

# Vacuum Systems

## Lecture 2

V. Baglin

CERN TE-VSC, Geneva



# Outline

1. Elements of adsorption/desorption
2. Outgassing
3. Qualification of materials

# 1. Elements of adsorption/desorption

# Reminder: Pressure in a system

- The **Pressure**, is the ratio of the flux of molecules in the vacuum vessel to the pumping speed

$$P = \frac{Q}{S}$$

mbar →

mbar.l/s

l/s

- S range from 10 to 20 000 l/s
- Q range from  $10^{-14}$  mbar.l/s for metallic tubes to  $10^{-5} - 10^{-4}$  mbar.l/s for plastics

3 orders of magnitude for pumping

vs

10 orders of magnitude for outgassing

**Outgassing MUST be optimised to achieve UHV**

# Reminder: Mass flow & quantities

- The mass flow can be derived from the ideal gas law

$$R = \mathcal{N} k$$
$$Q = p \frac{dV}{dt} = \frac{1}{\mathcal{N}} \frac{dn}{dt} RT =$$

- It has the unit of [Pa.m<sup>3</sup>/s] which is equivalent to molecules/s

| PV       | G                               |
|----------|---------------------------------|
| 1 mbar.l | 4.35 10 <sup>19</sup> molecules |
| 1 Torr.l | 3.27 10 <sup>19</sup> molecules |

- Langmuir: 1 L = 10<sup>-6</sup> Torr for 1 s.

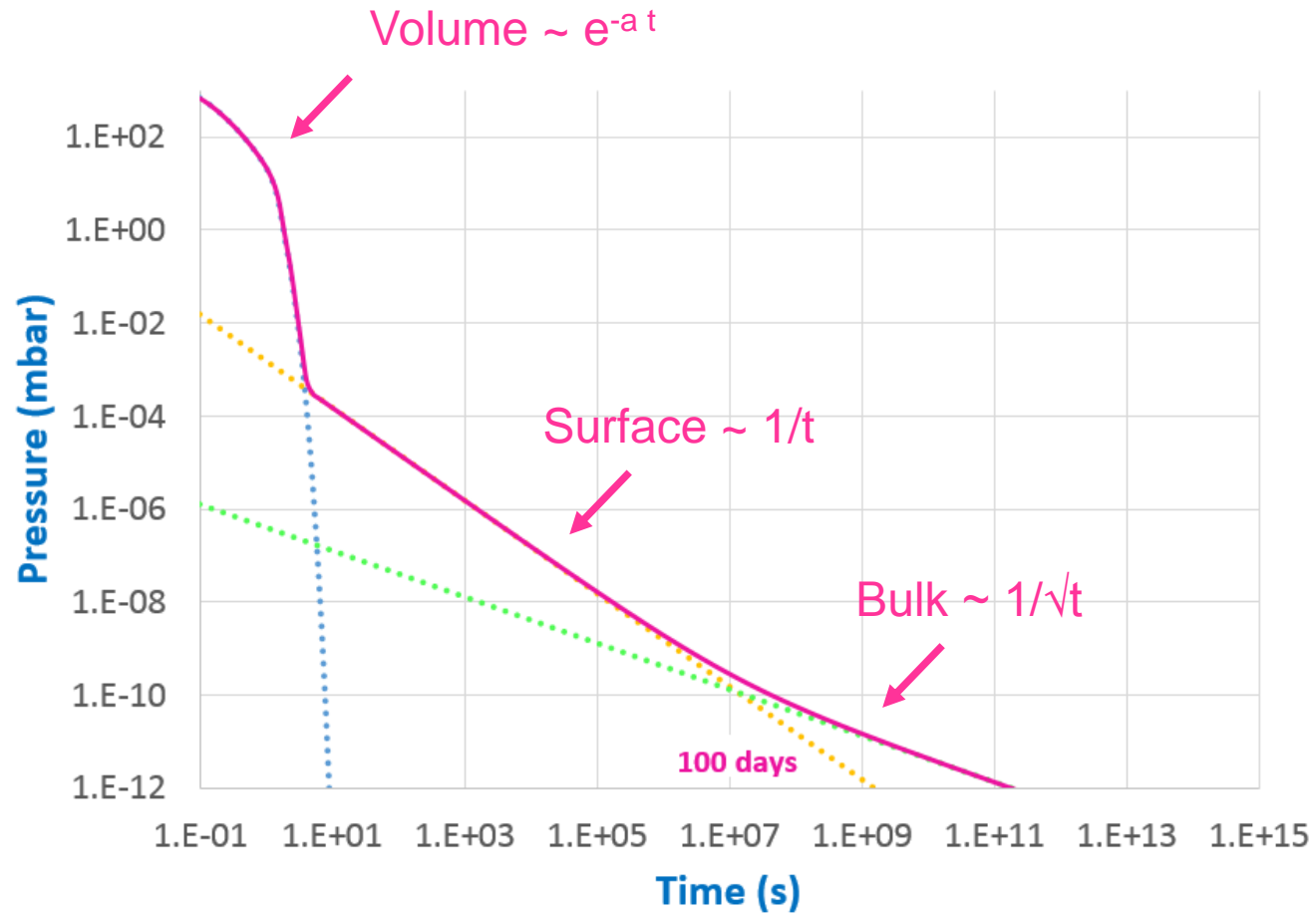
# Material for Vacuum Technology

- Metals are used for vacuum chambers building parts:
  - Stainless steel, copper, aluminum, beryllium
- Insulating material are used for instrumentation or assembly:
  - Minerals:
    - Ceramics, glass
  - Polymeres (plastics):
    - Kapton, PEEK
    - Glues
    - Elastomeres e.g. Viton,
- During the manufacturing process of these materials, atoms and molecules are sorbed *i.e.* **adsorbed** or **absorbed** on the material surface or the bulk
- The surface can be very rough and the material highly porous
- **Quantities** of gas adsorbed / absorbed in materials can be very large:
  - 1 cm<sup>3</sup> of stainless steel can contain 0.05 – 0.5 mbar.l of hydrogen
  - Under vacuum, Nylon can lose 4% of its weight *i.e.* 5 mbar.l per cm<sup>3</sup>

# Pump down of a vessel

- Consider 1 m long, Ø10 cm stainless steel tube pumped by 30 l/s
- 4 regimes

- 1) Volume pumping
- 2) Surface desorption
- 3) Diffusion from the bulk
- 4) Permeation through the wall (solubility+diffusion)





# A schematic description

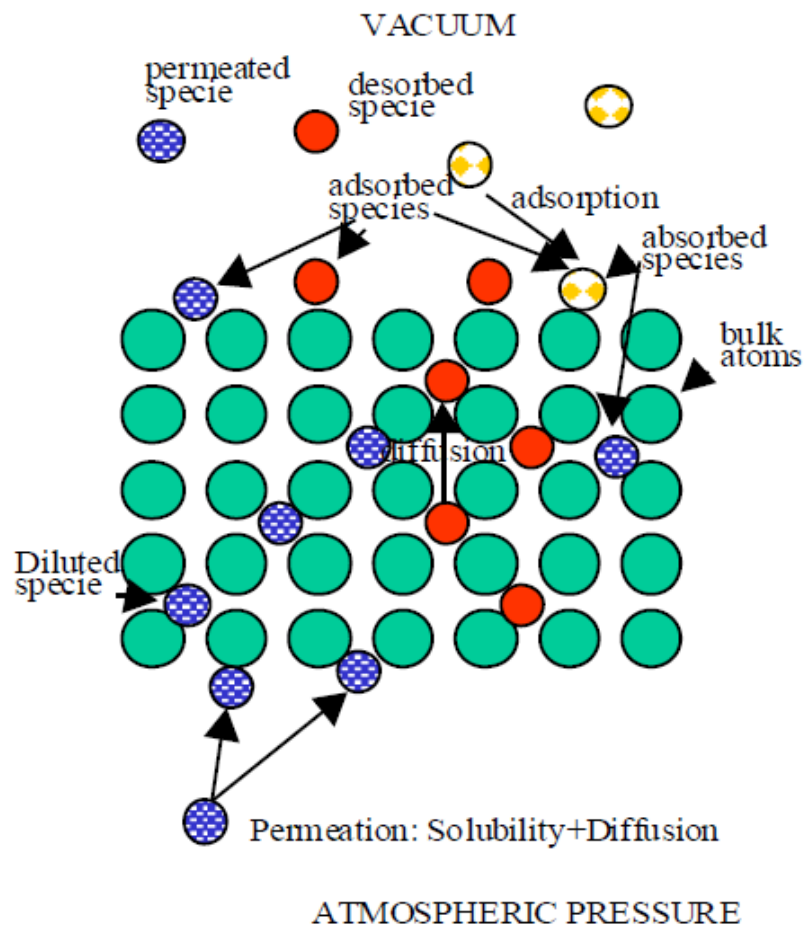


Fig. 1 Surface and bulk phenomena in vacuum.

J De Segovia, Physics of Outgassing, CAS, CERN-99-05

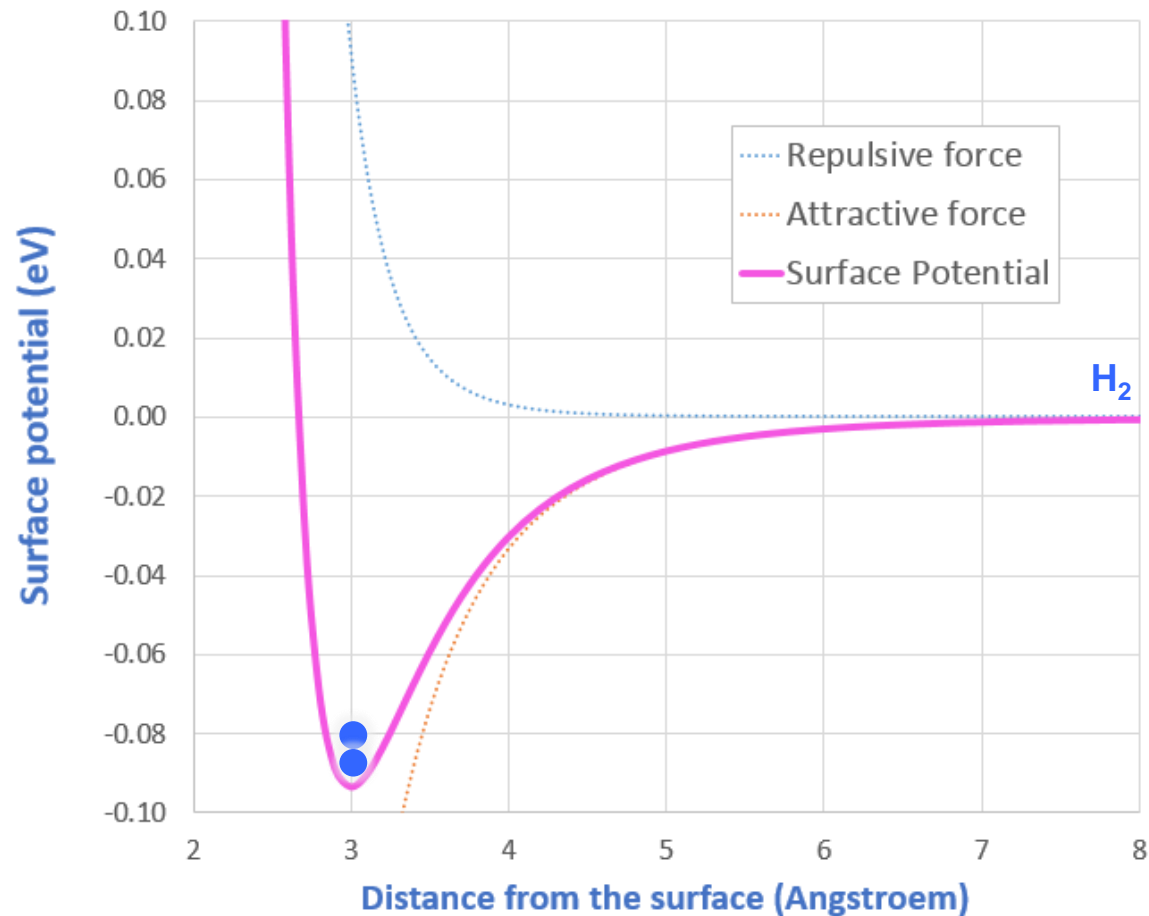
# Adsorption-Desorption

- The process is controlled by the interaction energy between the molecule or atom with the surface
- Depending of the “binding energy” level, two types of adsorption exist
- Weak binding energy:
  - **Physical adsorption** process
  - Van der Waals forces
  - E: 6-30 kJ/mole or 60-300 meV per particle
- Strong binding energy:
  - **Chemical adsorption** process
  - Electron sharing
  - E: 30-10000 kJ/mole or 0.3-10 eV per particle
- The surface interaction can be described by Lennard-Jones potentials, E, as a function of the distance from the surface, r.

$$E = E_m \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right]$$

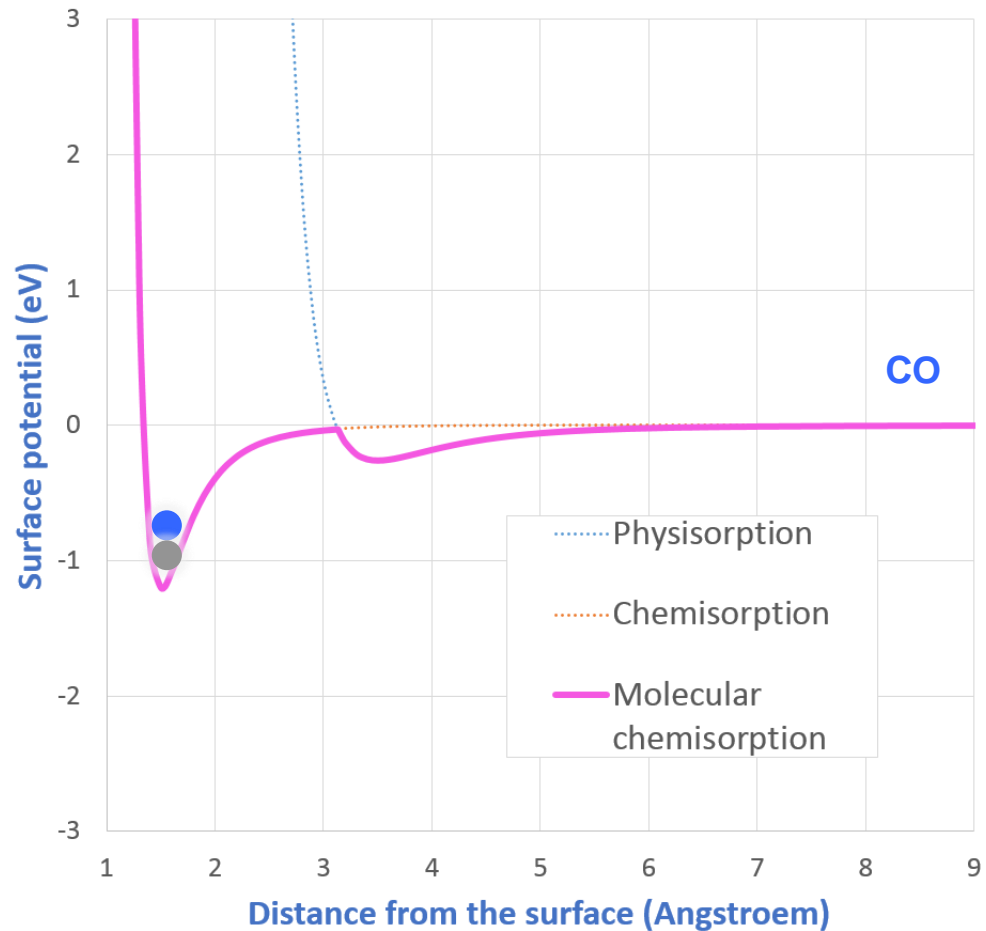
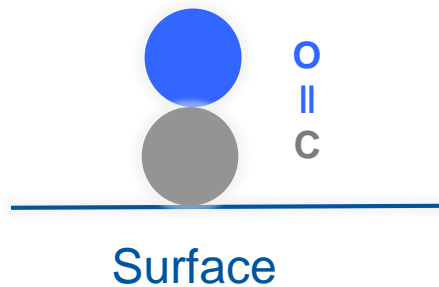
# Physisorption

- A molecule, say  $H_2$ , approaches towards the surface
- The molecule is physisorbed onto the surface at  $\sim 3 \text{ \AA}$  with a “binding” (adsorption/desorption) energy of  $\sim 10 \text{ meV}$  (twice the H heat of vaporization)
- Due to the nature of the physisorption process, several monolayers can be physisorbed in this state



# Non-Dissociative Chemisorption

- Non-dissociative chemisorption: case of CO onto metals
- The molecule is chemisorbed onto the surface at  $\sim 1.5 \text{ \AA}$  with a “binding” energy of  $\sim 6 \text{ eV}$
- A maximum of one monolayer can be adsorb on the surface
- The carbon atom is oriented towards the surface

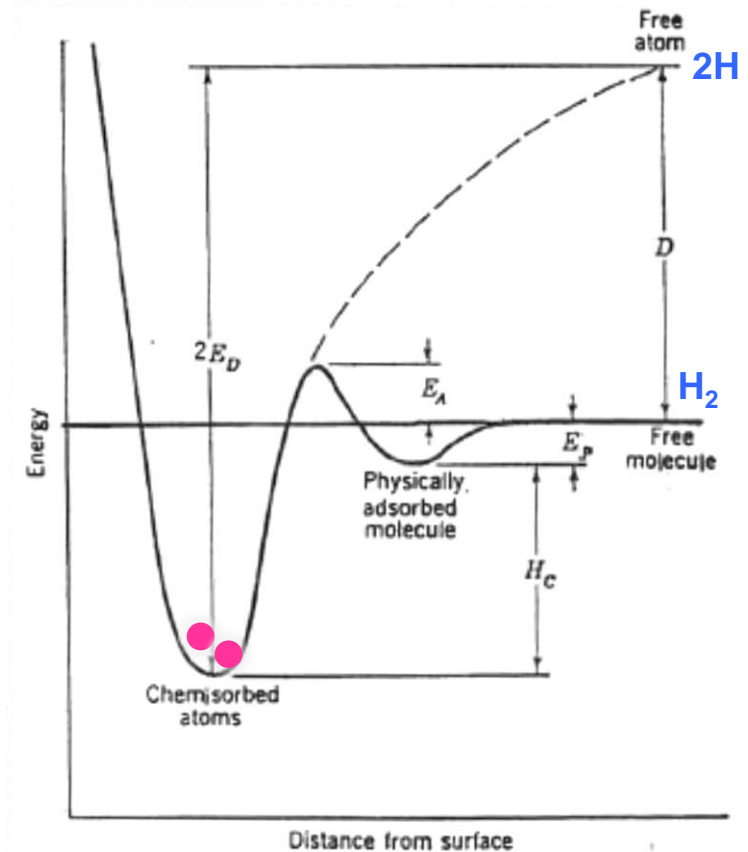
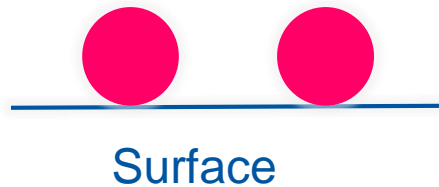


# Dissociative Chemisorption

- Dissociative chemisorption: case of  $H_2$  onto metals
- The molecule is physisorbed on the surface
- If the molecule has enough energy to overcome the activation barrier ( $E_A \sim 0.4$  eV), the molecule is dissociate and the H atoms are chemisorbed (H-H binding energy:  $E_{diss} \sim 4.5$  eV)
- The atoms are chemisorbed onto the surface at  $\sim 1.5$  Å with a adsorption energy of  $\sim 3.7$  eV
- A maximum of one monolayer can be adsorbed on the surface
- Activation energy  $\sim 0.4$  eV

$$E_{Des} = E_A + E_{ads}$$

$$E_{diss} = E_{Des} + E_{ads}$$



# Conversion between energy units

Complementary  
information

|  → | eV    | kJ/mole | kcal/mole |
|---|-------|---------|-----------|
| 1 eV  | 1     | 96      | 23        |
| 1 kJ/mole   | 0.01  | 1       | 0.24      |
| 1 kcal/mole   | 0.043 | 4.2     | 1         |

# 1<sup>st</sup> order desorption

- The rate of molecular desorption from a surface is given by:

$$-\frac{d\theta}{dt} = \nu_1 \theta e^{-E_D/kT}$$

- $\theta$ , surface coverage,  $\nu_1$  frequency of vibration of an adsorbed molecule ( $10^{13}$  Hz),  $E_D$ , activation energy for desorption
- Applicable for **physisorbed** molecules and **non-dissociated chemisorbed** molecules
- Solution:

$$\theta(t) = A e^{-t/\tau}$$

$$\tau = \frac{1}{\nu_1} e^{E_D/kT} = \tau_0 e^{E_D/kT}$$

# 2<sup>nd</sup> order desorption

- For **dissociatively chemisorbed** molecules (H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>) on metals
- Collision at surface of atoms is needed before molecular desorption occur
- The rate of molecular desorption from a surface is given by:

$$-\frac{d\theta}{dt} = v_2 \theta^2 e^{-E_D/kT}$$

- $\theta$ , surface coverage,  $v_2$ , second order rate desorption constant (10<sup>-2</sup> cm<sup>2</sup>/s),  $E_D$ , activation energy for desorption



# TPD or TDS

- The order of desorption and the desorption energy can be evaluated from **Temperature Programmed Desorption or Thermal Desorption Spectroscopy**
- Applying a linear change of the temperature sample  $T = T_0 + \beta t$ , the desorption rate is maximum at temperature  $T_p$  for:

- For first order:

$$\frac{E}{R T_p^2} = \frac{\nu_1}{\beta} e^{-E/R T_p}$$

P.A. Redhead, Vacuum 12 (1962), 203.

