# Vacuum Systems
# Lecture 2

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# 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 $\rightarrow$ P

Q $\rightarrow$ mbar.l/s

S $\rightarrow$ l/s

- S ranges from 10 to 20 000 l/s

- Q ranges from $10^{-14}$ mbar.l/s for metalic 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

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

$$R = \mathcal{N}\,k$$

- It has the unit of [Pa.m³/s] which is equivalent to a number of molecules/s (or Watt)

| PV | G |
| --- | --- |
| 1 mbar.l | 2.46 10$^{19}$ molecules |
| 1 Torr.l | 3.27 10$^{19}$ molecules |

at 300 K

- Langmuir: 1 L = 10$^{-6}$ Torr for 1 s.

- 1 monolayer ~ 10$^{15}$ molecules/cm$^2$



1 Torr.l injected inside a 10m long, 10 cm diameter chamber gives 1 monolayer on the surface!
=> the LHC experimental beam pipe would be saturated and unusable

# 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 $cm^3$ 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 $cm^3$

# Long term pump down of a vessel

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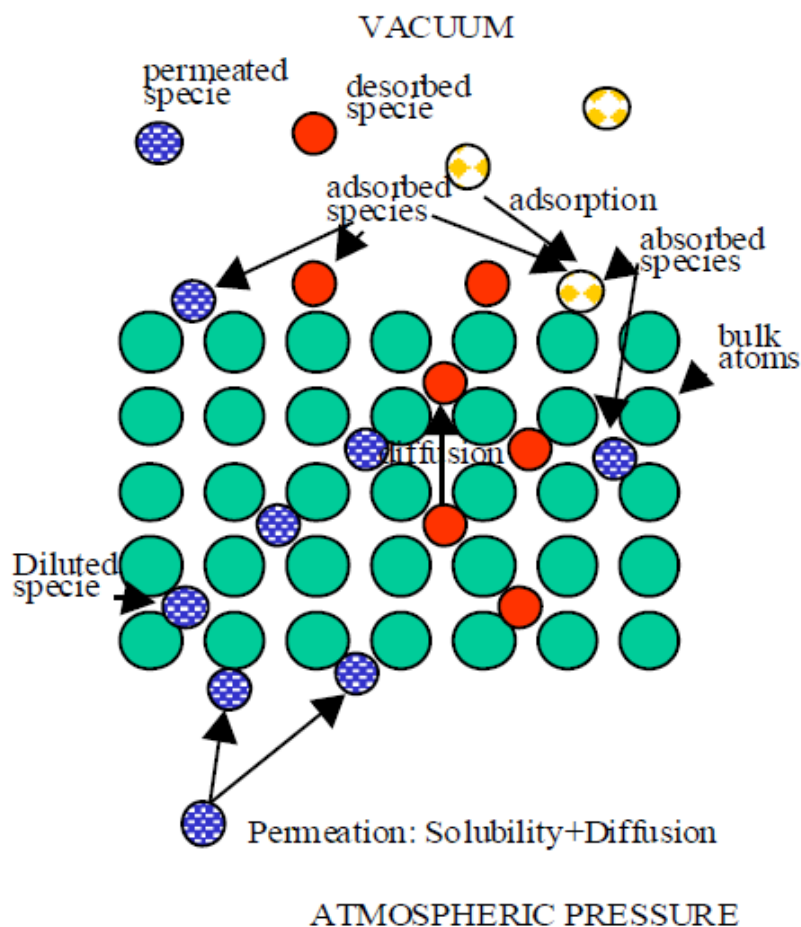
- 4 regimes

1) Volume pumping

2) Surface desorption

3) Diffusion from the bulk

4) Permeation trough the wall (solubility+diffusion)

Volume ~ $e^{-a\,t}$

Surface ~ $1/t$

Bulk ~ $1/\sqrt{t}$

100 days
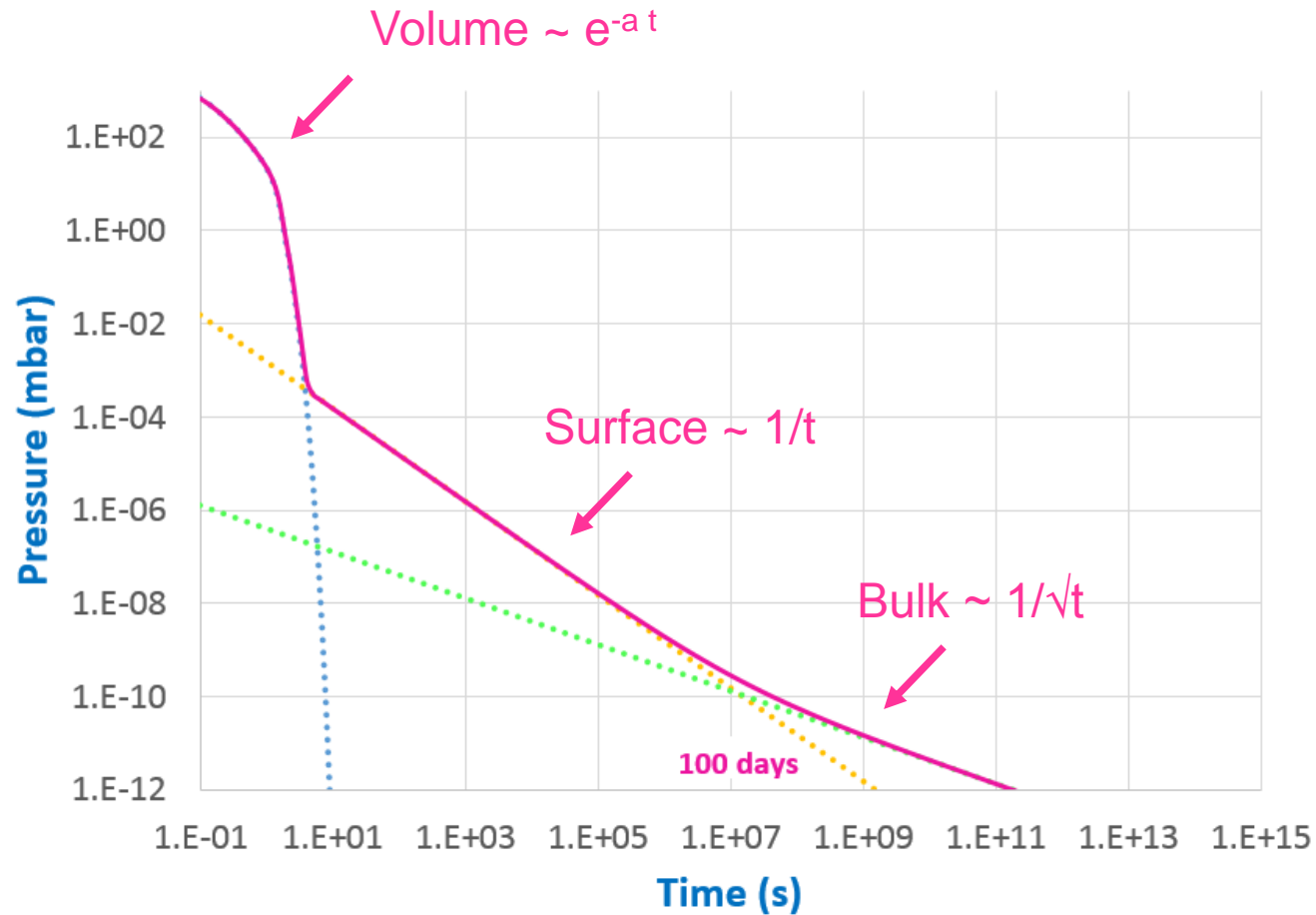
# A schematic description

The release of these molecules into the vacuum is named OUTGASSING

• Desorbed molecules originates from:

  • Adsorption

  • Absorption

  • Diffusion

  • Permeation

VACUUM

permeated specie
desorbed specie
adsorbed species
adsorption
absorbed species
bulk atoms
diffusion
Diluted specie
Permeation: Solubility+Diffusion

ATMOSPHERIC PRESSURE

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.

