Energy and Buildings 162 (2018) 198–207

Contents lists available at ScienceDirect

Energy and Buildings

journal homepage: www.elsevier.com/locate/enbuild

Evaluation of VIPs after mild artificial aging during 10 years: Focus on the core behavior

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ARTICLE INFO

Article history:
Received 1 September 2017
Received in revised form 6 December 2017
Accepted 7 December 2017
Available online 11 December 2017

Keywords:
VIP
Long term aging
Performance
Characterization
Silica core
Sorption isotherms
Drying tests
Thermal conductivity
Pressure
Weight gain

ABSTRACT

The prediction of the long term performance of VIPs remains challenging. To improve the forecast, the evaluation of VIPs aged for very long periods can help significantly. This study reports the characterization method which was implemented on VIPs after an artificial aging of 10 years in the laboratory, at room temperature in two different relative humidities: quite low and high (23 °C at 33 and 80 %RH). The aim is to evaluate the aging of the fumed silica core thanks to the detailed study of the hygrothermal and structural evolutions of the core material. The evaluation reveals that the silica core has been partly aged at high relative humidity (80 %RH), as highlighted by: (i) the moisture content at equilibrium which is not so high as the moisture content that could be reached by short-term additional aging of the sole silica at high humidity levels, (ii) the evolution of the specific area (decrease of only several percents). For the VIP aged at relatively high humidity, the water sorption isotherm indicates that the moisture content inside the VIP corresponds to a humidity level of 44 %: in comparison with the permeation at the beginning of the accelerated aging, the WVTR decreased approximately by a factor 2 (humidity gradient from 80 to 44 %). Furthermore, thanks to the follow-up on the weight and internal pressure of the VIPs, the permeances of the barrier laminate to water vapor and air are also estimated.

1. Introduction

The prediction of the long term performance of VIPs remains challenging. It is important that the thermal conductivity of VIPs after a long aging in laboratory or in service is not underestimated for their increasing application in buildings. There are many reasons for the deviation towards too low predicted values: e.g. the relevance of the model used or the accuracy of the data. According to the most commonly used models, the degradation of the thermal performance (conductivity increase) is due firstly to the increase of the internal pressure (main contribution: dry air), that leads to the increase of the gaseous contribution to the thermal conductivity and secondly to the increase of the solid conduction [1]. This increase of the solid conduction is due (i) to the physisorbed water on the silica skeleton and (ii) to the smoothing and coalescence of the primary particles of silica, both resulting in enhanced connection between the particles. Indeed, as it was extensively studied by Zhuravlev [2] and first observed by Transmission Electron Microscopy (TEM) by Morel for pyrogenic silica [3,4], the silica skeleton undergoes surface modifications during aging at 80 %RH (20–60 °C). TEM examinations show that the surface of the aged material appears smoothened and a coalescence of the primary particles is evidenced without any modification of the aggregates architecture [3,5] (Fig. 1). This is linked to the decrease of the measured specific surface area and suggests an enhancement of the structural contribution to the thermal conductivity.

Aging models developed a decade ago to predict the evolution of the centre-of-panel thermal conductivity do not take into consideration the aging of the core itself. Recently, difference between prediction and measurements has been pointed out by Brunner [6] whose measurements on monitored VIPs installed on a roof for about 8 years have shown an underestimation by the model by an amount of 1.1–1.4 mW/(m.K) in their centre-of-panel thermal conductivity [6]. The authors presume that aging of the core is the more likely explanation: a redistribution of Si and O atoms around the neck of SiO_2 particles enhances the structural heat transfer trough the SiO_2 skeleton.

To improve the knowledge and then the forecast, the evaluation of VIPs aged for very long periods can help significantly. It is the object of this study, which reports the characterization pro-

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https://doi.org/10.1016/j.enbuild.2017.12.016

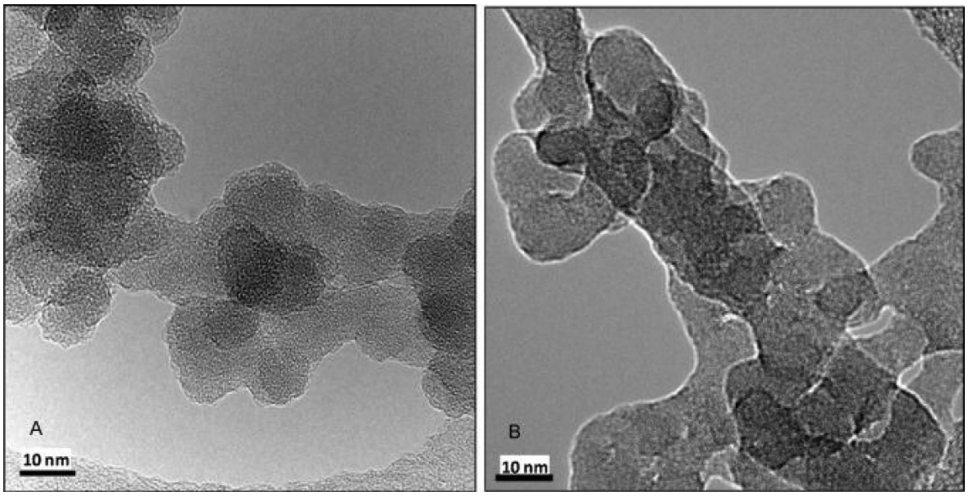

Fig. 1. TEM examination of the microstructure of pyrogenic silica HDK T30 in the fresh state (left) and after 205 days aging at 60 °C 80 %RH (right) (picture obtained by courtesy of B. Morel [3]).

cedure which was developed on VIPs aged during 10 years in the laboratory. The subject is of interest, and was also discussed during IEA EBC Annex 65 Kick-off Meeting in Grenoble in 2014 [7] and by R. Caps at the 2015 International Vacuum Insulation Symposium (IVIS) [8].

The aim is to evaluate the hygrothermal[1] and structural evolutions of the core material, thanks to water sorption measurements, drying tests, and nitrogen sorption measurements. The main issue is to evaluate the irreversible modifications of the silica core after 10 years of aging. The tests were proceeded on the core as the VIPs were opened but also after an additional aging of the core outside the VIPs during 1 month at high humidity level (90 %RH at 23 or 50 °C). The evolutions can be interpreted thanks to the detailed study of the aging of the fumed silica core. Concerning the barrier laminate, the follow-up on the weight and internal pressure of the VIPs gives an assessment of the water vapor and air permeances.

This paper investigates and discusses these points with the goal to improve the prediction of the conductivity evolution.