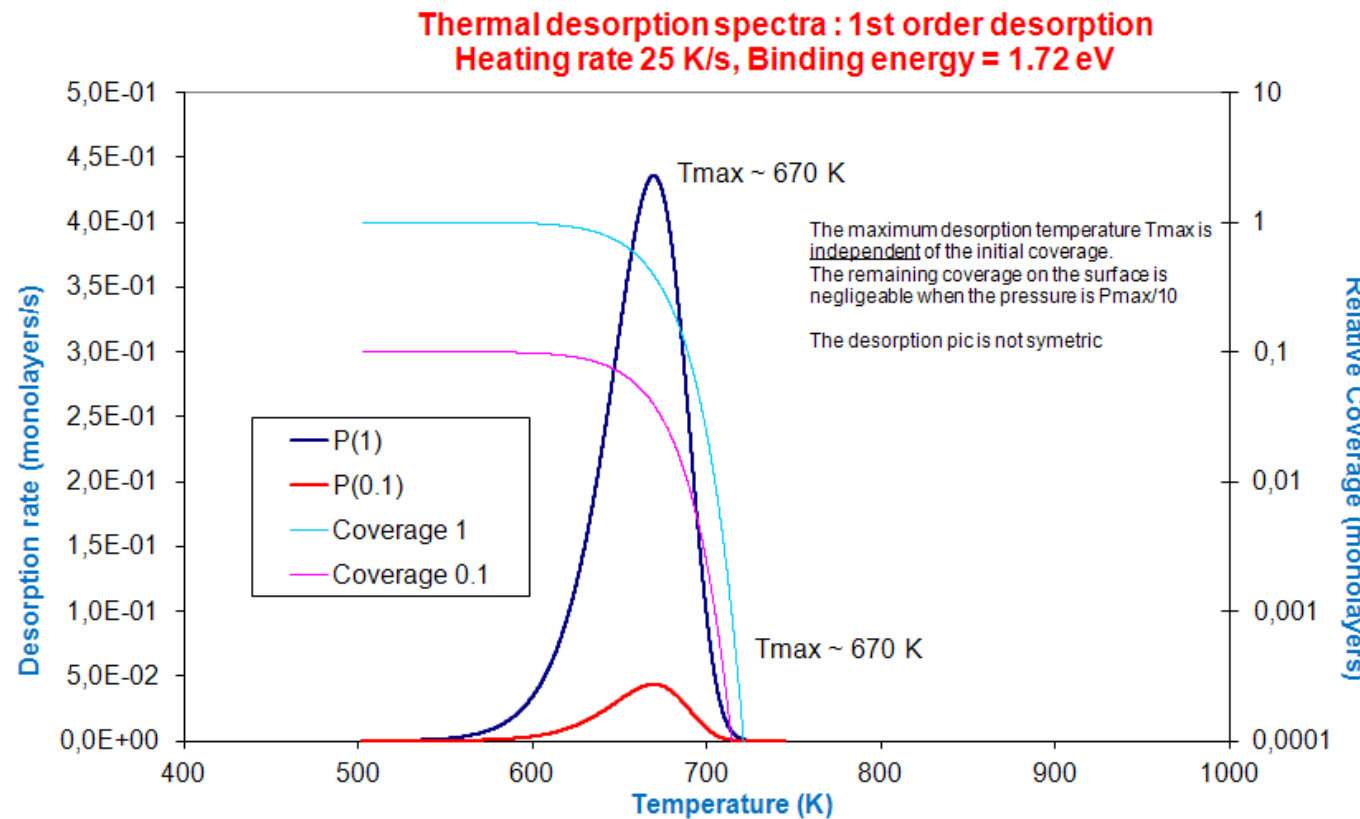
- For second order:

$$\frac{E}{R T_p^2} = \frac{\theta_{initial} \nu_2}{\beta} e^{-E/R T_p}$$

- Solving the above equations with  $\beta$  and  $T_p$  as inputs give the activation energy

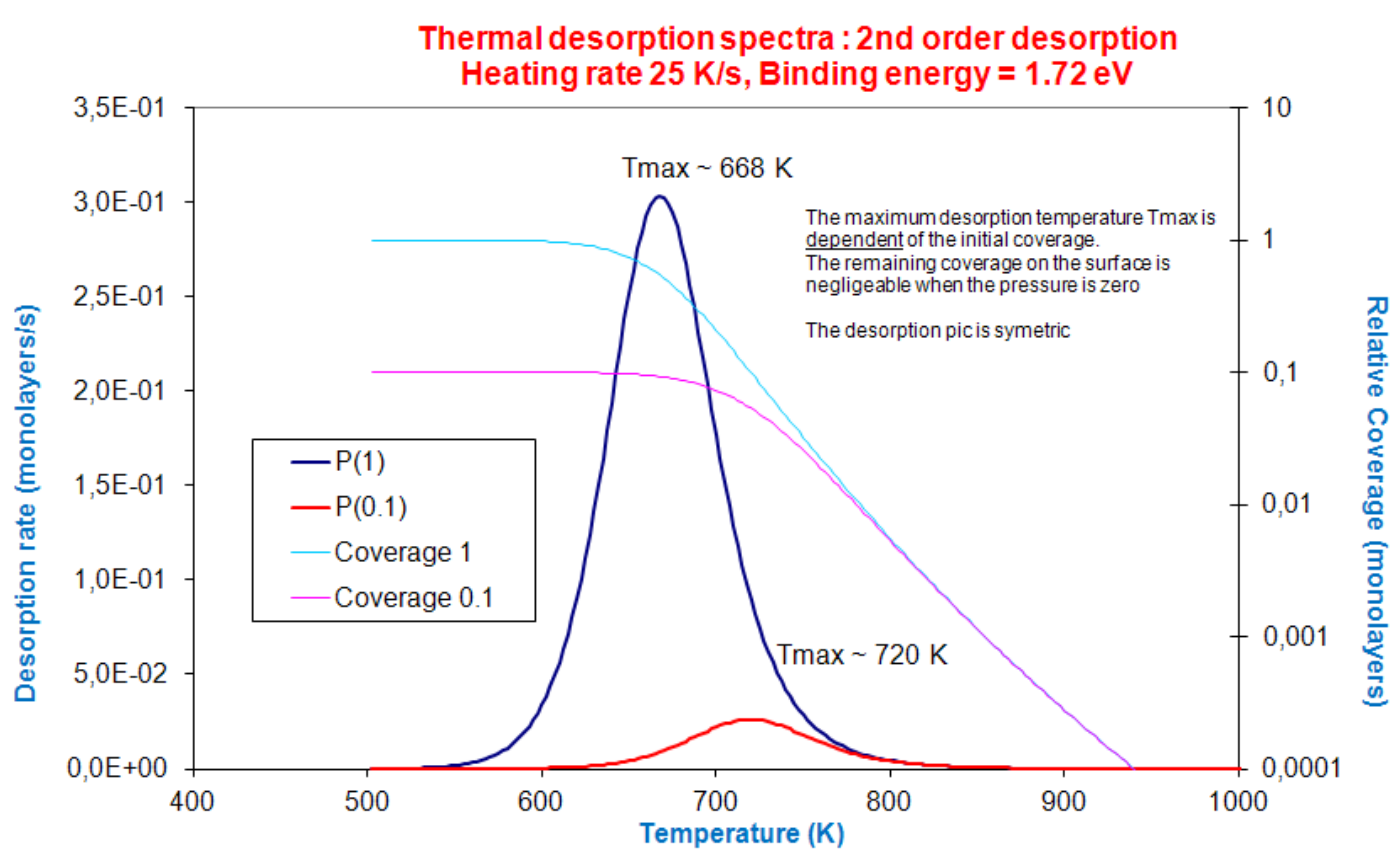
# TDS spectra: 1<sup>st</sup> Order

- The maximum temperature  $T_{\max}$ , is **independent** of the initial surface coverage
- The remaining coverage on the surface is negligible when the pressure is  $P_{\max}/10$
- The desorption peak is **not symmetric**



# TDS spectra: 2<sup>nd</sup> Order

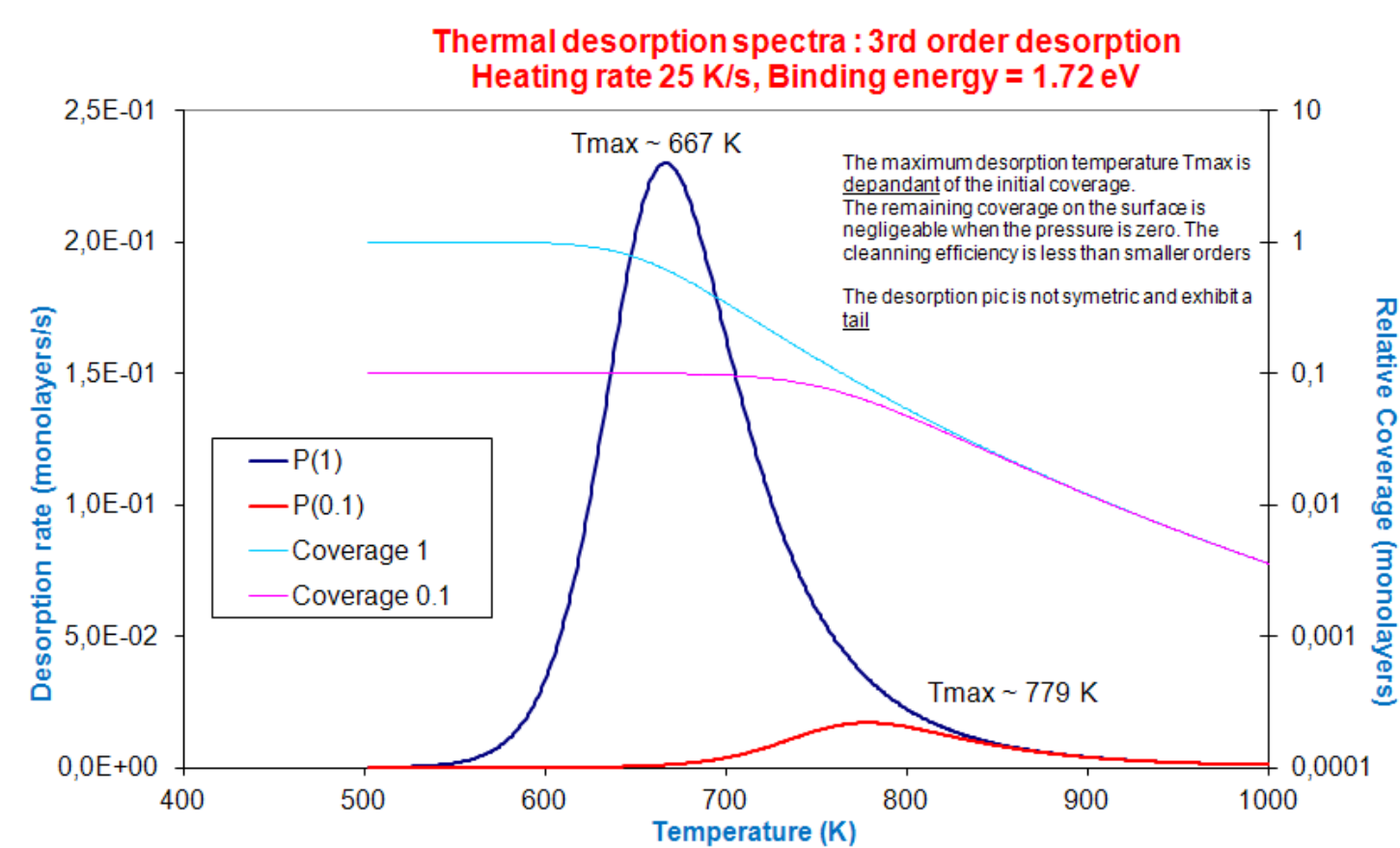
- The maximum temperature is **dependent** of the initial surface coverage
- The remaining coverage on the surface is negligible when the pressure is 0.
- The desorption peak is **symmetric**



# TDS spectra: 3<sup>rd</sup> Order

Complementary information

- The maximum temperature is **dependent** of the initial surface coverage
- The remaining coverage on the surface is negligible when the pressure is 0.
- The desorption peak is **not symmetric and exhibit a tail**



# Evaluation of the activation energy

- Measure with several heating rates

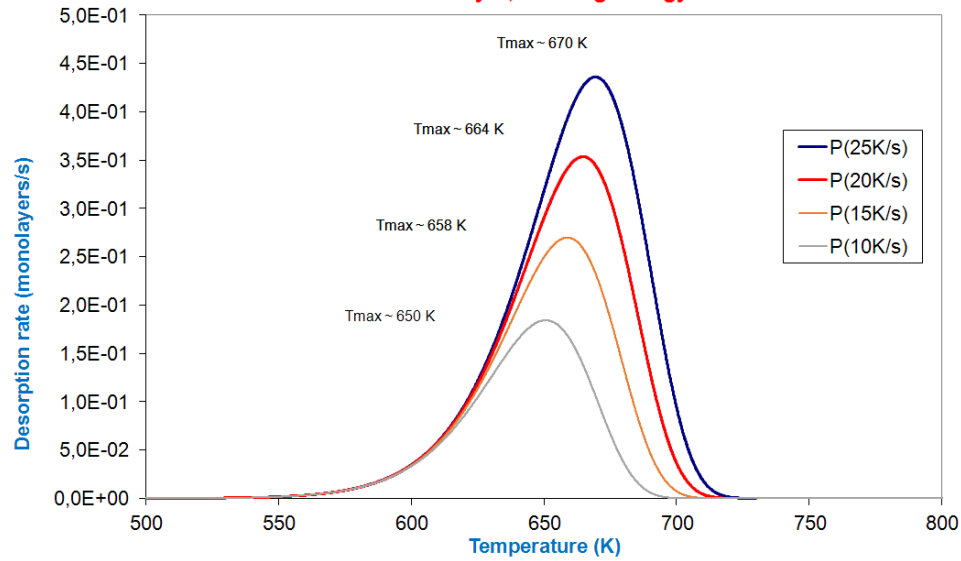
- First order 
$$\frac{E}{R T_p^2} = \frac{\nu_1}{\beta} e^{-E/R T_p}$$

- Taking natural log and rearranging

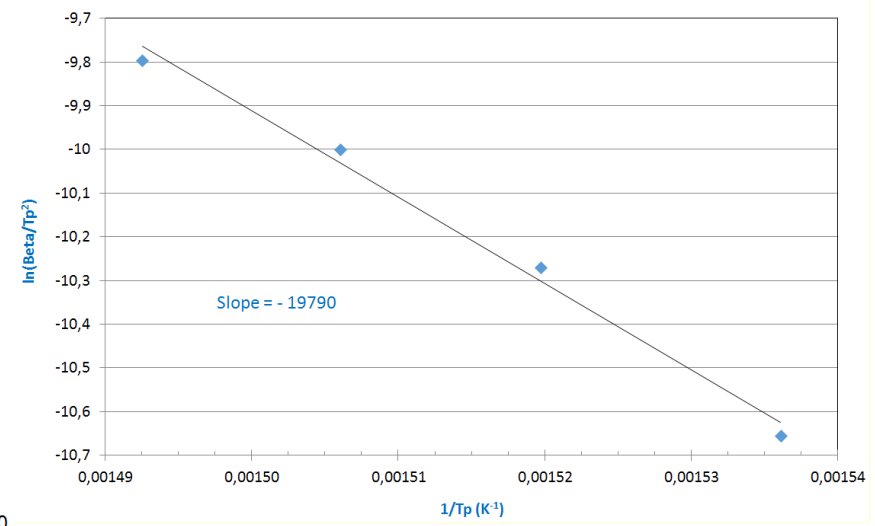
$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E}{R T_p} + \ln\left(\frac{\nu_1 R}{E}\right)$$

- Plot  $\ln(\beta/T_p^2)$  vs  $1/T_p$  gives a straight line with slope proportional to E

Thermal desorption spectra : 1st order desorption  
1 monolayer, Binding energy = 1.72 eV



$\ln(\beta/T_p^2)$  vs  $1/T_p$

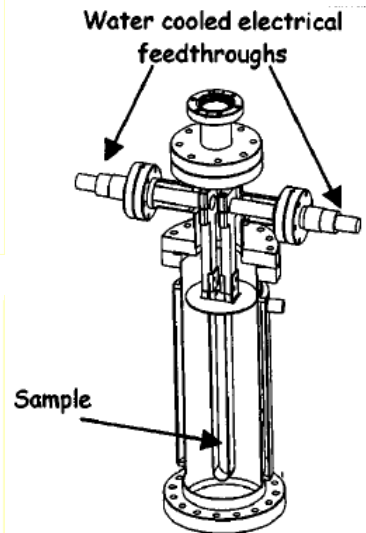
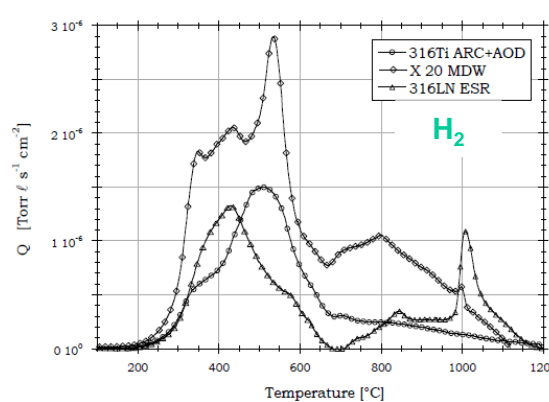


