

HYGROSCOPICITY OF NON-MATURED AND MATURED PLASTERS

Olga Koronthalyova¹, Peter Matiasovsky¹

¹Institute of Construction and Architecture, Slovak Academy of Sciences, Dubravská cesta 9, SK-84503 Bratislava 45, Slovakia

Email: usarkoro@savba.sk, usarmat@savba.sk

Abstract

The pore structure and consequent the moisture accumulation parameters changes due to the carbonation process were investigated for characteristic types of the contemporary lime/cement plasters: multi-purpose masonry and plastering mortars, renovation plasters and thermal insulation plasters. The most important parameter changes due to carbonation were noticed in the values of specific surface area.

Key words: sorption curve, specific surface area, BET, mercury intrusion porosimetry

1 Introduction

At the simulation of the building envelopes hygro-thermal performance the use of simulation models, based on the numerical solution of heat and moisture transfer equations has become an important tool. The reliability of the simulation results depends not only on the correctness of the numerical code but also on the reliability of the material parameters used. The building material hygroscopicity is dependent on its porous system and therefore, in cases when the porous system has been changed during its service life, it is possible to expect that the real hygroscopicity is different from the one determined in laboratory conditions, a few months after manufacturing the samples. One of the sources of the pore structure change in time is the process of carbonation. In natural conditions the plasters are during their service life exposed to the carbonation due to the carbon dioxide presence in the indoor or outdoor environment.

In the paper the pore structure and consequent the hygroscopicity changes due to the carbonation process were investigated for some characteristic types of the contemporary lime/cement plasters.

It can be concluded from the previous works that the carbonation of cementitious materials causes the increase in bulk density, the reduction of porosity and the changes in pore size distribution. In case of hardened cement pastes (HCP), the reduction of small pores portion with radii below 100 nm and consequently the reduction of the specific surface area has been noticed [5, 7, 8]. On the other hand, in case of the ordinary portland cement (OPC) concrete, it was observed that the carbonation had caused the more crooked pore structure (resulting in the reduction of porosity and the increase in small pores portion) and consequently, a decrease of the water absorption coefficient [3] and the increase in the specific surface area [2]. In case of cement mortars the presented results are not unique. A significant reduction of small pores portion has been observed [9] but, on the other hand, in [6] only very small changes in the specific surface area have been reported.

2 Experimental

The specimens were prepared from the industrially produced dry plaster mixtures. A description of the plasters is presented in Table 1. The inorganic silicate/carbonate aggregate was used in all but thermal insulation plasters. The thermal insulation plaster mixtures also contained the lightweight aggregates - expanded polystyrene (PS) or expanded perlite (EP).

The manufactured samples were conditioned under laboratory conditions at the 19°C temperature and the 45% relative humidity for 70 days in order to stabilize their moisture content.

When the samples had been stabilized the pore structure parameters and the parameters of moisture accumulation were determined. After finishing the tests, the part of the specimens was exposed to the accelerated carbonation process in the chamber with the 17% concentration of carbon dioxide, the temperature of 30°C and a the relative humidity of 60% for the period of 30 days. It was assumed that the 30 days period was sufficient for the ultimate carbonation of the tested samples. Afterwards, the same pore structure and material parameters as in the case of normally conditioned samples were determined for the carbonated ones.

Table 1. Description of tested plasters

Type of plaster	Purpose	Symbol	Binder
Lime – cement	universal	LCP	lime + cement
Cement	– multi- purpose	CP	cement + lime (cem. prevailing)
Lime		LP	lime + cement (lime prevailing)
Thermal insulation	thermal	TIP-PS	hydraulic binder (cement)
Thermal insulation	insulation	TIP-EP	hydraulic binder (special cement)
Base renovation (hydrophobic)	renovation	BRP	cement + lime (cem. prevailing)
Renovation (hydrophobic)		RP	cement (white cement)
Renovation-insulation		RIP	hydraulic lime + cement

The pore size distribution, the open porosity and the specific surface area of pores were studied using the mercury intrusion porosimetry (MIP): the high-pressure porosimeter mod. 2000 and the macro-porosimeter mod. 120 (both Carlo Erba, Milan). This system enables to determine micropores with the radius ranging from 3.7 up to 7500 nm and larger pores with the radius up to 0.06 mm. A porosimetry measurement is carried out by the fraction of broken dried (up to 105°C) samples. The TIP-PS samples were dried at 50°C. The specific surface area of pores was determined using the cylindrical model.