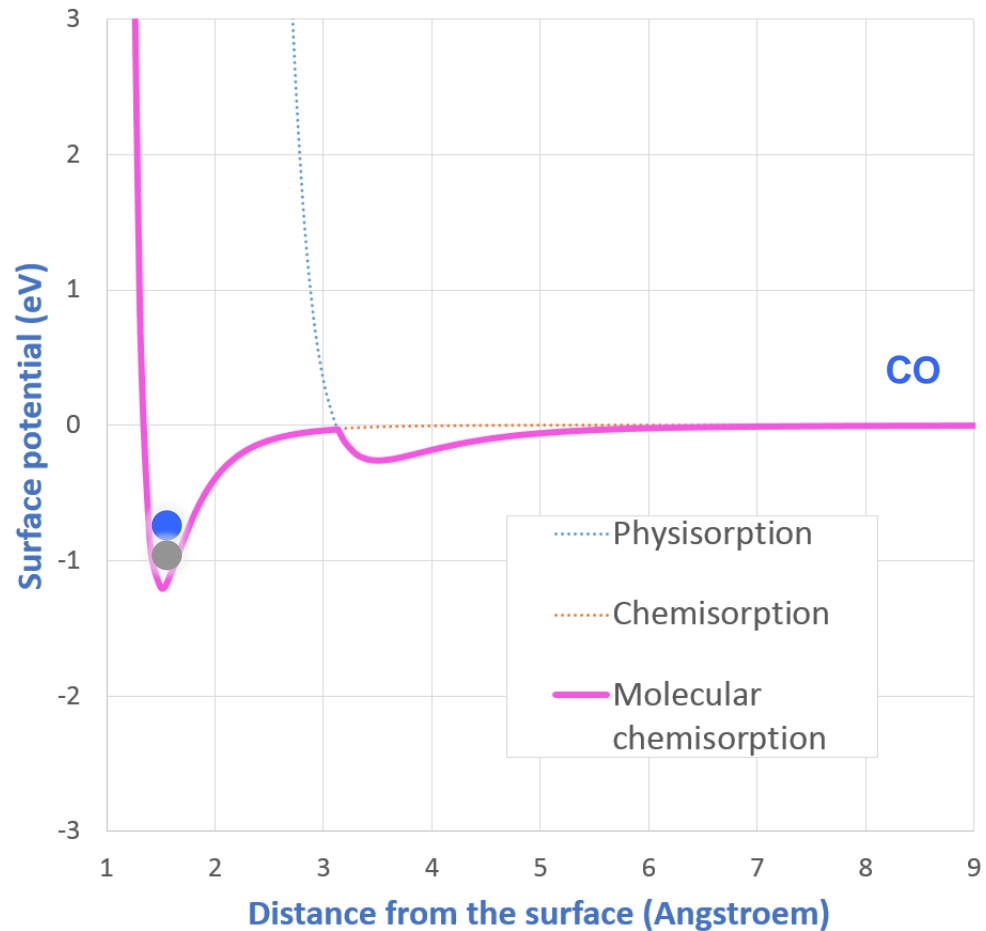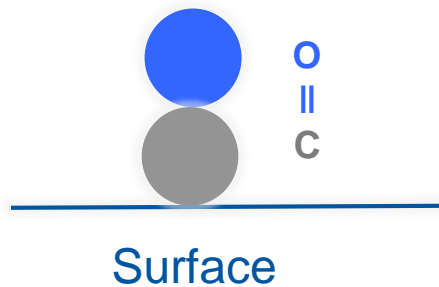$$E = E_m \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right]$$

# Physisorption

• A molecule, say $H_2$, approaches towards the surface
• The molecule is physisorbed onto the surface at ~ 3 Å with a "binding" (adsorption/desorption) energy of ~ 10 meV (twice the H heat of vaporization)
• Due to the nature of the physisorption process, several monolayers can be physisorbed in this state
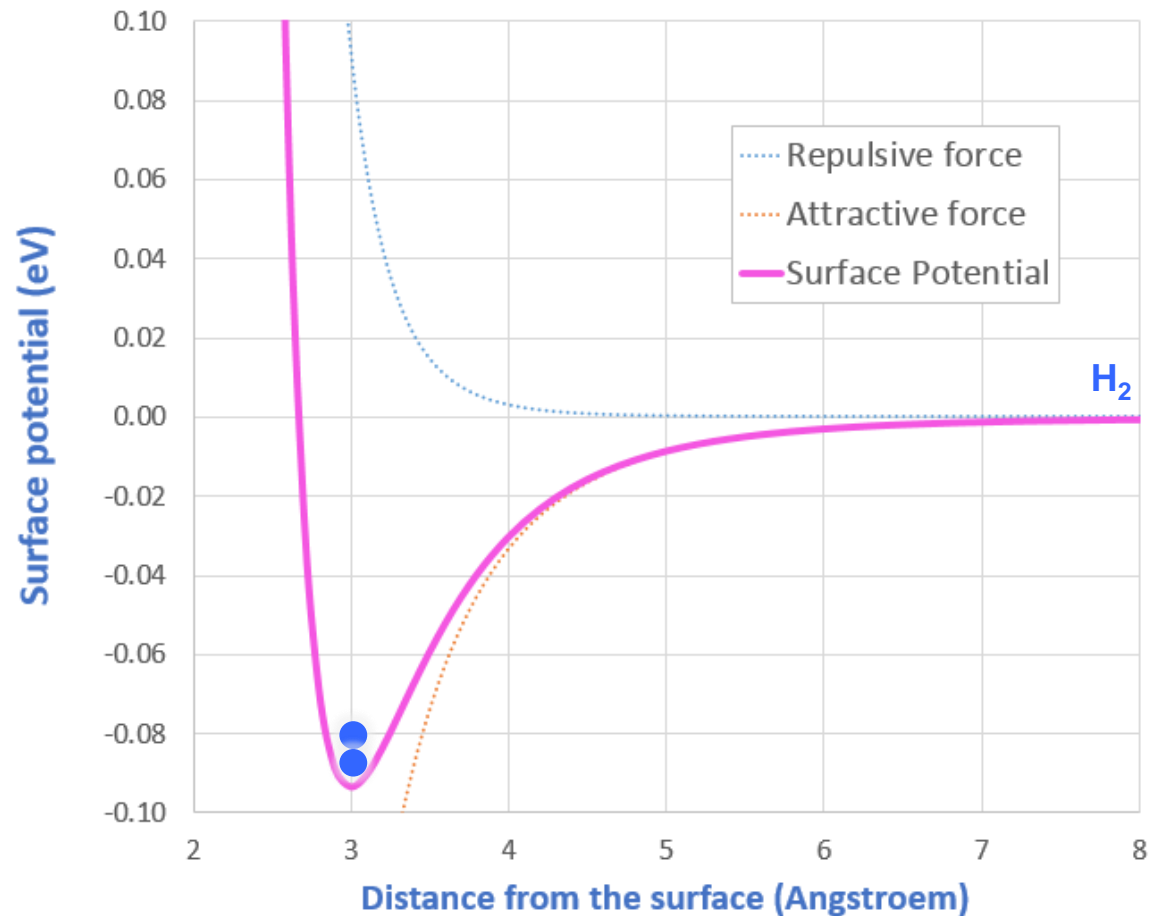
# Non-Dissociative Chemisorption

