Study on Carbonation Process of Several Types of Advanced Lime-Based Plasters

Z. Pavlík, H. Benešová, P. Matiašovský, and M. Pavlíková

Abstract —In this paper, study on carbonation process of several types of advanced plasters on lime basis is presented. The movement of carbonation head was measured by colorimetric method using phenolphtalein. The rate of carbonation was accessed also by gravimetric method. Samples of studied materials were placed into the climatic chamber for simulation of environment with high concentration of CO_2. The particular samples were on all lateral sides and on the bottom side provided by epoxy resin in order to arrange 1-D transport of CO_2 into the studied samples. The carbonation rates of particular materials pointed to the time dependence of diffusion process of CO_2 for all the studied plasters. From the quantitative point of view, the carbonation of advanced modified plasters was much faster than for the reference lime plaster, what is beneficial for the practical application of the tested newly developed materials.

Keywords—Carbonation, colorimetric method, gravimetric method, lime-based plasters, pozzolana admixtures.

I. INTRODUCTION

THE process of hardening of lime-based plasters is driven by the reaction of CO_2 from the ambient air with $Ca(OH)_2$ that represents reaction product of burnt lime (CaO) hydration. The rate of carbonation is one of the decisive factors that affect the final strength and durability properties of lime-based mortars and plasters. The lime-based mortars and plasters find application in civil engineering because of their high hygroscopicity that allows optimal conditioning of buildings' interior. The lime materials exhibit also good adhesion to the substrates, and partial self-consolidation in the case of substrate deformation. On the other hand, the lime materials have very low durability in case of their longer contact with liquid water. Here, the significant weathering of lime materials can be observed. On that account, several admixtures mainly on pozzolana basis are applied within the mix design of lime-based mortars and plasters.

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Hardening of lime mortar with addition of pozzolanic admixtures proceeds in two competitive reactions: classical carbonation (reaction of calcium hydroxide and carbon dioxide) and pozzolanic reaction [1]. The process of carbonation of pure lime mortars and plasters is nowadays well understood and experimentally researched. However, application of new materials in composition of lime materials makes the process of carbonation more complex and complicated. Therefore, experimental testing and monitoring of the velocity and propagation of carbonation must be performed in order to obtain necessary information for application of newly developed materials in building practice.

In this paper, accelerated carbonation tests were performed in order to investigate carbonation process of several types of newly developed lime-based plasters. The carbonation process was monitored using the colorimetric method, whereas the gravimetric analysis was performed as well.

II. CARBONATION PROCESS

A. Carbonation of Lime Plaster

Carbonation is a reaction of slaked lime $(Ca(OH)_2)$ with carbon dioxide (CO_2). Within this reaction, the calcite $(CaCO_3)$ is created. This reaction runs in all of lime based materials, and is accompanied by pH decrease in the carbonated areas. This is negative phenomenon in the case of concretes due to reducing of corrosive protection of embedded steel reinforcement. On the other hand, it is fundamental process for lime plasters and mortars hardening [2].

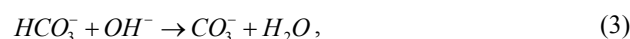There were discovered five phases of carbonation process [3]:

1. diffusion of CO_2 gas through the porous structure of material,

2. dissolving of $Ca(OH)_2$ in pore solution according to the following reaction

$$(Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \qquad (\text{pH}>10), \qquad (1)$$

3. dissolving of CO_2 in pore solution

$$CO_2 + OH^- \rightarrow HCO_3^-, \qquad (2)$$

4. achievement of chemical balance of dissolved CO_2 in pore solution

$$HCO_3^- + OH^- \rightarrow CO_3^- + H_2O, \qquad (3)$$

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5. precipitation of $CaCO_3$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \, . \tag{4}$$

Finally, the carbonation process of lime plasters can be expressed as

$$Ca(OH)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2H_2O \, . \tag{5}$$

This reaction is accompanied by the mass and volume growth of hardened particles, because portlandite (molar weight 74 g/mol and molar volume 33.0 ml/mol) is changing to calcite $CaCO_3$ (or laterite, and aragonite, molar weight 100g/mol and molar volume 36.9 ml/mol).

B. Carbonation of Modified Lime Plasters

Pozzolanic admixtures appeared to have positive effect on properties of lime binder in the past [4]. According to the composition of the applied pozzolana, compounds similar to Portland cement products are formed within the hydration process. Here, also the compounds of zeolite character were found, such as phillipsite $3CaO \cdot 3Al_2O_3 \cdot 10SiO_2 \cdot 12H_2O$ and analcime $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$, in connection with microcrystalline calcite. These compounds are the cause of the plasters resistance against environmental conditions and in this way of the durability of these plasters [5].

