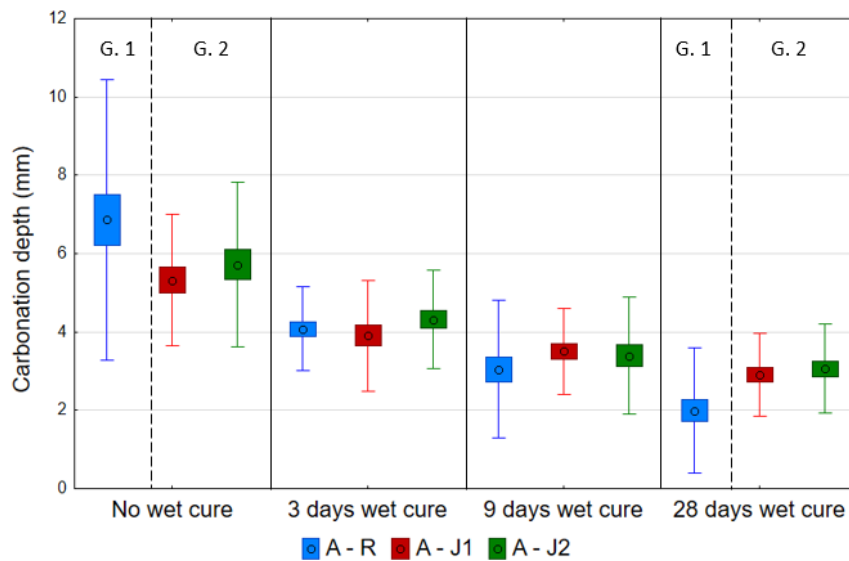


Figure 2. Carbonation depth results analyzed with multiple comparison of means.

3.3 Relationship Between pH Indicators

Figure 3 shows the relationship between the carbonated depth measurements made with thymolphthalein and phenolphthalein, and the strong correlation between these two variables ($R^2 = 0.89$). It is noted that, in general, the thymolphthalein indicated greater depths than the phenolphthalein, which can be attributed to the difference between the indicators' pH turning ranges (phenolphthalein from 8.0 to 9.8 and thymolphthalein from 9.3 to 10.5). Other authors (such as: Kazmierczak; Lindenmeyer, 1996; Yu; Lee; Chung, 2010; Reis; Camões; Ribeiro, 2016; Revert *et al.*, 2016, Thiel; Gehlen, 2019) have worked with indicators and discussed the relationships between the measurements obtained.

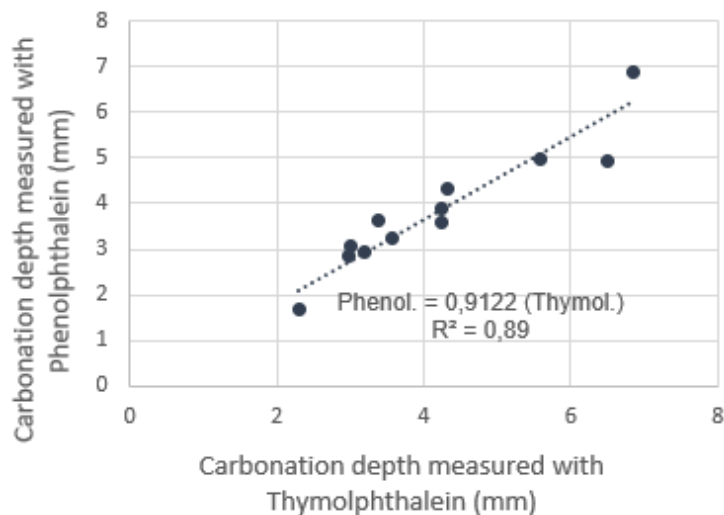


Figure 3. Relationship between carbonated depths with different pH indicators.

The equation obtained for this correlation can be highlighted; the carbonated depth readings with phenolphthalein are equivalent to 0.9 times the readings taken with thymolphthalein. An interesting aspect, and perhaps new, was noticed: this relationship between the variables matches the relationship between the two extremes of the pH ranges nominated by the different pH indicators ($9.3 / 10.5 = 0.9$; where 9.3 is the maximum pH indicated by phenolphthalein and 10.5 is maximum by thymolphthalein).

4 Conclusions

Based on the research presented, the following conclusions can be drawn:

Despite of the chemical, coloring and fineness differences of both metakaolins studied, there were no statistically significant differences regarding the carbonated depths of the mortars prepared with them. These metakaolins had similar pozzolanic activity (measured by the Chapelle method), showing that this characteristic is very relevant to explain the carbonation of mortars with metakaolin.

The curing condition had a strong influence on carbonated depths of mortars. This depth is reduced with wet curing and with the increased time of immersion in water, showing the importance of wet curing for increasing the durability of reinforced concrete. However, metakaolin mortars are less affected by wet curing when compared to the non-pozzolan mortars (reference cementitious mortars). This is certainly due to a self-healing action exerted by a microstructure with refined pores, referring to systems with metakaolin, with greater water retention capacity.