- Non-dissociative chemisorption: case of CO onto metals
- The molecule is chemisorbed onto the surface at ~ 1.5 Å with a "binding" energy of ~ 6 eV
- A maximum of one monolayer can be adsorbed on the surface
- The carbon atom is oriented towards the surface



O
‖
C

**Surface**

CO

Distance from the surface (Angstroem)

Surface potential (eV)

......... Physisorption

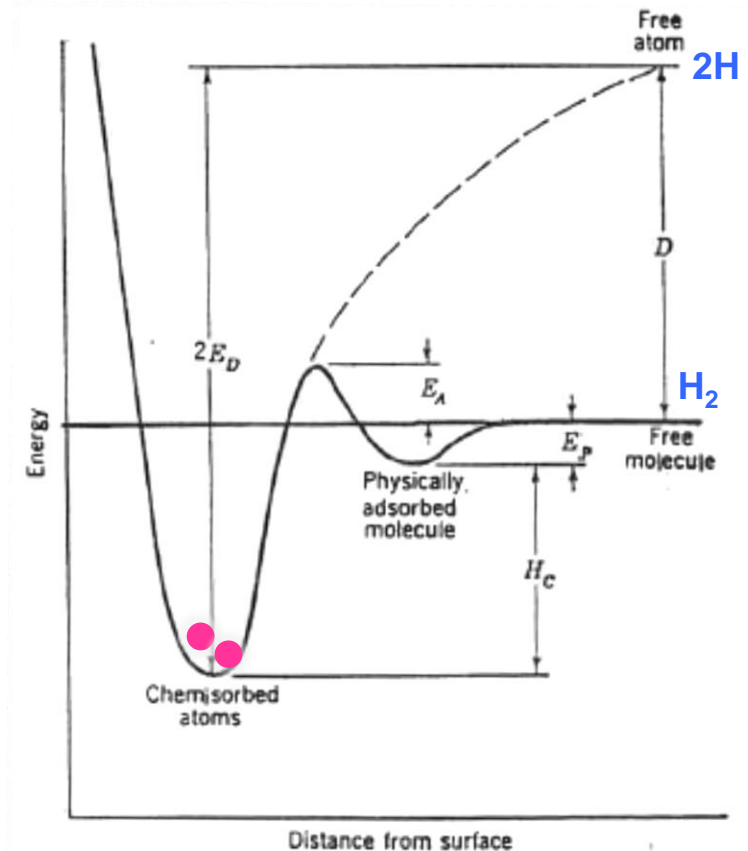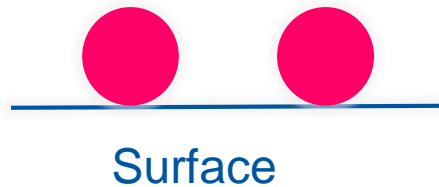......... Chemisorption

—— Molecular chemisorption

# 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 dissociated 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

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

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

Surface

# 1st 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:

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

time constant: $\tau = \dfrac{1}{\nu_1} e^{E_D/kT} = \tau_0 \, e^{E_D/kT}$

# 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 $T = T_o + \beta t$, the desorption rate is <u>maximum</u> at temperature Tp for:

    • For first order:
$$\frac{E}{R\,T_p{}^2} = \frac{\nu_1}{\beta}\,e^{-E/R\,T_p}$$

    • 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 β and Tp as inputs give the activation energy

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

Hiden TPD/TDS station
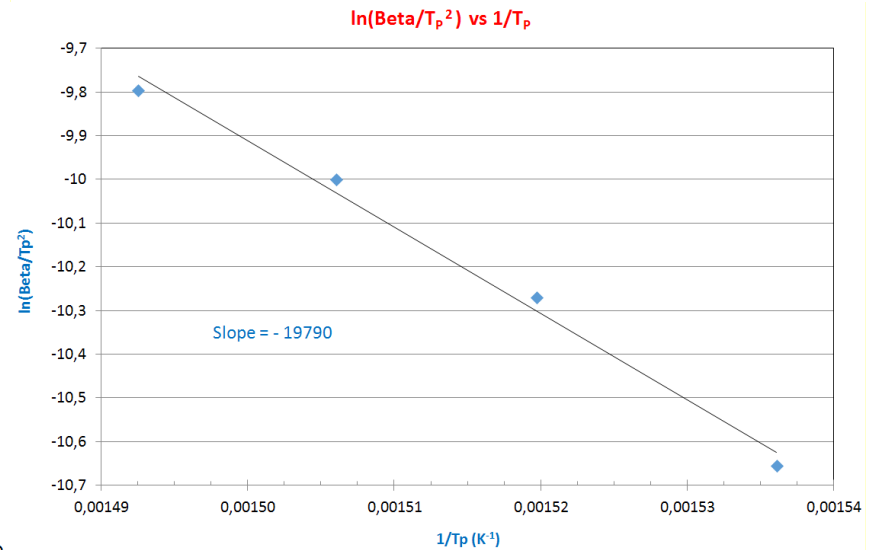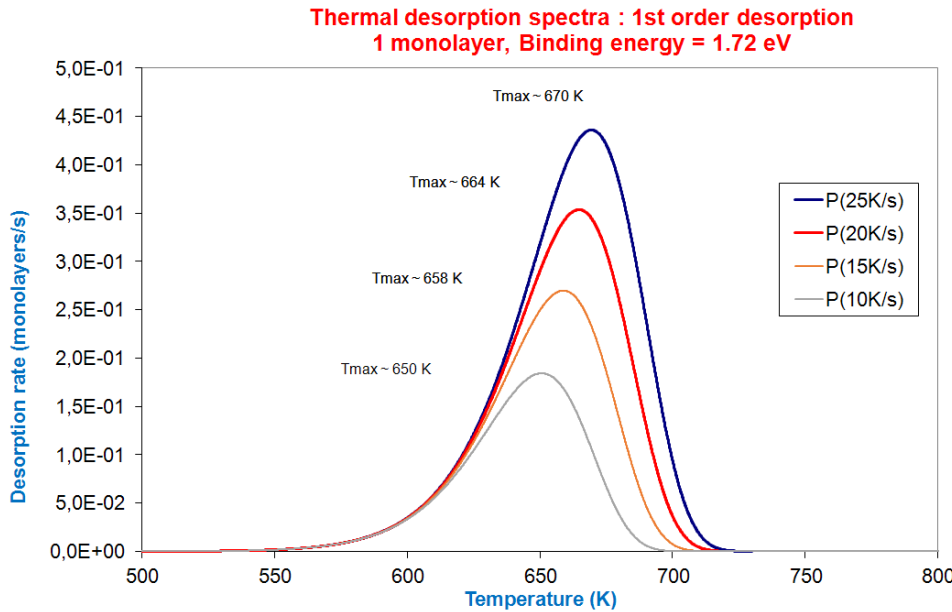
# Evaluation of the activation energy

- 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 the activation energy, E



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

Tmax ~ 670 K
Tmax ~ 664 K
Tmax ~ 658 K
Tmax ~ 650 K

P(25K/s)
P(20K/s)
P(15K/s)
P(10K/s)

Desorption rate (monolayers/s)
Temperature (K)

**ln(Beta/Tp²) vs 1/Tp**

Slope = - 19790

ln(Beta/Tp²)
1/Tp (K⁻¹)

# 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, Ed, and the surface temperature, T:

$$\tau = \tau_0 \, e^{\left(\frac{E_D}{k\,T}\right)}$$

• With $\tau_0$ the oscillation period of the molecules on the surface ~ $10^{-13}$ s.