The mineral admixtures interact chemically with the hydrating Portland cement in cement-lime plasters to form a modified paste microstructure [6]. Major component of a pozzolana, the amorphous or glassy silica, reacts with calcium hydroxide formed from calcium silicates hydration

$$CH + S + H \rightarrow C - S - H \, . \tag{6}$$

The composition of $C - S - H$ is not very different from that form in regular hydration, however, with very reactive pozzolanas of high silica content (metakaoline), the C/S ratio is significantly different being close to 1.0, and the H/S ratio is slightly lower, which indicates a secondary pozzolana reaction

$$C_3S + 2S + 10.5H \rightarrow 3[CSH_{3.5}] \, . \tag{7}$$
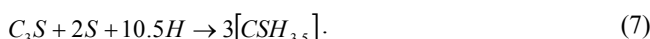
Small quantities of reactive alumina in a pozzolana generally substitute silica as a part of the $C - S - H$. In the case of metakaolin, which contains appreciable quantities of reactive alumina, a separate set of secondary reactions can occur, leading to the calcium aluminate hydrates formation

$$CH + A + H \rightarrow C - A - H \, . \tag{8}$$

The exact composition of the calcium aluminate hydrates depends on the particular pozzolana. Here, also AFm compounds, gehlenite hydrates, or monosulfoaluminate may form.

The pozzolana reaction has kinetics similar to the slow rate of hydration of C_2S, whereas the reaction heat is about -12 kJ/mol. The pozzolana addition raises the C_2S content of the cement, thereby lowers the amount of early heat evolution and reduces early strength, but not long-term strength [7]. Since pozzolana reaction has an overall increase in solid volume, the porosity of the paste will be reduced, resulting in higher strength and durability in the comparison with a plain paste of comparable reaction [8].

Plasters on the lime and cement basis combine the benefits of the both materials. Portland cement is highly reactive binder; it reacts immediately with water during hydration. Then, after several minutes the reaction is stopped for 1.5 – 2.5 hours. There is formation of ettringite with the help of gypsum on the cement grains surface. Thus water has to diffuse through the cover and reactive products like as CSH and CAH gels. Together with the hydration of clinker minerals, the portlandite supersaturation of pore solution proceeds. pH of pore solution increased up to 12.4. The rest of $Ca(OH)_2$ carbonates to calcite. The pores of lime-cement plaster have smaller diameter than pores of lime plaster, what causes higher diffusion resistance to CO_2 and retardation of carbonation [9].

C. Factors Affecting Carbonation

The carbonation process is affected by many factors. Firstly, it is CO_2 concentration, the higher the concentration the quicker is the reaction [10]. The temperature rise causes the increasing of CO_2 reaction rate and slower carbonation head moving [11]. Relative humidity over 95% causes the capillary condensation in the pores of material and aggravation of CO_2 permeability. On the other hand, carbonation proceeds only providing that sufficient water amount is inside the material pores. It was further discovered that CO_2 diffusion slows with increasing of filler concentration [12]. Also large calcite grains slow down the carbonation reaction [13].

III. EXPERIMENTAL INVESTIGATION

A. Materials and Samples

Within the experimental testing, new lime-metakaoline plaster developed in our laboratory was tested together with three commercially produced plasters. For the comparative reasons, the reference lime plaster was studied as well. The lime-metakaoline plaster (VOM) and the reference plaster (VO) mixtures were prepared from hydrate lime L90 produced by limekiln Mokrá, Carmeuse Czech Republic Ltd. The lime hydrate consists mainly of $Ca(OH)_2$ (92.2-96.6%). The rest are admixtures and impurities, nominally CO_2 (0.4-1.5%), MgO (0.4-0.8%) and SO_3 (0.1-0.3%). The applied silica aggregates mixed of three fraction 0.08/0.5; 0.5/1 and 1/2 mm in portion 1:1:1 were produced by Heidelberg Cement Group, Brněnské písky Inc., affiliate Bratčice. Metakaoline MEFISTO K05, produced by ČLUZ Inc., Nové Strašecí, was used as a pozzolana active admixture. Metakaoline is kaolinite burnt at temperatures between 500 – 850°C, i.e. above the temperature of kaolinite dehydration. It is a highly active pozzolana material with average particle size in the interval of 3 to 5 μm. Dominant parts of metakaoline MEFISTO represent SiO_2

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(55%) and Al_2O_3 (41%). The minority of compounds include Fe_2O_3, TiO_2, CaO, MgO, and Na_2O. The products of their chemical reaction during hydration are CSH gels and crystallization products. Furthermore, three factory-produced dry plaster mixtures were tested, namely lime-cement priming plaster Baumit, denoted as VOC, and restoration system plasters; outer fine plaster Baumit 64, denoted as VOS 1, and buffer plaster Baumit 68, denoted as VOS 2. The water/dry mixture ratio of these plasters was modified according to mixture workability. The composition of mixtures for sample preparation is presented in Tables I, II.