The specific surface area of the pores (SSA) is an important parameter from the point of view of the moisture accumulation in porous materials. The MIP determined SSA is, to be more exact, the cumulative pore surface area of pores accessible to the mercury at the used pressures, calculated under the assumption of cylindrical geometry of pores. In our case the mercury accessible pores are pores with radii above 3.7 nm. Therefore it can be expected that the MIP determined SSA will be lower than the whole surface of pores, taking part in water vapour accumulation in materials having pores smaller than 3.7 nm. The comparison between the BET SSA, calculated from the water vapour adsorption and the MIP SSA offers a possibility for the better understanding of microstructural changes in the tested materials.

The water vapour adsorption moisture contents were determined by the storing of the pre-dried specimens in climate chambers with the corresponding relative humidity and the temperature 19°C until the equilibrium moisture content has been reached.

The BET specific surface area was determined from water vapour adsorption data, using the relation (1) for a calculation of the specific surface area on the base of the amount of mono-layer adsorbate completely covering the pores surface [4]:

$$SSA = m_m \cdot N_A \cdot \sigma / M \quad (1)$$

Where:

SSA is the BET specific surface area [m^2 / g],

m_m is the amount of mono-layer adsorbate [kg / kg],

N_A is the Avogadro number, $N_A = 6.023 \cdot 10^{23} \text{ mol}^{-1}$,

σ is the area occupied by each adsorbed molecule of adsorbate, in case of H_2O molecules and if the hexagonal arrangement of the molecules is assumed, the σ value is $1.05 \cdot 10^{-19} \text{ m}^2$,

M is the molar weight of H_2O .

Taking into account the actual values for the H_2O molecules the relation (1) can be rewritten as follows:

$$SSA_{H_2O} = m_m \cdot 3.5 \cdot 10^3 \quad (2)$$

The amount of mono-layer adsorbate m_m was calculated from the adsorption data at 15% and 30% RH using the BET equation. The BET (Brunauer, Emmet, Teller) equation gives a relation between the amount of adsorbate and relative humidity during the adsorption on material surfaces. In case of an unlimited number of the adsorbate layers the BET equation can be expressed as follows:

$$m_a(\varphi) = \frac{m_m \cdot c \cdot \varphi}{(1 - \varphi) \cdot (1 - \varphi + c \cdot \varphi)} \quad (3)$$

Where:

m_a is the amount of adsorbate [kg / kg]

φ is the relative humidity of air [-]

c is the constant.

The equation (3) can be rewritten to the following form:

$$\frac{\varphi}{m_a(\varphi) \cdot (1 - \varphi)} = \frac{1}{m_m \cdot c} + \frac{(c - 1)}{m_m \cdot c} \varphi \quad (4)$$

Using the equation (4) the material constants m_m and c can be calculated from the slope and intercept of the straight line part of the function.

3 Results and discussion

The results of the MIP presenting the changes of bulk density, open porosity and specific surface area of pores caused by the carbonation are shown in Table 2 [1]. The LP samples were included in the tested set in the function of reference samples.

The bulk density has increased in case of all tested plasters with the exception of LP. The highest increase of bulk density was achieved in case TIP-PS and all renovation plasters. The changes of open porosity were negligible in case of universal mortars. In case of renovation plasters a small decrease has been noticed, in case of thermal

insulation plasters with relatively coarse filler (PS) a significant decrease has been found.

Table 2. Pore structure parameters of normally conditioned and ultimately carbonated plasters obtained from MIP

Plaster	Normally conditioned				Ultimately carbonated		
	BD kg/m ³	TP %	OP %	SSA m ² /g	BD kg/m ³	OP %	SSA m ² /g
LCP	1364	44	39	6.702	1423	39.9	5.791
CP	1686	29	29.6	3.255	1698	29.7	1.82
LP	1574	40	31	2.269	1582	33	2.557
TIP-PS1	252	89	81	56.03	276	66	17.68
TIP-EP	577	74	68	16.90	605	65	8.92
BRP	1637	29	30	5.6	1732	25	4.65
RP	811	63	60	16.4	872	54	3.28
RIP	558	76	74	18.22	590	69	14.85

BD – bulk density, TP – total porosity, OP – open porosity, SSA – specific surface area of pores.

