Permeation of water vapor through high performance laminates for VIP

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3. Vacuum Insulation Panels
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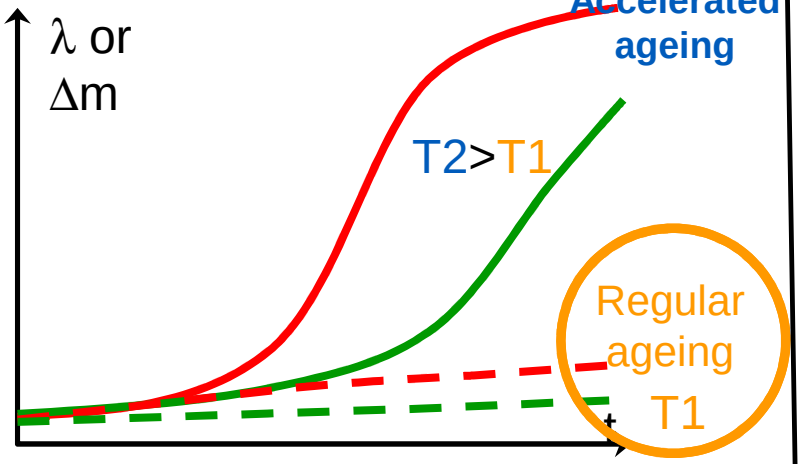
5. Conclusions

Introduction

Ageing of VIP



- Based on :
  - 10 different commercial laminates
  - over 400 measurements
  - 4 different aging conditions
  - up to 28 month duration

Ageing of barrier film

Delamination
⇔ T

Corrosion
⇔ RH

No ageing
(permeance point of view)

This presentation only covers water vapor permeation

[G. Garnier, PhD thesis. Institut Polytechnique de Grenoble (2009)]
[B. Yrieix et al. Rapport final du projet ADEME PREBAT "Barisol" (2010)]

Introduction

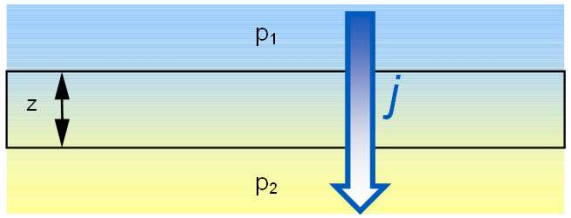
- expectations from end-users and VIP manufacturers regarding the long term performance of VIP, dictated by the permeance of the barrier films :
  - maintain core under vacuum
  - limit uptake of humidity

- quality of the metallization and the laminating adhesives is key to the performance of the barrier film

- various techniques available :
  - direct measurements on barrier foils :
    - applicable on a single layer or on the multilayer structure
    - several methods available, including :
      - manometric method
      - cup method
      - radioactive tracers
      - coulometric method
      - mass spectrometry
  - indirect mesurement on VIP

