Hydration of Nuclear Waste Glass in Vapor Phase
- Jeet PATEL

Joint ICTP-IAEA International School on Nuclear Waste Vitrification
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Laboratory Introduction

Subatomic Physics and Associated Technologies (SUBATECH) Laboratory

- High energy universe
- Nuclear and environment (Radiochemistry Group)
- Nuclear and Health (Radiochemistry Group)

Under the Guidance of

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(SUBATECH Laboratory)

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Ph.D. fellow
(SUBATECH Laboratory)

Subatech laboratory & IMT Atlantique (Nantes)

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Outlines

- Background

- Objectives

- Literature review

- Materials and Methods

- Characterization Techniques
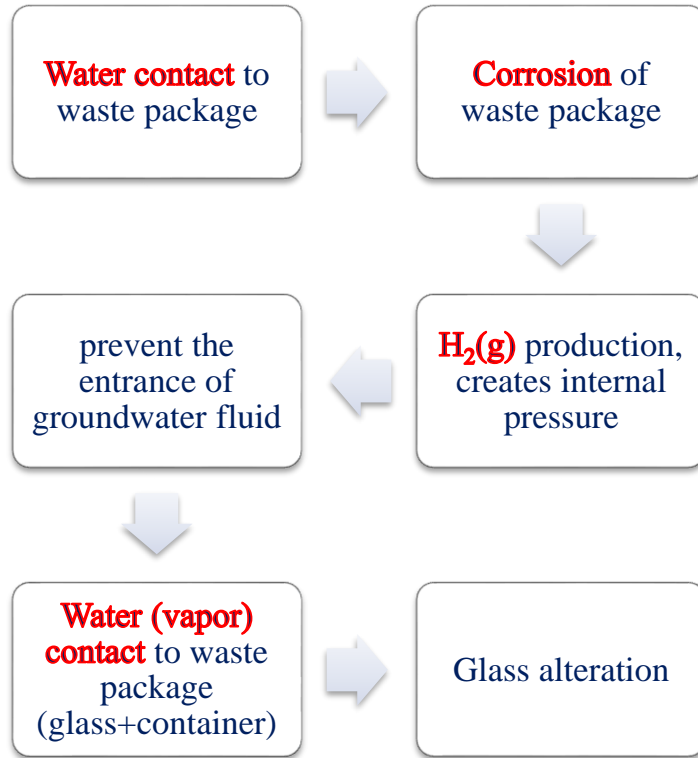
- Results and Discussion

- Conclusion

Background

- French policy for Spent Nuclear Fuel

  - recycling/reprocessing

- Immobilization of fission products and minor actinides in **borosilicate glass** named R7T7

- High level nuclear waste glass in **Deep geological repository**

  - Current project at Meuse/Haute-Marne centre (Cigéo project- ANDRA)
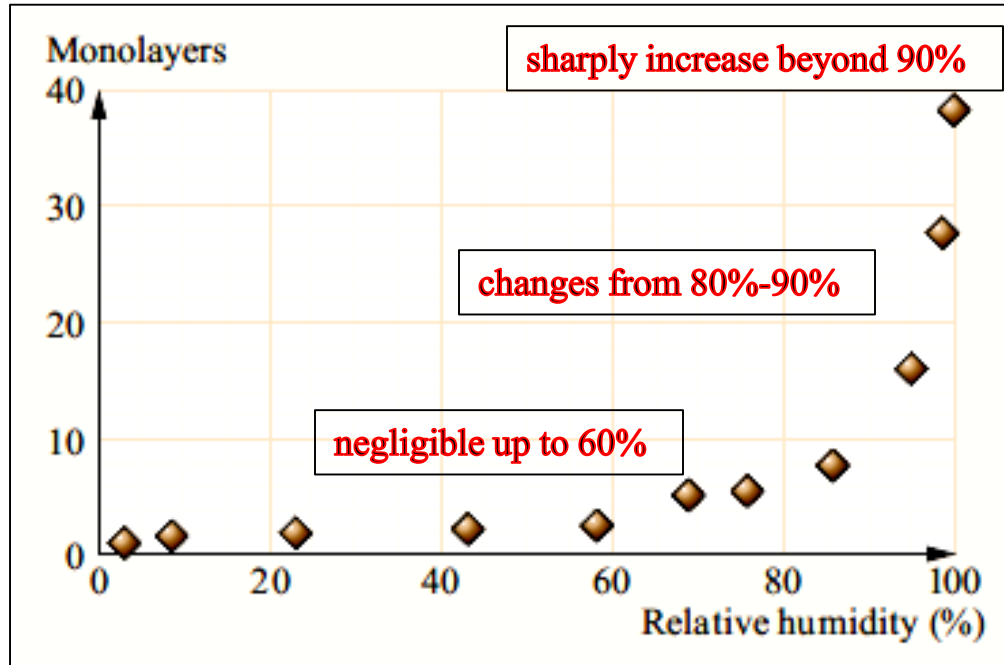

Picture- ANDRA.fr

Background (cont.)