2. Experimental

2.1. Samples

The VIP samples were aged in Empa laboratory at 23 °C and in two different relative humidities, quite low (33 %) and high (80 %). 6 VIPs were studied (Table 1): 2 VIPs aged at 33 %RH (samples #12 & #13) and 4 VIPs aged at 80 %RH (samples #3 & #4 & #6 & #7). Both panels of smaller size (250*500*20 mm^3 whereas the others are 500*500*20 mm^3) were intended to optimize the handling for each analysis. The beginning of the aging discussed here was 2003, and it was ended in 2014.

The core is made up of fumed silica (Wacker WDS 200 $m^2.g^{-1}$), fibers and opacifier. Concerning the details of their composition and conditioning, the hypotheses done are:

- fibers: a mass ratio of 2 % of PET fibers was supposed but it could be also cellulose fibers.
- opacifier: SiC with a mass ratio of 5 %.
- drying at 140 °C.

[1] This paper uses the wording ≪hygro≫ to refer to water vapor, while the wording ≪hydro≫ is used for liquid water.

The barrier laminate is a three-fold metalized polymer laminate (previously studied in [9–13]). It was referenced MF4 in the Annex 39 of the IEA [9] and MF2 in the linked paper [10]. It was also called L1 in [11,12] and Type B in [13]. There is no gluing tape for labelling nor for fixing the folded seams (only a 2 cm^2 identification tag) so no perturbation of the weight gain is expected.

The measurements during aging are the following (VIPs of 500*500*20 mm^3):

- Mass and internal pressure at the beginning, after about 200 days and at the end with about 3950 days.
- Thermal conductivity at the beginning and at the end.

2.2. Evaluation method of the silica core

The evaluation method of the core is as follows:

1) Quantification of the water mass content τ_{VIP} by the weight measurements of the VIP. It was checked that the water content adsorbed in the sample τ_{ads} can be approximated by the water content of the VIP (negligible influence of the masses of water dissolved in the envelope and as vapor in the core porosity). Practically, depending on the quality of the initial drying the water content adsorbed in the sample τ_{ads} is the sum of the rate of initial water remaining in the core before sealing the VIP τ_{ini} and the rate of water uptake during aging $\Delta m\%$:

$$\tau_{ads} = \tau_{ini} + \Delta m\% \quad (1)$$

2) Quantification of the chemi- and physisorbed water by the drying method. The VIP is opened to sample the core, and then it is re-sealed. The drying is done thanks to a vacuum pretreatment instrument Belprep (*Bel Japan*) and an analytical balance (model AT261 DeltaRange, *Mettler Toledo*, resolution of 0.01 mg for samples weighed up to 62 g) as follows:

- first drying during 2 h at 140 °C, which is the temperature usually employed by the VIP manufacturers, for which the low energy physisorbed water is removed;
- second drying during 2 h at 200 °C, to be sure having dried all the physisorbed water including the high energy one [5,2]; the dried amount gives τ_{phys}.
- the chemisorbed amount can then be deducted:

$$\tau_{chem} = \tau_{ads} - \tau_{phys} \quad (2)$$

Table 1
samples characteristics and their aging conditions.

Sample #	Dimensions (mm³)	Aging			
		Conditions	Start date	End date	Duration
12	500*500*20	23 °C, 33 %RH	19/05/2003	31/03/2014	3969
13	500*500*20	23 °C, 33 %RH	19/05/2003	31/03/2014	3969
3	250*500*20	23 °C, 80 %RH	25/07/2003	31/03/2014	3902
4	250*500*20	23 °C, 80 %RH	28/07/2003	31/03/2014	3899
6	500*500*20	23 °C, 80 %RH	25/07/2003	31/03/2014	3902
7	500*500*20	23 °C, 80 %RH	25/07/2003	31/03/2014	3902

3) Water sorption isotherm at 25 °C after preparation under vacuum at 140 °C. The preparation is made with the Belprep and the isotherm $\tau_{ads} = f(p_v)$ is established on a very accurate apparatus (Belsorp Aqua, *Bel Japan*) using the volumetric method. The main parameters deducted from the isotherms for this work is the macroscopic hygrophilicity $\tau_{ads@50\ \%RH}$. This value could be used to evaluate the surface hygrophilicity $\psi_{ads} = \tau_{ads@50\ \%RH}/A_{BET}$ which is a way to characterize the surface chemistry. The comparison with the classical new silica gives the intensity of the aging of the core.

4) Water sorption isotherm at 25 °C after a treatment in climatic chamber (50 °C, 90 %RH, 1 month) to age the core close to a fully aged state.

5) Nitrogen sorption at −196 °C (77 K) to determine the specific area A_{BET} (BET method) and the pore size distribution (BJH method, on the desorption isotherm) and therefore evaluate aging. The same preparation than for water sorption measurement is made with the Belprep and the adsorption and desorption isotherms are recorded with a Belsorp Max (*Bel Japan*).

The nitrogen adsorption isotherm is close to the type IV(a), making it possible to assess the specific area by the Brunauer-Emmett-Teller (BET) method, within the p/p_0 range of ~0.05 – 0.30–0.35 [14,15]. This type of isotherm corresponds to mesoporous adsorbents. Its first part for the lowest p/p0 ratio (<0.42 in the case of nitrogen adsorption at 77 K) reflects the initial monolayer – multilayer adsorption on the mesopores walls. Then, increasing p/p0, pore condensation occurs. While continuing to increase the p/p_0 ratio, a plateau (of variable length, sometimes reduced to an inflexion point) corresponds to the saturation of the mesopores. In the case of a type IV(a) isotherm, the capillary condensation is accompanied by a hysteresis between adsorption and desorption (this hysteresis takes place for mesopores wider than ~4 nm in the case of nitrogen desorption in cylindrical pores at 77 K).The isotherms recorded on VIP cores do not show a plateau but an inflexion point.

As the reference state of the silica is no more available, the silica aged at (23 °C, 33 %RH) is considered to be very little modified.