• The inverse of the sojourn time is the desorption probability of a molecule

• For some bounding values the residence time of a molecules is of the order of a week

• Increasing the temperature decrease the residence time

• Decreasing the temperature, increase the residence time

• Strongly bound molecules have long residence time

# 2. Outgassing

# Units of outgassing rate

- The (intrinsic) outgassing rate is the quantity of gas leaving the surface per unit time per unit of exposed geometric surface: $Pa \ m^3 \ s^{-1} \ m^{-2}$ (or $Pa \ m \ s^{-1}$ or $W \ m^{-2}$ )

| | $Pa \ m \ s^{-1}$ | $Torr \ l \ s^{-1} \ cm^{-2}$ | $mbar \ l \ s^{-1} \ cm^{-2}$ | $molecules \ s^{-1} \ cm^{-2}$ |
|---|---|---|---|---|
| $1 \ Pa \ m \ s^{-1}$ | 1 | $7.5 \times 10^{-4}$ | $10^{-3}$ | $2.46 \times 10^{16}$ |
| $1 \ Torr \ l \ s^{-1} \ cm^{-2}$ | $1.33 \times 10^{3}$ | 1 | 1.33 | $3.27 \times 10^{19}$ |
| $1 \ mbar \ l \ s^{-1} \ cm^{-2}$ | $10^{3}$ | 0.75 | 1 | $2.46 \times 10^{19}$ |

- Examples:
  - $3 \ 10^{-10}$ Torr $l/(s \ cm^2)$ is converted to $1.33 \ 10^3 \ x \ 3 \ 10^{-10} = 4 \ 10^{-7} \ Pa \ m \ s^{-1}$
  - $5 \ 10^{-13}$ Torr $l \ s^{-1} \ cm^{-2}$ is converted to $1.33 \ x \ 5 \ 10^{-13} = 6.7 \ 10^{-13} \ mbar \ l \ s^{-1} \ cm^{-2}$
  - $5 \ 10^{-15} \ mbar \ l \ s^{-1} \ cm^{-2}$ is converted to $10^3 \ x \ 5 \ 10^{-15} = 5 \ 10^{-12} \ Pa \ m \ s^{-1}$
  - $5 \ 10^{-15} \ mbar \ l \ s^{-1} \ cm^{-2}$ is converted to 123 000 molecules / $(s \ cm^2)$

P. Redhead, Recommended practices for measuring and reporting outgassing data, J. Vac. Sci. Technol. A 20(5), Sep/Oct 2002, 1667-1675
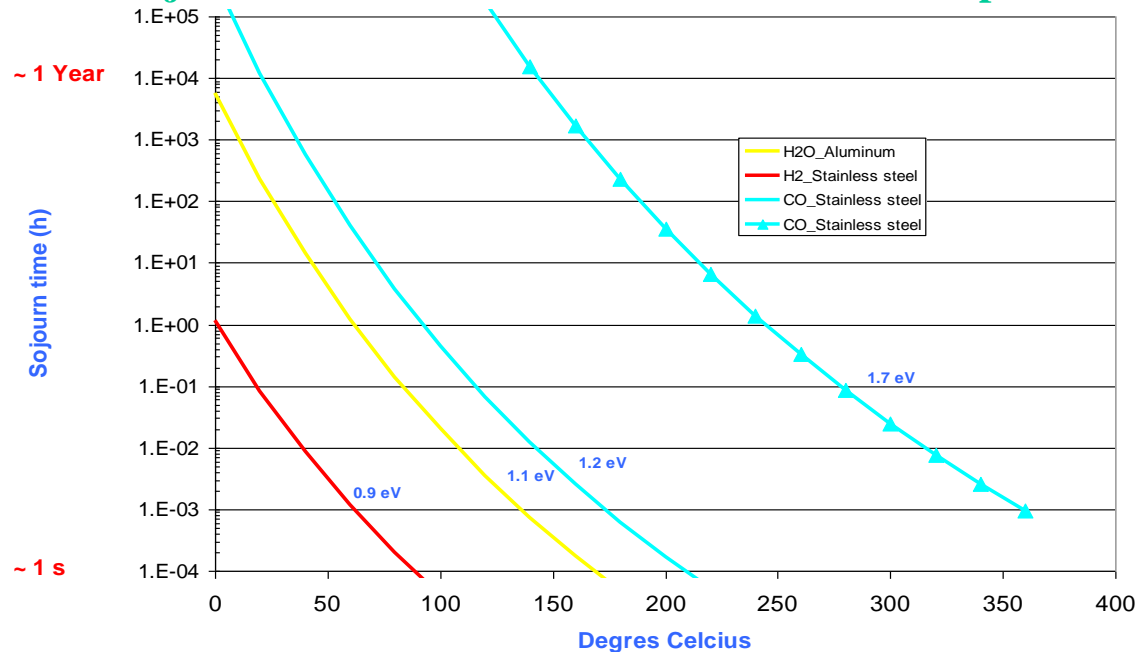
# 2.1 Unbaked system

# H₂O - 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:

$$Fe_xO_y + 2H \rightarrow Fe + H_2O$$
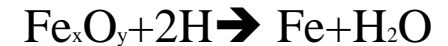
### Sojourn time of a molecule as a function of temperature

# Unbaked system: water outgassing

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

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

- In practical units

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

- 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 Tempkin 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)

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



$q = q_0(1-\alpha\theta)$
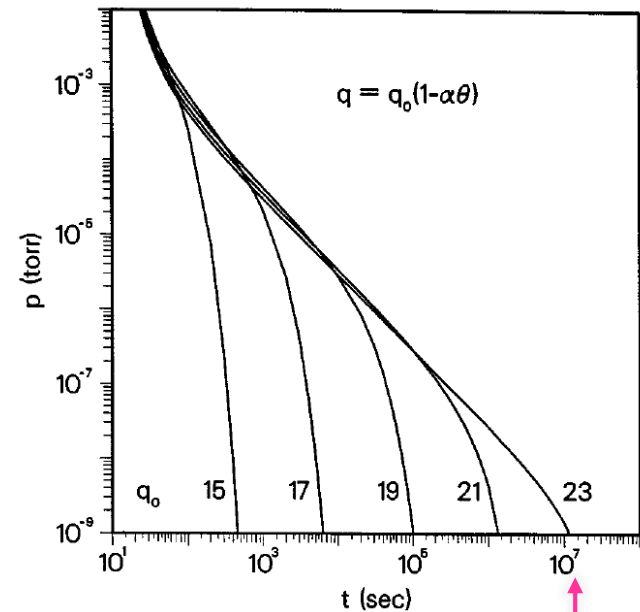
100 days

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:

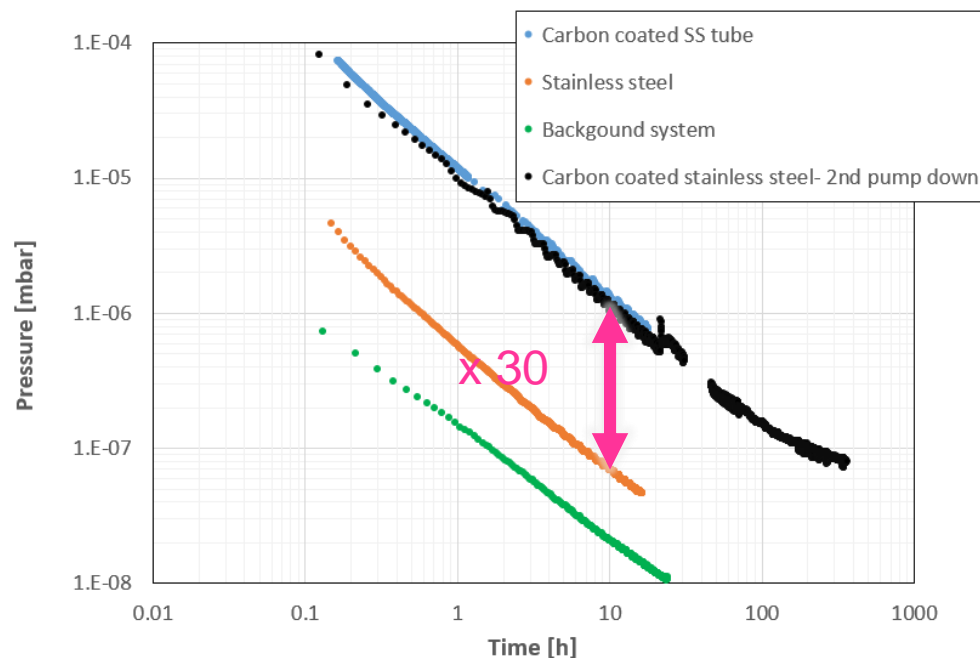  Mass spectrum is water dominated
  ~ x 30 unbaked stainless steel
  2nd pump down very similar to 1st one