Water contact to waste package → **Corrosion** of waste package

↓

H$_2$(g) production, creates internal pressure → prevent the entrance of groundwater fluid

↓

Water (vapor) contact to waste package (glass+container) → Glass alteration

Picture- Retrieval Test of HLW package in the Cigeo Project, Andra (IGD-TP Technical Forum, Berlin- 2018)

Literature review: evolution of glass under vapor condition

- Number of water layers adsorbed on the glass surface

Monolayers

sharply increase beyond 90%

changes from 80%-90%
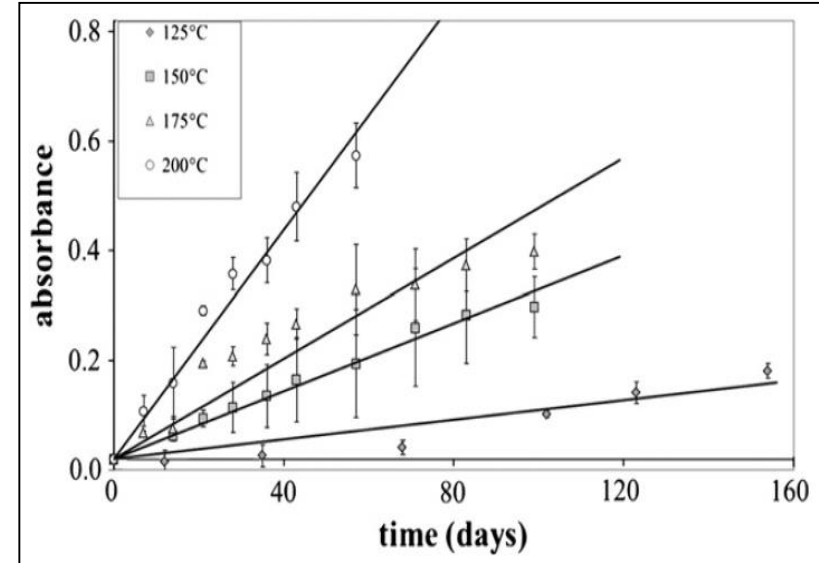
negligible up to 60%
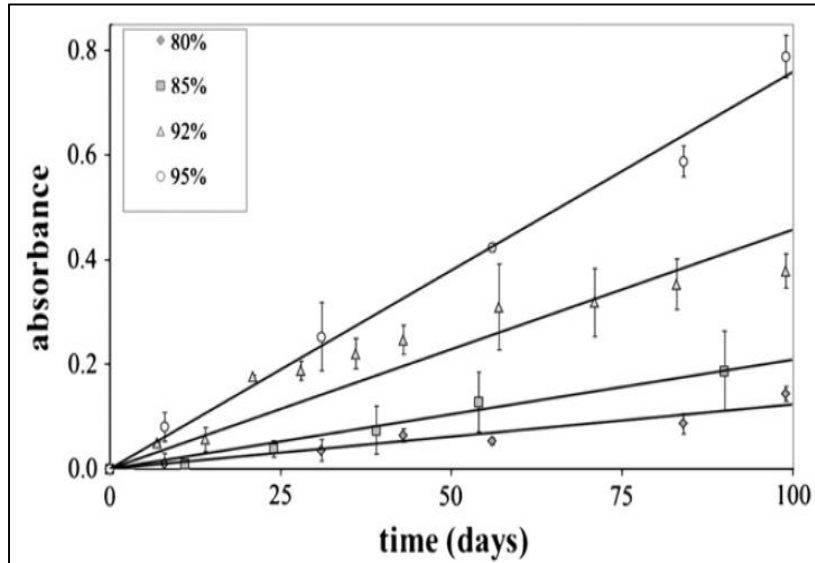
Relative humidity (%)

W.L.Ebert et al., The Sorption of Water on Obsidian and a Nuclear Waste Glass (1991)

Figure- Chemical durability of Glasses (Abdelouas et al.- 2019)

Literature review: evolution of glass under vapor condition (cont.)

- The hydrated layer thickness depends on **RH (%)**, **Temperature (°C)**, **Hydration time** and also **Glass composition**.

- Hydration rate increases with the RH and Temperature increases

Figures- Vapor hydration of SON68 glass from 90°C to 200°C: A kinetic study and corrosion products investigation (J. Neeway et al.- 2012)
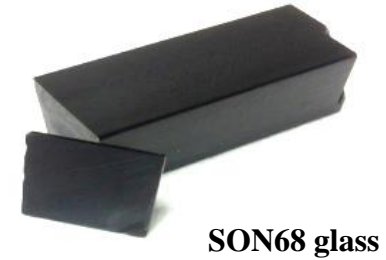
Objectives

I.   Investigation of hydration kinetics in Vapor phase of French surrogate SON68 glass and ISG (International Simple Glass).