2.3. Evaluation method of the multilayer barrier laminate

The weight and internal pressure increases of the VIPs were recorded, so the water vapor and air permeance of the barrier laminate can be estimated. The following equations were used:

$$j = \pi \cdot A \cdot (p_{ext} - p_{int}) \tag{3}$$

where

j = mass flux (kg s^{-1})
π = permeance (kg.m^{-2} s^{-1} Pa^{-1})
A = barrier laminate area (m^2)
p_{ext}, p_{int} = partial pressures outside, inside the VIP (Pa)

For water vapor, the weight increase during the aging is used and Eq. (4) directly gives the permeance of water vapor:

$$\pi_{wv} = \frac{dm}{dt} \cdot \frac{1}{A \cdot (p_{wv,ext} - p_{wv,\mathrm{int}})} \tag{4}$$

For air, the pressure increase inside the VIP during the aging is used to calculate the mass permeance by Eq. (5):

$$\pi_a = \frac{M_a \cdot V_{pores}}{R \cdot T} \cdot \frac{dp_{a,int}}{dt} \cdot \frac{1}{A \cdot \left(p_{a,ext} - p_{a,int}\right)} \tag{5}$$

where

$dp_{a,int}/dt$ = evolution of the internal pressure of air with time (Pa.s^{-1})
$p_{a,ext} - p_{a,int}$ = difference of the partial pressure of air outside and inside the VIP
M_a = molar mass of air (kg mol^{-1})
V_{pores} = porous volume of the VIP core (m^3)
R = universal gas constant (8.314 m^3 Pa K^{-1} mol^{-1})
T = temperature (K)

The value required for the calculation of the air permeance is the partial pressure of dry air in the panel after aging. Two different methods were used to determine it:

1 The first is the more indirect, it needs the total pressure inside the panel and the partial pressure of water vapor, obtained via the water vapor sorption isotherm. The air pressure is therefore:

$$p_{a,int} = P_{t,int} - p_{wv,int} \tag{6}$$

2 The second uses the determination of the pressure inside the panel at low temperature (< −20 °C) that approximates the partial pressure of air.

Both suppose that the initial pressure of the VIP is due to air.

Concerning the first method, the measurement of the total internal pressure of the VIP was made at EDF with the lift-off method of the envelope in a vacuum climatic chamber [9,16]. The measurement principle is based on the lift-off of the barrier film as soon as the internal pressure of the VIP becomes higher than the surrounding pressure.

The water vapor pressure was assessed thanks to the weight gain measurement, Δm_w – assumed to be due only to water – that is reported next on the water vapor adsorption isotherm of the core in order to find the equilibrium pressure $p_{wv,int}$.

The second method, lift-off at low temperature, is to our insights first time used in this scientific paper, as it was just published [17]. The principle is to perform the lift-off method on VIPs at very low temperature that is the temperature where the saturation pressure of water (p_{sat}) is lower than the needed accuracy on the pressure. Typically at T < −20 °C, P_{sat} for water vapor is less than 1 mbar. In this case, the partial pressure of air can be approximated by the total internal pressure. The air pressure must then be converted at room temperature by Eq. (7) (temperatures expressed in K):

$$p_{a,int@23\,^\circ C} = P_{t,int@T<-20\,^\circ C} \frac{296.15}{T} \tag{7}$$

In order to calculate the air permeance (Eq. (5)), the pressure $p_{a,int}$, the temperature T and the porous volume V_{pores} should be

coherent; a simple way is to express the three parameters at ambient conditions or STP conditions.

As for the classical method the true volume of pores must be used); the volumes of the solid skeleton as well as the volume of the adsorbed water must be subtracted from the total volume of the VIP at the equilibrium pressure $V_{pores} = V_{total@Pt}$:

$$V_{pores} = V_{total@Pt} - \frac{m_{core}}{\rho_s} - \frac{m_w}{\rho_w} \quad (8)$$

with:

m_{core} and ρ_s = mass and skeleton density of the core ($\sum \frac{m_i}{\rho_{0i}}$ if the core contains several constituents). Remark: The real mass of the core is calculated from the mass of the VIP by subtracting that of the film.

m_w and ρ_w = mass and density of water

$V_{total@Pt}$ = total volume of the VIP at the equilibrium pressure

The influence of the temperature on the skeleton and water densities and on the core thermal expansion are neglected.

The total volume at the equilibrium pressure $V_{total@Pt}$ is classically obtained by the dimensions of the VIP core at atmospheric pressure. In the lift-off method at low temperature, the mechanical behavior of the core and the expansion of volume due to the decrease of the pressure are taken into account. For the silica based cores, a linear elastic behavior is observed:

$$V_{total@Pt} = V_{total@Patm} \cdot \left(1 + \frac{P_{atm} - P_{t,int}}{E}\right)^3 \quad (9)$$

where:

$V_{total@Patm}$ = total volume of the VIP at the atmospheric pressure (obtained by the dimensions of the core)

E = Young modulus of the core

The Young modulus of the core can be determined by compression tests or during the decompression of the VIP in the vacuum climatic chamber by the slope of the curve $d = f(p)$ if the laser mounting system at the vacuum chamber is done in a way that there is no or small influence of the vacuum chamber wall deformation.

3. Results

3.1. Weight, pressure and conductivity increase over 10 years

The evolutions of the mass, internal pressure and conductivity for just over 10 years are listed in Tables 2a and 2b. After aging at EMPA at low and high humidity levels over 10 years, the VIPs were stored at EDF at (23 °C, 50 %RH).

During aging, the mass and pressure of the VIPs increase because of the water vapor and air permeations through the envelope (Table 2a). For the VIPs aged at (23 °C, 33 %RH), these increases are moderate (0.57 % mass, 5 mbar), but relatively important for the VIPs aged at 80 %RH (about 3.25 % mass, 17.5 mbar). The weight gain is to be compared to the one of a fully aged fumed silica core which could uptake about 5 % of mass or more at 80 %RH (cf. [5] and the results hereafter). The pressure inside the VIPs places them roughly always on the lower plateau of conductivity versus pressure for the aging at 33 %RH and in the beginning of the increase for the aging at 80 %RH. As a consequence of this water and pressure uptakes, the conductivity of the panels increases respectively by 0.6 and 2.2 mW/(m.K) (Table 2b). In comparison with vented VIPs, the conductivity values remained low and the insulation performance of the VIP was good even after 10 years at (23 °C, 80 %RH).

The VIPs can even be dried, if the environmental conditions change, as it was confirmed by the weight loss of the VIPs firstly aged for 10 years at (23 °C, 80 %RH) over the last years, where they were placed at (23 °C, 50 %RH).