# Some results of TDS

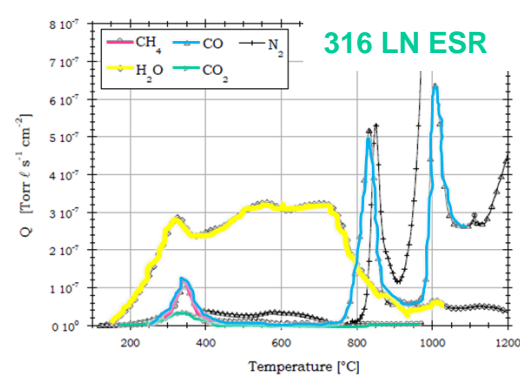
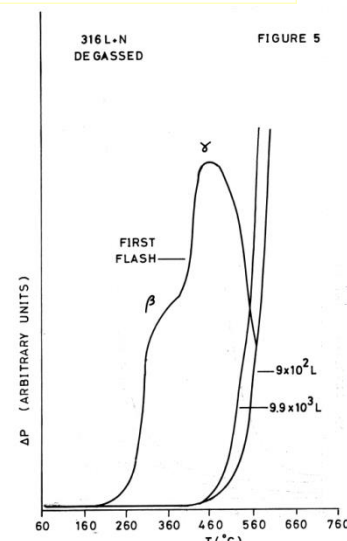
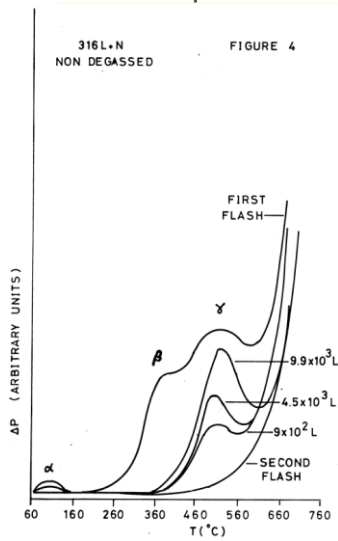
- The binding energy of CO range from 0.9 to 2.8 eV
- Vacuum fired material cannot be repopulated with CO

- 200°C bakeout
- H<sub>2</sub> is desorbed at different temperature
- H<sub>2</sub>O is still present

|                | E (eV)                 |                    |       |       |
|----------------|------------------------|--------------------|-------|-------|
|                | 316 L + N non-degassed | 316 L + N degassed | 316 L | NS 21 |
| α-CO           | 0.97                   |                    | 1.2   | = 0.9 |
| β-CO           | 1.72                   | 1.67               | 1.7   | 1.55  |
| γ-CO           | 2.05                   | 1.91               | 2.2   | 1.96  |
| δ-CO (?)       |                        |                    | 2.8   |       |
| H <sub>2</sub> |                        |                    |       | 0.89  |



25 K/s



5 K/s

A.G. Mathewson *et al*, Proc. 7<sup>th</sup> Int. Vac. Congr, Vienna, 1977

JP Bacher *et al*, JVSTA 21 Jan/Feb 2003, 167

# Sojourn time

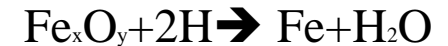
- This is the characteristic time for a first order desorption process
- The sojourn time (residence time) of a molecule on a surface is a function of the desorption energy,  $E_D$ , and the surface temperature,  $T$ :

$$\tau = \tau_0 e^{\left(\frac{E_D}{kT}\right)}$$

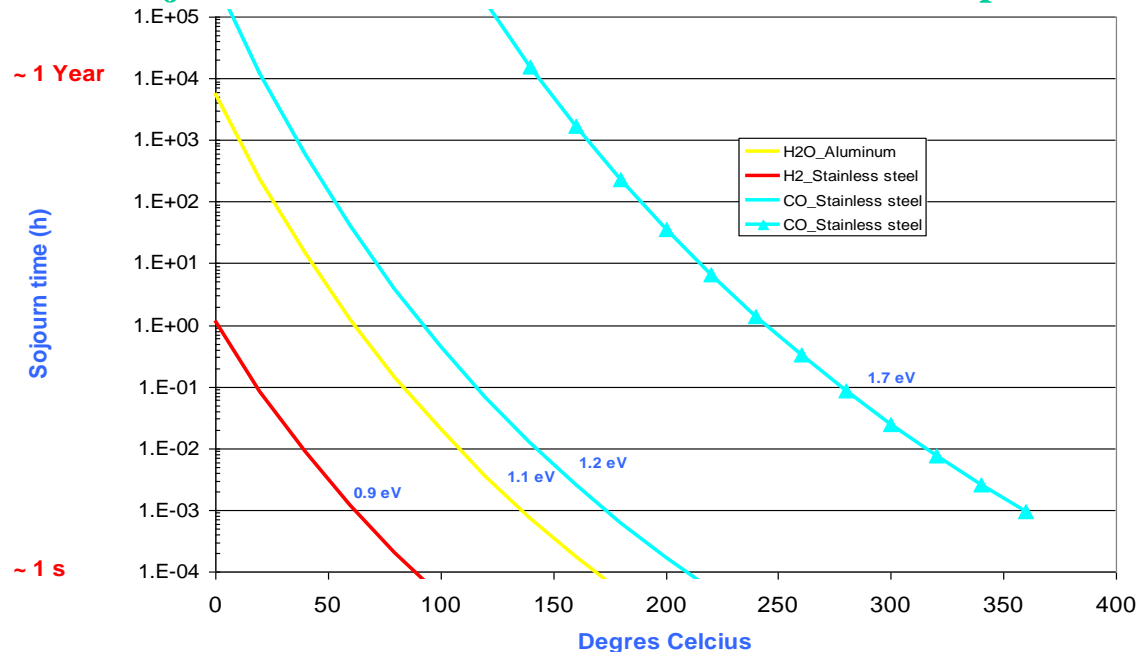
- With  $\tau_0$  the oscillation period of the molecules on the surface  $\sim 10^{-13}$  s.
- The inverse of the sojourn time reflects the probability of desorption
- Strongly bound molecules have long residence time
- Increasing the temperature decrease the residence time
- Decreasing the temperature, increase the residence time

# H<sub>2</sub>O - Sojourn time

- At room temperature, the sojourn time of water on the surface is very large ~ 1 week
  - The surface coverage of water is therefore reduced by 1/e in a week
- Water desorption is dominating the pumping process and several months are needed to evacuated fully the water adsorbed on the surface
- Water originates from previously adsorbed molecules and also from reaction with oxides



Sojourn time of a molecule as a function of temperature





## 2. Outgassing

# 2.1 Water outgassing

# Water outgassing

- It is observed that the desorption of water follows a law of the form, with a  $\sim 1$ :

$$q(t) = q_0 t^{-a}$$

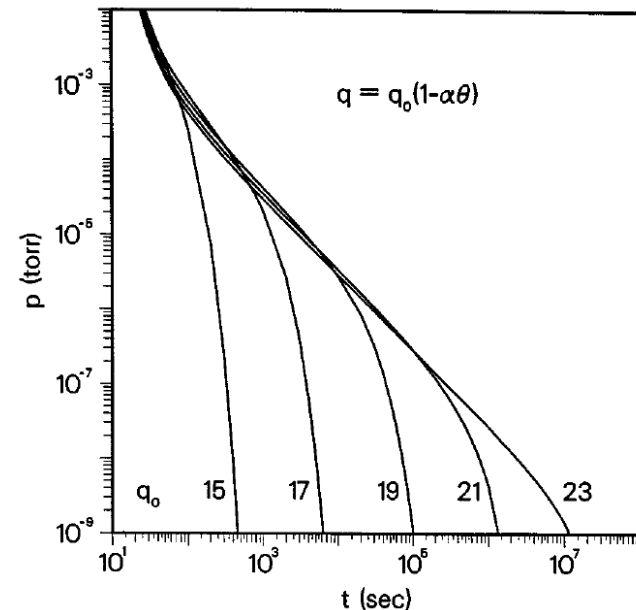
- In practical units

$$q(t) = \frac{3 \cdot 10^{-9}}{t [h]} \text{ mbar.l.s.cm}^{-2}$$

- Model of Redhead:

- Desorption/adsorption is assumed to be reversible
- The surface coverage can be expressed as a function of pressure by a suitable isotherm
- Assumes a Temptkin isotherm with several possible adsorption energies,  $q_i$ , due to the complexity of the technical surface (15-23 kcal/mole *i.e.* 0.6 - 1 eV)

$$P(t) = \frac{\theta_m RT V/S}{GV(q_0 - q_1)} t^{-1}$$



P.A. Redhead, J. Vac. Sci. Technol. A 13(2), Mar/Apr 1995

# Impact of roughness

- Case of unbaked a-C coated stainless steel tube, 450-500 nm thick:

Mass spectrum is water dominated

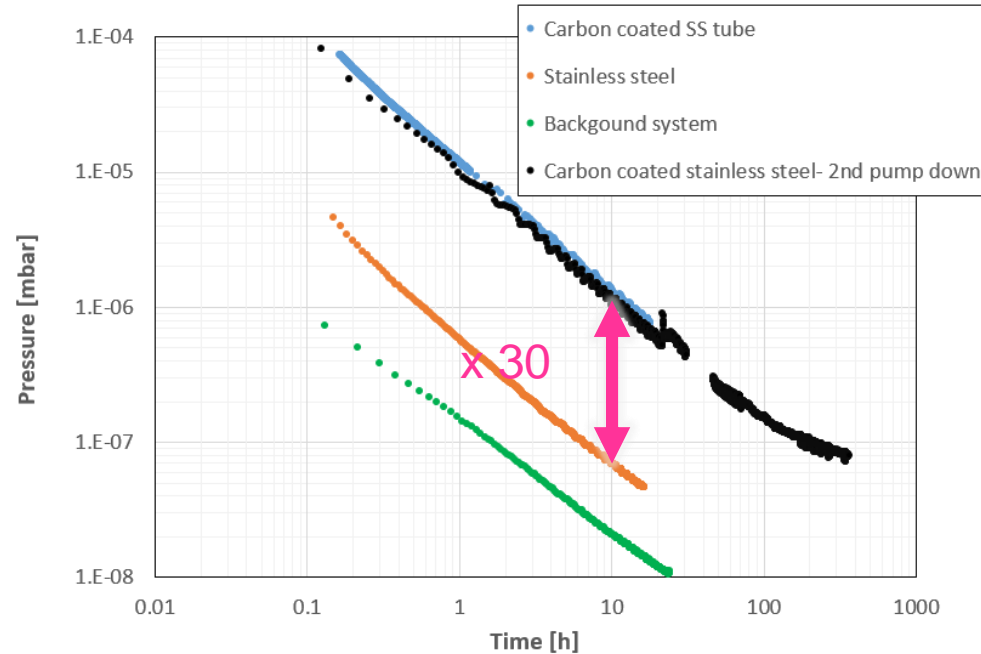
~ x 30 unbaked stainless steel

2nd pump down very similar to 1st one

After 10h pumping:

Stainless steel =  $2 \cdot 10^{-10}$  mbar.l/s/cm<sup>2</sup>

a-C coating =  $6 \cdot 10^{-9}$  mbar.l/s/cm<sup>2</sup>



Courtesy I. Wevers

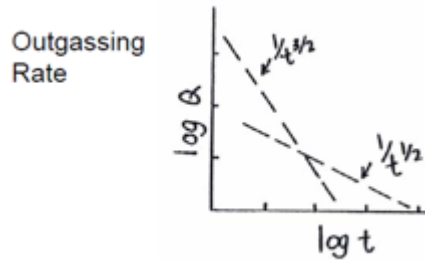
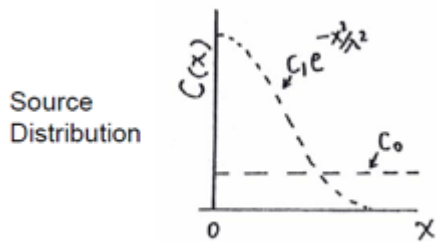
The amount of water chemisorbed on the surface increases when increasing the surface roughness

- Mechanical polishing or electropolishing are used to reduce the outgassing rate of materials

# Water outgassing & exposition to water

$$Q(t) = Q_0 t^{-a} = \frac{q_1}{t^{3/2}} + \frac{q_2}{t^{1/2}}$$

- The exponent,  $a$ , varies with the quantity of water exposed:
- Large water exposure (17 ML): 1.3
- ambient air (8L): 1
- low water exposure (0.02 ML): 0.65
- The observation can be modeled by the superposition of:
  - a water surface concentration  $\Rightarrow a \sim 3/2$
  - a water bulk concentration  $\Rightarrow a \sim 1/2$



F. Dylla, CAS 2006 & J. Vac. Sci. Technol. A 11(4), Jul/Aug 1993

Venting with dry N<sub>2</sub> reduces pump down times

TABLE I. H<sub>2</sub>O absorption/desorption data for various venting conditions of the stainless-steel (304) test chamber.<sup>a</sup>

| Trial | H <sub>2</sub> O absorbed (ML) | H <sub>2</sub> O exposed (ML) | $Q = Q_{10}/t^a$           |      | $Q = q_1/t^{3/2} + q_2/t^{1/2}$ |                         | Venting gases   |
|-------|--------------------------------|-------------------------------|----------------------------|------|---------------------------------|-------------------------|---|
|       |                                |                               | $Q_{10}$ ( $\times 10^4$ ) | $a$  | $q_1$ ( $\times 10^3$ )         | $q_2$ ( $\times 10^3$ ) |   |
| T010  | 7.8                            |                               | 2.67                       | 1.22 | 1.96                            | 3.73                    | Ambient air   |
| T020  | 16.8                           | 600                           | 8.21                       | 1.30 | 4.23                            | 3.86                    | Controlled mixture of H <sub>2</sub> O and N <sub>2</sub> |
| T021  | 9.2                            | 400                           | 3.12                       | 1.18 | 3.15                            | 5.86                    |   |
| T022  | 7.2                            | 200                           | 2.36                       | 1.19 | 2.11                            | 6.11                    |   |
| T023  | 3.6                            | 100                           | 0.87                       | 1.09 | 1.55                            | 6.33                    |   |
| T024  | 2.3                            | 10                            | 0.52                       | 1.07 | 0.86                            | 5.89                    |   |
| T030  | 0.7                            |                               | 0.12                       | 0.96 | 0.29                            | 14.0                    | N <sub>2</sub> gas (> 10 ppm H <sub>2</sub> O)            |
| T040  | 0.017                          |                               | $5.07 \times 10^{-4}$      | 0.65 | $8.91 \times 10^{-2}$           | 1.05                    | Highly dry N <sub>2</sub> gas                             |

<sup>a</sup>Note: The unit for the outgassing rate ( $Q$ ) is (Torr  $\ell/\text{cm}^2 \text{ s}$ ) and the unit of time ( $t$ ) is (s).

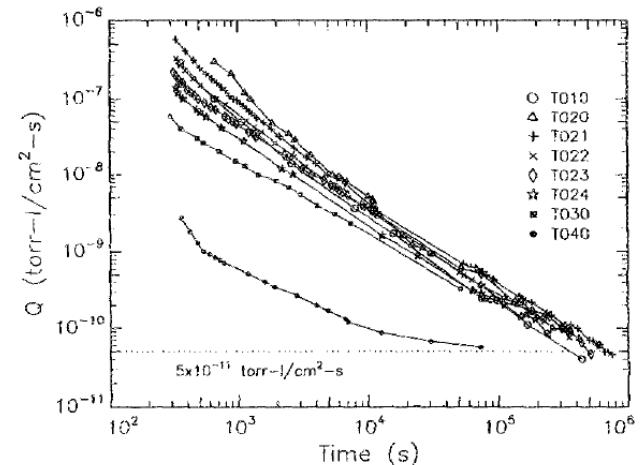


FIG. 2. Outgassing measurements for different H<sub>2</sub>O exposures in a log ( $Q$ ) vs log( $t$ ) plot. (See Table I for key to trial numbers, T010-T040.)

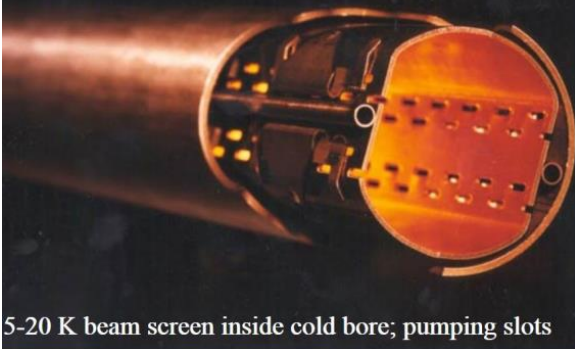
# Typical design value of outgassing rates

- The outgassing rate of unbaked surfaces is **dominated by H<sub>2</sub>O**.
- For metallic surfaces, unbaked after 10h (or 100h tbc) of pumping (Torr.l.s<sup>-1</sup>.cm<sup>-2</sup>)

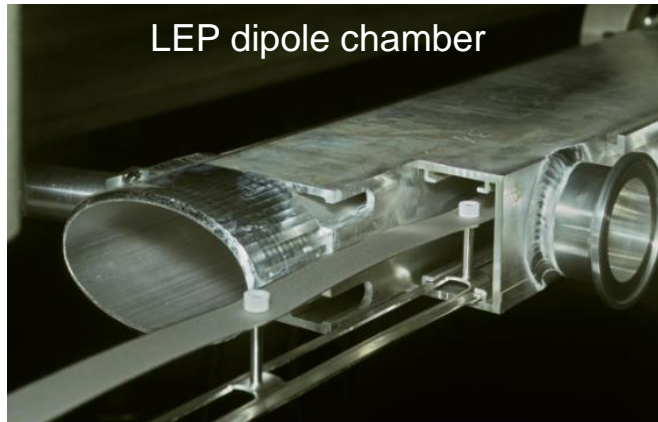
| Gas              | Al                  | Cu                    | St. Steel           | Be                    |
|------------------|---------------------|-----------------------|---------------------|-----------------------|
| H <sub>2</sub>   | 7 10 <sup>-12</sup> | 1.4 10 <sup>-11</sup> | 7 10 <sup>-12</sup> | 1.4 10 <sup>-11</sup> |
| CH <sub>4</sub>  | 5 10 <sup>-13</sup> | 5 10 <sup>-13</sup>   | 5 10 <sup>-13</sup> | 1 10 <sup>-12</sup>   |
| H <sub>2</sub> O | 3 10 <sup>-10</sup> | 3 10 <sup>-10</sup>   | 3 10 <sup>-10</sup> | 6 10 <sup>-10</sup>   |
| CO               | 5 10 <sup>-12</sup> | 1 10 <sup>-12</sup>   | 5 10 <sup>-12</sup> | 1 10 <sup>-11</sup>   |
| CO <sub>2</sub>  | 5 10 <sup>-13</sup> | 2.5 10 <sup>-13</sup> | 5 10 <sup>-13</sup> | 1 10 <sup>-12</sup>   |

A.G. Mathewson *et al.* in Handbook of Accelerator Physics and Engineering, World Scientific, 1998

LHC cold vacuum chamber



LEP dipole chamber



ISR intersection "bicone" chamber



## 2.2 Bake-out

# Sojourn time at high temperature

$$\tau = \frac{e^{\frac{E}{kT}}}{V_0}$$

- The sojourn time decrease strongly with increasing temperature
- Heating the material allows a degassing of molecules with binding energies  $< 2 \text{ eV}$