- at two temperatures (90°C and 125°C)

- at two RH- Relative Humidities (95% and 99%)

II.   In **Autoclave** and **Climate Test Chamber** (which is not widely used).
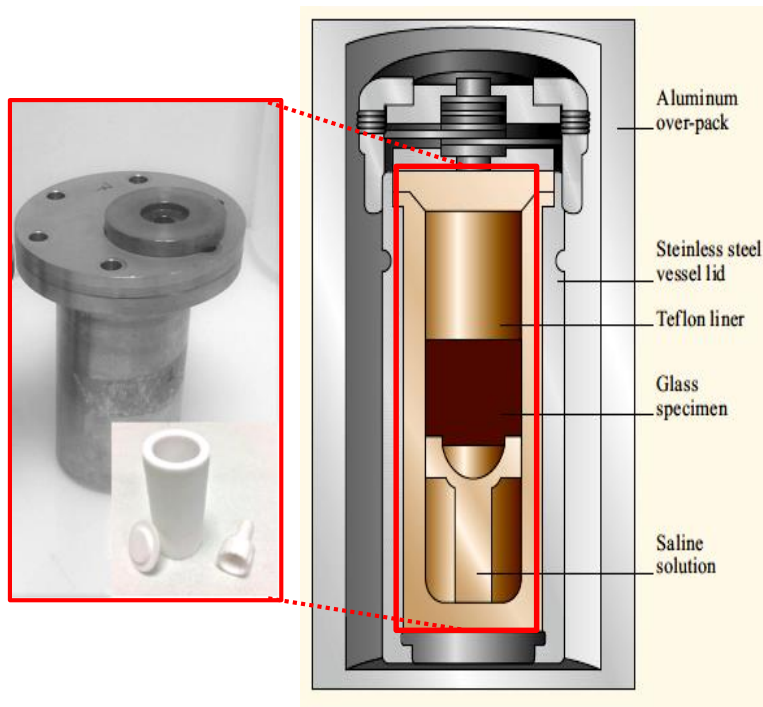
Materials & Methods

Materials

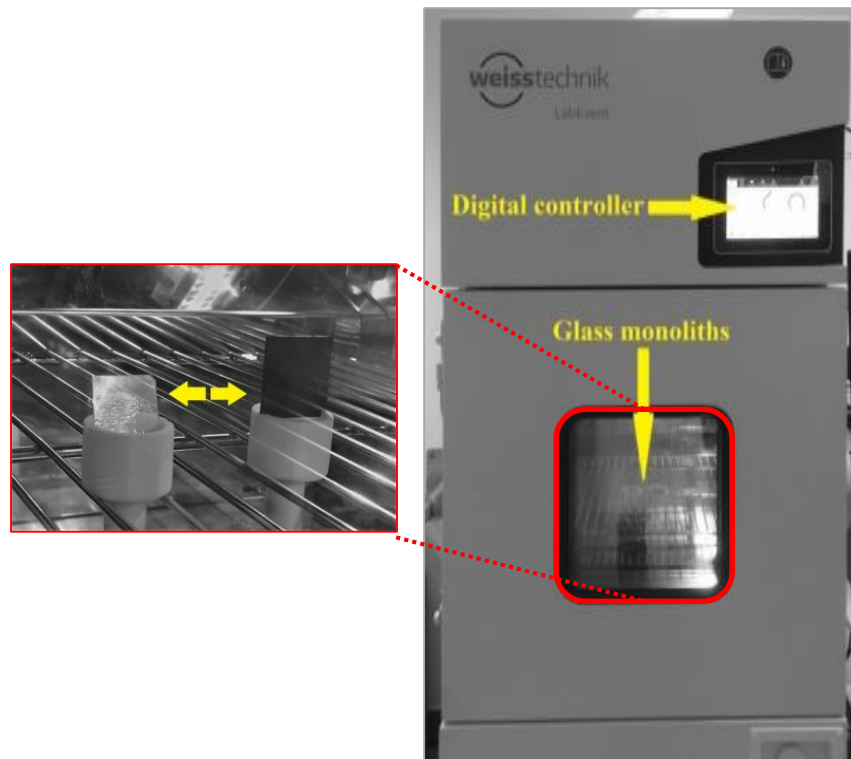| Oxides	ISG (wt %)	SON68 (wt %)
SiO_2	56.2	45.85
B_2O_3	17.3	14.02
Na_2O	12.2	9.86
Al_2O_3	6.1	4.91
CaO	5.0	4.04
ZrO_2	3.3	2.65
Fe_2O_3	-	2.91
Li_2O	-	1.98
MoO_3	-	1.70
Others	-	12.08

SON68 glass

ISG glass
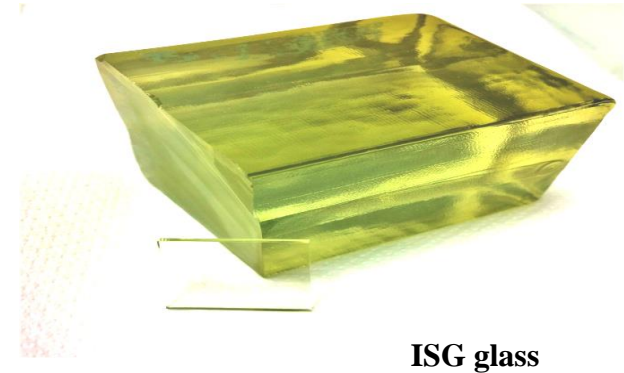
Glass composition- ISG (Chaoua et al.- 2014), SON68 (K M Davis et al.- 1996)