From the MIP results detailed analysis it has followed that in most of the ultimately carbonated plasters a portion of the small pores with radii below 50 nm (CP, TIP-EP) or below 100 nm (renovation plasters) has been reduced in favour of the increase in capillary pores in the range of 1000 – 3000 nm. As a result of the small pores portion reduction - taking into account the applied cylindrical model for the specific surface area calculation – the specific surface area of pores has decreased. The highest decrease in the specific surface area was achieved in case of renovation plaster RP and thermal insulation plaster TIP-PS.

The BET specific surface areas calculated from the water vapour adsorption values (SSA_{H_2O}) compared with the ones obtained from MIP are reported in Tab. 3 and in Fig. 1. The noticed differences between the SSA_{H_2O} and SSA_{Hg} values were mainly due to fact that the used method for SSA_{H_2O} determination took into account also the pores with radii from 0.5 to 3.7 nm, which were not accessible to the mercury. This statement can be confirmed by the evaluation of an additional volume of small pores by the cylindrical model (using the SSA_{H_2O} and SSA_{Hg} difference and the median radius of 2 nm). The evaluation gave for normally conditioned samples the pore volume values from 3 to 11 %, which were in a sufficient agreement with the difference between the total porosity and the MIP determined open porosity (Tab. 2).

The carbonation has significantly reduced the BET specific surface area and consequently, the moisture accumulation capacity of the all tested plasters with the exception of LP. A degree of reduction was very different for different types of plasters. The strongest reduction of the SSA_{H_2O} was achieved in the case of lime-cement plaster LCP on the contrary to the relatively low SSA_{Hg} reduction. It could be caused by the worse pore connectivity of carbonated LCP, which was in MIP pores size distribution represented as a relatively high portion of small pores (a bottleneck effect). The lowest but still significant SSA_{H_2O} reduction (25%) has been observed in case of CP. The significant changes in SSA_{H_2O} implicate the significant changes in sorption isotherms. This result is important from the point of view of hygro-thermal performance simulation

models material parameters, especially in case of evaluating moisture buffer effect of indoor hygroscopic surfaces.

Table 3. BET specific surface areas (SSA_{H_2O}) and MIP specific surface areas (SSA_{Hg}) of normally conditioned and ultimately carbonated plasters

Plaster	Normally conditioned		Ultimately carbonated	
	SSA_{H_2O} m^2 / g	SSA_{Hg} m^2 / g	SSA_{H_2O} m^2 / g	SSA_{Hg} m^2 / g
LCP	87.5	6.702	29.2	5.791
CP	24.3	3.255	19.4	1.82
LP	19.4	2.269	19.4	2.557
TIP-PS	218.8	56.03	130.3	17.68
TIP-EP	-	16.90	97.2	8.92
BRP	77.8	5.6	58.3	4.65
RP	131.3	16.4	97.2	3.28
RIP	194.2	18.22	116.6	14.85