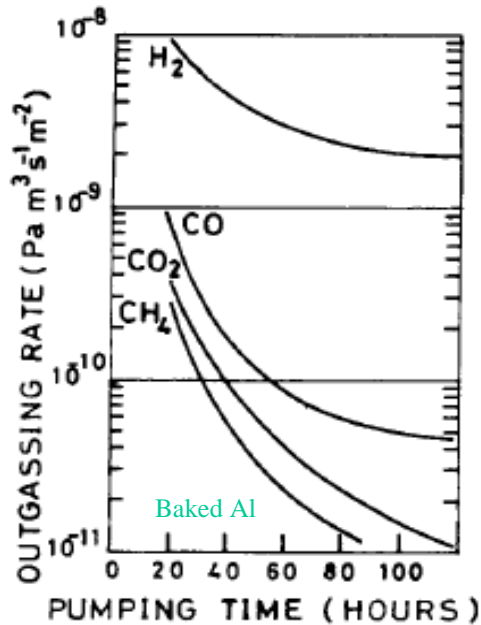
| E(eV) | 120°C                           | 200°C                        | 300°C                        | 400°C                       |
|-------|---------------------------------|------------------------------|------------------------------|-----------------------------|
| 0.9   | $4 \cdot 10^{-2} \text{ s}$     | $4 \cdot 10^{-4} \text{ s}$  | $8 \cdot 10^{-5} \text{ s}$  | $6 \cdot 10^{-7} \text{ s}$ |
| 1.1   | 13 s                            | $5 \cdot 10^{-2} \text{ s}$  | $5 \cdot 10^{-4} \text{ s}$  | $2 \cdot 10^{-5} \text{ s}$ |
| 1.7   | 20 years                        | 1.5 days                     | 88 s                         | 0.5 s                       |
| 2.0   | $1 \cdot 10^5 \text{ years}$    | 6 years                      | 10h                          | 95 s                        |
| 2.8   | $3 \cdot 10^{15} \text{ years}$ | $2 \cdot 10^9 \text{ years}$ | $1 \cdot 10^4 \text{ years}$ | 3 years                     |

- Molecules with larger binding energies than 1.7-2 eV will not be depleted by a bake-out  
→ those molecules will be available for subsequent desorption by e.g. ion bombardment



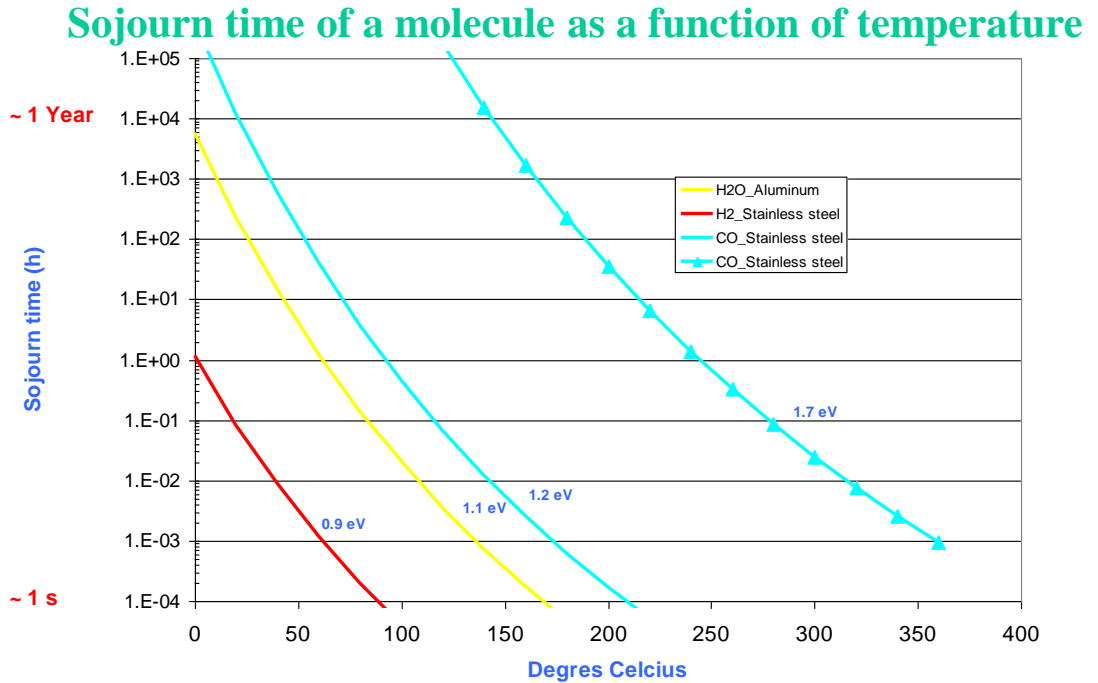
# In Situ Bake Out

- A bake-out above 150 degrees increase the desorption rate of H<sub>2</sub>O and reduce the H<sub>2</sub>O sojourn time in such a way that H<sub>2</sub> become the dominant gas



A.G. Mathewson *et al.*  
 J.Vac.Sci. 7(1), Jan/Fev 1989, 77-82

$$\tau = \frac{e^{\frac{E}{kT}}}{V_0}$$



# Material for bakeout



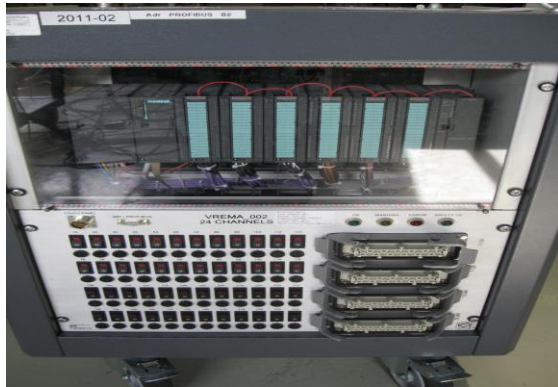
Collars



thermocouples



bakeout jackets



racks

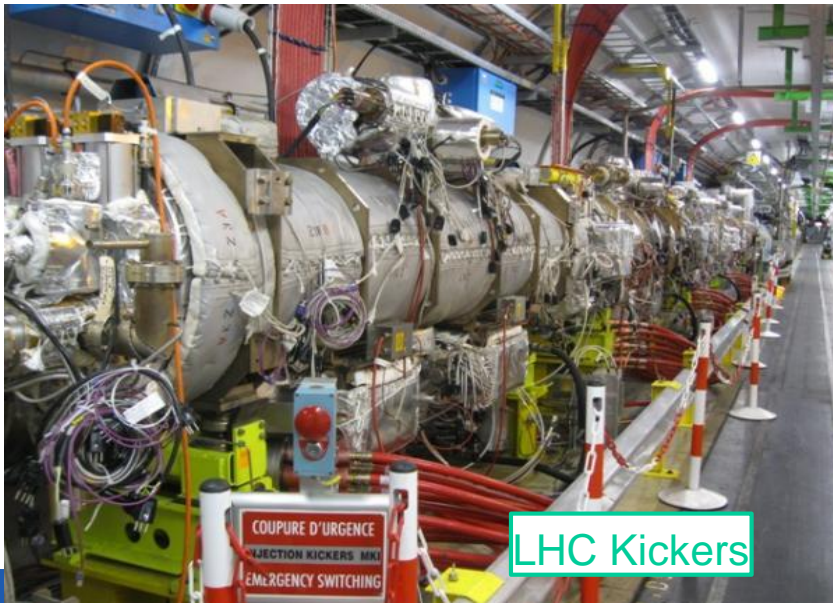
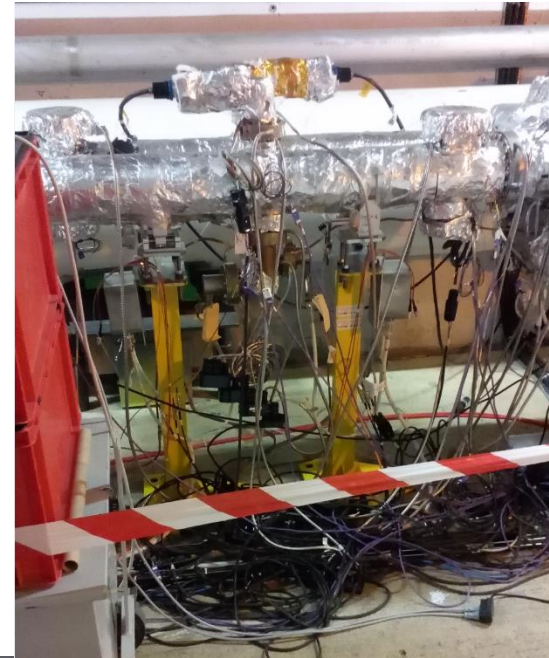
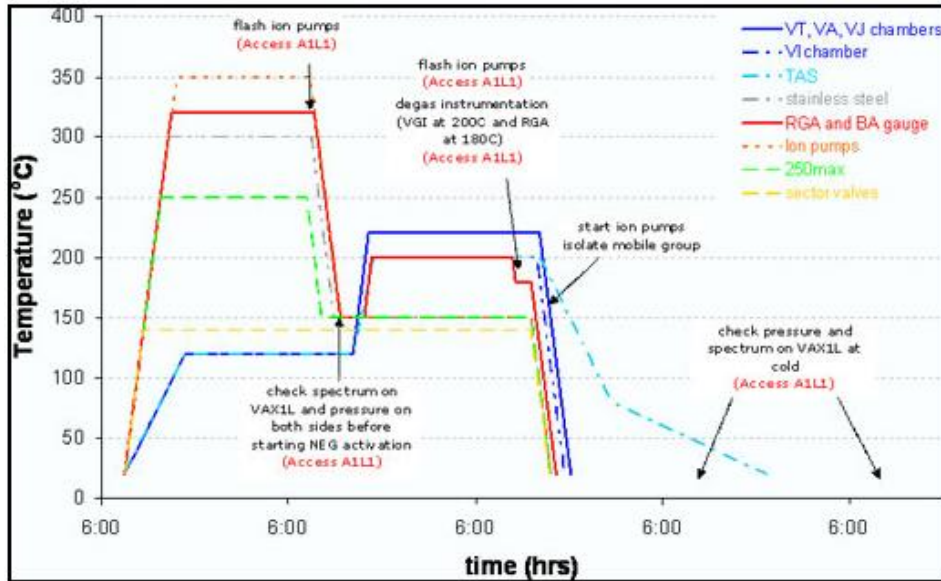


heating tape



Storage area

# Bakeout systems



“Combined” sector  
Both beams circulates in the same beam pipe

# Amount of gas removed after a bake-out

- After a laboratory bake-out of a stainless steel chamber at 200°C for 20 h

| Gas species                                  | H <sub>2</sub> | CH <sub>4</sub> | H <sub>2</sub> O | CO  | CO <sub>2</sub> | Total |
|--|----------------|-----------------|------------------|-----|-----------------|-------|
| Molecule.cm <sup>-2</sup> x 10 <sup>15</sup> | 11             | 0.7             | 7                | 4.4 | 5.7             | 28.8  |

C. Herbeaux *et al.*, J. Vac. Sci. Technol. A 17(2), Mar/Apr 1999, 635

Several monolayers of gas are removed from the vacuum system during a bake out

# Diffusion

- The diffusion coefficient is a function of the diffusion energy and temperature:

$$D(T) = D_0 e^{-E_{diff}/kT}$$

- In 304L, 316L stainless steel:

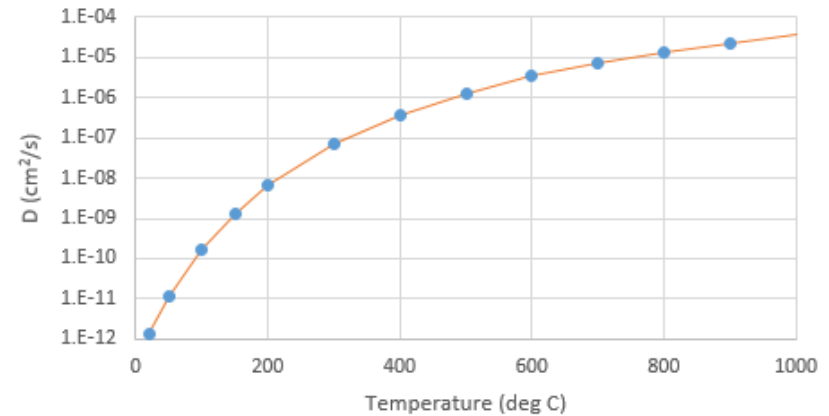
| T°C                    | 20                    | 900                  |
|------------------------|-----------------------|----------------------|
| D [cm <sup>2</sup> /s] | 1.4 10 <sup>-12</sup> | 2.3 10 <sup>-5</sup> |

$$D_0 = 5.8 \cdot 10^{-3} \text{ cm}^2/\text{s}$$

$$E_{diff} = 0.558 \text{ eV}$$

P. Tison, Le Vide, 264, Dec 1992, 377

Stainless steel diffusion coefficient



- The hydrogen diffusion in materials is governed by **Fick Laws**:

- 1<sup>st</sup> Law: The gaseous flux,  $q$ , is equal to the production of the diffusion coefficient,  $D$ , by the gradient of hydrogen concentration

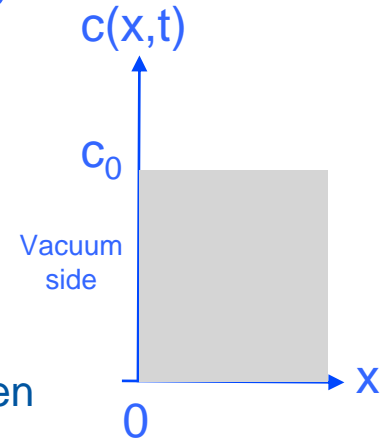
$$q(x, t) = -D \frac{\partial c(x, t)}{\partial x}$$

- 2<sup>nd</sup> Law: The time variation of the hydrogen concentration is equal to the product of the diffusion coefficient by the second derivative of the hydrogen concentration in the solid

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2}$$

# Diffusion in a semi-infinite slab

- Assume a stainless steel slab of infinite thickness with a uniform initial concentration along the slab at  $t=0$  i.e.  $c(x,0) = c_0$
- For  $t>0$ , the pumping is started in such a way the diffused hydrogen is evacuated from the surface i.e.  $c(0,t)=0$
- This is the case of a vacuum chamber under pumping
- Solving the 2<sup>nd</sup> Fick law with these boundary conditions gives for the hydrogen concentration:



$$c(x, t) = \frac{2c_0}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} e^{-y^2} dy = c_0 \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad \bullet \text{ with: } \operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} dy$$

- The hydrogen outgassing rate,  $q$ , after a pumping time,  $t$ , can be derived from the 1<sup>st</sup> Fick law:

$$q(t) = D \left( \frac{\partial c(x,t)}{\partial x} \right)_{x=0} = c_0 \sqrt{\frac{D}{\pi}} \frac{1}{\sqrt{t}} \propto \sqrt{D} t^{-1/2}$$

The outgassing rate varies inversely with the square root of the pumping time

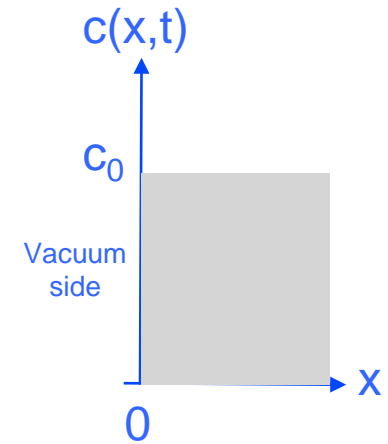
R.J. Eisey, Vacuum 25, 7 (1975), 299

# Diffusion in a semi-infinite slab

Complementary  
information

- The total amount of gas desorbed from the surface at time  $t$  is:

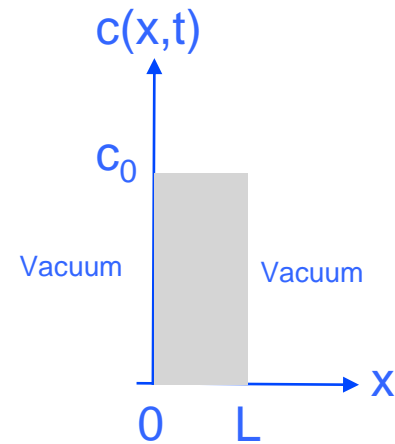
$$\int_0^t q(t) dt = c_0 \sqrt{\frac{2}{\pi}} \sqrt{Dt} \propto \sqrt{t}$$



R.J. Eisey, *Vacuum* 25, 7 (1975), 299

# Diffusion in a finite slab

- Assume a stainless steel slab of thickness,  $L$ , with a uniform initial concentration along the slab at  $t=0$  i.e.  $c(x,0) = c_0$
- For  $t>0$ , the pumping is started in such a way the diffused hydrogen is evacuated from the surface i.e.  $c(0,t)=0$  and  $c(L,t)=0$
- This is the case of a wall totally enclosed in a vacuum system



- Solving the 2<sup>nd</sup> Fick law with these boundary conditions gives:

$$c(x, t) = c_0 \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin\left(\frac{2n+1}{L} \pi x\right) e^{-\left(\frac{\pi(2n+1)}{L}\right)^2 Dt}$$

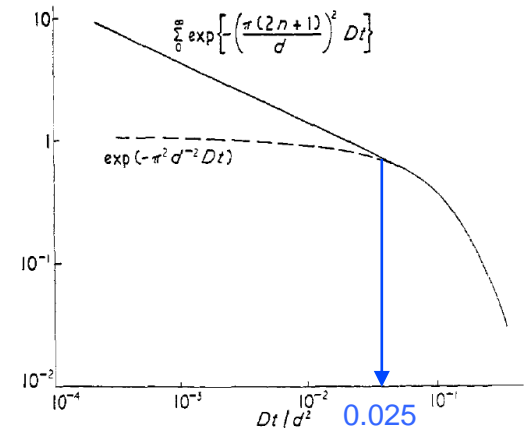
- The hydrogen outgassing rate from both surfaces,  $q$ , after a pumping time,  $t$ , can be derived from the 1<sup>st</sup> Fick law:

$$q(t) = 2 D \left( \frac{\partial c(x, t)}{\partial x} \right)_{x=0} = \frac{8 c_0 D}{L} \sum_{n=0}^{\infty} e^{-\left(\frac{\pi(2n+1)}{L}\right)^2 Dt}$$

- when:  $Dt/L^2 > 0.025$ , all values above  $n>0$  are negligible leading to:

$$c(x, t) = c_0 \frac{4}{\pi} \sin\left(\frac{\pi}{L} x\right) e^{-\left(\frac{\pi}{L}\right)^2 Dt}$$

$$q(t) = \frac{8 c_0 D}{L} e^{-\left(\frac{\pi}{L}\right)^2 Dt}$$



R.J. Eelsey, Vacuum 25, 7 (1975), 299

R. Calder, G. Lewin,  
Br J Appl. Phys, 18, 1967, 1459



# Diffusion in a finite slab: bake-out

- Following an in-situ bake out at temperature  $T_{BO}$  for a long enough time duration  $t_{BO}$ , the **outgassing rate at room temperature (RT)** of one face of the slab is **constant** and equal to:

$$q_{RT}(t) = \frac{4 c_o D(T_{RT})}{L} e^{-\left(\frac{\pi}{L}\right)^2 D(T_{BO})t_{BO}} \times \underbrace{e^{-\left(\frac{\pi}{L}\right)^2 D(T_{RT})t}}_{=1} \approx \frac{4 c_o D(T_{RT})}{L} e^{-\left(\frac{\pi}{L}\right)^2 D(T_{BO})t_{BO}}$$