Autoclave (AC)

Climate Test Chamber (CC)

- Aluminum over-pack
- Steinless steel vessel lid
- Teflon liner
- Glass specimen
- Saline solution

- Digital controller
- Glass monoliths

Autoclave figure- Chemical durability of Glasses (Abdelouas et al.- 2019)

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Experimental conditions

	Glass	RH (%)	Temperature (°C)	Time of hydration (days)
Autoclave (AC)	SON68	99	125	112
			90	112
		95	90	47
				37
	ISG	99	125	112
			90	112
		95	90	47
				37
Climate Test Chamber (CC)	SON68	95	90	44
				37
	ISG			44
				37

Characterization Techniques

Hydration of Nuclear Waste Glass in Vapor Phase by Jeet PATEL

Characterization Techniques

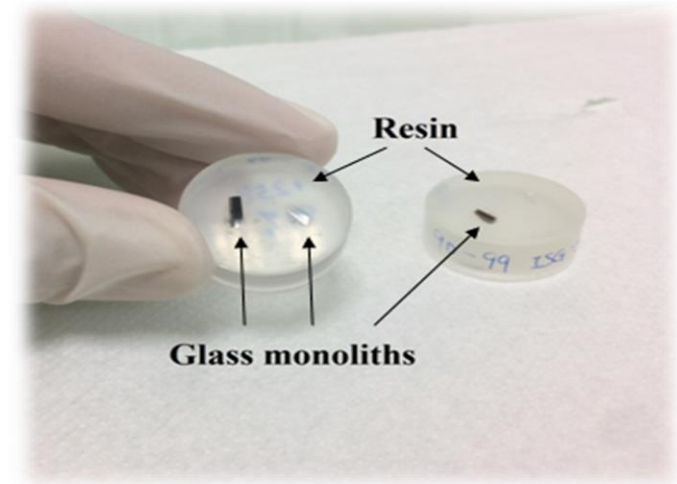## SEM

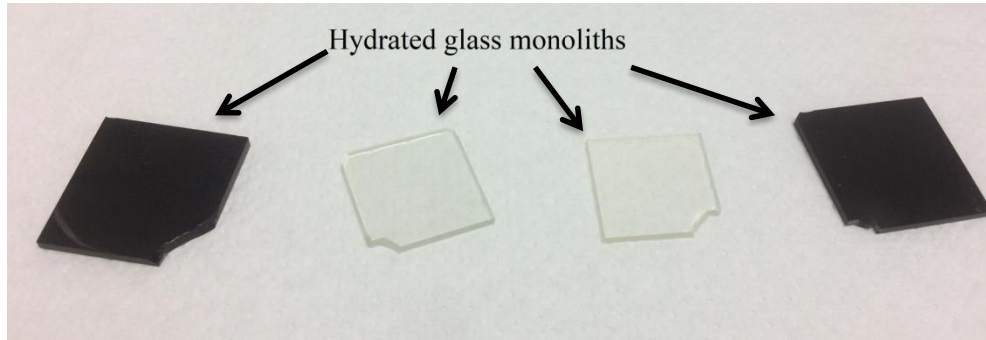• Determination of hydrated thickness

FTIR

• To follow the glass hydration
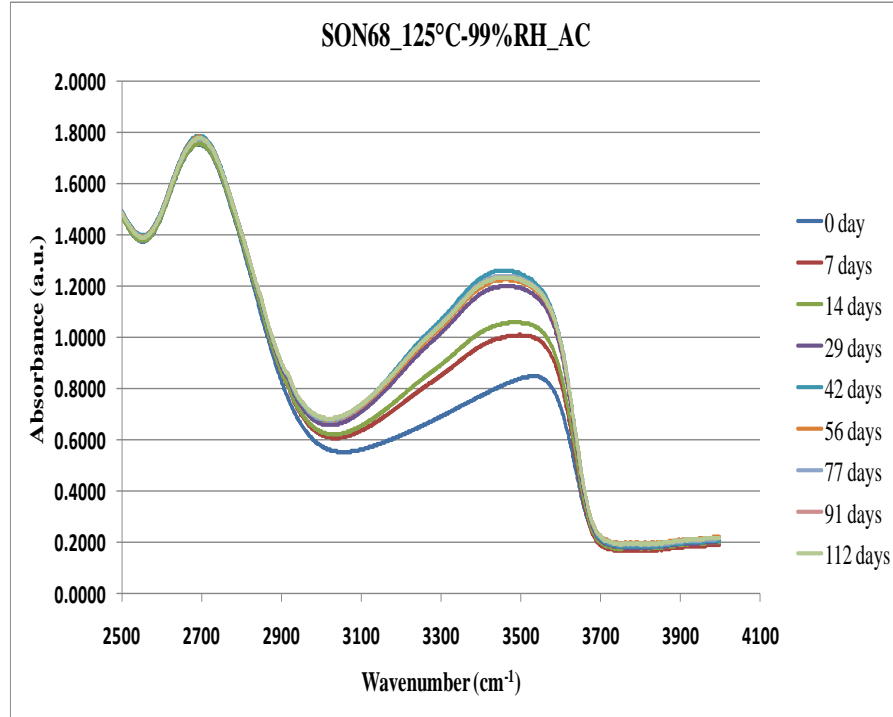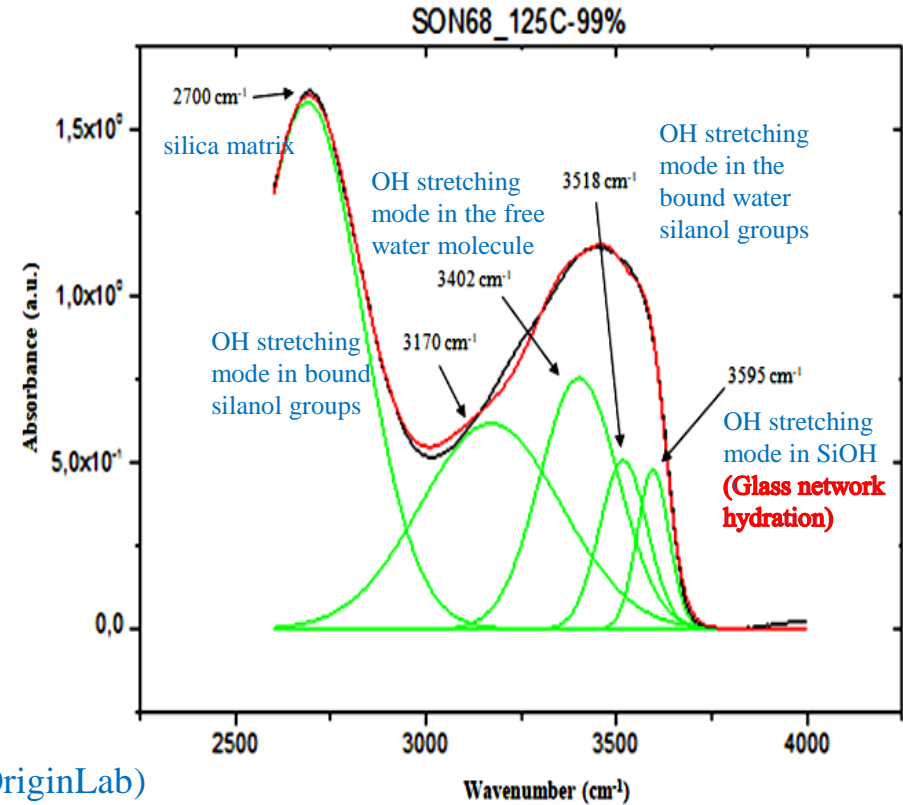• To determine the physical hydration thickness

ICP-MS

• Determination of chemical hydration thickness