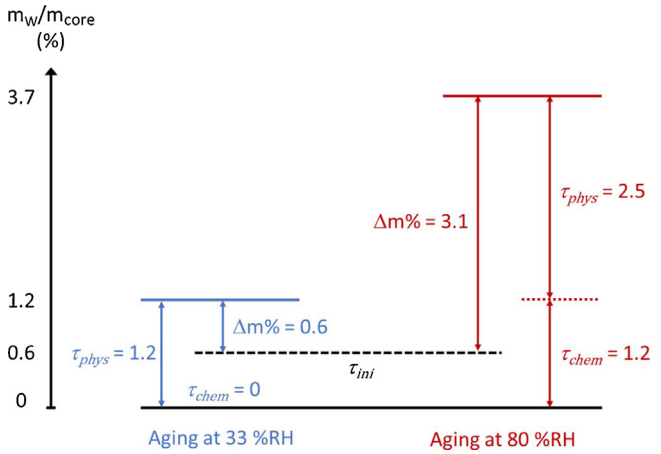

Fig. 2. water mass content of the VIP cores after aging over ten years at 23 °C and 33 or 80 %RH deducted from weight measurements during aging (Δm%) and from drying tests at 200 °C (τ_{phys}). Details of chemisorbed (τ_{chem}) and physisorbed (τ_{phys}) contributions.

In Table 2b, the differences in conductivity values measured at EMPA ("aged 1") and at EDF ("aged 2") could come from the difference in instruments and to a small amount from the different time of measurement. The apparatuses used for the conductivity measurement are different: heat flow meter at EDF, guarded hot plate at EMPA.

While at Empa a symmetrical measurement was done, that uses the assumption that nominal identical samples are the same, the measurement made at EDF on each sample confirms that the pairs stored at the same conditions had the same thermal conductivity.

3.2. Drying tests

The weight loss of the core dried 2 h at 140 and 200 °C is given in Table 3 (% of the wet initial mass).

The amount of physisorption τ_{phys} is about 1.2 % for the VIPs aged at 33 %RH and 2.5 % for the VIPs aged at 80 %RH.

According to the results obtained for the samples aged at 33 %RH, it can be noted that after drying at 140 °C some physisorbed water remains (0.32 % of the sample mass), which corresponds mainly to high energy physisorption. The amount of high energy physisorbed water is lower for samples aged at 80 %RH (0.17 %). The results confirm the need to dry at 200 °C to completely dry the physisorbed amount of water.

Fig. 2 gives the details of the water mass content of the VIP cores, deducted from the weight measurements during aging and from the drying tests at 200 °C. As the humidity inside samples #12 and #13 is low (< 33 %RH thanks to the external conditions and ≈21 % thanks to the weight gain and the water adsorption isotherm Fig. 3, cf. § *Water vapor sorption*), it can be assumed that no chemisorption coming from the aging occurred in these cores (of course some chemisorbed water exists which comes from the production of the silica). It can then be concluded that the weight loss by drying, which is higher than the water uptake during aging (Table 3), indicates that the initial drying wasn't fully completed; the remaining amount of water was thus 0.6 % (Eq. (1)).

The initial internal pressure measured for VIP samples # 12 and # 13 was 0.94 and 0.99 mbar at 23 °C (Table 2a), that corresponds to a humidity of p/psat <3.4 % (considering that the water vapor pressure is a fraction of total pressure, psat = 2810 Pa at 23 °C). According to the initial water sorption isotherms (Fig. 4, VIP #12), this humidity corresponds to a water content lower than 0.3 %.

Table 2a
weight gain and pressure increase in the VIP after low and high humidity aging in climate chambers over more than 10 years.

Sample #	Aging		$m_{initial}$ (g)	m_{aged1} (g)	Δm (%)	$p_{initial}$ (mbar)	p_{aged1} (mbar)	Δp (mbar)
	Conditions T °C – RH %	Duration (days)						
12	23–33	3948	964.61	970.07	0.57	0.94	6.02	5.1
13	23–33	3948	948.61	954.05	0.57	0.99	5.80	4.8
3	23–80	3902	508.27	*524.95*	*3.28*	0.91	–	–
4	23–80	3899	477.81	*494.21*	*3.43*	1.10	–	–
6	23–80	3881	956.23	986.47	3.16	0.96	18.62	17.8
7	23–80	3881	940.06	969.26	3.11	0.89	18.39	17.5

In italics: weighing performed at EDF laboratory after storage at (23 °C, 50 %RH) during 213 days.

Table 2b
weight gain, pressure increase in the VIP and conductivity evolution after low and high humidity aging over more than 10 years.

Sample #	$\lambda_{cop\ initial}$ (mW m^{-1} K^{-1})	Aging		$\lambda_{cop\ aged\ 1}$ (mW m^{-1} K^{-1})	$\Delta\lambda_{cop}$ (mW m^{-1} K^{-1})	Storage		$\lambda_{cop\ aged\ 2}$ (mW m^{-1} K^{-1})
		Conditions T °C – RH %	Duration (days)			Conditions T °C – RH%	Duration (days)	
12	3.9	23–33	3969	4.5	0.6	23–50	199	4.8
13		23–33	3969			23–50	199	4.8
3	–	23–80	3902	–	–	23–50	218	7.0
4	–	23–80	3899	–	–	23–50	218	7.0
6	3.9	23–80	3902	6.1	2.2	23–50	200	6.6
7		23–80	3902			23–50	211	6.6

Table 3
weight loss of the core by drying (assessment of the physisorbed water τ_{phys}) and comparison with the weight gain during aging.

VIP Sample #	Aging		Test sample	Weight loss by drying (%)		Δm (%)*
	Conditions T °C – RH %	Duration (days)		at 140 °C	at 200 °C	
12	23–33	3969	12–1	0.85	1.16	0.57
13	23–33	3969	13–2	0.94	1.25	0.57
			Mean 12-1/13-2	0.89	1.21	0.57
3	23–80	3902	3–1	2.29	2.38	
			3–3	2.32	2.56	
			Mean 3-1/3-3	2.30	2.47	3.13

* From the weight measurements of VIPs. For the conditions (23 °C, 80 %RH), the value comes from the largest VIPs # 6 & # 7, because the uncertainty is lower.