- In practice, long enough duration time means a couple of hours:

$$\frac{D(T_{BO}) t_{BO}}{L^2} > 0.025$$

| L (mm) | 200°C | 250°C | 300°C |
|--------|-------|-------|-------|
| 1      | 11    | 3     | 1     |
| 2      | 42    | 11    | 4     |

- In practice, increasing the **bake out temperature** is more efficient than increasing the bake out duration time:

Table of equivalences between  
bake out temperature

|         | 200°C  | 250°C | 300°C |
|---------|--------|-------|-------|
| 1 day   | 7h     | 2h    |       |
| 4 days  | 1 day  | 8h    |       |
| 10 days | 2 days | 1 day |       |

R.J. Eley, Vacuum 25, 7 (1975), 299

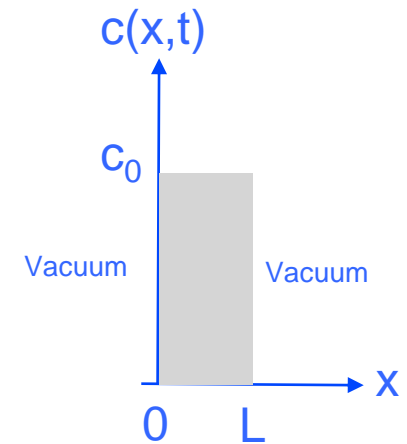
R. Calder, G. Lewin, Br J Appl. Phys, 18, 1967, 1459

# Diffusion in a finite slab

Complementary  
information

- The total amount of gas desorbed from the surface at time  $t$  is:

$$\int_0^t q(t) dt = c_o D \left( 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{\sqrt{2n+1}} e^{-\left(\frac{\pi(2n+1)}{L}\right)^2 D t} \right)$$



R.J. Eley, *Vacuum* 25, 7 (1975), 299

R. Calder, G. Lewin, *Br J Appl. Phys.* 18, 1967, 1459

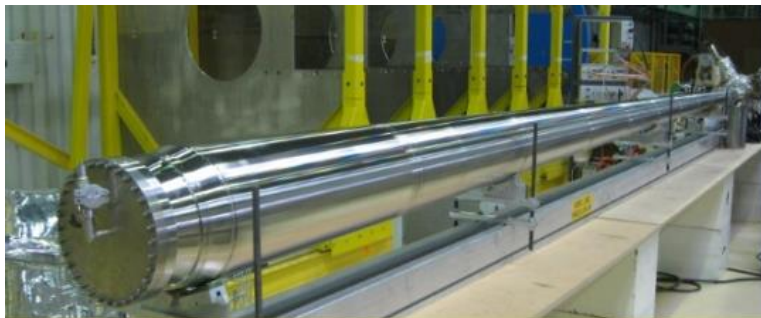
# Typical design value outgassing rates

- The outgassing rate of baked surfaces is **dominated by H<sub>2</sub>**
- Metal, baked (24 h at 150°C for Cu and Al, 300°C for SS) after 50h of pumping (Torr.l.s<sup>-1</sup>.cm<sup>-2</sup>)

| Gas              | Al                  | Cu                   | St. Steel           | Be                  |
|------------------|---------------------|----------------------|---------------------|---------------------|
| H <sub>2</sub>   | 5 10 <sup>-13</sup> | 1 10 <sup>-12</sup>  | 5 10 <sup>-13</sup> | 1 10 <sup>-12</sup> |
| CH <sub>4</sub>  | 5 10 <sup>-15</sup> | 5 10 <sup>-15</sup>  | 5 10 <sup>-15</sup> | 1 10 <sup>-14</sup> |
| H <sub>2</sub> O | 1 10 <sup>-14</sup> | <1 10 <sup>-15</sup> | 1 10 <sup>-14</sup> | 2 10 <sup>-14</sup> |
| CO               | 1 10 <sup>-14</sup> | 1 10 <sup>-14</sup>  | 1 10 <sup>-14</sup> | 2 10 <sup>-14</sup> |
| CO <sub>2</sub>  | 1 10 <sup>-14</sup> | 5 10 <sup>-15</sup>  | 1 10 <sup>-14</sup> | 2 10 <sup>-14</sup> |

A.G. Mathewson *et al.* in Handbook of Accelerator Physics and Engineering, World Scientific, 1998

Outgassing rate of baked material are 2-3 order of magnitude less than unbaked materials



CMS End cap chamber



Copper tubes

# Successive bakeout of a finite slab

- n successive bakeout at  $T_{BO}$  of long enough time duration  $t_{BO}$  give the following outgassing rate at room temperature:

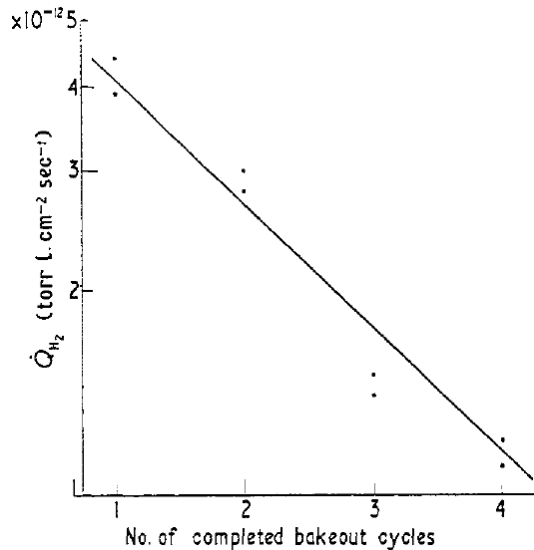
$$q_n(t) = \frac{4 c_o D(T_{RT})}{L} e^{-n \left(\frac{\pi}{L}\right)^2 D(T_{BO}) t_{BO}}$$

R. Calder, G. Lewin, Br J Appl. Phys, 18, 1967, 1459

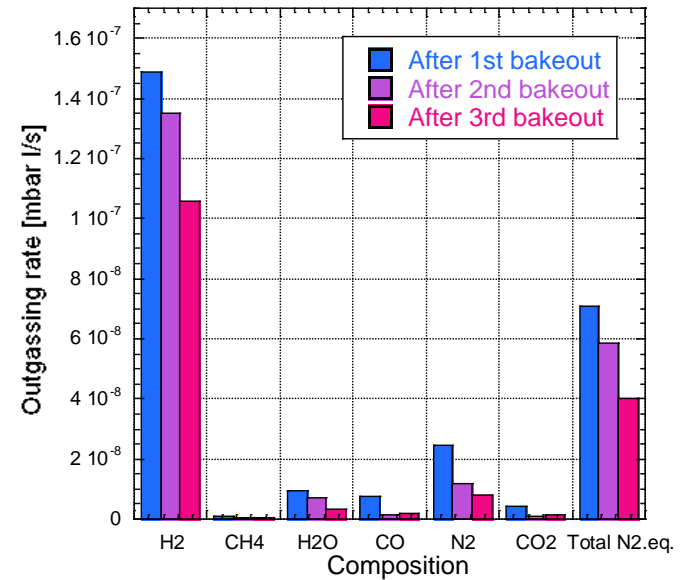
- A plot  $\ln(q)$  vs number of bakeout cycles is **linear** with a slope proportional to the diffusion coef.
- So each bakeout **reduce** the outgassing at room temperature by a **constant value**:

$$\frac{q_{n+1}(t)}{q_n(t)} = e^{\left(\frac{\pi}{L}\right)^2 D(T_{BO}) t_{BO}}$$

Stainless steel sample: a reduction of x1.3-1.5 after each cycle



LHC collimator: a reduction of x1.3 after each cycle



R. Calder, G. Lewin, Br J Appl. Phys, 18, 1967, 1459

J. Kamiya *et al.*, Vacuum 85 (2011) 1178-1181

# Outgassing vs temperature

- Due to the diffusion term, the outgassing rate of a baked material follows an Arrhenius law:

$$q(T) = q_0 e^{-\frac{E_a}{kT}}$$

- A plot  $\ln(q)$  vs  $1/T$  gives a straight line which slope is proportional to the activation energy

- Baked stainless steel:

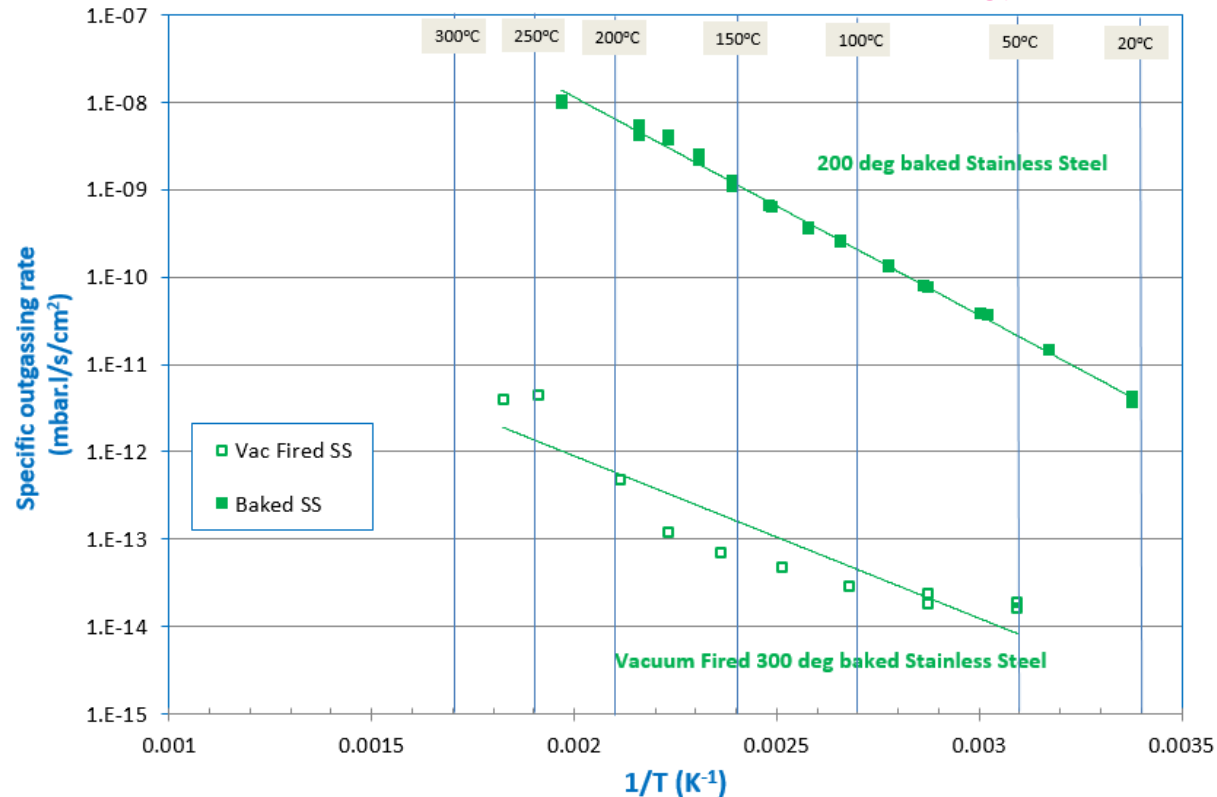
$$E_a \sim 0.5 \text{ eV}$$

| °C                 | 30 | 50 | 100 | 150 |
|--------------------|----|----|-----|-----|
| $\frac{q}{q_{RT}}$ | 2  | 5  | 70  | 450 |

- Vacuum fired baked s. steel:

$$E_a \sim 0.4 \text{ eV}$$

| °C                 | 30 | 50 | 100 | 150 |
|--------------------|----|----|-----|-----|
| $\frac{q}{q_{RT}}$ | 2  | 5  | 30  | 150 |



Courtesy P. Chiggiato, TE-VSC

Laboratory measurements are sensitive to day & night temperature!

## 2.3 Hydrogen reduction

# Vacuum firing

- A method to **reduce hydrogen content in stainless steel** (316 series)
- Outgassing the material is performed in an oven at 950°C under vacuum ( $<10^{-5}$  mbar) for 2 h
- The high temperature allows to enhance hydrogen diffusion



Courtesy P. Chiggiato, TE-VSC

## CERN large furnace

Length: 6 m

Diameter: 1 m

Maximum charge weight: 1000 Kg

Ultimate pressure:  $10^{-9}$  mbar

P at the end of the treatment:  
high  $10^{-6}$  mbar range

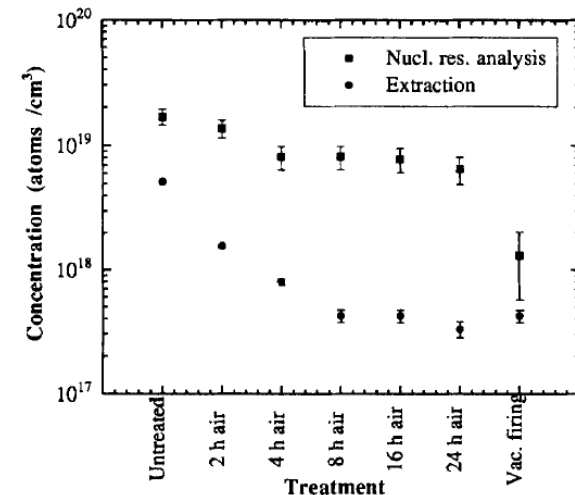
# Impact on structural properties

- Under the heat surface treatment 304 series stainless steel are recrystallized due to carbide precipitation at the grain boundaries
  - ➔ cannot be used as material for flanges (leak at the level of the knife)!
  - ➔ low carbon and low carbon nitrogen alloys stainless steel are used
- The hardness of the material is not modified
- The surface is enriched in Fe due to the Cr evaporation during the treatment
- When the material is bring back to atmospheric pressure, it keeps the memory of the treatment since the hydrogen diffusion at room temperature is small
  - ➔ A **single** treatment is needed in the life of the material

**Table 1.** Deduced hydrogen concentration in the samples from the nuclear resonance analysis (NRA) and an extraction method

| Treatment    | Time(h) | Temperature (°C) | NRA Hydrogen conc. (At/cm <sup>-3</sup> ) | Extraction Hydrogen conc. (At/cm <sup>-3</sup> ) |
|--------------|---------|------------------|---|--|
| Untreated    |         |                  | $1.70(25) \cdot 10^{19}$                  | $5.17(5) \cdot 10^{18}$                          |
| Air baked    | 2       | 400              | $1.37(22) \cdot 10^{19}$                  | $1.56(5) \cdot 10^{18}$                          |
| Air baked    | 4       | 400              | $8.2(17) \cdot 10^{18}$                   | $8.0(5) \cdot 10^{17}$                           |
| Air baked    | 8       | 400              | $8.2(17) \cdot 10^{18}$                   | $4.2(5) \cdot 10^{17}$                           |
| Air baked    | 16      | 400              | $7.8(17) \cdot 10^{18}$                   | $4.2(5) \cdot 10^{17}$                           |
| Air baked    | 24      | 400              | $6.5(16) \cdot 10^{18}$                   | $3.3(5) \cdot 10^{17}$                           |
| Vacuum Fired | 1       | 950              | $1.3(7) \cdot 10^{18}$                    | $4.2(5) \cdot 10^{17}$                           |

$c \sim 2 \cdot 10^{19} \text{ H/cm}^3$  reduced to  $10^{18} \text{ H/cm}^3$



**Figure 1.** The average hydrogen concentration in the 0.05–0.7 μm depth range of the virgin, air baked and the vacuum fired samples. The results from the extraction method are also included.

L. Westerberg *et al.*, Vacuum 48 (1997) 771-773



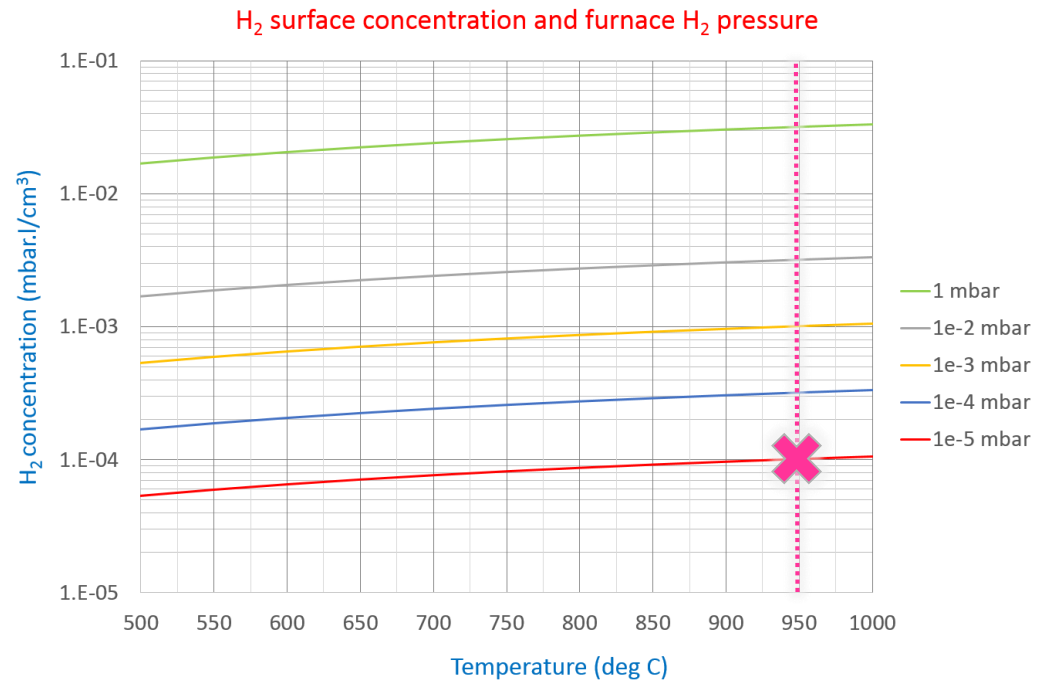
# Hydrogen Solubility

- During the thermal process, the hydrogen can dissolve into the material, in particular at high temperature
- The hydrogen solubility in stainless steel increase with increasing temperature and exposed pressure according to the Seivert's law:

$$c_F = 3 \sqrt{P} e^{-\frac{E_S}{kT}}$$

With  $E_S = 0.115$  eV,  $P$  in bar and  $c_F$  in mbar.l/cm<sup>3</sup>

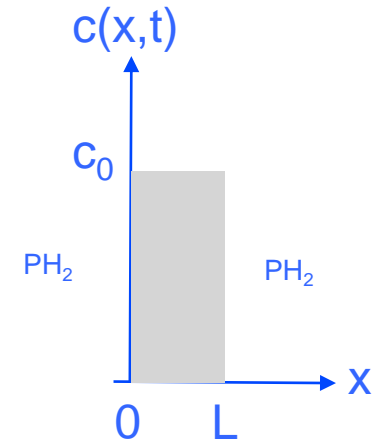
- A furnace pressure < 1 mbar is needed to reduce the “natural” H surface concentration
- At 10<sup>-5</sup> mbar and 950°C, the minimum H<sub>2</sub> concentration is 10<sup>-4</sup> mbar.l/cm<sup>3</sup> *i.e.* ~ 5 10<sup>15</sup> H/cm<sup>3</sup>
- 3 to 4 order magnitude less than in “natural” stainless steel !