Sample preparation for SEM analysis

Hydrated glass monoliths

Resin

Glass monoliths

SEM- Scanning Electron Microscopy

FTIR Spectroscopy

SON68_125°C-99%RH_AC

SON68_125C-99%

2700 cm⁻¹ — silica matrix
OH stretching mode in the free water molecule — 3402 cm⁻¹
OH stretching mode in the bound water silanol groups — 3518 cm⁻¹
OH stretching mode in bound silanol groups — 3170 cm⁻¹
OH stretching mode in SiOH **(Glass network hydration)** — 3595 cm⁻¹

Deconvolution - five Gaussian using Origin 8.0 software (OriginLab)
H.Tomozawa, M.Tomozawa. Diffusion of water into a borosilicate glass

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NL calculation

Boron

Normalized mass loss: $NL_i = \dfrac{NC_i}{(S/V)} = \dfrac{(C_i/X_i)}{(S/V)}$

NL_i - normalized mass loss (g/m^2)

S - surface area of the sample (m^2)

V - volume of solution (m^3)

NC_i - normalized elemental concentration

C_i - concentration of the element i in the solution (g/m^3)
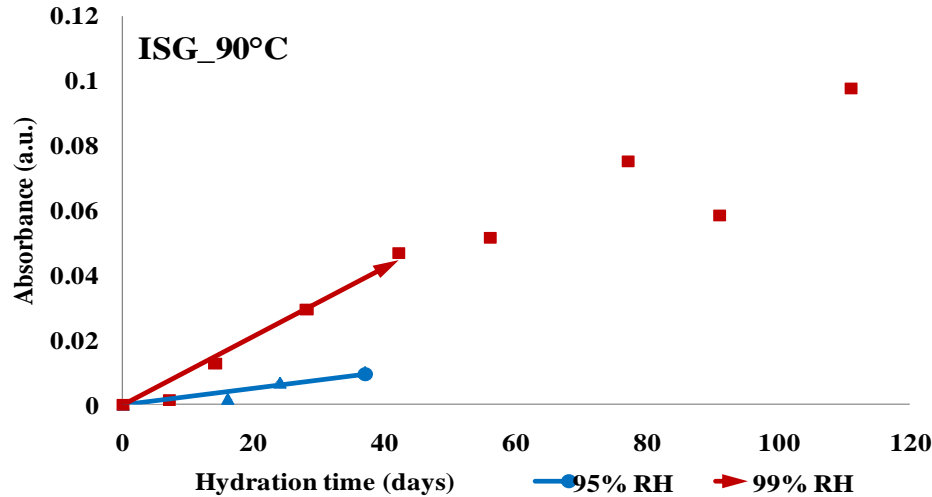
X_i - weight fraction of element i in the glass