Permeance of barrier films

- **permeation through a membrane :**



$p_1 > p_2$

$$j = D.S.\frac{\Delta p}{z} = \delta\frac{\Delta p}{z}$$

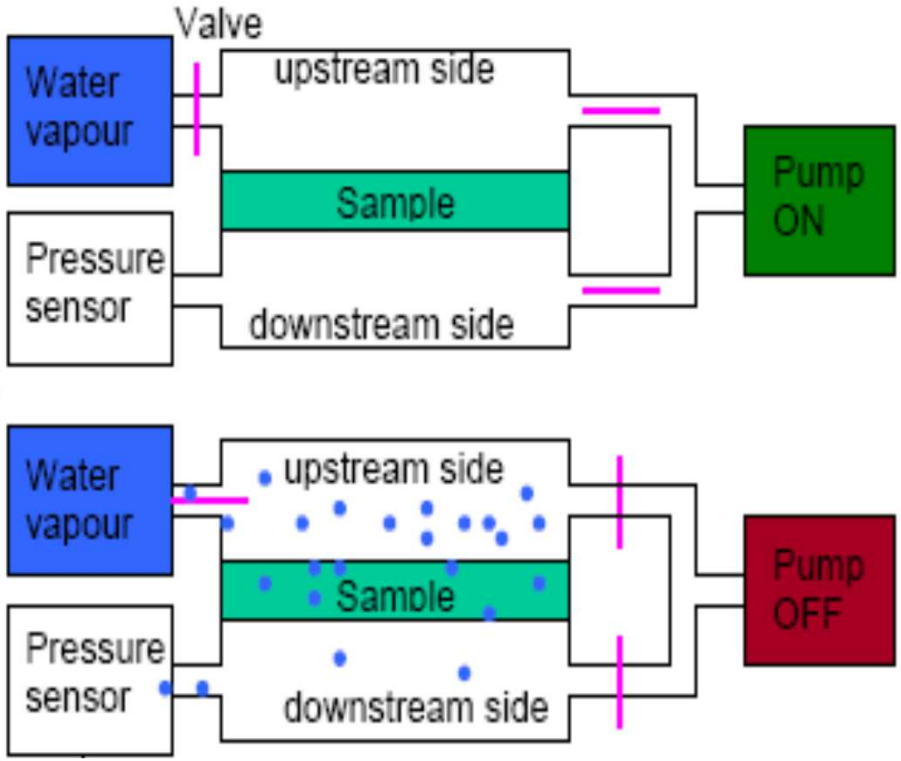
- **for non-homogeneous films :**

$$\Pi = \frac{\delta}{z} \qquad (kg.m^{-2}.s^{-1}.Pa^{-1})$$

where Π = permeance, δ = permeability, z = thickness

- **results obtained on single metallized layers allow the modelling of bi- and trilayer structures, and comparison with the results of indirect measurements on VIP**

Evaluation of barrier films - Manometric method



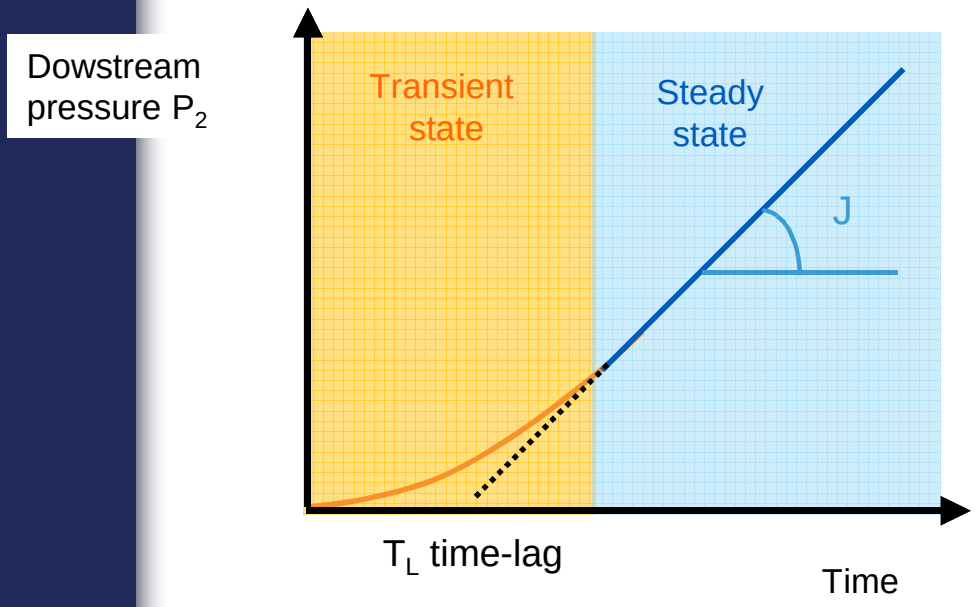
Drying, under vacuum and at temperature (40°C, 24h)

Insertion of water vapor in the upstream chamber and continuous measurement of the pressure downstream

[Equipment : Deltaperm by Technolox (UK)]