# Diffusion in a finite slab with residual H<sub>2</sub> pressure

- Assume a stainless steel slab of thickness, L, with a uniform initial concentration along the slab at t=0 *i.e.*  $c(x,0) = c_0$
- For t>0, the pumping is started in such a way the diffused hydrogen is in equilibrium with the oven pressure *i.e.*  $c(0,t)=c_F$  and  $c(L,t)=c_F$
- Solving the 2<sup>nd</sup> Fick law with these boundary conditions gives:

$$c(x,t) \approx c_F + (c_0 - c_F) \frac{4}{\pi} \sin\left(\frac{1}{L} \pi x\right) e^{-\left(\frac{\pi}{L}\right)^2 Dt}$$

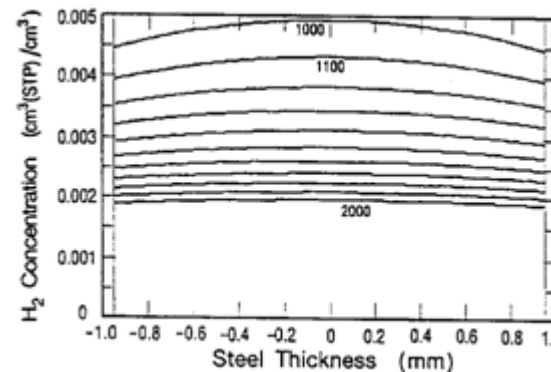
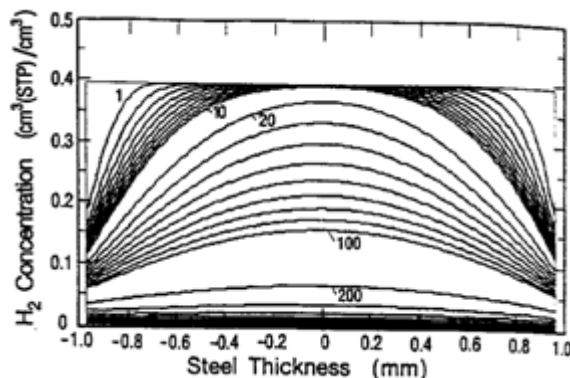


- After the vacuum firing in the furnace at temperature  $T_F$  for a duration  $t_F$ , the hydrogen concentration  $c_H$ , in the solid is:

R. Calder, G. Lewin, Br J Appl. Phys, 18, 1967, 1459

$$c_H(x,t_F) \approx c_F + (c_0 - c_F) c_0 \frac{4}{\pi} \sin\left(\frac{1}{L} \pi x\right) e^{-\left(\frac{\pi}{L}\right)^2 D(T_F)t_F}$$

- Hydrogen profile in a stainless steel sheet as a function of time (in second)



B.C. Moore, J. Vac. Sci. Technol. A 13 (1995), 545.

# Subsequent bakeouts following vacuum firing

- As previously, taking into account the achieved hydrogen surface concentration following the vacuum firing, the hydrogen outgassing rate after  $n$  successive bakeout at temperature  $T_{BO}$  and duration  $t_{BO}$  is obtained from the 1<sup>st</sup> Fick Law:

$$q(t) = D \left( \frac{\partial c(x, t)}{\partial x} \right)_{x=0}$$

$$q_{n,F}(t) = \left[ c_F + (c_O - c_F) e^{-\left(\frac{\pi}{L}\right)^2 D(T_F)t_F} \right] \frac{4 D(T_{RT})}{L} e^{-n \left(\frac{\pi}{L}\right)^2 D(T_{BO})t_{BO}}$$

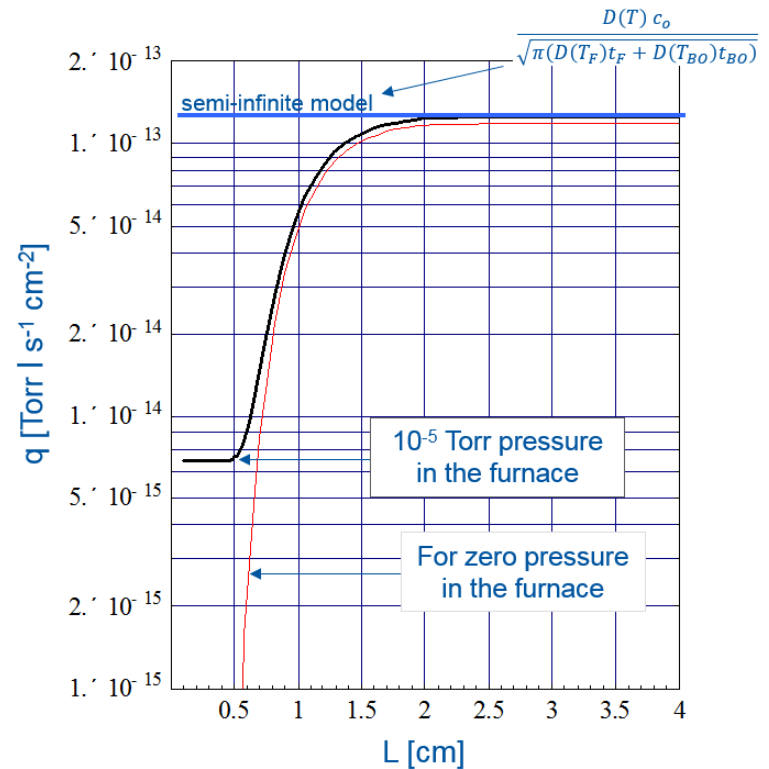
R. Calder, G. Lewin, Br J Appl. Phys, 18, 1967, 1459

- For **thin sheets**, the initial content of hydrogen is fully removed. The final outgassing is defined by the  $H_2$  pressure in the furnace:

$$q \sim 5 \cdot 10^{-15} \text{ mbar.l/cm}^2$$

- For **thick slab**, the pressure in the furnace as limited influence:

$$q \sim 10^{-13} \text{ mbar.l/cm}^2$$



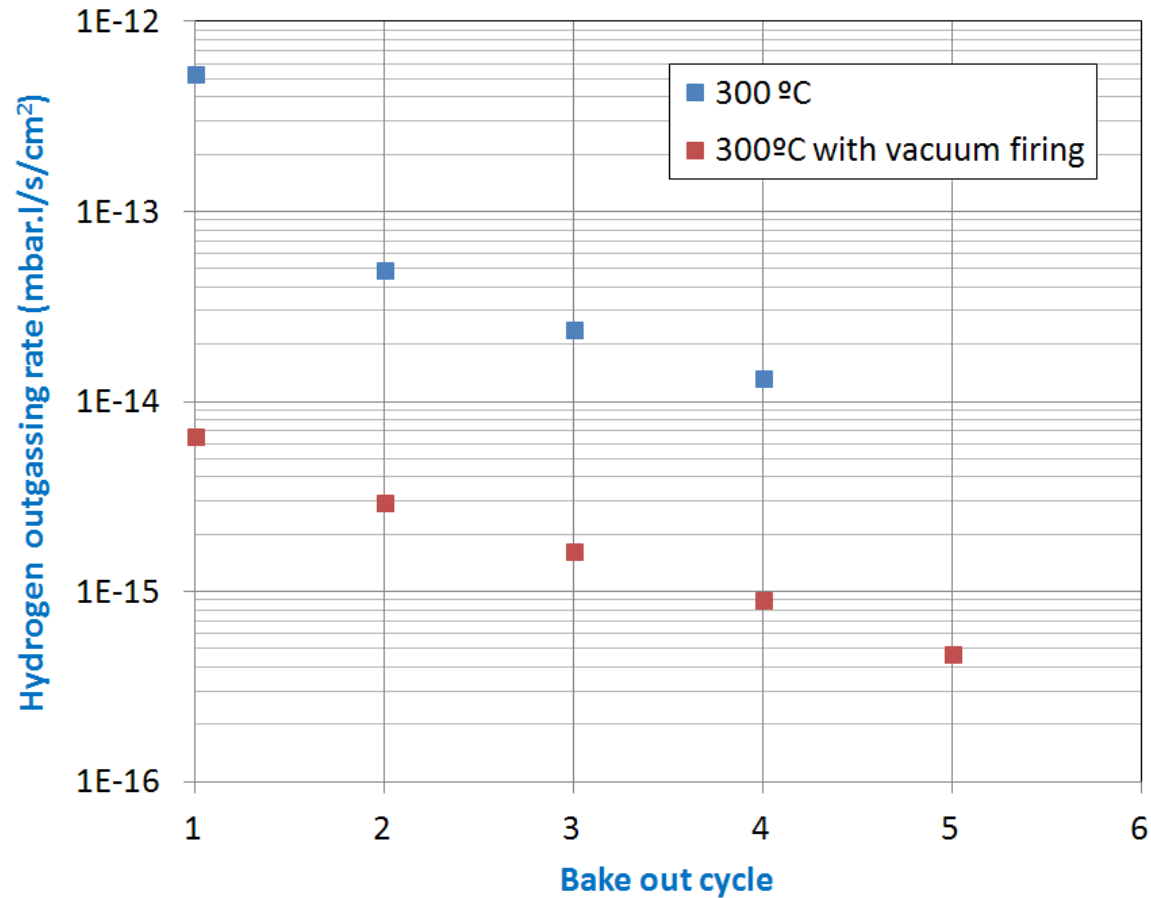
Courtesy P. Chiggiato, TE-VSC

# Stainless steel 316 LN

- 1.5 mm thick sheet held at 300°C for 24 h, rate measured 120 h after then end of bake-out
- A reduction of ~ 1.8 between each cycle



316 LN stainless steel hydrogen outgassing rate



B. Versolatto, N. Hilleret, CERN Vacuum Technical Note 2002

# Diffusion barrier: air baking

- The hydrogen diffusion is reduced by a diffusion barrier created during the air bake-out
- Stainless steel tube:
  - 8 m length, 1.2 m diameter, 2mm thick
- Air fired at 400 deg for 38h
- Then baked at 150 deg for 7 days
- Oxide thickness x 10
- $q = 10^{-15}$  mbar.l/s/cm<sup>2</sup>
- Diffusion energy increased from 0.5 to 0.6 eV
- **Low cost!**

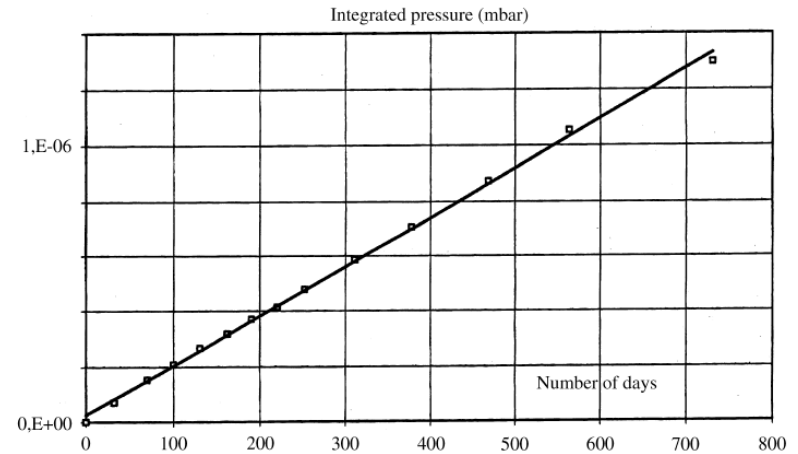
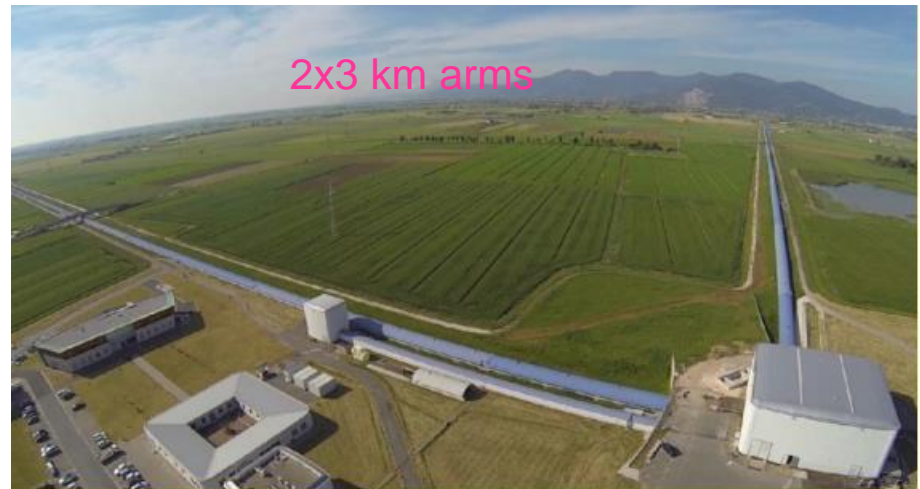


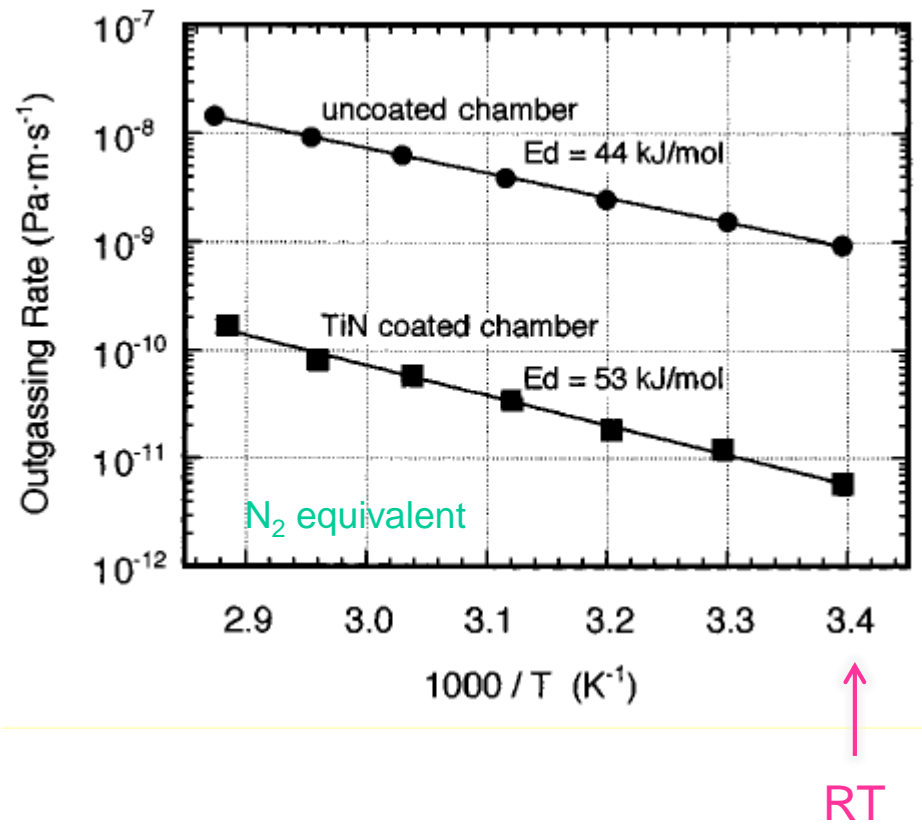
Fig. 1. Hydrogen accumulation over a long period of time in the Orsay corrugated prototype tube for VIRGO.

Outgassing performance of an industrial prototype tube for the Virgo antenna, P. Marin *et al.* , Vacuum 49 (1998) 309



# Diffusion barrier: coating ?

- The hydrogen diffusion is reduced by a diffusion barrier created by a coating e.g. TiN
- At least 1  $\mu\text{m}$  film thickness
- The film **reduce** the hydrogen **permeation**
- Extrapolation from coupons measurements predicts  $10^{-14} \text{ Pa}\cdot\text{m s}^{-1}$  ( $10^{-17} \text{ mbar}\cdot\text{l/s/cm}^2$ )
- 3D object: **difficulties** to realise a uniform coating without pinholes which compromised the observed performance on a tube or vacuum chamber
- Reduction of 2 orders of magnitude of the hydrogen outgassing rate:
  - Uncoated chamber:  $10^{-10} \text{ mbar}\cdot\text{l/s/cm}^2$
  - TiN coated chamber:  $7 \cdot 10^{-13} \text{ mbar}\cdot\text{l/s/cm}^2$



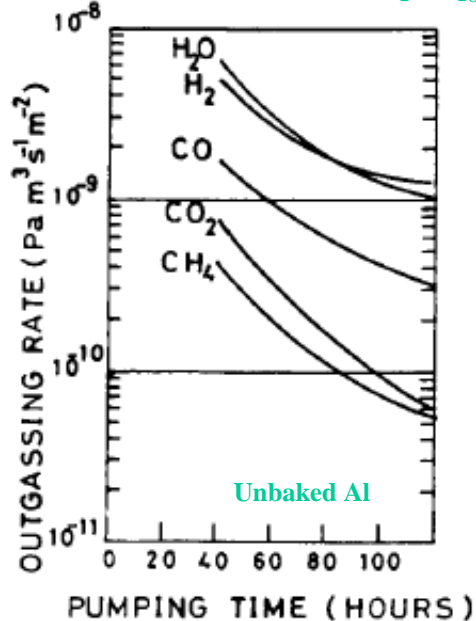
TiN thin film on stainless steel for extremely high vacuum material, K. Saito *et al.* , J. Vac. Sci. Technol. A 13(3) May/Jun 1995, 556

## 2.4 Other materials

# Outgassing of plastics

- Plastic material are **highly porous** and contains much more water than metallic surface
- Their outgassing rate is limited by a **diffusion process**