As for the carbonate depth measurements performed with phenolphthalein and thymolphthalein based indicators, a strong linear correlation was observed between the two variables ($R^2 = 0.89$). The carbonated depth readings with phenolphthalein are equivalent to 0.9 times the measured readings with thymolphthalein. This relationship between the variables is exactly the relationship between the two extremes of the indicators' pH turning ranges (phenolphthalein = 9.8 and thymolphthalein = 10.5).

Acknowledgements

The authors would like to thank: Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) – Brazil, Eletrobras FURNAS and the technicians of LABITECC-UFG - Brazil.

ORCID

Helena Carasek: <https://orcid.org/0000-0002-1170-0980>

Mônica E. Jungblut: <https://orcid.org/0000-0003-2111-0666>

Paulo M. Passos: <https://orcid.org/0000-0002-2934-9279>

Oswaldo Cascudo: <https://orcid.org/0000-0003-1879-6396>

References

- Cascudo, O. and Carasek, H. (2011). Ação da Carbonatação no Concreto. In G. C. ISAIA (Ed.), *Concreto: Ciência e Tecnologia*. São Paulo, SP: IBRACON, 849-885.
- Castro, A., Ferreira, R., Lopes, A., Couto, A. P., Braun, V., Carasek, H. and Cascudo, O. (2007). Influência das adições minerais na durabilidade do concreto. In *IV Congresso de Inovação Tecnológica em Energia Elétrica*. Araxá: ANEEL, 1-8.
- Couto, A. B. P. ; Cascudo, O. ; Carasek, H. and Lopes, A. N. M. (2003). Influência das condições de cura na

- durabilidade de diferentes concretos. In *45. Congresso Brasileiro do Concreto*, Vitória. Anais de CD-ROM. São Paulo: IBRACON, 1, 1-15.
- Duan, P., Shui, Z., Chen, W. and Shen, C. (2012). Influence of metakaolin on pore structure-related properties and thermodynamic stability of hydrate phases of concrete in seawater environment *Construction and Building Materials*, 36, 947-953. doi: 10.1016/j.conbuildmat.2012.06.073
- Duan, P., Shui, Z., Chen, W. and Shen, C. (2013). Enhancing microstructure and durability of concrete from ground granulated blast furnace slag and metakaolin as cement replacement materials *Journal of materials Research and Technology*, 2(1), 52-59. doi: 10.1016/j.jmrt.2013.03.010
- Hossain, M. M., Karim, M. R., Hasan, M., Hossain, M. K. and Zain, M. F. M. (2016). Durability of mortar and concrete made up of pozzolans as a partial replacement of cement: A review *Construction and Building Materials*, 116, 128-140. doi: 10.1016/j.conbuildmat.2016.04.147
- Kazmierczak, C. S. and Lindenmeyer, Z. (1996). Comparação entre metodologias utilizadas para a determinação da profundidade de carbonatação em argamassas. In *Proceedings of the International Congress on High-performance and Quality of Concrete Structures*, Florianópolis, Brazil, 402-413.
- Lim, S. and Mondal, P. (2015). Effects of incorporating nanosilica on carbonation of cement paste *Journal of Materials Science*, 50(10), 3531-3540. doi: 10.1007/s10853-015-8910-7
- Meddah, M. S., Ismail, M. A., El-Gamal, S. and Fitriani, H. (2018). Performances evaluation of binary concrete designed with silica fume and metakaolin *Construction and Building Materials*, 166, 400-412. doi: 10.1016/j.conbuildmat.2018.01.138
- Papadakis, V. G. (2000). Effect of supplementary cementing materials on concrete resistance against carbonation and chloride ingress *Cement and concrete research*, 30, 291-299. doi: 10.1016/S0008-8846(99)00249-5
- Reis, R., Camões, A. and Ribeiro, M. (2016). Using Thymolphthalein for Accelerated Carbonation Testing of High Volume Fly Ash Cementitious Blends. In *Service Life and Durability of Reinforced Concrete Structure*, Marne-la-Vallée, France, 17-30.
- Revert, A., De Weerd, K., Hornbostel, M. and Geiker, M. (2016), Carbonation Characterization of Mortar with Portland Cement and Fly Ash, Comparison of Techniques, Nordic Concrete Research, publication N. 54 1/2016, 60-76
- Rossignolo, J. A. and Oliveira, I. L. (2006). Concreto leve estrutural com metacaulim *Revista Minerva: Pesquisa e Tecnologia*, 3(2), 177-187.
- Sulapha, P., Wong, S. F., Wee, T. H. and Swaddiwudhipong, S. (2003). Carbonation of Concrete Containing Mineral Admixtures *Journal of Materials in civil engineering*, 15, 134-143. doi: 10.1061/(ASCE)0899-1561(2003)15:2(134)
- Thiel, C. and Gehlen, C. (2019) On the Determination of Carbonation in Cementitious Materials. In *RILEM Spring Convention and Sustainable Materials, Systems and Structures Conference*, Rovinj, Croatia, 373-380.
- Thomas, M. D. A. and Matthews, J. D. (1992). Carbonation of fly ash concrete *Magazine of Concrete Research*, 44(160), 217-228. doi: 10.1680/mac.1992.44.160.217
- Yu, M., Lee, J and Chung, C. (2010), The Application of Various Indicators for the Estimation of Carbonation and pH of Cement Based Materials, *Journal of Testing and Evaluation* 38, no. 5: 534-540