- **method described in ASTM D-1434 and ISO 15105-1**
- **measurement as a function of temperature and relative humidity possible**

Evaluation of barrier films - Manometric method



$$\Pi = \frac{j_\infty}{\Delta p} \quad \text{with } j_\infty = \frac{M.V}{R.T.A}\frac{dP_2}{dt}$$

[Equipment : Deltaperm by Technolox (UK)]

Evaluation of barrier films - Manometric method

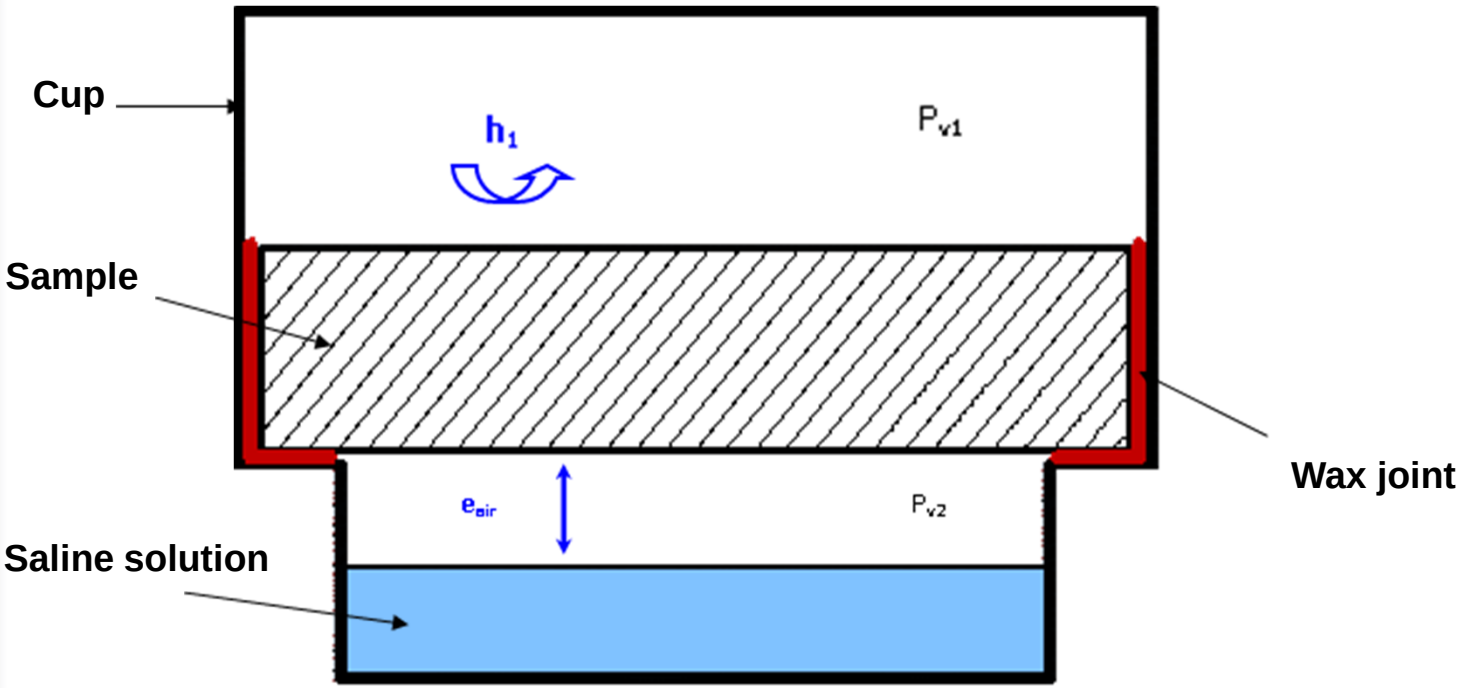
- as in the case of the other indirect methods, the manometric method looks at relatively small samples, thus it remains important to look for defects and test several samples

- measurement as a function of temperature and relative humidity possible :
  - permeance increases with temperature
  - above 40 - 50 % RH the increase of the permeance depends on the polymers in the laminate