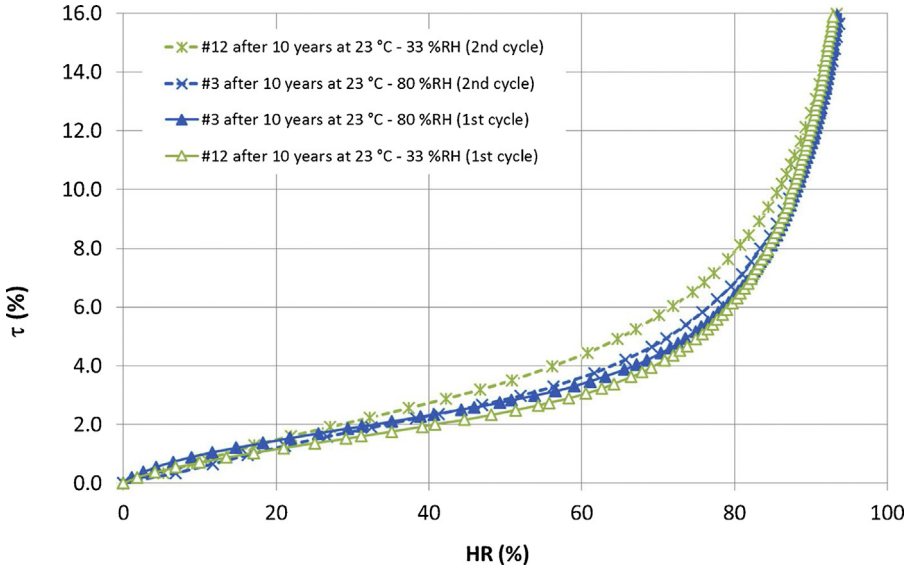

Fig. 3. adsorption isotherms at 25 °C on VIP samples # 3 & # 12 (2 successive cycles). Preparation of the samples: vacuum drying at 140 °C during 2 h.

Comparing the results obtained by drying tests τ_{phys} and the weight gain of the VIP aged at 80 %RH (Table 2a and 3), the amount of chemisorbed water τ_{chem} is 1.2 % (Eqs. (1)–(2)) which is a typical value of fumed silica [5].

To conclude, the most significant points are that there is no chemisorption and no aging of the core detected over 10 years in samples aged at 33 %RH, and that there is some chemisorption and some aging of the core in samples aged at 80 %RH.

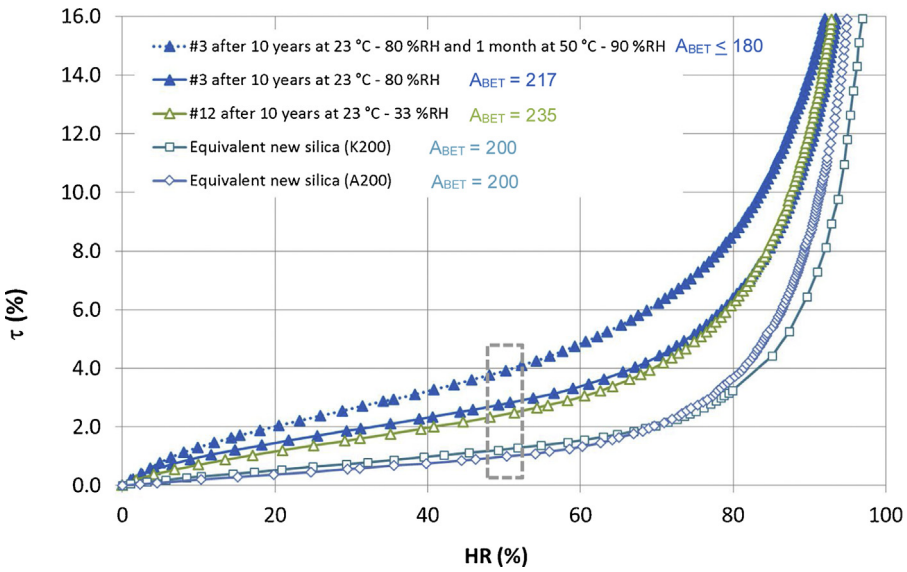

Fig. 4. adsorption isotherms at 25 °C on formulated cores after aging and on new equivalent product for the initial state. Preparation of the samples: vacuum drying at 140 °C during 2 h.

3.3. Water vapor sorption

The water sorption isotherms were recorded on the core just as the VIP was opened and also after an additional aging of the core outside the VIP during over 1 month at high humidity level for one VIP aged at 80 %RH. This additional aging was performed at 23 °C to evaluate the level of the long-term aging at (23 °C, 80 %RH) and at 50 °C to compare with the maximum level that the silica core could reach.

For the VIPs aged at 80 %RH during 10 years, the silica core does not undergo any additional aging during the sorption isotherm recording, as it was evidenced by the comparison of the 1st and 2nd cycles recorded on one sample of VIP #3 (Fig. 3). It is not the case for the core samples of the VIPs aged at 33 %RH during 10 years, as illustrated on one sample of VIP # 12 on Fig. 3 and in Table 4. The comparison of the 1st and 2nd cycles shows for this core sample a significant evolution of the silica during recording. For both conditions, the maximum humidity level reached when recording the isotherm was about 95 %, thereby confirming that the unaged core has the potential to evolve more easily than a more aged one.

Another point is that the macroscopic hydrophilicity is only a little bit higher for the core aged at 80 %RH than those on aged at 33 %RH.

The isotherms of VIPs aged during 10 years at the two levels of relative humidity are compared with isotherms recorded on new equivalent pyrogenic silicas Aerosil® 200 and Konasil® 200 on Fig. 4. Table 4 gives the equilibrium water content at 50 %RH for the samples tested, just as aged and also after short-term additional aging of the core for the VIP aged at 50 °C 90 %RH.

The water adsorption isotherm of the core aged at 33 %RH appears higher than those of reference silicas. A small part of this difference is due to their highest specific area and the main part is relative to a more hydrophilic surface.

The water content after both aging conditions during 10 years is relatively moderate in comparison with the levels reached after additional aging of the core (Table 4). This highlights that VIP cores are able to age further.

The water vapor isotherms allow also to estimate the humidity level reached inside the VIPs:

- For the VIPs aged at 33 %RH, 1.2 % of physisorbed water corresponds to a humidity level inside the VIP of 21 % or 6.6 mbar at 23 °C (p/p0 = 0.21 and p0 = $p_{sat@25\,°C}$ = 3169 Pa –> $p_{@25\,°C}$ = 6.65, then converted to 23 °C by p1/p2 = T1/T2);
- For the VIPs aged at 80 %RH, 2.5 % of physisorbed water corresponds to a humidity level inside the VIP of 44 % or 13.9 mbar at 23 °C.

An important point is that in comparison with the permeation at the beginning of the accelerated aging, the WVTR therefore decreased respectively by a factor 3 and 2 (humidity gradients from 33 to 12 and from 80 to 36 %).

3.4. Nitrogen sorption: evolution of the specific area and of the pore size distribution

Table 5 gives the BET specific areas (A_{BET}) deducted from the nitrogen adsorption.

To assess the value of the specific area of the sole silica, the hypothesis made on the composition of the real core (2 wt% of fibers and 5 wt% of opacifier) leads to a correction of 7 % (only the average value is given for the silica in Table 5).