  After 10h pumping:
  Stainless steel = $2 \cdot 10^{-10}$ mbar.l/s/cm²
  a-C coating = $6 \cdot 10^{-9}$ mbar.l/s/cm²
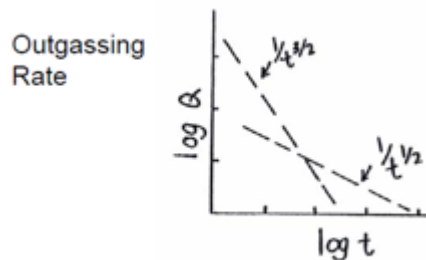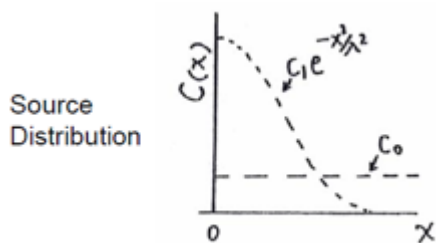


Courtesy I. Wevers

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 & venting

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

• The exponent, a, varies with the quantity of water absorbed:
  • ambient air (8 ML): 1.2
  • large water exposure (17 ML): 1.3
  • low water exposure (0.02 ML): 0.65

• The observation can be modeled by the superposition of:
  • a water surface concentration => a ~ 3/2
  • a water bulk concentration => a ~ 1/2

TABLE I. $H_2O$ absorption/desorption data for various venting conditions of the stainless-steel (304) test chamber.[a]

| Trial | $H_2O$ absorbed (ML) | $H_2O$ exposed (ML) | $Q = Q_{10}/t^a$ | | $Q = q_1/t^{1/2} + q_0/t^{1/2}$ | | Venting gases |
|---|---|---|---|---|---|---|---|
| | | | $Q_{10}$ ($\times 10^4$) | $\alpha$ | $q_1$ ($\times 10^3$) | $q_0$ ($\times 10^8$) | |
| 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 |
| T021 | 9.2 | 400 | 3.12 | 1.18 | 3.15 | 5.86 | mixture of |
| T022 | 7.2 | 200 | 2.36 | 1.19 | 2.11 | 6.11 | $H_2O$ and $N_2$ |
| 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 | $N_2$ gas (> 10 ppm $H_2O$) |
| T040 | 0.017 | | 5.07 $\times 10^{-4}$ | 0.65 | 8.91 $\times 10^{-2}$ | 1.05 | Highly dry $N_2$ gas |

[a]Note: The unit for the outgassing rate ($Q$) is (Torr $\ell$/cm$^2$ s) and the unit of time ($t$) is (s).



Source Distribution



Outgassing Rate

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

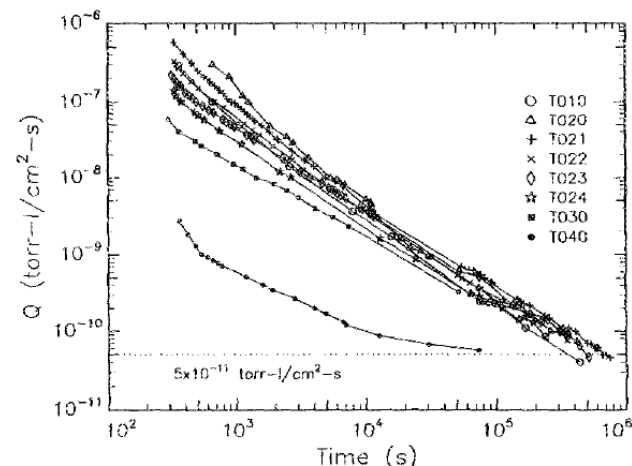Venting with dry N2 reduces pump down times



FIG. 2. Outgassing measurements for different $H_2O$ 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 $H_2O$.

- For metallic surfaces, unbaked after 10h of pumping (Torr.l.s$^{-1}$.cm$^{-2}$)

| Gas | Al | Cu | St. Steel | Be |
|---|---|---|---|---|
| $H_2$ | $7\ 10^{-12}$ | $1.4\ 10^{-11}$ | $7\ 10^{-12}$ | $1.4\ 10^{-11}$ |
| $CH_4$ | $5\ 10^{-13}$ | $5\ 10^{-13}$ | $5\ 10^{-13}$ | $1\ 10^{-12}$ |
| $H_2O$ | $3\ 10^{-10}$ | $3\ 10^{-10}$ | $3\ 10^{-10}$ | $6\ 10^{-10}$ |
| CO | $5\ 10^{-12}$ | $1\ 10^{-12}$ | $5\ 10^{-12}$ | $1\ 10^{-11}$ |
| $CO_2$ | $5\ 10^{-13}$ | $2.5\ 10^{-13}$ | $5\ 10^{-13}$ | $1\ 10^{-12}$ |

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



LHC cold vacuum chamber

5-20 K beam screen inside cold bore; pumping slots
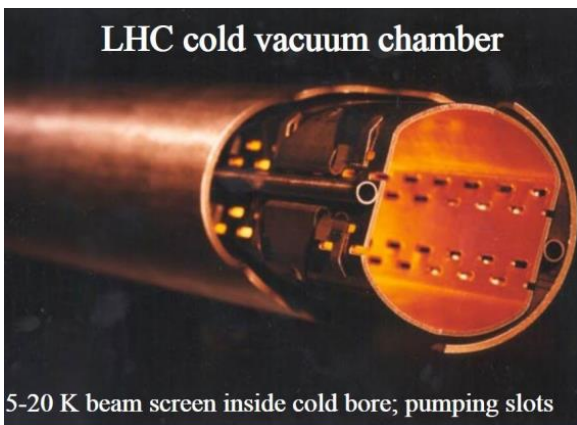


LEP dipole chamber
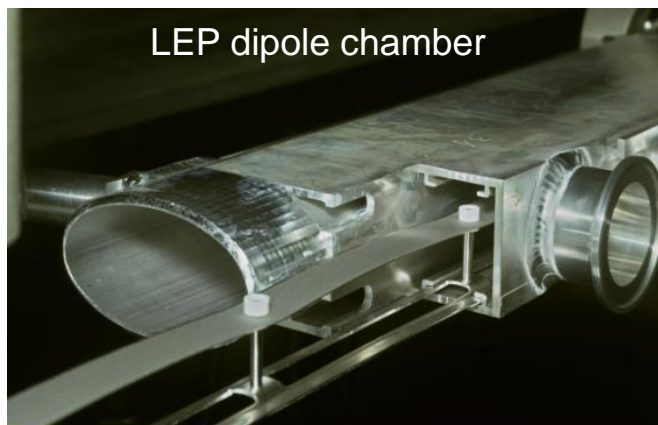


ISR intersection "bicone" chamber
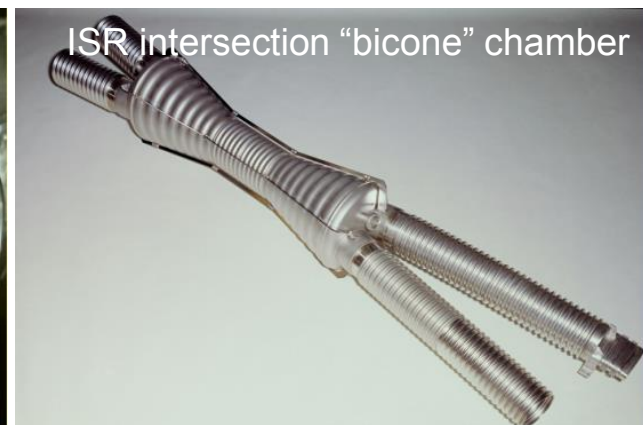
# 2.2 Baked system