Metallic surfaces  $q \sim q_0/t$

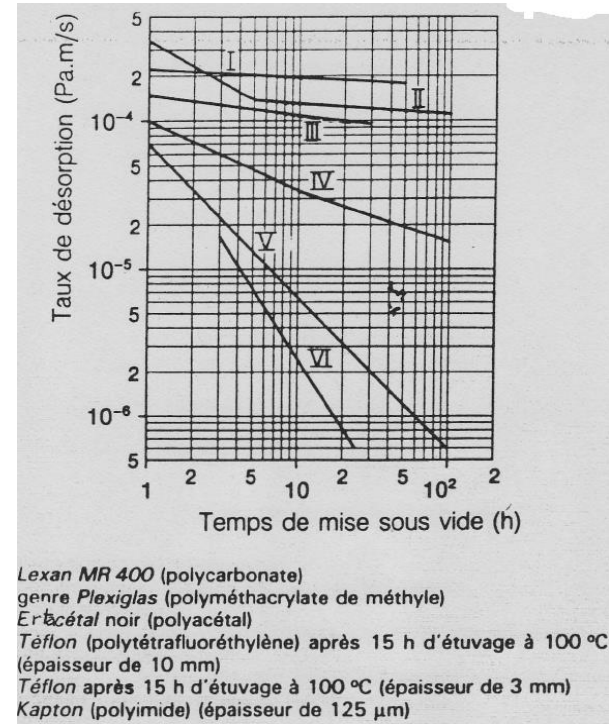


A.G. Mathewson *et al.*  
 J.Vac.Sci. 7(1), Jan/Fev 1989, 77-82

x 5 000



Plastic surfaces  $q \sim q_0/\sqrt{t}$



## Good Vacuum Design :

Use **ONLY** metallic surfaces and reduce to **ZERO** the amount of plastics

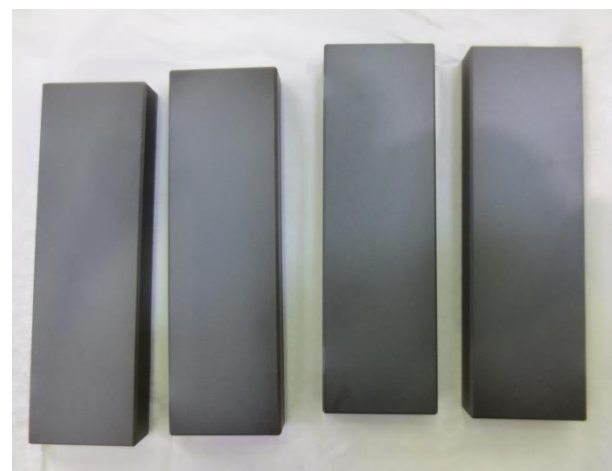
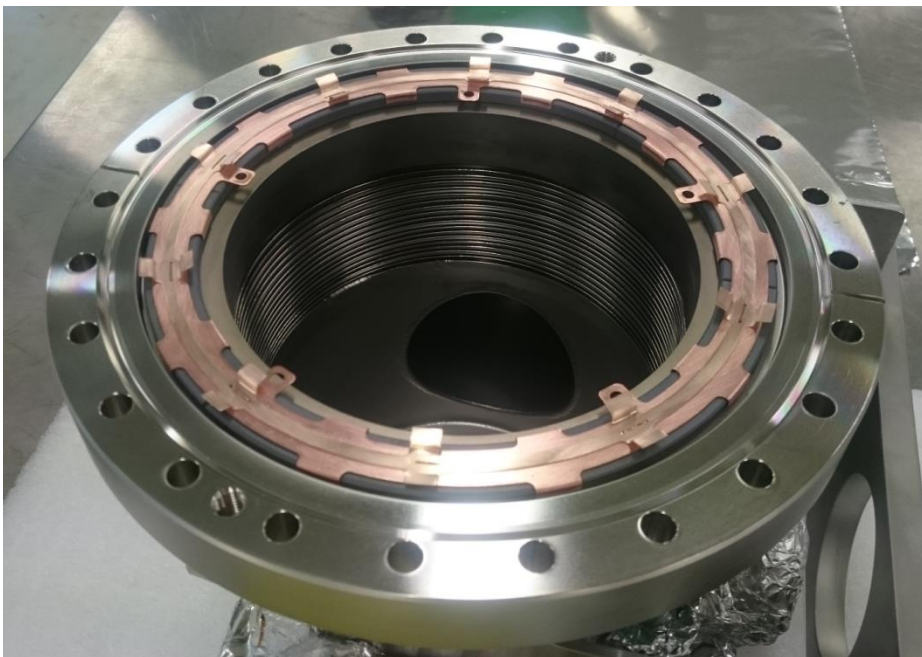
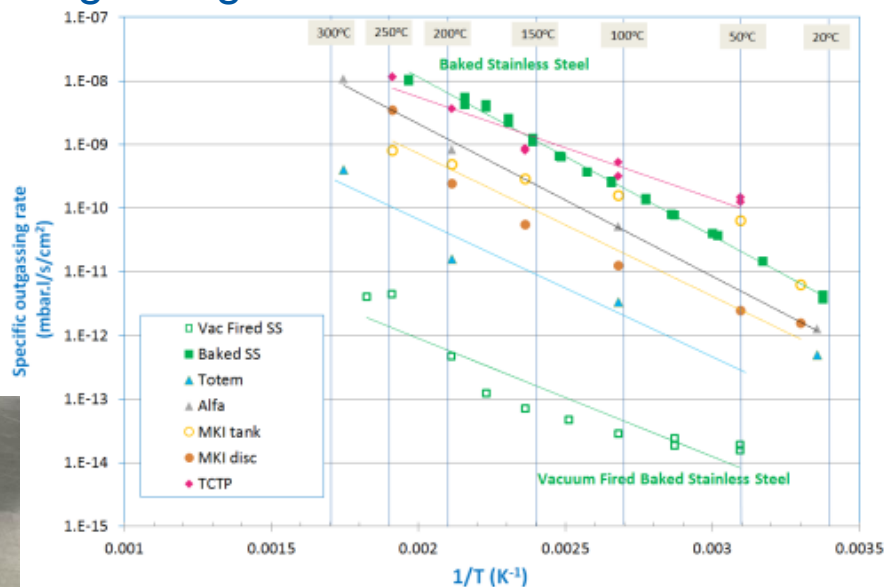


# Outgassing of ferrites

Complementary information

- Ferrites inserted in devices (XRP, TCSP, TCTP, MKI, TDI ...) can heat up during operation => **increase** of outgassing rate
- TT2-111R, CMD5005 and CMD10
- Treated at 400°C – 1000°C

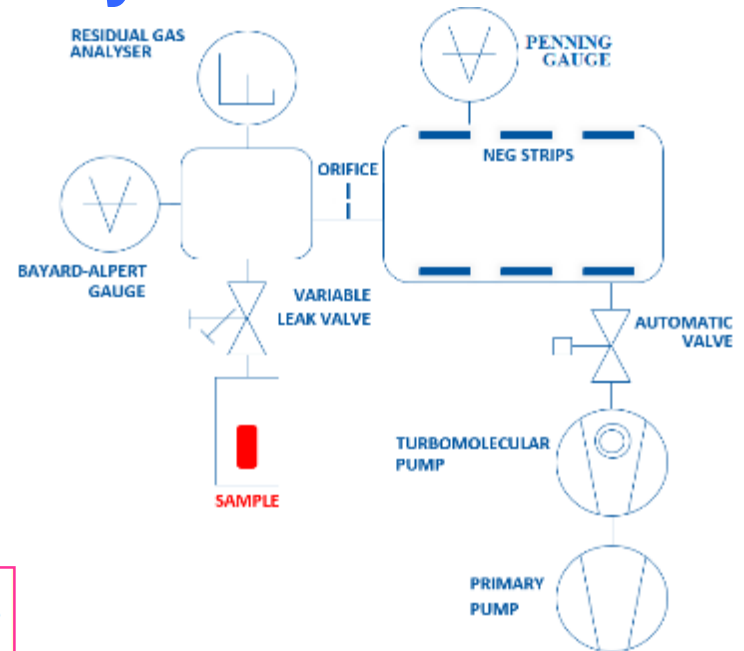
| °C                 | 50 | 100 | 150 | 200 |
|--------------------|----|-----|-----|-----|
| $\frac{q}{q_{RT}}$ | 5  | 40  | 150 | 600 |



# 3. Qualification of materials

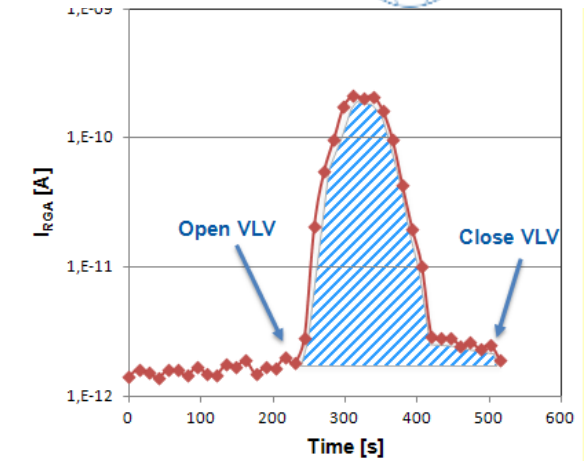
# Outgassing measurement by Accumulation

- A sample is placed in an evacuated vessel and the leak valve closed
- Gas accumulates into the sample chamber
- After some accumulation time  $t_{acc}$ , the leak valve is opened and the mass spectra measured
- The leak valve is closed again and the procedure repeated every 1 to 72 h



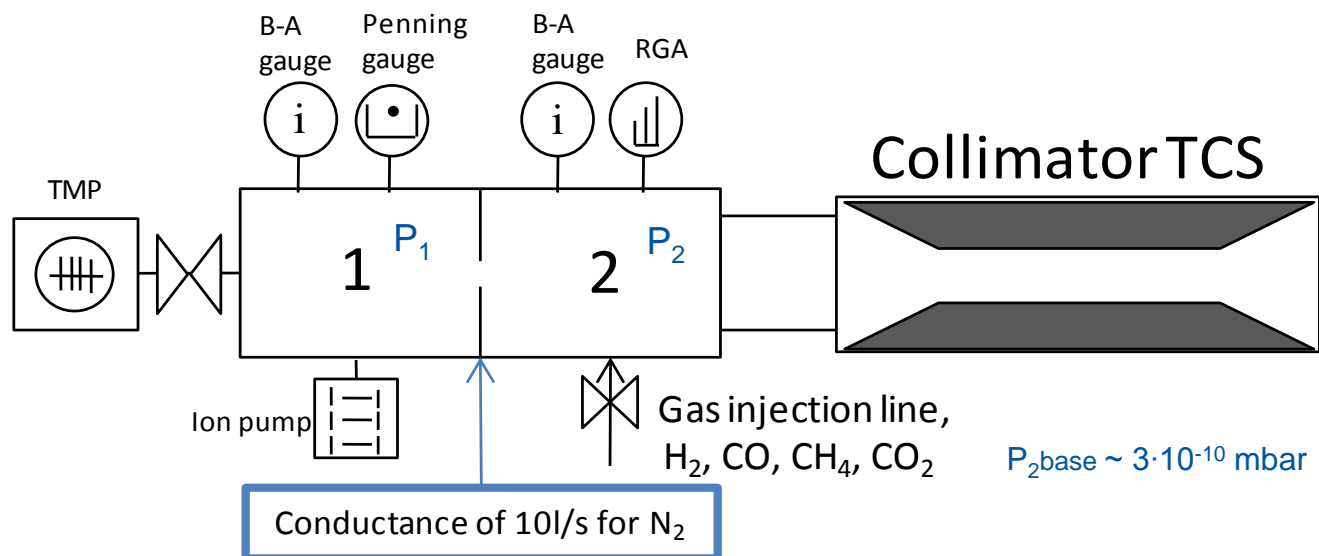
$$Q(\Delta t_{ac}) = \frac{S_i \int_0^{\Delta t} \alpha_i I_{RGA}(t) dt}{\Delta t_{ac}}$$

- With:
  - $S_i$  the pumping speed for gas, i
  - $\alpha$  the RGA calibration factor for gas, i
  - $I_{RGA}$  the current recorded during the leak valve opening
  - $\Delta t$  the RGA recording duration
  - $\Delta t_{ac}$  the accumulation time
- Sensitive measurement



Courtesy I. Wevers

# Outgassing measurement - Throughput



J. Kamiya *et al.*, *Vacuum* 85 (2011) 1178-1181

- The component is connected to a pumping system via a conductance,  $C$
- Background is determined by a blank run
- The outgassing rate is

$$Q_{N_2\text{eq}} = C (P_2 - P_1)$$

In N<sub>2</sub> equivalent no RGA is needed!

$$Q_i = S_{\text{eff}} P_{2,i} = C_i (P_{2,i} - P_{1,i})$$

$$S_{\text{eff}} = \frac{C_i (P_{2,i} - P_{1,i})}{P_{2,i}} = C_i \left(1 - \frac{P_1}{P_2}\right)$$



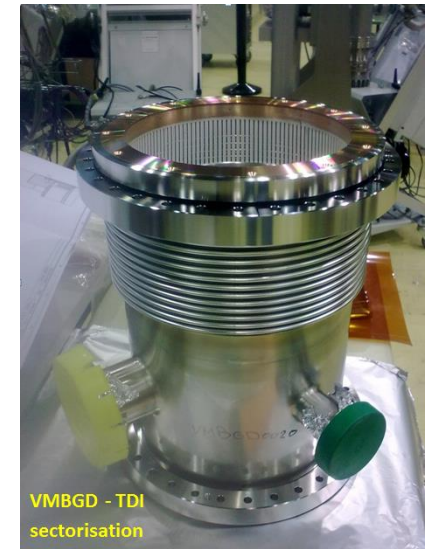
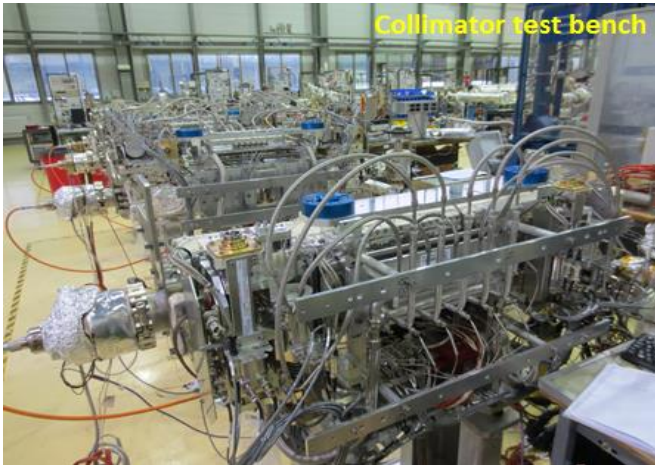
$$Q_i = C_i \alpha_i I_i \left(1 - \frac{P_1}{P_2}\right)$$

$\alpha$  the RGA calibration factor for gas,  $i$   
 $I_i$  the RGA current for gas  $i$   
 $c_i$  the conductance for gas  $i$

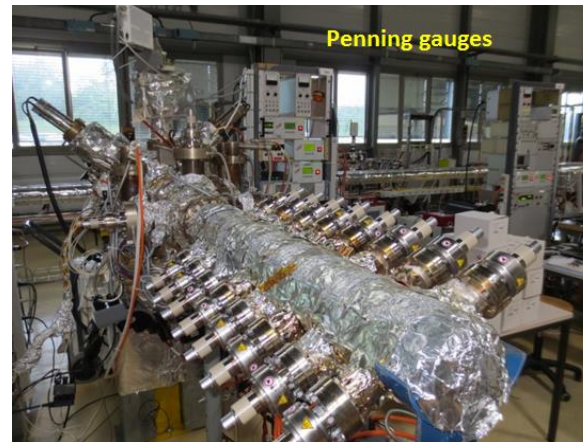
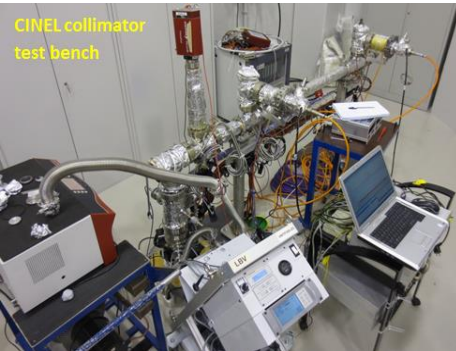
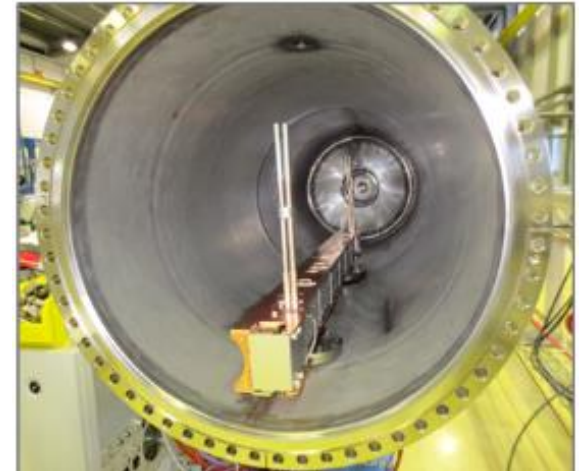
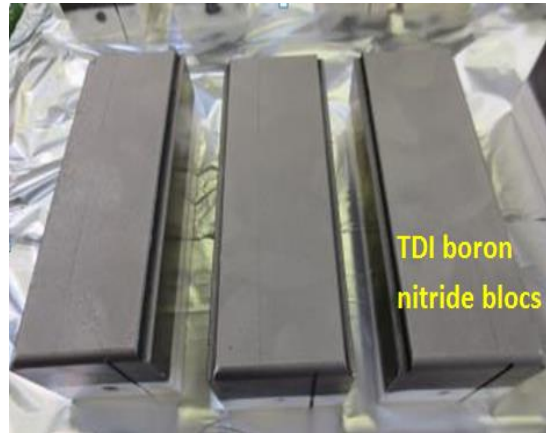
# Vacuum Acceptance Test Laboratory



# Example of tested parts

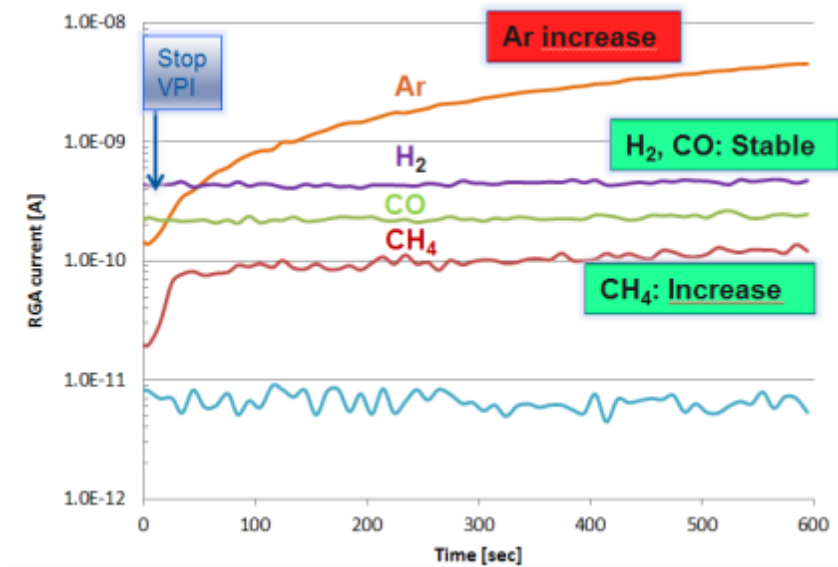


# Example of tested parts

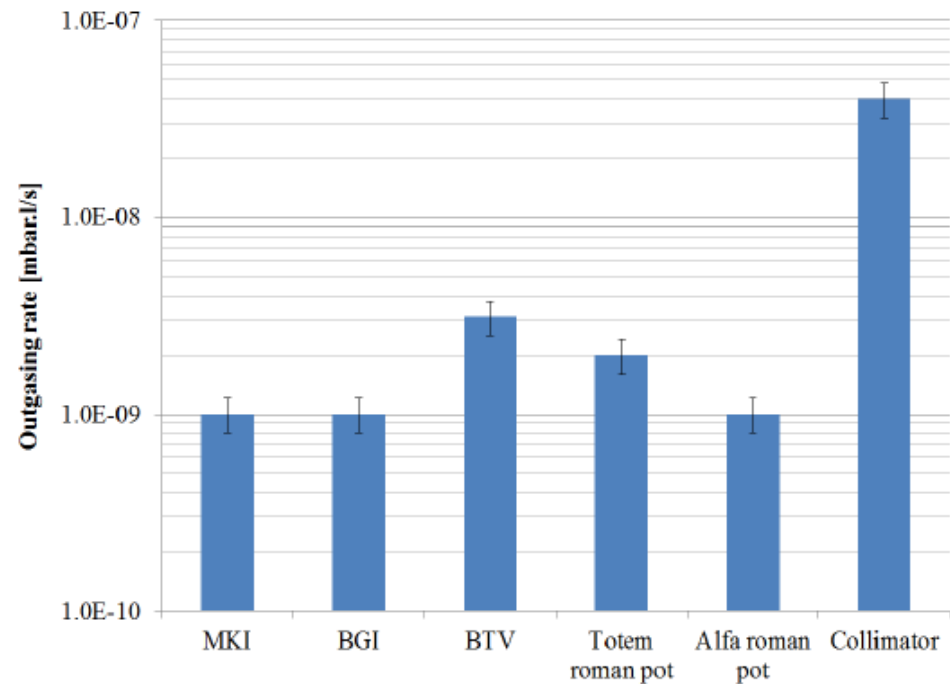


# Vacuum Acceptance Tests

- Prior LS1 installation ~1200 LSS's equipments have been baked and validated at the surface :
  - functional test
  - pump down
  - leak detection
  - residual gas composition
  - total outgassing rate