In comparison with the A_{BET} of the sample aged at (23 °C, 33 %RH), the A_{BET} for an aging at 80 %RH appears nearly stable with a very small decrease of only 6 %. This small decrease of A_{BET} confirms that the aging was not so important to induce a collapse of the specific surface. As expected, the A_{BET} of the core additionally aged outside the VIP shows a greater decrease (17 % decrease by the additional aging). The specific area of equivalent pyrogenic silicas fully aged can decrease down to 135 $m^2\,g^{-1}$ (value measured in our laboratory on Konasil® 200 after 96 days at (70 °C, 90 %RH)) [unpublished results].

Moreover, the pore size distribution (Fig. 5), calculated by the BJH method on the desorption isotherm which is of type IV(a) [18], of VIPs aged during 10 years at (23 °C, 80 %RH) is not significantly modified in comparison with the one of VIPs aged 10 years at (23 °C, 33 %RH) – likened to the pore size distribution of the core in a new state. This is another argument to highlight the moderate aging of the core despite the high and stationary external humidity level. The same observation can be done for VIP cores aged 10 years at high relative humidity, followed by an additional aging of a few weeks of the silica core outside the VIP at higher humidity, as illustrated on Fig. 5.

Table 4
water content deducted from the adsorption isotherm.

Sample #	Aging	$\tau_{ads@50\%RH}$ (%)	
		1st cycle	2nd cycle
12	10 years at (23 °C, 33 %RH)	2.43	3.45
13	10 years at (23 °C, 33 %RH)	2.44	–
13	10 years at (23 °C, 33 %RH)	2.34	–
3	10 years at (23 °C, 80 %RH)	2.79	2.87
4	10 years at (23 °C, 80 %RH)	2.88	3.04
4	10 years at (23 °C, 80 %RH)	2.94	3.05
3	10 years at (23 °C, 80 %RH) + core during 1 month at (50 °C, 90 %RH)	3.9	–

Table 5
BET specific area (nitrogen measurements) of the core and estimation for the silica.

Sample #	Aging	$A_{BET\ core}$ *measured* ($m^2\ g^{-1}$)	$A_{BET\ silica}$ *calculated* ($m^2\ g^{-1}$)
12	10 years at (23 °C, 33 %RH)	219–220	235
3	10 years at (23 °C, 80 %RH)	205	219
4	10 years at (23 °C, 80 %RH)	199–205	216
3	10 years at (23 °C, 80 %RH) + core during 1 month at (23 °C, 90 %RH)	168	180

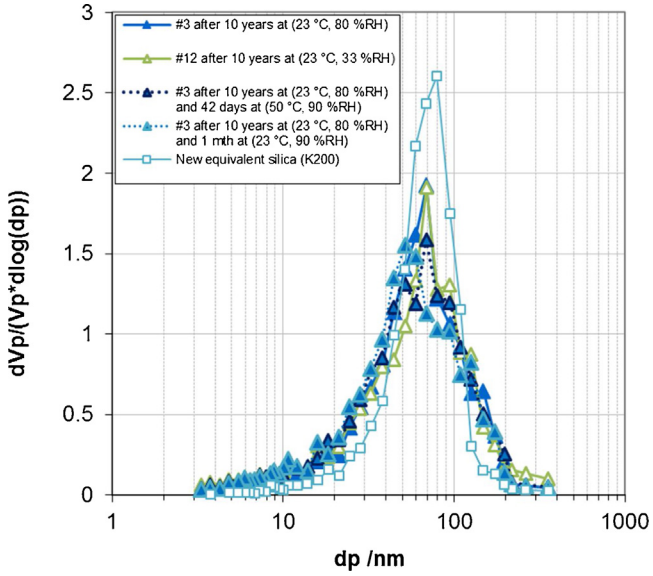

Fig. 5. pore size distribution of VIPs aged during ten years at 23 °C – 33 and 80 %RH (normalized to the porous volume). Comparison with new equivalent products and with additional aging of the core at 90 %RH.

3.5. Evaluation of the laminate

The permeances of water vapor and air calculated from Eqs. (4)–(5) are given in Table 6.

For air, the permeance is given based on three different method and pressures: the first without considering the contribution of water vapor (referenced (1) in Table 6) and the two others as exposed in the method section with only the dry air pressure deducted from the water isotherm ((2) in Table 6) or measured at low temperature ((3) in Table 6).

For this last method, the internal partial pressure assessed by the lift-off method at −39.6 °C for the VIP sample # 13 after aging, was measured equal to 3.7 mbar, or 4.7 mbar converted at room temperature (23 °C). The pressure can be determined by the intersection of the tangents of the de-compression and lift-off parts of the curve or by the naked eye, choosing the first point that emerges from dispersion (Fig. 6 shows the lift-off behavior at −28.6 °C for the VIP sample # 13). The Young modulus of the silica core can be determined by linear regression on the de-compression part of the curve (before the lift-off of the envelope): with the experiment shown in Fig. 6, the modulus is found to be about 1.6 MPa.

Table 6 shows a clear disagreement between the results obtained with the first method and the two others for the samples aged at 80 %RH. Of course the first method overestimates the air pressure and thus the air permeance. The overestimation is slighter on the samples aged at 33 %RH. This is fully consistent because the overestimation increases with humidity and thus with water pressure (14 mbar for the VIPs aged at 80 %RH compared to 5.9 mbar at 33 %RH). The two other methods which distinguish the contribution from air and vapor give similar results considering the moderate accuracy of the second method.

The values of water vapor permeance match very well with the one measured twelve years ago by Simmler and Brunner [9,10], on this laminate: 4E–14 kg $m^{-2}\ s^{-1}\ Pa^{-1}$. The same comment applies on the results for air permeance where the previous work leads to 2.4E–18 kg $m^{-2}\ s^{-1}\ Pa^{-1}$ (0.016 $cm^3_{STP}\ m^{-2}\ d^{-1}$). The ratio between the water vapor and air permeances is about 4 orders of magnitude, that corresponds to bibliographic data [19].

Table 6
permeance of water vapor assessed from weight and permeance of air/gas from pressure increases over 10 years (mean values over 2 VIPs).