- suitable for the measurement of low permeance values, down to values of 2.10^{-15} to 4.10^{-17} $kg.m^{-2}.s^{-1}.Pa^{-1}$

- this method reproduces the best the loading conditions on the barrier film of a VIP, e.g. with a mixture of air and water vapor upstream

Evaluation of barrier films - Cup method



method described in ISO 12572 and 2528, and ASTM E 96M-05

Evaluation of barrier films - Cup method

- amount of water vapor absorbed by a desiccant (dry cup) or evaporated by a saline solution (wet cup) from the interior of the cup, is monitored

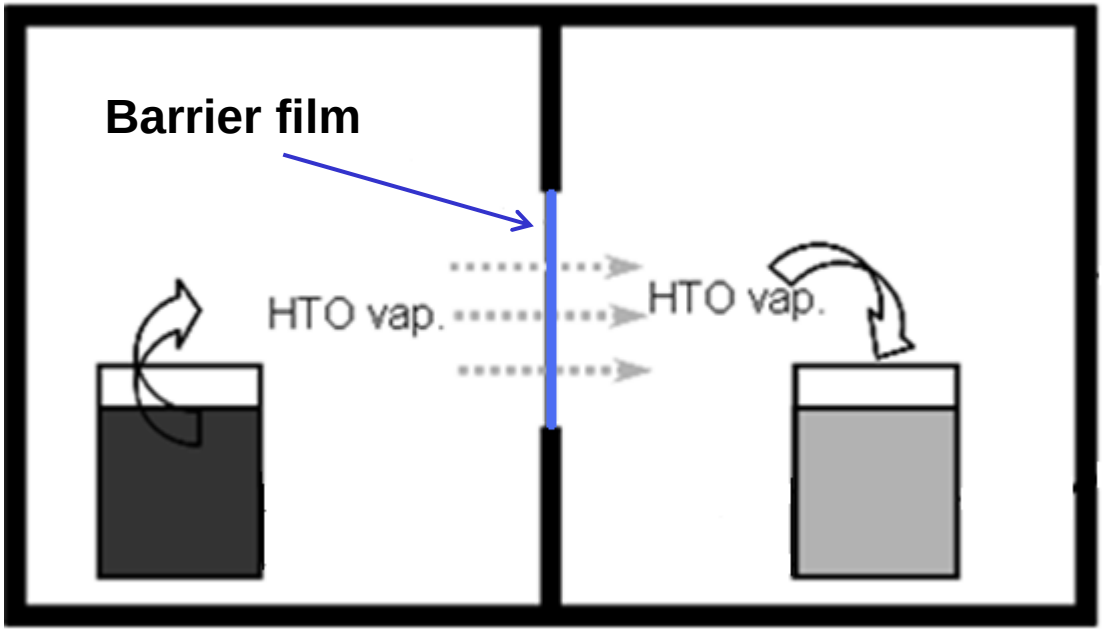
- quantity of water vapor going through the barrier film is measured as a weight change of the cup, i.e. Δm = f(t), thus

$$\Pi = \frac{j_\infty}{A.\Delta p_v} \quad \text{where} \quad j_\infty = \frac{\Delta m}{\Delta t} \qquad (kg.m^{-2}.s^{-1}.Pa^{-1})$$

- measurement as a function of temperature and humidity possible (in a limited T range)

- sensitivity remains limited, i.e. thus not suitable for very high performance barrier films

Evaluation of barrier films - Tritium test



Evaluation of barrier films - Tritium test

- method implies the use of a radioactive tracer, namely tritium, to improve the precision of the measurement of the flux through (very) high performance barrier films
- small part of the water molecules on one side of the film are marked through the addition of tritium, thereby forming HTO
- concentration of tritiated water molecules is measured after their passage through the film sample
- measurement as a function of temperature and humidity possible
- more difficult to implement