Equivalent thickness: $Eq_i = \dfrac{NL_i}{\rho_i}$

ϱ_i is the glass density
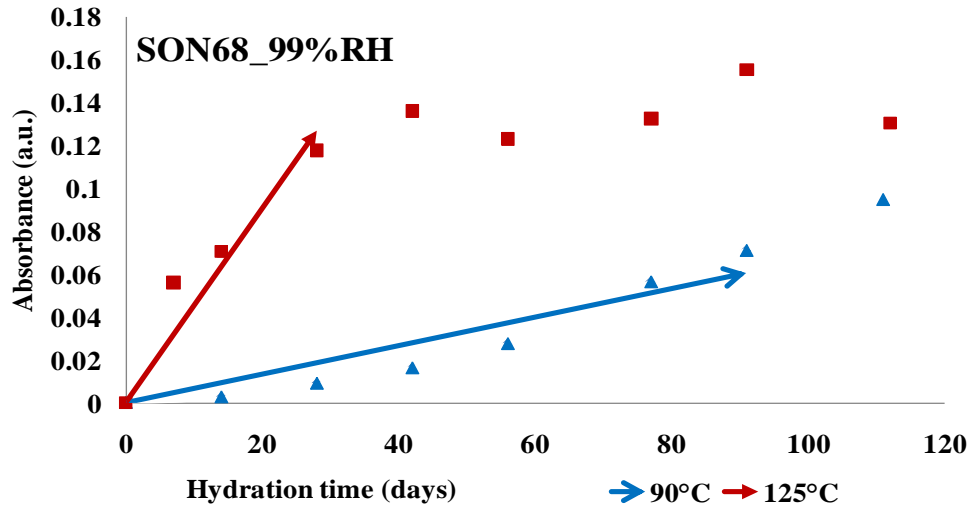
Results & Discussion

Effect of relative humidity at 90°C

ISG_90°C

90°C	ISG glass
95% RH	$2.6×10^{-4}$ per day
99% RH	$9.8×10^{-4}$ per day
Factor	3.8

• Hydration rate increases with the RH increases
• The results consistent with the literature[@]

@ literature (Abdelouas et al.- 2013) (Neeway et al.- 2012) (Chaou et al.- 2017)
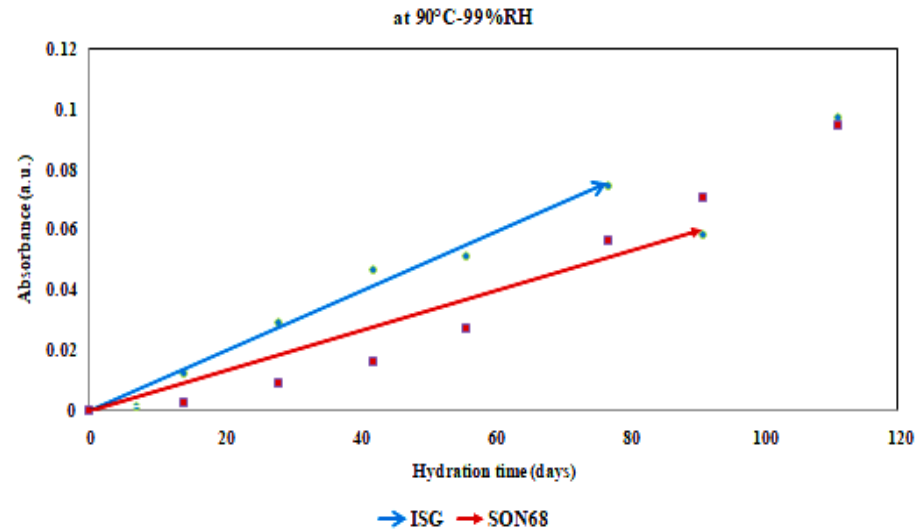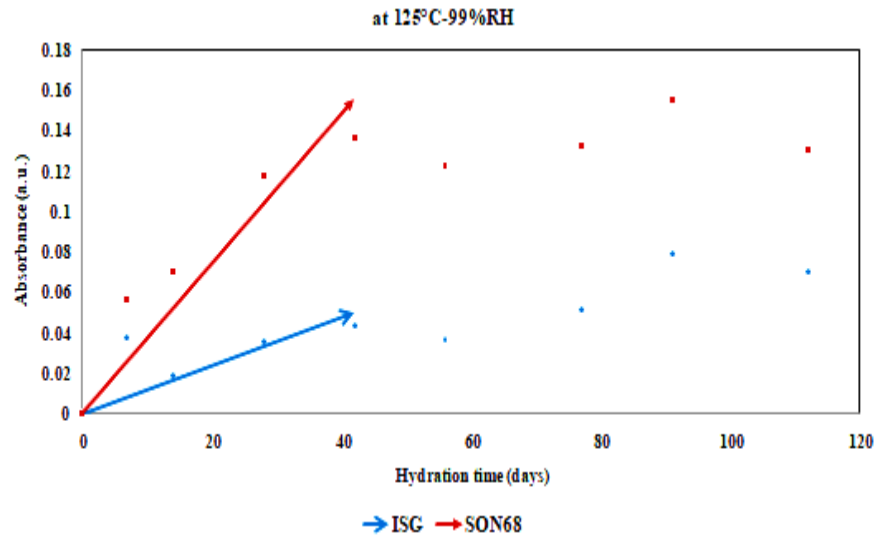
Effect of temperature at 99% RH