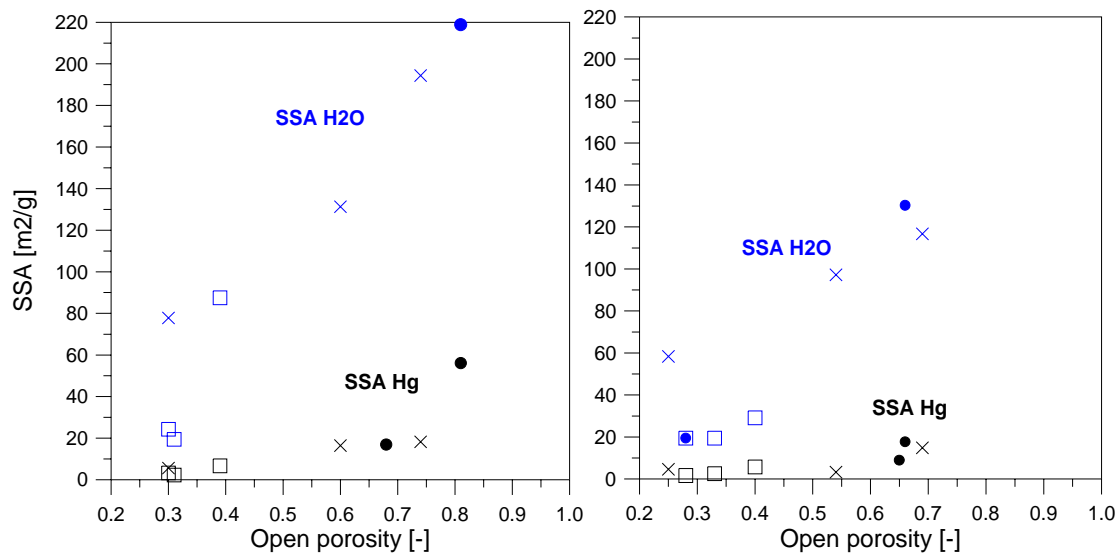


Fig. 1. Comparison of SSA_{Hg} and SSA_{H_2O} for normally conditioned (left) and ultimately carbonated (right) plasters. (\square - universal, \bullet - thermal-insulation, \times - renovation plasters)

The correlations between the SSA_{H_2O} and SSA_{Hg} are shown in Fig. 2 for a complete set of tested plasters and in Fig. 3 for case that the TIP-PS was not involved. The TIP-PS represents a special case because of the expanded polystyrene aggregate compressibility. This fact can yield to some distortion in MIP pore size distribution curve resulting in an overestimation of the small pores portion and consequently to an overestimation of SSA_{Hg} value (Tab. 3, Fig. 2). This effect seems to be more significant in case of normally conditioned samples.

From the achieved results it follows that the correlation relations between the SSA_{H_2O} and SSA_{Hg} were similar for the normally conditioned and the ultimately carbonated

plasters. As it can be seen from the Fig. 3 the SSA_{Hg} represented approximately 12 % of SSA_{H_2O} for all tested plasters with the exception of TIP-PS.

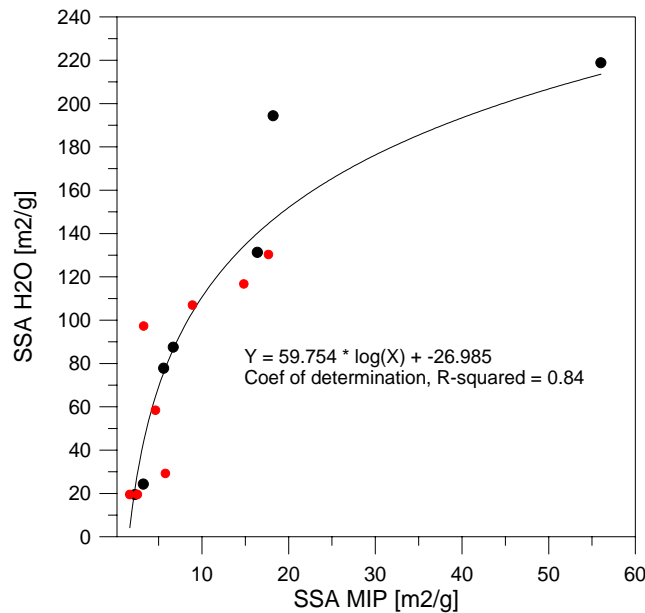


Fig. 2 Correlation between SSA_{Hg} and SSA_{H_2O} for normally conditioned (●) and ultimately carbonated plasters (●). Complete set of tested plasters.

Conclusion

The pore structure and the consequent moisture accumulation parameters changes due to the carbonation process were investigated for the characteristic types of contemporary lime/cement plasters: multi-purpose masonry and plastering mortars, renovation plasters and thermal insulation plasters.

The carbonation has not significantly influenced the open porosity of the tested universal and renovation plasters, but it has caused the changes in pore size distribution in all tested plasters: the reduction of the portion of pores with radii below 50 or 100 nm.

The reduction of these pores has caused the reduction of the surface area of pores. The degree of the reduction was different for different types of plasters.