# Sojourn time at high temperature

- The sojourn time <span style="color:magenta">decrease strongly</span> with increasing temperature

$$\tau = \frac{e^{\frac{E}{kT}}}{\nu_0}$$

- Heating the material allows a degassing of then molecules having binding energies <span style="color:magenta">< 2 eV</span>

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

- Molecules with larger binding energies than 1.7-2 eV will not be depleted by a bake-out
  → However, those molecules will be available for <span style="color:magenta">subsequent</span> desorption by e.g. ion bombardment

# In Situ Bake Out

• A bake-out above 150°C increase the desorption rate of $H_2O$ and reduce the $H_2O$ sojourn time in such a way that $H_2$ becomes the dominant gas
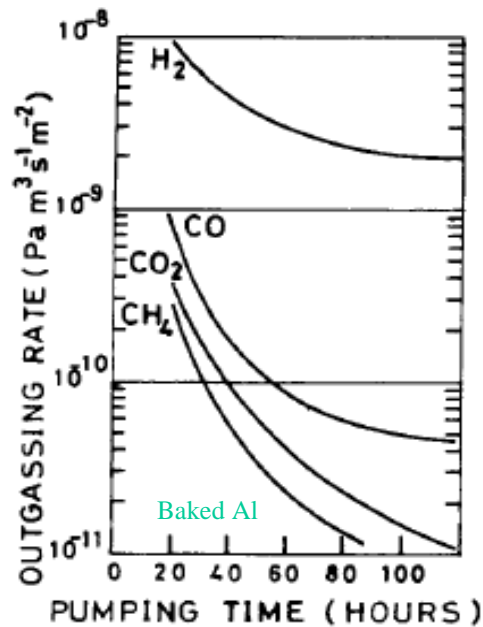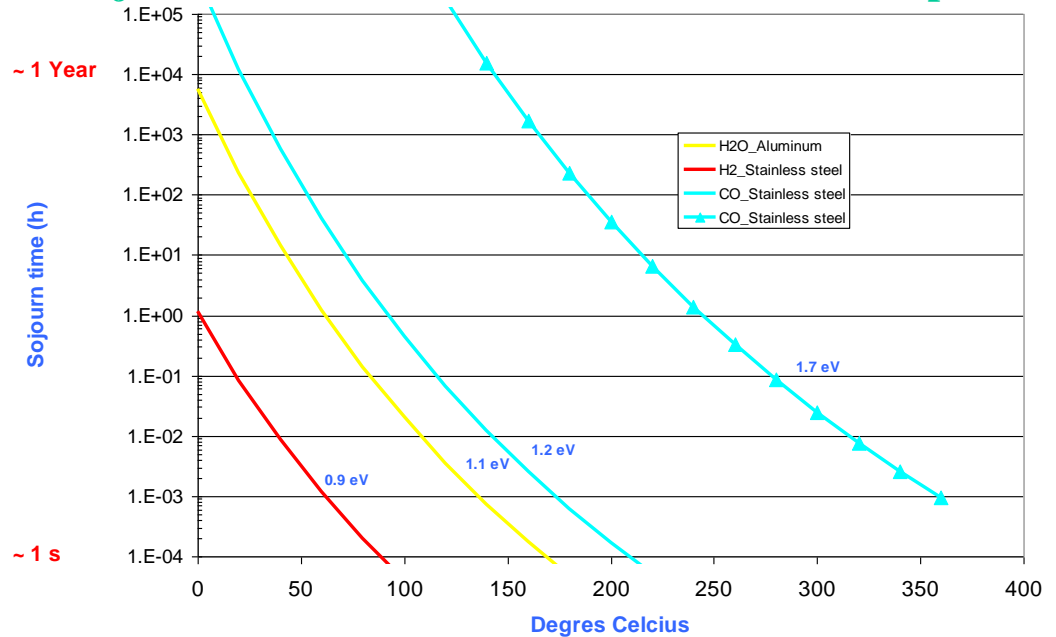


A.G. Mathewson *et al*.
J.Vac.Sci. 7(1), Jan/Fev 1989, 77-82

### Sojourn time of a molecule as a function of temperature

$$\tau = \frac{e^{\frac{E}{kT}}}{\nu_0}$$

# Material for bakeout


Collars


thermocouples


bakeout jackets
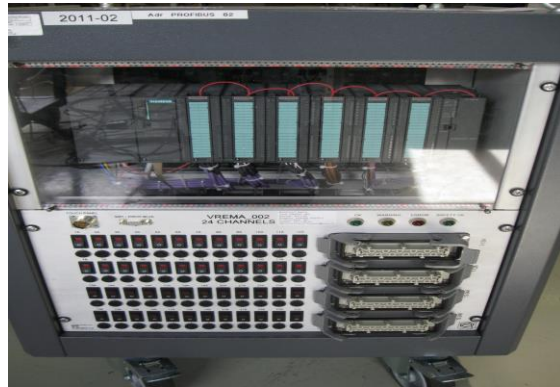

racks


heating tape


Storage area

# Typical design values of outgassing rates

- The outgassing rate of baked surfaces is dominated by $H_2$

- Metal, baked (24 h at 150ºC for Cu and Al, 300ºC for SS) after 50h of pumping (Torr.l.s$^{-1}$.cm$^{-2}$)

| Gas | Al | Cu | St. Steel | Be |
|-----|-----|-----|-----------|-----|
| $H_2$ | $5\ 10^{-13}$ | $1\ 10^{-12}$ | $5\ 10^{-13}$ | $1\ 10^{-12}$ |
| $CH_4$ | $5\ 10^{-15}$ | $5\ 10^{-15}$ | $5\ 10^{-15}$ | $1\ 10^{-14}$ |
| $H_2O$ | $1\ 10^{-14}$ | $<1\ 10^{-15}$ | $1\ 10^{-14}$ | $2\ 10^{-14}$ |
| CO | $1\ 10^{-14}$ | $1\ 10^{-14}$ | $1\ 10^{-14}$ | $2\ 10^{-14}$ |
| $CO_2$ | $1\ 10^{-14}$ | $5\ 10^{-15}$ | $1\ 10^{-14}$ | $2\ 10^{-14}$ |

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

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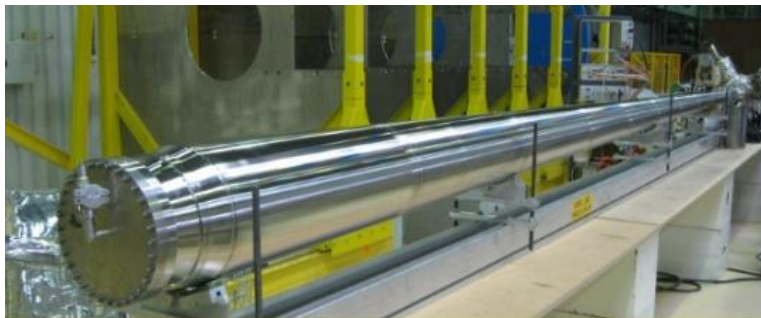