SON68_99%RH

99% RH	SON68 glass
90°C	$4.3×10^{-4}$ per day
125°C	$45.0×10^{-4}$ per day
Factor	10.5

- Hydration rate increases with the Temperature increases
- The results consistent with the literature@

@ literature (Abdelouas et al.- 2013) (Neeway et al.- 2012) (Chaou et al.- 2017)
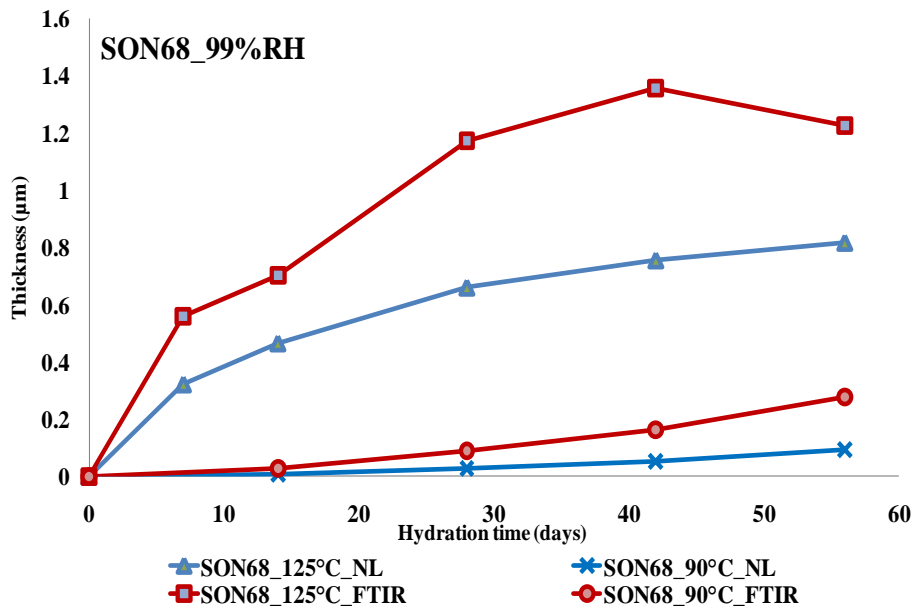
Effect of Glass Composition

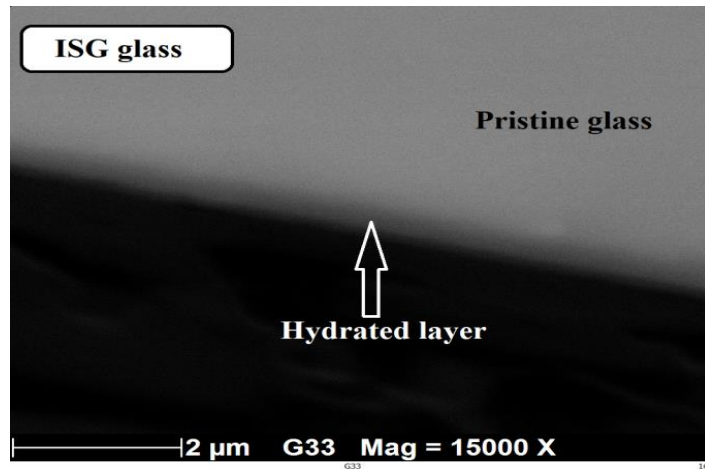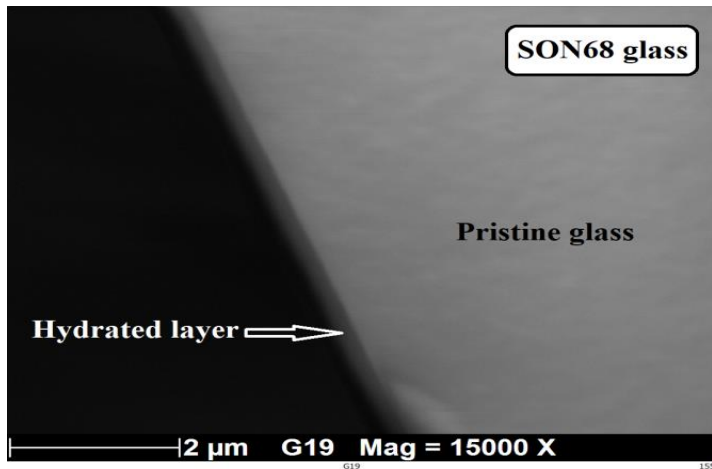|	SON68 glass	ISG glass
At 125°C-99%RH	45.0×10^{-4} per day	12.0×10^{-4} per day
At 90°C-99%RH	4.3×10^{-4} per day	9.8×10^{-4} per day

- The glass composition also affect the hydration rate

Physical & Chemical Thicknesses

SON68_99%RH

• The physical thicknesses (FTIR) shows the maximum hydration.