TABLE I
COMPOSITION OF TESTED PLASTERS

Mixture	Lime	Sand	Metakaoline	Water
	Amount of material (kg)			
VO	4.8	14.4	-	4.8
VOM	4.8	14.4	1.2	5.5

TABLE II
COMPOSITION OF FACTORY PREPARED PLASTERS

Mixture	Dry mixture	Water
	Amount of material (kg)	
VOC	40.0	7.2
VOS 1	35.0	6.3
VOS 2	35.0	7.0

Plaster mixtures were prepared using laboratory mixing machine with forced rotation for 3 minutes. Each mixture was casted into two special forms, the PVC cylindrical tubes, first one with 7 cm diameter and 10 cm height, see Fig. 1. These samples were compacted using vibrating machine. The second type of form were tubes with 3 cm in diameter and 5 cm height, see Fig. 2. These samples were filled only to a half of their height and then compacted gently with hand according to Cultrone and his colleagues [8]. Then the samples were daily wetted for a three day period before they were taken out of forms and then cured for 25 days at $22\pm5°C$ and $40\pm10\%$ of relative humidity.
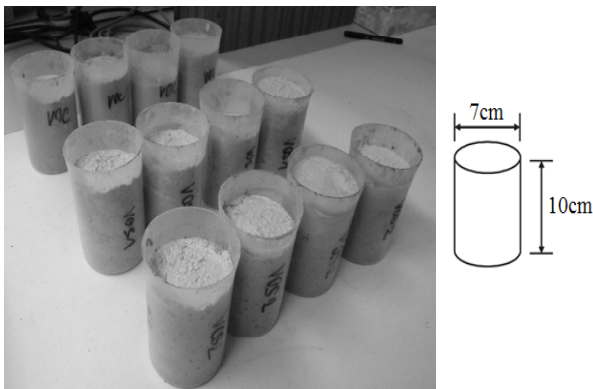

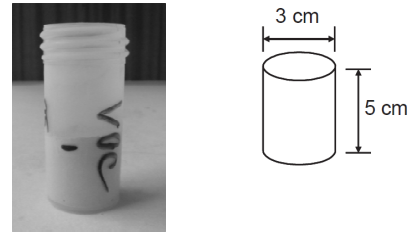Fig. 1 Cylindrical tubes for sample preparation

Fig. 2 Example of smaller cylindrical tube for sample preparation

B. Colorimetric Method

Despite a lot of modern instrumental methods for carbonation measurement exists, the most known method for carbonation head detection is colorimetric analysis using phenolphtalein. A part of sample which stays dark pink (pH>9) contains highly alcalic portlandite. Colourless place indicates neutral calcite which is a reaction product of lime carbonation, see Fig. 3. This information often faces to a fault result that sharp border between carbonated and non carbonated part of material exists [12, 14, 15]. It was explored that head of carbonation is a large area, which width and position during carbonation changes.
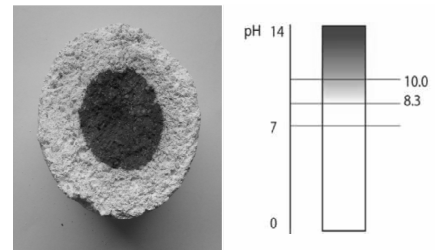

Fig. 3 Colorimetric method

C. Gravimetric Method

During carbonation reaction the weight of lime plasters apparently increases. Cultrone and his colleagues used gravimetric method for determination of $CaCO_3$ weight, which arose in certain time interval of carbonation [8]. Within their tests, the studied lime-based plasters were exposed to very high CO_2 environment and the differences in plasters samples mass were monitored for 30 days. The maximum of weight of studied samples was reached until 8 days of CO_2 exposure for all the researched materials.

This method requires constant temperature and moisture conditions [3]. On this account, the gravimetric method is used for small samples of lime and cement-lime plasters measurement. The advantage of this method is short time of the experiment in the case of quick carbonation tests. The results of gravimetric measurement give information about the amount of carbonated calcium hydroxide [2].