The noticed differences between the SSA_{H_2O} and SSA_{Hg} values were mainly due to the presence of small pores with radii below 3.7 nm, which were not accessible to the mercury. The correlations between the SSA_{H_2O} and SSA_{Hg} were similar for the normally conditioned and ultimately carbonated plasters. The SSA_{Hg} represent approximately 12 % of SSA_{H_2O} for practically all tested plasters.

The noticed reduction of water vapour specific surface area is important from the point of view of the actual sorption isotherms of the plasters.

The sorption curves are crucial material parameters in hygro-thermal performance simulations and therefore, their possible changes due to carbonation should be taken into account in the numerical calculations. The sorption isotherm changes can especially be of importance in simulations of the moisture buffering effect of the inner surfaces of the building structures.

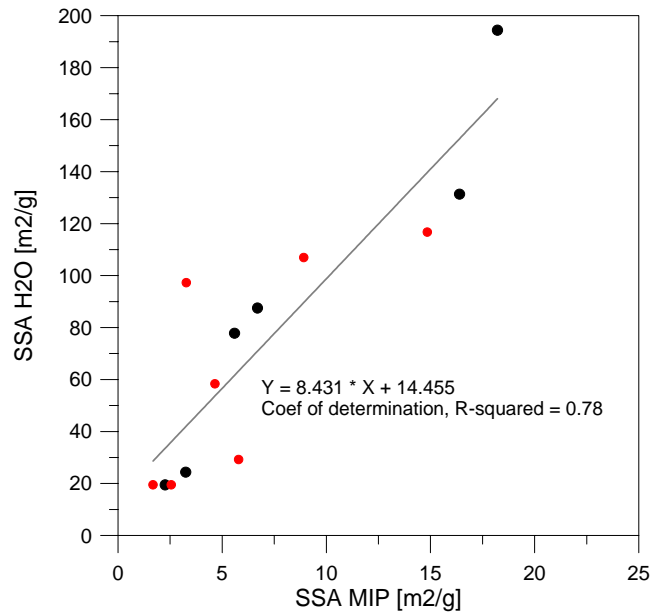


Fig. 3 Correlation between SSA_{Hg} and SSA_{H2O} for normally conditioned (●) and ultimately carbonated plasters (●). Thermal insulation plaster containing PS aggregate is excluded.

Acknowledgement

Financial support of the projects APVT-51-030704 and VEGA 2/4077/24 is gratefully acknowledged.

References

- [1] Bagel, L. Structural parameters of plasters. Internal report. Institute of Construction and Architecture, SAS, Bratislava 2002. (in Slovak)
- [2] Da Silva, C. A. R. at al. Carbonation-Related Microstructural Changes in Long-Term Durability Concrete. *Materials Research*, Vol. 5, No. 3, (2002) pp. 287-293.
- [3] Dias, W. P. S. Reduction of concrete sorptivity with age through carbonation. *Cem Concr Res* 30 (2000) pp. 1255 – 1261.
- [4] Gregg, S. J. & Sing, K. S. W. Adsorption, Surface Area and Porosity. Academic Press. London 1982.
- [5] Houst, Y. F. & Wittman, F. H. Influence of porosity and water content on the diffusivity of CO₂ and through hydrated cement paste. *Cem Concr Res* 24 (1994) pp 1165-1176.
- [6] Johannesson, B. & Utgenannt, P. Microstructural changes caused by carbonation of cement mortar. *Cem Concr Res* 31. (2001) pp. 925 - 931.
- [7] Ngala, V. T. & Page, C. L. 1997. Effects of carbonation on pore structure and diffusional properties of hydrated cement pastes. *Cem Concr Res* 27 (1997) pp. 995-1007.
- [8] Thomas, J., J. at al. Effect of Carbonation on the Nitrogen BET Surface Area of Hardened Portland Cement Paste. *Advn. Cem. Bas. Mat* 4, (1996) pp 76-80.
- [9] Ying-yu, Li & Qui-dong, W. The Mechanism of Carbonation of Mortars and the Dependence of Carbonation on Pore Structure, in *Concrete Durability – Katharine and Bryant Mather International Conference*, American Concrete Institute, Detroit. SP 100. Vol. 2, 1987, pp. 1915-1943.