**CMS End cap chamber**



**Copper tubes**

# Amount of gas removed after a bake-out

- After a laboratory bake-out of a stainless steel chamber at 200⁰C for 20 h

| Gas species | $H_2$ | $CH_4$ | $H_2O$ | CO | $CO_2$ | Total |
|---|---|---|---|---|---|---|
| Molecule.cm$^{-2}$ x $10^{15}$ | 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

# Model of diffusion

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

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

- In 304L, 316L stainless steel:

| TºC | 20 | 900 |
|---|---|---|
| D [cm²/s] | $1.4 \cdot 10^{-12}$ | $2.3 \cdot 10^{-5}$ |

$D_o = 5.8 \cdot 10^{-3}$ cm²/s
$E_{diff} = 0.558$ eV

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

**Stainless steel diffusion coefficient**
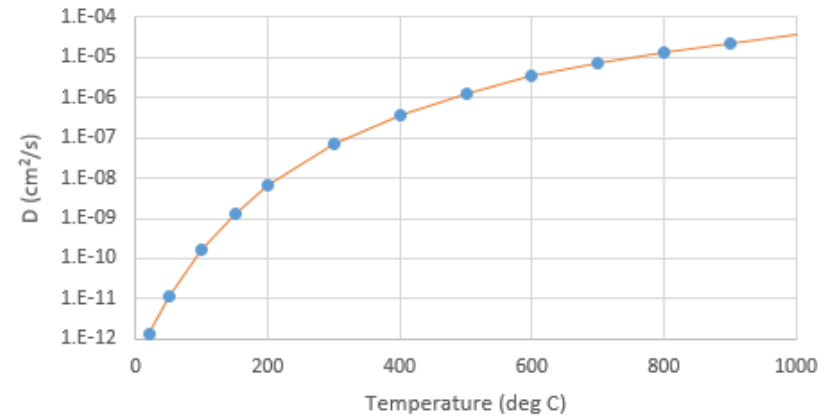


- The hydrogen diffusion in materials is governed by Fick Laws:



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

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

- 2nd 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
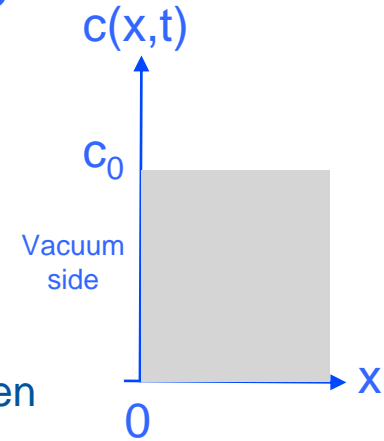
$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}$$
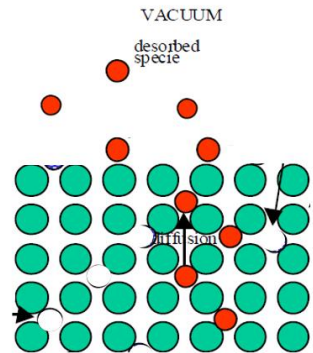
# Diffusion in a semi-infinite slab

- Case of a vacuum chamber under pumping:
    - 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.* $c(0,t)=0$

$c(x,t)$

$c_0$

Vacuum side

$0$ → $x$

- Solving the 2nd Fick law with these boundary conditions gives for the hydrogen concentration:

$$c(x,t) = \frac{2c_o}{\sqrt{\pi}} \int_0^{\frac{x}{2}\sqrt{Dt}} e^{-y^2} \, dy = c_o \, erf\left(\frac{x}{2}\sqrt{Dt}\right)$$

- with: $erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} \, dy$

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

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

The H$_2$ outgassing rate varies inversely with the square root of the pumping time

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

# Diffusion in a finite slab: bake-out

- Assume a stainless-steel slab of thickness, L, with a uniform initial concentration
- Following an in-situ bake out at temperature $T_{BO}$ for a long enough time of duration $t_{BO}$, the $H_2$ outgassing rate at room temperature (RT) of one face of the slab is constant and equals 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 several hours:

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

| L (mm) | 200ºC | 250ºC | 300ºC |
|--------|-------|-------|-------|
| 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

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

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

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

# Successive bakeout of a finite slab

• n succesive bakeouts at $T_{BO}$ with long enough time duration $t_{BO}$ give the following outgassing rate at room temperature:
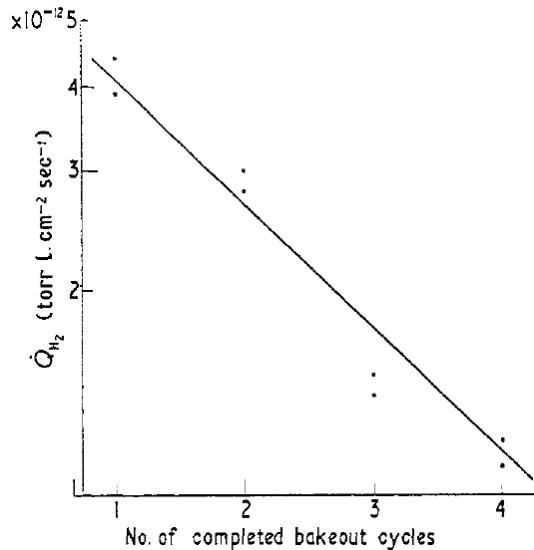
$$q_n(t) = \frac{4\, c_o\, D(T_{RT})}{L}\, e^{-n\left(\frac{\pi}{L}\right)^2 D(T_{BO})t_{BO}}$$

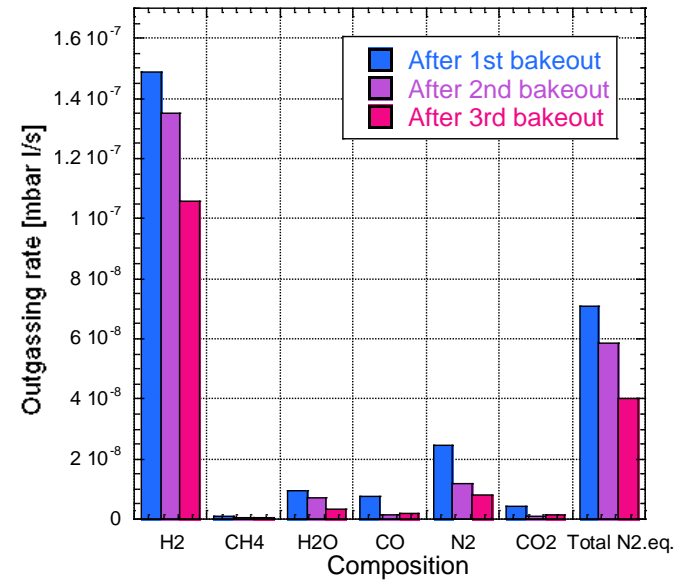R. Calder, G. Lewin, Br J Appl. Phys, 18, 1967, 1459

• A plot ln(q) vs number of bakeout cycles, n, is linear with a slope proportional to the diffusion coef.