• The difference between physical (FTIR) and chemical (NL) thicknesses is maybe boron were not released from hydrated layer to the solution.

Comparison of Autoclave (AC) and Climate Test Chamber (CC)

SON68_90°C-95%RH

ISG_90°C-95%RH

	SON68 glass	ISG glass
Autoclave (AC)	2.1×10^{-4} per day	2.6×10^{-4} per day
Climate test chamber (CC)	3.3×10^{-4} per day	7.6×10^{-4} per day
Factor	1.6	3.0

- The hydration rate in the climate test chamber is higher than the autoclave

Surface analysis

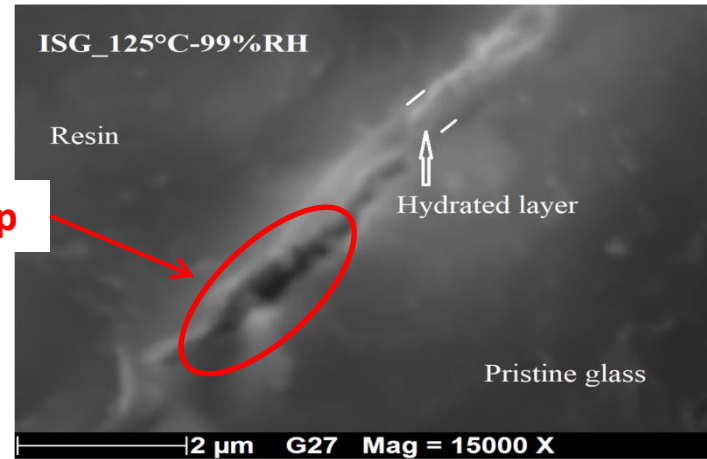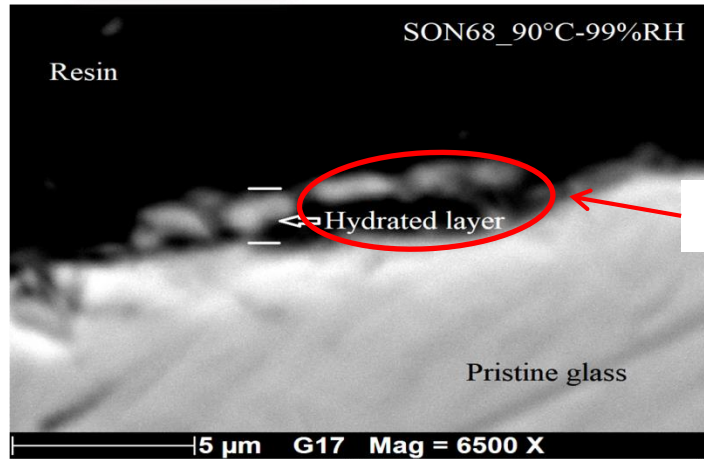| 90°C-95%RH_CC	SON68 glass	ISG glass
SEM analysis	0.24 μm	0.37 μm

- Hydrated layer is not clearly visible in SEM images, not sure about the hydrated layer thickness

CC- Climate Test Chamber
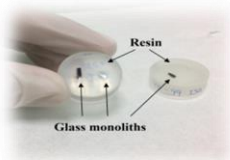
Surface analysis (cont.)

99% RH_AC	SON68 glass	ISG glass
SEM analysis	1.44 μm	0.69 μm
FTIR	1.10 μm	0.63 μm

- Found a gap between Resin and Glass sample

AC- Autoclave

Conclusion

- Correlation factor,

  - **ISG** 0.1 SiOH absorbance unit per 0.99 μm of hydrated layer (125°C-99%RH)

  - **SON68 glass** 0.1 SiOH absorbance unit per 1.5 μm of hydrated layer (90°C-99%RH)

Jeet PATEL (for ISG_125°C-99%RH)	Abdelouas et al. @ (for ISG_175°C-98%RH)	Jeet PATEL (for SON68_90°C-99%RH)	J. Neeway # (for SON68 glass)
0.1	0.11	0.07	0.09

- Verifying,

  - The hydration rate increasing with the RH and temperature increases

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@ Primary Investigation of the ISG Glass Vapor Hydration (Abdelouas et al.- 2013), # Ph.D. thesis, University of Nantes (J. Neeway- 2010)

Acknowledgment

• Guillaume Blain (Subatech) for FTIR formation.
• Nicolas Stéphant from Centre of Micro-characterization, University of Nantes (France) for SEM analysis.

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