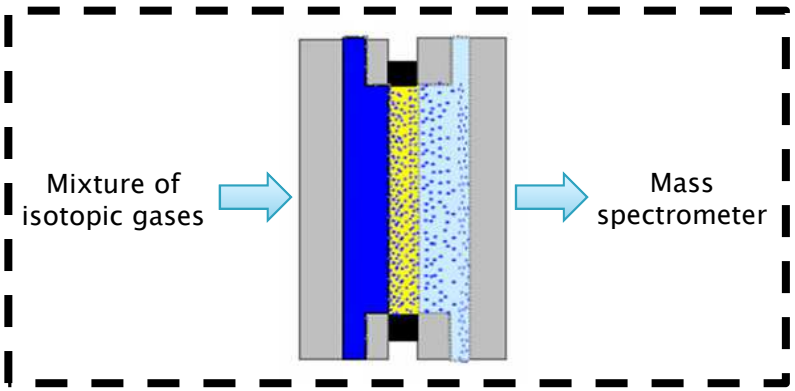
Evaluation of barrier films - other methods

- the coulometric method :
  - all permeating water vapor is swept to a coulometric sensor
  - the detector uses the P_2O_5 coulometric reaction (the water vapor entering the sensor is converted to a measurable amount of charge) to measure the amount of permeated water vapor

[Equipment by Mocon]

- permeation coupled with mass spectrometry :
  - the accumulation side in the equipment is swept to a mass spectrometer for water quantification
  - an option is to use a mixture of isotopic gases

[P. Hülsmann, Review of scientific instruments, 2009]



[M. Firon, P. Trouslard, S. Cros, CEA/DRT/LITEN/LCS, Patent US, 11/402230, 2006]

Evaluation of permeance on VIP

- barrier performance of the film covering the VIP core examined through an indirect measurement on the product

- aging in an environmental chamber at a selected temperature and relative humidity, e.g.