Sample #	Aging	π_{wv} (kg m^{-2} s^{-1} Pa^{-1})	π_g (kg m^{-2} s^{-1} Pa^{-1})	π_a (kg m^{-2} s^{-1} Pa^{-1})	
12/13	10 years at (23 °C, 33 %RH)	3.2E-14	1.8E-18	7.1E-19	9.8E−19 *
3/4	10 years at (23 °C, 80 %RH)	7.5E-14	–	–	–
6/7		7.4E-14	6.2E-18	1.3E-18	–
		Based on weight gain data of whole VIP	(1) Based on pressure increase data of whole VIP	(2) Based on estimation of the dry air pressure inside the VIP (cf. §. *Water vapor sorption*)	(3) Based on the measurement of the total pressure at low temperature

* The value of the total pressure considered here (8.2 mbar) was measured at EDF by the lift-off method at 25 °C (equal if converted to 23 °C) at the same time than the measurement was done at low temperature (−39.6 °C) to assess the air pressure, so after 3 years additional aging at (23 °C, 50 %RH).

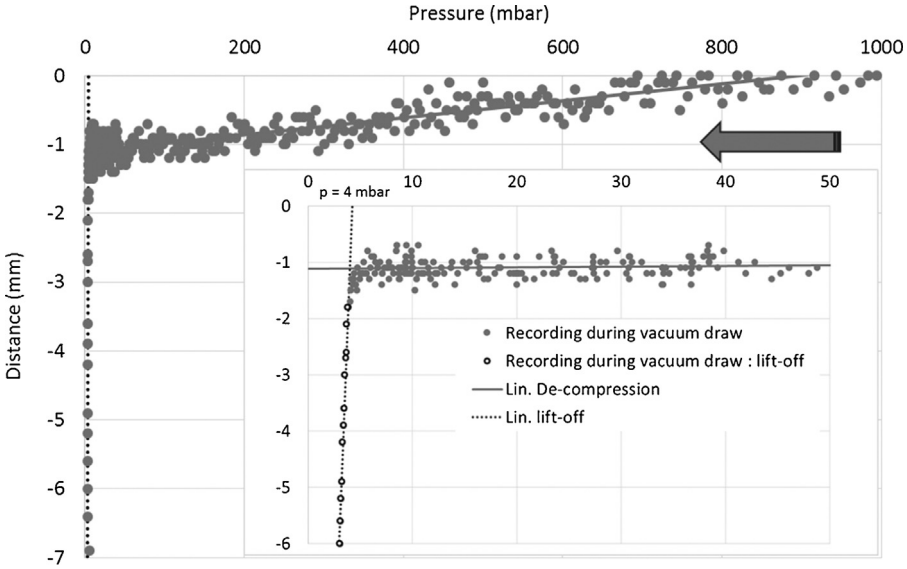

Fig. 6. lift-off behavior of the VIP # 13 aged 10 years at (23 °C, 33 %RH), measured at −28.6 °C. The upper and lower limits of the pressure intervals for de-compression and lift-off are chosen by the operator.

The values of the air and water vapor permeances correspond to current high quality metalized laminates. The real permeance over ten years is the same as the permeances at the beginning of the test showing that no significant degradation of the laminate occurs during this time. This is consistent with recent work about the degradation of similar laminates during aging of VIPs [20].

4. Discussion

4.1. Evaluation of the surface hygrophilicity

The ratio of the water content at equilibrium at 50 %RH divided by the specific area $\psi_{ads} = \tau_{ads@50\,\%RH}/A_{BET}$ is a fine way to express the surface hygrophilicity which can be strongly affected in the case of aging. The results are shown in Table 7.

The surface hygrophilicity of the core of the VIP aged at (23 °C, 33 %RH) during 10 years is intermediate between the one of standard fumed silica in fresh state and the value obtained on this silica aged 30 days at (23 °C, 80 %RH). Aging of the core began. The surface hygrophilicity of the core of the VIP aged at (23 °C, 80 %RH) during 10 years was multiplied by a factor 3 in comparison with the one of new equivalent silicas, that means that the physisorbed water is three times higher. The surface hygrophilicity is closer to the value of the silica aged 30 days at (23 °C, 80 %RH) outside any VIP. This shows that the core of the VIP aged 10 years at (23 °C, 80 %RH) is relatively aged, but not completely. This is consistent with the estimated humidity inside the VIP (only 44 % for an equilibrium value of 80 %, cf. section *Water vapor sorption*).

4.2. Prediction of the conductivity evolution

4.2.1. Impact coefficient of water and pressure intakes

The models developed in 2005 are expressed in the following equations [5,10]:

$$\lambda = B \cdot \tau_W + G \cdot p_g \tag{10}$$

$$\Delta\lambda_{(t)} = B \cdot \tau_{W\infty} \cdot \left(1 - \exp\left(\frac{-t \cdot \dot{m}_{t_0}}{\tau_{W\infty}}\right)\right) + G \cdot \Delta p_{g(t)} \cdot t \tag{11}$$

where

τ_w, $\tau_{w\infty}$ = water content of the VIP and at equilibrium

p_g = gas pressure inside the VIP (p_{int} in the simplified version or $p_g = p_{dry\ air} = p_{int} - p_{wv}$ in the version used in [10,21])

$\dot{m}_{t_0} = \left(\Delta m/\Delta t\right)_{t_0}$ = initial mass increase rate

The values of the parameters B and G, which don't consider any aging of the core, are the following [10], [21]:

B = 0.5 mW m^{-1} K^{-1}%$^{-1}$

G = 0.035 mW m^{-1} K^{-1} mbar^{-1}

This simple model has been applied with the values of the aging of 10 years (Table 1). The predicted values of the conductivity are given in Table 8 and compared with the measured values. They are in good agreement.

Table 7
assessment of the surface hygrophilicity of the VIP core.

Sample #	Aging	ψ_{ads} ($\mu g\,m^{-2}$)
12	VIP 10 years at (23 °C, 33 %RH)	102
3	VIP 10 years at (23 °C, 80 %RH)	136
4	VIP 10 years at (23 °C, 80 %RH)	145
4bis	VIP 10 years at (23 °C, 80 %RH)	143
Reference fumed silica	silica not aged	47
	silica, 30 days at (23 °C, 80 %RH)	170
	silica, 24 h at (70 °C, 90 %RH)	185

Table 8
calculated values by the model Eq. (10) and measured values of the thermal conductivity increase.

Sample #	Aging	Δm	Δp_{int}	$\Delta\lambda_{calc}$	$\Delta\lambda_{meas}$
		(%)	(mbar)	($mW\,m^{-1}\,K^{-1}$)	
12	3948 days at (23 °C, 33 %RH)	0.57	5.1	0.5	0.6
13	3948 days at (23 °C, 33 %RH)	0.57	4.8	0.5	0.6
6	3881 days at (23 °C, 80 %RH)	3.16	17.8	2.2	2.2
7	3881 days at (23 °C, 80 %RH)	3.11	17.5	2.2	2.2

Table 9
mass and pressure increase rates and permeances for different VIPs aged at 23 °C.