D. Experimental Procedure

To find out the carbonation rate of the studied materials, the particular samples were firstly insulated by the epoxy resin at the lateral sides and bottom. Thus, one-dimensional transport of CO_2 took place. Samples were then exposed to CO_2

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environment in Nuire GT2000 chamber at 30°C. High relative humidity, 70±10%, was simulated with water tank in the chamber bottom. The carbonation rate was investigated at two different CO_2 concentrations of 10% and 5% respectively, in order to speed up CO_2 diffusion into the plasters samples and accelerate carbonation reaction. Usual CO_2 concentration in cities is according to Dheilly 225-300 ppm [3]. To ensure our safety during the experiment, CO_2 concentration in the laboratory was monitored with CO_2 sensor ZG 106.

The tested samples were lengthwise cut at the specific time intervals and with the help of phenolphtalein analysis the depth of carbonation head was determined. Since we had no image how long does carbonation of modified lime plasters take, the studied samples were firstly tested after 24 hours of CO_2 exposure and the depth of carbonation head was analysed. According to the obtained results, the VO and VOM plasters samples were analysed after 16, 40, 66, 164, 652, and 816 hours, samples of VOS 1 and VOS 2 after 40, 96, and 108 hours, and finally samples of VOC after 16, 24, and 48 hours in both CO_2 concentrations.

Each tested sample was lengthwise cut immediately after it was taken out of the CO_2 chamber, whereas the dust was purified by brush. Freshly cut surface was sprinkled with 1% solution of phenolphtalein in ethanol. The determined depth of carbonation head was calculated as the average value of four measurement using micrometer.

IV. RESULTS AND DISCUSSION

The results of depth of carbonation head in dependence of time of CO_2 exposure are presented in Figs. 4, 5. From the measured data it is visible that higher CO_2 concentration caused growth of carbonation rate of about 20% for all the tested samples. The carbonation rate was nearly the same in the case of lime plaster and lime plaster modified with metakaoline addition. All factory produced plasters exhibited rapid carbonation head progress especially in case of lime-cement plaster VOC. Carbonation of all the VOC samples was completed after 72 hours, while carbonation of VO and VOM samples was not finished even at 820 hours.

The abnormal shape of carbonation head was in the case of factory produced plasters observed in comparison with VO and VOM plasters. They had a sharp straight border of phenolphtalein coloured part of samples. The other plasters had diffusion transition zone of coloured carbonation head. In the case of lime-cement plaster VOC, there were small regions, 0.5x0.5mm, which reacted with phenolphtalein. It means that their pH is higher than 9, in areas of carbonated sample. The presence of these non-carbonated particles can be caused due to very big grains of lime hydrate, which can be covered of gas impermeable layer of calcite. This layer defends to carbonation reaction inside particles. Thus phenolphtalein soaks through miscellaneous particles, reacts with basic $Ca(OH)_2$, and mixed calcite-portlandite grain becomes violet. The phenomenon of non reactive particles can also originate from the continuous portlandite formation during hydration reaction [16]. Moreover, hydrating allite produces three times over of portlandite than hydrating bellite

in fresh cement plasters. Due to these reactions the results of carbonation process in modified plasters can be distorted.
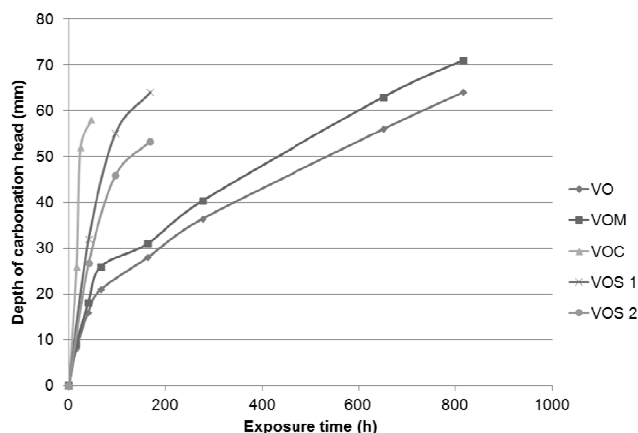

Fig. 4 The depth of carbonation head at 5% CO_2 concentration
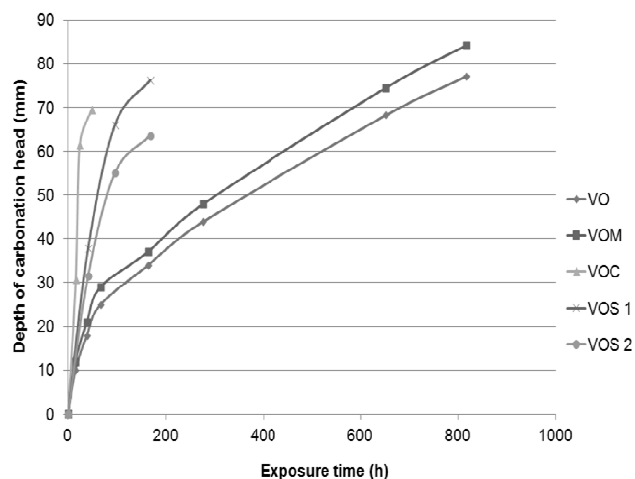