Identification of virtual leaks by accumulation test



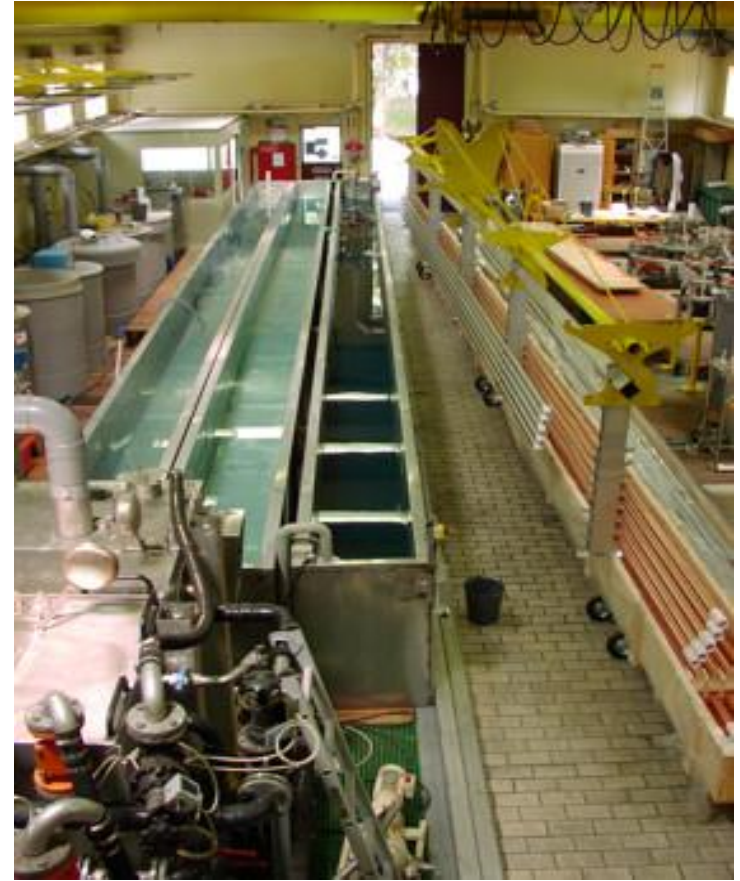
Outgassing rate of some LHC components

G. Cattenoz *et al.* , Proceeding of IPAC'14, Dresden, Germany



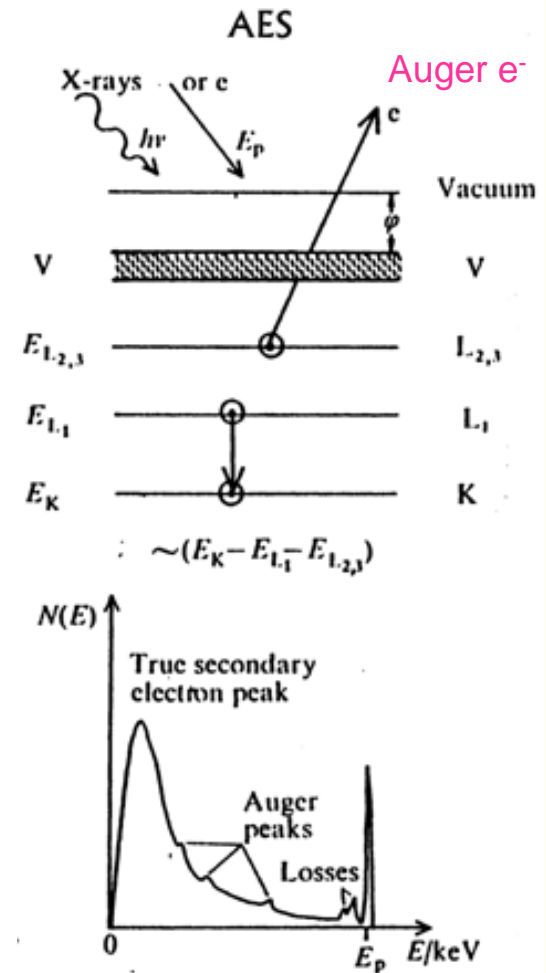
# Cleaning Methods

- **Chemical cleaning** is used to remove gross contamination such as grease, oil, finger prints.
- It can be needed to attack the surface with acids to etch the oxide layer
- Passivation can be helpful to produce a “stable” oxide layer on the surface
- Example of CERN LHC beam screens :
  - Degreasing with an alkaline detergent at 50°C in an ultrasonic bath
  - Running tap water rinse
  - Cold demineralised water rinse by immersion
  - Rinse with alcohol
  - Dry with ambient air



# Surface characterisation – AES

- Auger Electron Spectroscopy is surface sensitive (nm ?)
- Hydrogen and helium are not detected
- An incoming electron/photon eject an electron from a core level of an atom to create a hole
- This hole is filled by an electron falling from an higher energy level
- The energy released is transferred to a 3<sup>rd</sup> electron *i.e.* the Auger electron, which is ejected into the vacuum
- Measuring the electron energy of the emitted Auger electron allows to do a chemical analysis of the solid
- The e<sup>-</sup> gun source might induce surface modification
- Auger lines might overlap
- spot: 0.01x0.01 to 0.1x0.1 mm<sup>2</sup>
- Detection limit ~10<sup>14</sup> atoms/cm<sup>2</sup>



# C content after chemical cleaning and vacuum firing

- An in-situ bakeout after a vacuum firing produce a much cleaner surface than a baked surface

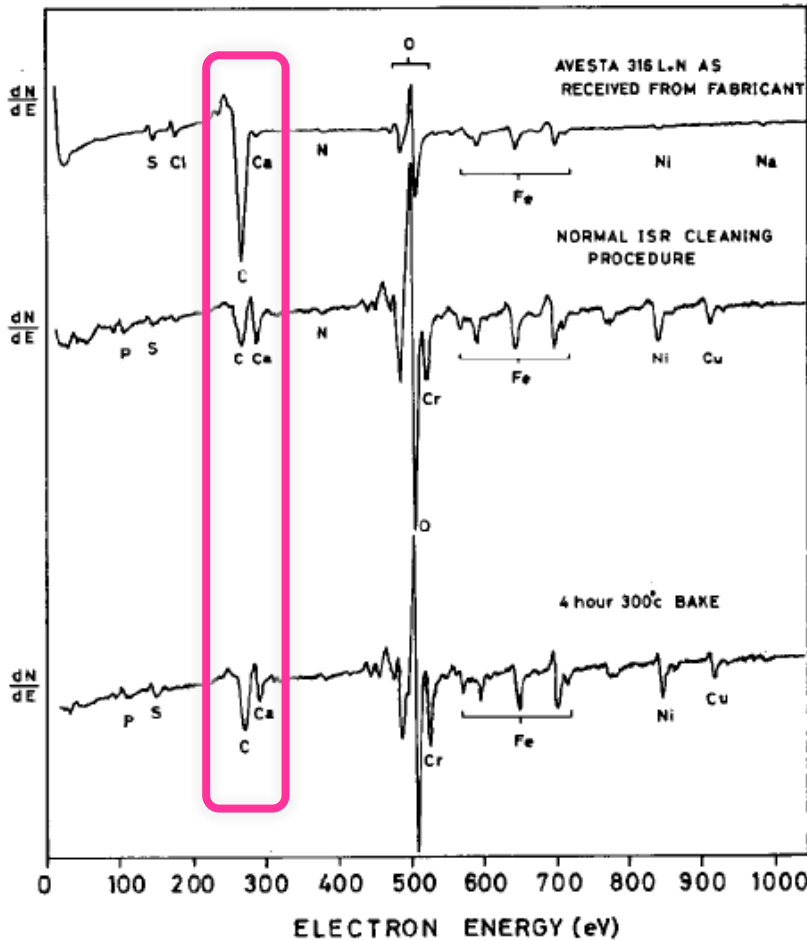


Figure 1. Auger spectra from a 316 L + N stainless steel specimen, as received (top) after solvent cleaning (centre) and after baking at 300°C for 4 h (bottom).

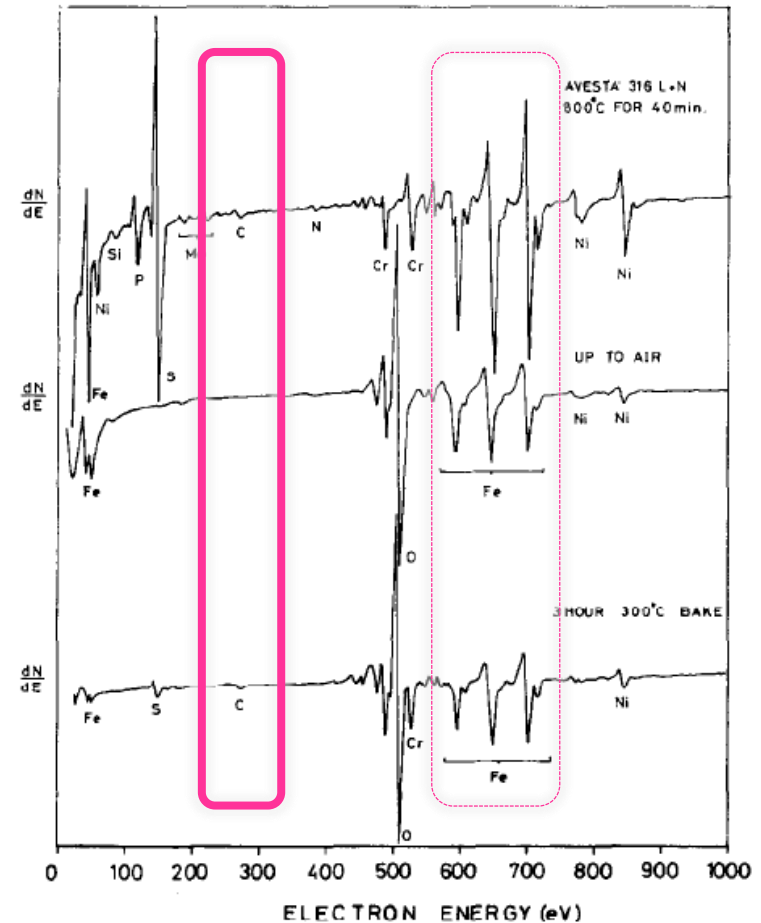


Figure 3. Auger spectra from a 316 L + N stainless steel specimen after heating to 800°C for 40 min *in vacuo* (top), after exposing to air (centre) and after a 3 h 300°C bake (bottom).

—The surface cleanliness of 316 LN stainless steel studied by SIMS and AES, A. G. Mathewson, Vacuum 24 (1974) 505

# Surface characterisation – XPS

- X-ray Photoelectron Spectroscopy is surface sensitive (1- 3 nm)
- Hydrogen and helium are not detected
- An X-ray photon ejects an electron i.e. a photoelectron from a core level of an atom to create a hole
- The energy of the ejected photoelectron is characteristic of the emitting species
- XPS is more sensitive than AES and provides rich information on the chemical state of the emitter.

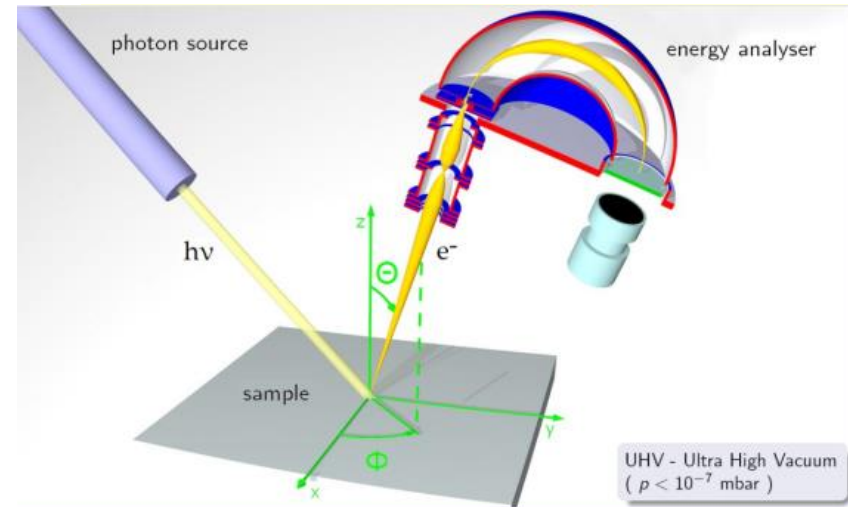
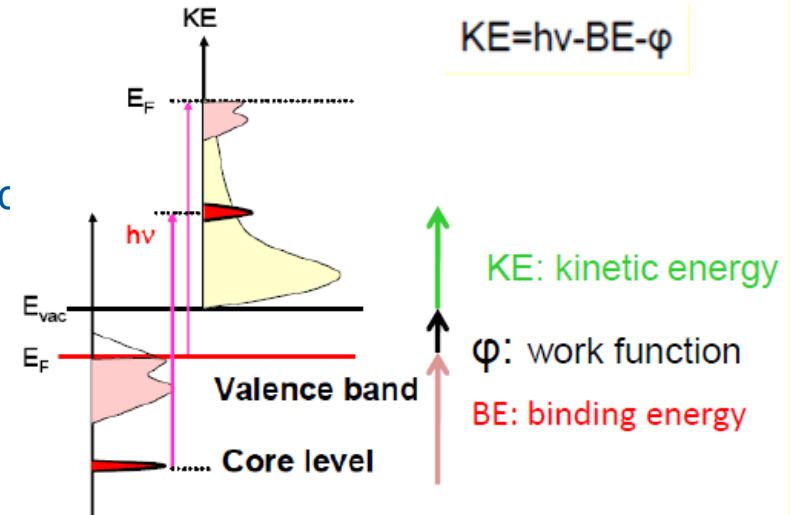
Detection limit  $\sim 10^{14}$  atoms/cm<sup>2</sup>

## X-Ray Sources:

- Al:  $E_{exc} = 1486.74$  eV;  $P_{max} = 400$  W
- Ag:  $E_{exc} = 2984.3$  eV;  $P_{max} = 600$  W
- spot size on the sample: 1x3.5 mm<sup>2</sup>

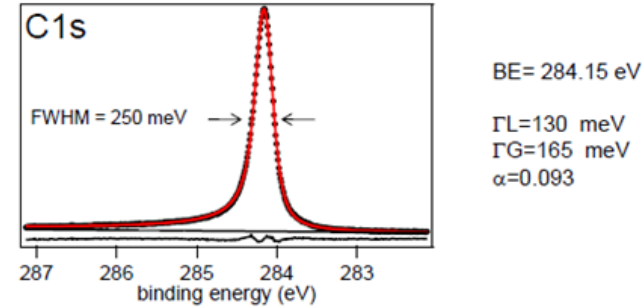
## Synchrotron radiation based X-Ray Sources:

- Monochromatic photon energy
- From IR to hard X-rays
- High flux

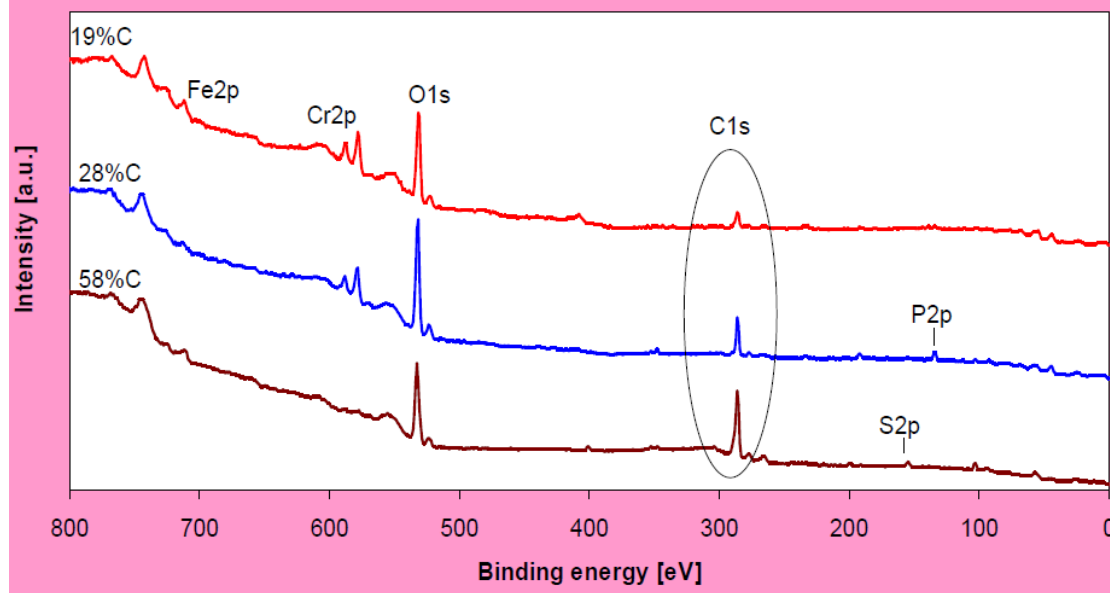


# Cleanliness evaluation

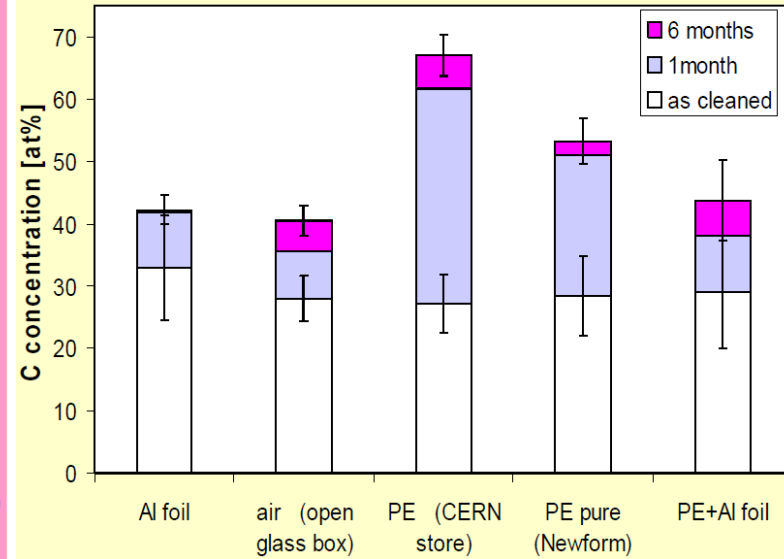
- 40% atoms of C on stainless steel is an upper acceptable limit
- Thickness of the layer ~ 0.5 nm
- Cleanliness is monitored by integrating the C1s peak



Stainless steel 316LN



Storage of cleaned OFE copper



The assessment of metal surface cleanliness by XPS, C. Scheueurlein and M. Taborelli, Appl. Surf. Sci 252 (2006) 4279

# Lecture 2 summary

- The pressure in a vacuum vessel is determined by the outgassing of the **surface**
- The **sojourn time** of a molecule on a surface is a strong function of its binding energy and the temperature of the surface
- Unbaked materials are dominated by **water** outgassing. The desorption rate is  $1/t$
- Baked material are dominated by **hydrogen** outgassing. The desorption rate is  $1/\sqrt{t}$
- Several **methods** are available to decrease the outgassing rate of the materials (vacuum firing, chemical cleaning etc.)
- Components must be **characterised in the laboratory** with appropriate tools to guarantee a good performance in a machine

# Some References

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**Thank you for your attention !!!**