Sample #	Aging	Size	$\Delta m/\Delta t$	$\Delta p_{int}/\Delta t$	π_{wv}	π_g	π_a	
		(cm^3)	(% y^{-1})	(mbar y^{-1})	($kg\,m^{-2}\,s^{-1}\,Pa^{-1}$)	($kg\,m^{-2}\,s^{-1}\,Pa^{-1}$)	($kg\,m^{-2}\,s^{-1}\,Pa^{-1}$)	
12/13	3948 days at (23 °C, 33 %RH)	50 × 50 × 2	0.05	0.5	3.2E-14	1.8E-18	7.1E-19	9.8E-19
[10,22]	180 days at (23 °C, 50 %RH)	25 × 25 × 2	0.16	1.4	6.0E-14	4.0E-18		
		25 × 50 × 2	0.13	1.3	5.1E-14	3.8E-18		
		50 × 50 × 2	0.12	1.0	4.9E-14	3.0E-18		
3/4	222 days at (23 °C, 80 %RH) [22]	25 × 50 × 2	0.22	1.1	5.6E-14	4.1E-18		
	4115 days at (23 °C, 80 %RH)		0.30	–	7.5E-14	–		
6/7	236 days at (23 °C, 80 %RH) [22]	50 × 50 × 2	0.21	1.3	5.3E-14	4.8E-18		
	3881 days at (23 °C, 80 %RH)		0.30	1.7	7.4E-14	6.2E-18	1.3E-18	
						Based on pressure increase data of whole VIP	*Based on estimation of the dry air pressure inside the VIP*	*Based on the measurement of the pressure at low temperature*

Table 10
mass and pressure increase rates for different VIP aged at 23 °C; comparison of the calculated and measured conductivity increases.

Sample	Aging	Size	$\Delta m/\Delta t$	$\Delta p_{int}/\Delta t$	$\Delta\lambda$forecasted Eq.10	$\Delta\lambda$forecasted Eq.11	$\Delta\lambda$measured
		(cm^3)	(%.y^{-1})	(mbar.y^{-1})	($mW.m^{-1}.K^{-1}$)		
6/7	236 days at (23 °C, 80 %RH) [22]	50x50x2	0.21	1.3			
	3881 days at (23 °C, 80 %RH)		0.30		1.6	1.5	2.2

This shows that the parameters *B* and *G* are suitable and accurate for the VIPs aged during 10 years. In other words this means that the core is not sufficiently aged to exhibit thermal modified behavior, and thus to modify the parameters *B* and *G*. This conclusion is consistent with the one deducted from the surface hygrophilicity and A_{BET}. Remark: The conductivity increase due to water estimated from Eq. (10), assuming that all the gas inside VIP is air and that water only contributes to solid conduction, is about 60 % for the VIPs aged at (23 °C, 33 %RH) (# 12 and # 13) and about 70 % for the VIPs aged at (23 °C, 80 %RH) ((# 6 and # 7).

4.2.2. Relevance of short-term determination of the permeances

Another question is the relevance for very long durations of the permeances of water and air determined by short-term tests. The short-term values for these VIPs for water vapor (previously estimated [10] and deducted from the present work and [22]) are compared in Table 9 to the long-term ones (this publication and the presentation of R. Caps at the Annex 65 of the IEA in September 2014 [23]).

The water vapor permeance is calculated from the mass uptake. In Table 9, the gas/air permeance is calculated by the 3 methods described above and already used in Table 6.

The experimental results reveal no significant dispersion in the couples of samples tested (individual results not given in the Table). The following observations can be made (Table 9):

- Unlike other works [9,10,21], no influence of the geometry (ratio between surface area and perimeter of the VIPs) is observed. This might be related to the small difference in dimension of samples considered here.
- The water vapor and gas permeances at 80 %RH are close to those at 50 %RH and slightly higher than those at 33 %RH.

Using the short-term tests, it is finally possible to estimate the long-term conductivity increase using Eqs. (10) and (11). For this last equation, the parameter $\tau_{W\infty}$ is taken equal to 8 % (Fig. 4).[2] The comparison with the measured conductivity increase is done for samples 6 and 7 in Table 10. The two methods underestimate this increase for one third; this is consistent with already cited work [6]. Keeping in mind that in the present case the core is not fully aged, the underestimation with Eqs. (10) and (11) should increase with longer duration. The link between the conditions, the aging of the core and the impacts on conductivity needs further works to be finer assessed; some are already in progress.

5. Conclusions and outlook

The evaluation of VIPs after mild artificial aging during 10 years revealed that the silica core has not been fully aged, even at high relative humidity (80 %RH). This was highlighted by different results: i) the amount of chemisorbed water, ii) the moisture content at equilibrium, which is below the moisture content that could be reached by short-term additional aging at higher humidity levels, iii) the decrease of the specific area, iv) the increase of the surface hygrophilicity, and v) the validity of the parameters *B* and *G* for the simplified model.

The water sorption isotherm indicates that the moisture content inside the VIPs, deducted from the weight increase, corresponds to a humidity level of 40–50 % for the VIPs aged at 80 %RH. So the water ingress has slowed down, the WVTR has been divided by a factor 2 in comparison with the one at the beginning of aging. And the VIPs can even be dried, if the environmental conditions change, as it was confirmed by the weight loss of the VIPs over the last year, where they were placed at (23 °C, 50 %RH).

As the main lever to age the silica is the humidity, it can be deducted that the VIP aging is divided in two steps: the first where no aging of the silica occurs because of too dry conditions inside, and a second one where the silica ages because of the high humidity inside. For the studied samples the results above lead to estimate the duration of the first period over ten years. In the second step, the increase of the surface hydroxylation precedes the textural evolutions. To go further, similar investigations of VIPs from real applications with changing boundary conditions should give clearer answers.

Acknowledgements

The authors acknowledge the ANR (French National Research Agency) for their financial support of the EMMA-PIV project (ANR-12-VBDU-0004) and the SFOE (Swiss federal office of energy) for the financial support of Empa in the Annex 65 project. Special thanks to Dr. Roland Caps (va-Q-tec) for the fruitful discussion and to Christophe Gourgues (EDF R&D) for the experimental tests.

[2] This value corresponds to the core "SIL2" [9] which is in fact a value corresponding to an unexpected aging during testing the water isotherm as evidenced in [5]. If this choice wasn't relevant in 2005, it is more relevant in the present case because it corresponds to the water content of a similar core fully aged at 80 %RH.

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