Fig. 5 The depth of carbonation head at 10% CO_2 concentration

The samples of plaster mixtures were investigated also by the gravimetric method. The mass changes during carbonation depending on time at both CO_2 concentrations are presented in Figures 6, 7.
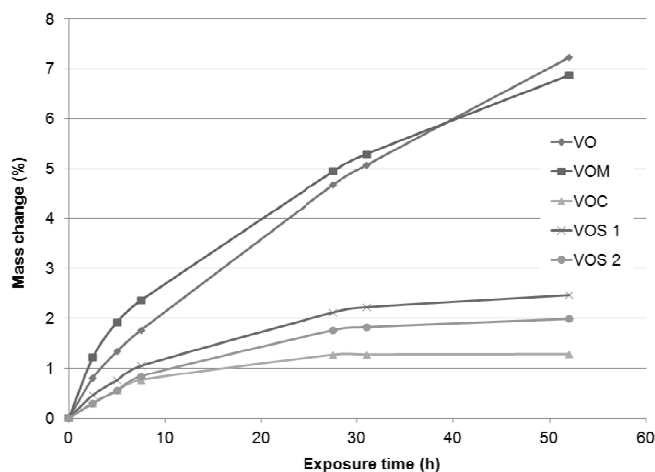

Fig. 6 The mass increase during carbonation at 5% CO_2 concentration

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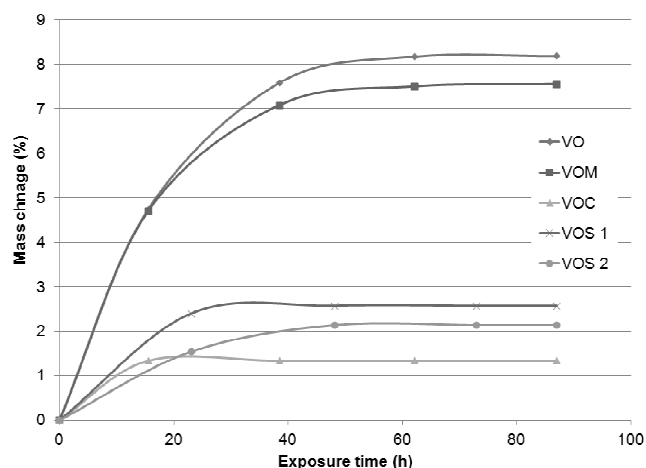International Journal of Materials and Metallurgical Engineering
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Fig. 7 The mass increase during carbonation at 10% CO_2 concentration

The mass of samples grew up markedly for 4 days. After that, the mass increments were in the range of measuring error, thus, experiments were finished. The greatest mass change was observed for plasters VO and VOM. It is evident that it was due to the high content of $Ca(OH)_2$ in these plasters. On the other hand, these plasters reached mass maximum very slowly. The factory produced restoration system plasters VOS 1 and VOS 2 showed lower mass changes than laboratory produced lime plasters, but the carbonation reaction ran faster. The lowest $Ca(OH)_2$ content in lime-cement plaster VOC caused the least mass increment. However, the mass maximum was obtained fastest.

V. CONCLUSION

In this paper, the carbonation process of several types of lime based plasters was studied. For the experimental assessment of carbonation rate and carbonation head movement, phenolphthalein colorimetric and gravimetric methods were used. The gravimetric measurement of carbonation process dynamics corresponded to the analysis of carbonation rate using phenolphthalein indicator. The accelerated carbonation tests used in the presented work made carbonation process possible in short time. Thus a lot of different plasters could be tested and different laboratory techniques used to monitor carbonation process. In the case of colorimetric method, it was explored that the carbonation rate of pure and modified lime plaster was nearly the same, while all the factory produced plasters exhibited rapid carbonation head progress. From the application of gravimetric method, there was observed the mass of samples growth for 4 days. After that, the mass increments were in the range of measuring error. The greatest mass change was observed for plasters on hydrated lime basis, what was due to the high content of $Ca(OH)_2$ in these plasters. The factory produced restoration system plasters exhibited lower mass changes, but the carbonation reaction ran faster. In future work we plan perform other acceleration carbonation tests, whereas the analysis will be done except phenolphtalein and gravimetric methods also by IR spectroscopy.

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