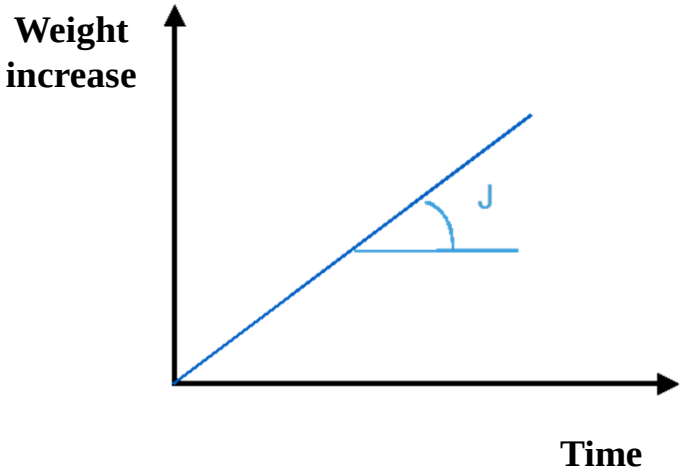
  40 °C / 40 % RH

  50 °C / 90 % RH

  70 °C / 90 % RH

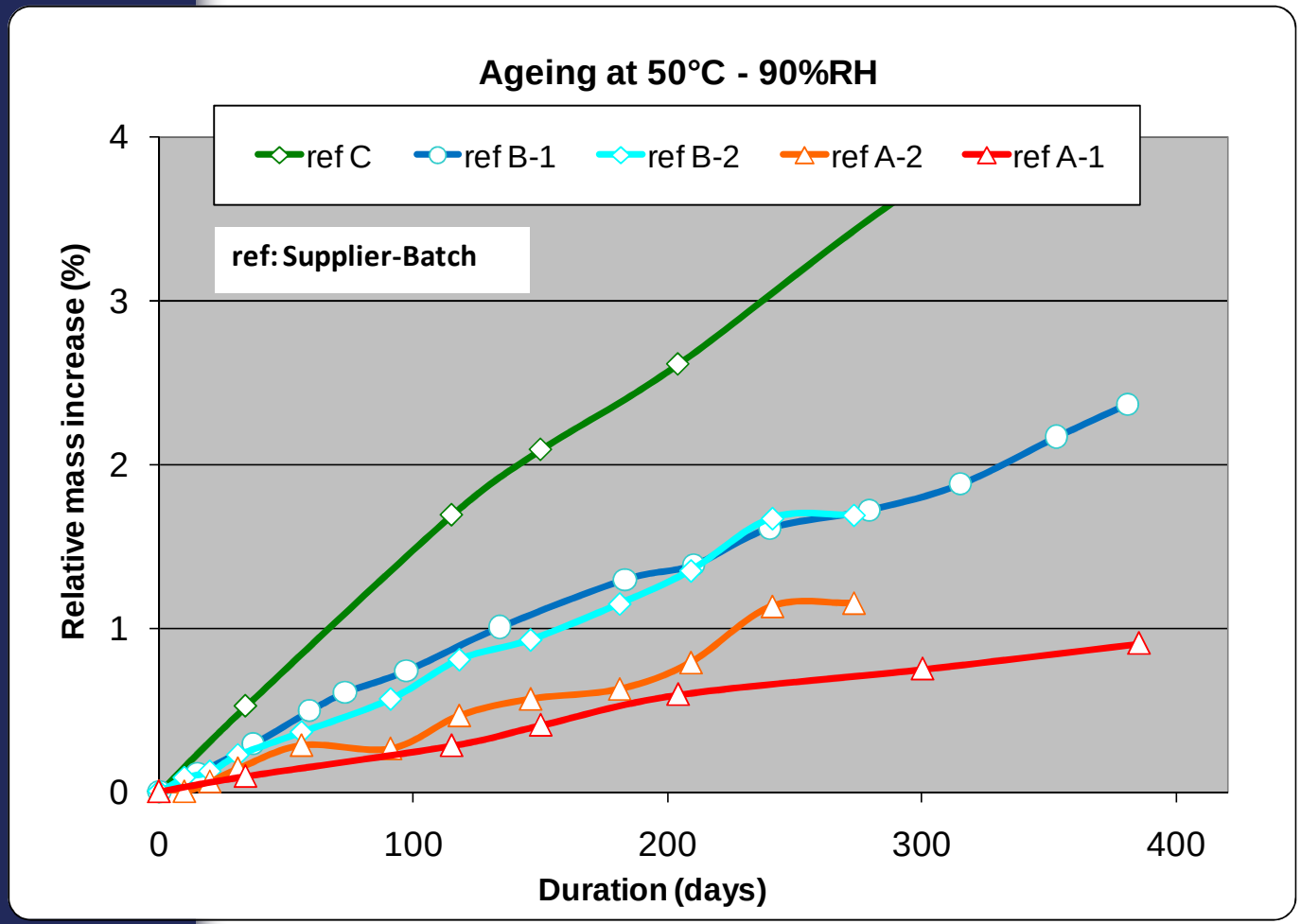
- method :
  - weight gain as a function of time recorded at regular intervals, i.e. $\Delta m = f(t)$
  - assumptions :
    - weight gain only due to water vapor
    - apparent permeation through flat surfaces of VIP
    - internal pressure = 0
  - calculation of Π in linear part of the recorded graph

Evaluation of permeance on VIP



$$\Pi = \frac{j_\infty}{\Delta p}$$

Evaluation of permeance on VIP



Π kg/(m².s.Pa)*10¹⁴
16.0
8.2
5.4
3.3

Higher values than those measured directly on laminates

Evaluation of permeance on VIP

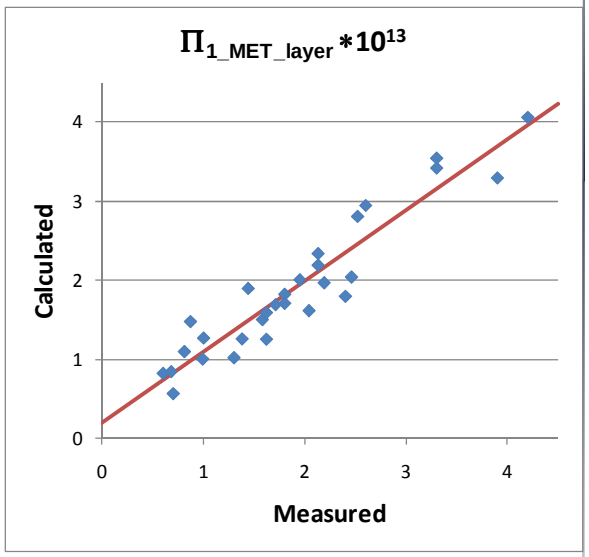
- Influence of temperature and humidity

$$\Pi_{1\_MET\_layer} = \Pi_0 . e^{-\frac{Q_\delta}{RT}} . e^{\eta . X_W}$$

  - 10 references of 3 suppliers
  - with 1 to 3 metallized layer(s)
  - tested between 23 and 70°C and 40 to 90 % RH

$e^{\eta . XW} \approx 0.90$
no or weak plasticizing effect

$Q_\delta = 26$ kJ.mol^{-1}
low activation energy *



* For the respective contributions of diffusion and solubility see [E. Pons, IVIS 2013]

Evaluation of permeance on VIP

- results indicate a different behavior between the various barrier films tested
- different behavior observed as a function of aging conditions
- results presented all concern aging at 50 °C & 90 % RH, other conditions have been covered in the series of tests
- the apparent activation energy of the water vapor permeation appears quite low w.r.t. the influence of the temperature
- no differences observed between small and large samples
- often variations observed within a batch or between different batches of same material
- highlights “damage” to VIP due to the manufacture of the product

Method	Suitability	Surface analyzed, cm^2	Sensitivity (flux), $g/(m^2.day)$	Permeance, $kg.m^{-2}.s^{-1}.Pa^{-1} * 10^{14}$
Manometric method	pressure gradient similar to VIP	50	$> 5\ 10^{-5}$	**0.002 to 0.02**
Cup Method	• suitable for single films • limited for high performance barrier films	80	$4\ 10^{-2}$	**1.7 to 17**
Coulometric method		50	$5\ 10^{-5}$	**0.002 to 0.02**
VIP	• represents real situation • many different conditions • slow method	> 800	$1.8\ 10^{-3}$	**0.06 to 0.6**
Target values				**0.5 to 1**

Discussion

- the cup method (lower sensitivity) and tritium based method (complexity) appear less suitable for the measurement of the permeance of barrier films
- among the direct methods looked at in this study the manometric method reproduces the best the actual loading conditions on barrier films ; approach to be optimized further
- ranking of the analyzed samples similar in all methods
- direct methods are suitable for the development of barrier films
- satisfactory agreement between the manometric method (barrier film) and the results obtained on VIP

Discussion

- permeance values measured on VIP often exceed values of manometric method due to :
  - possible damage to VIP during manufacture
  - possible water vapor influx through the edges
- indirect measurement on VIP remains our reference approach today
- quality of the metallization and the laminating adhesives is key to the performance of the barrier film in order to :
  - maintain core under vacuum
  - limit the uptake of humidity

Summary

- the permeance of barrier films is a key parameter to evaluate the long term performance of vacuum insulation panels

- various techniques available :
  - direct measurement on barrier films
  - indirect measurement on VIP

- among the methods looked at in this study, the manometric method appears the most relevant method regarding the evaluation of the permeance of barrier films

- indirect measurement on VIP provides valuable data in good agreement with this manometric method

Acknowledgements

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  - **ADEME (France)**
  - **IWT (Belgium)**

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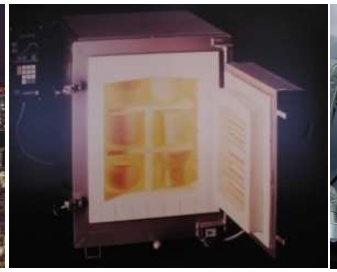


Thank you for your attention