• So each bakeout reduce the outgassing at room temperature by a constant value (as observed):

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

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:

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

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

- Baked stainless steel:
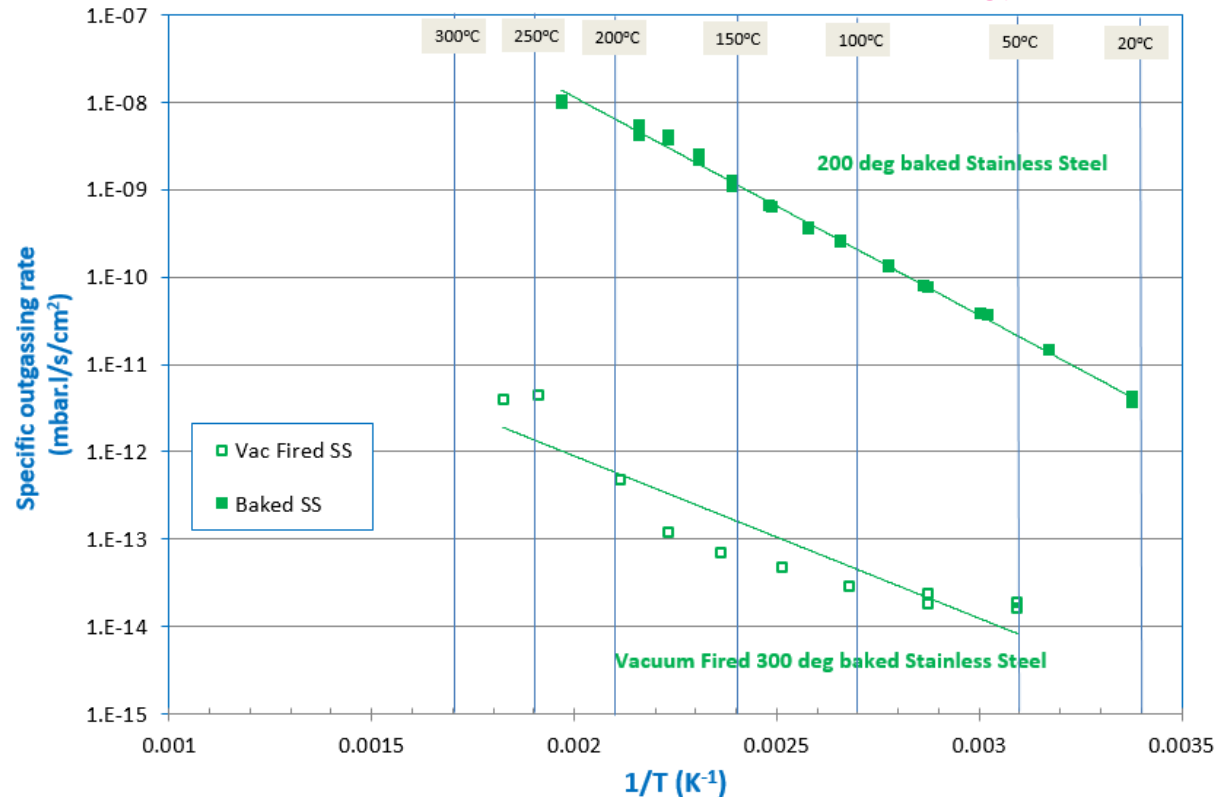  $E_a \sim 0.5$ eV

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

- Vacuum fired baked s. steel:
  $E_a \sim 0.4$ 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 of 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 heat treatment

• When the material is brought 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 for the full 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$^{-3}$) | Extraction Hydrogen conc. (At/cm$^{-3}$) |
|-----------|---------|------------------|-----------------------------------|-------------------------------------------|
| 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              | $1.3(7) \cdot 10^{18}$            | $4.2(5) \cdot 10^{17}$                    |

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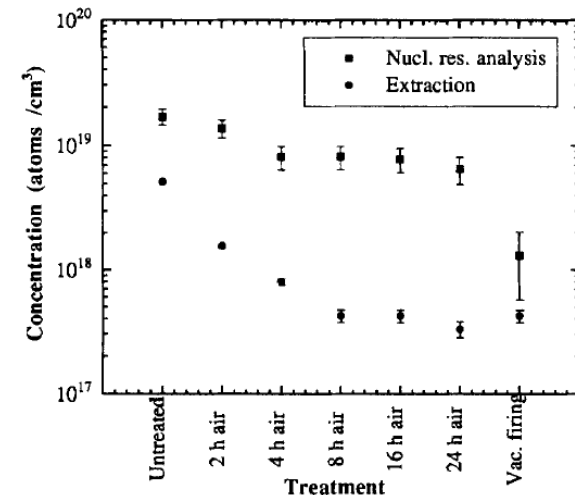


**Figure 1.** The average hydrogen concentration in the 0.05–0.7 $\mu$m depth range of the virgin, air baked and the vacuum fired samples. The results from the extraction method are also included.

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

# Subsequent bakeouts following vacuum firing

- As previously, considering 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 1st 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 (tubes), the initial content of the hydrogen is fully removed. The final outgassing is defined by the $H_2$ pressure in the furnace:
  q ~ 5 $10^{-15}$ mbar.l/(s.cm$^2$)

- For thick slab (flanges), the pressure in the furnace as limited influence:
  q ~ $10^{-13}$ mbar.l/(s.cm$^2$)

$$\frac{D(T)\, c_o}{\sqrt{\pi(D(T_F)t_F + D(T_{BO})t_{BO})}}$$

semi-infinite model

10$^{-5}$ Torr pressure in the furnace

For zero pressure in the furnace

q [Torr l s$^{-1}$ cm$^{-2}$]

L [cm]
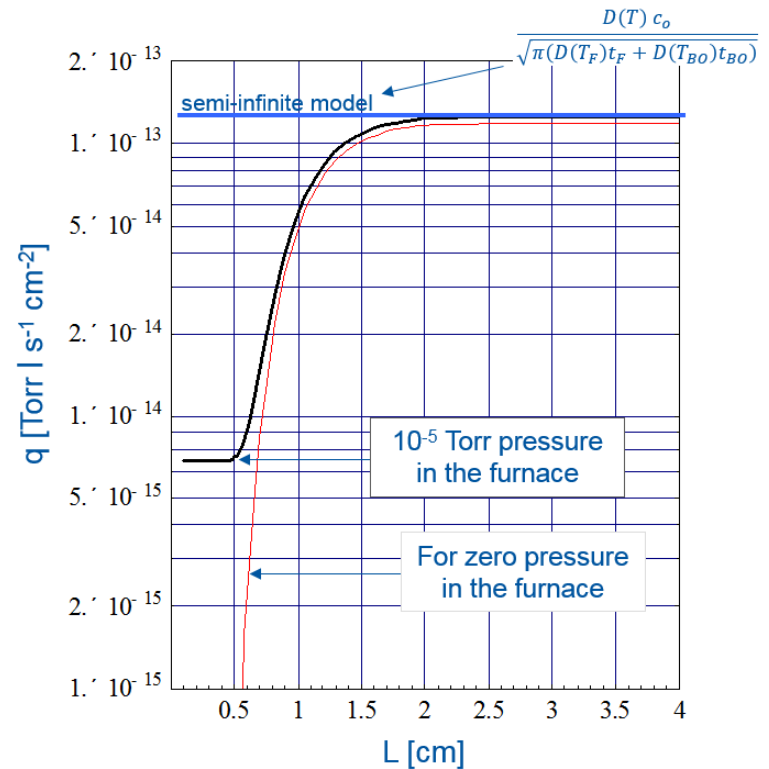
Courtesy P. Chiggiato, TE-VSC

# 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
- As expected from diffusion theory:
    - $H_2$ outgassing rate of 5 $10^{-15}$ mbar.l/(s.cm$^2$) and a reduction of ~ 1.8 between each cycle



**316 LN stainless steel hydrogen outgassing rate**

Legend:
- 300 ºC
- 300ºC with vacuum firing

Y-axis: Hydrogen outgassing rate (mbar.l/s/cm$^2$)
X-axis: Bake out cycle
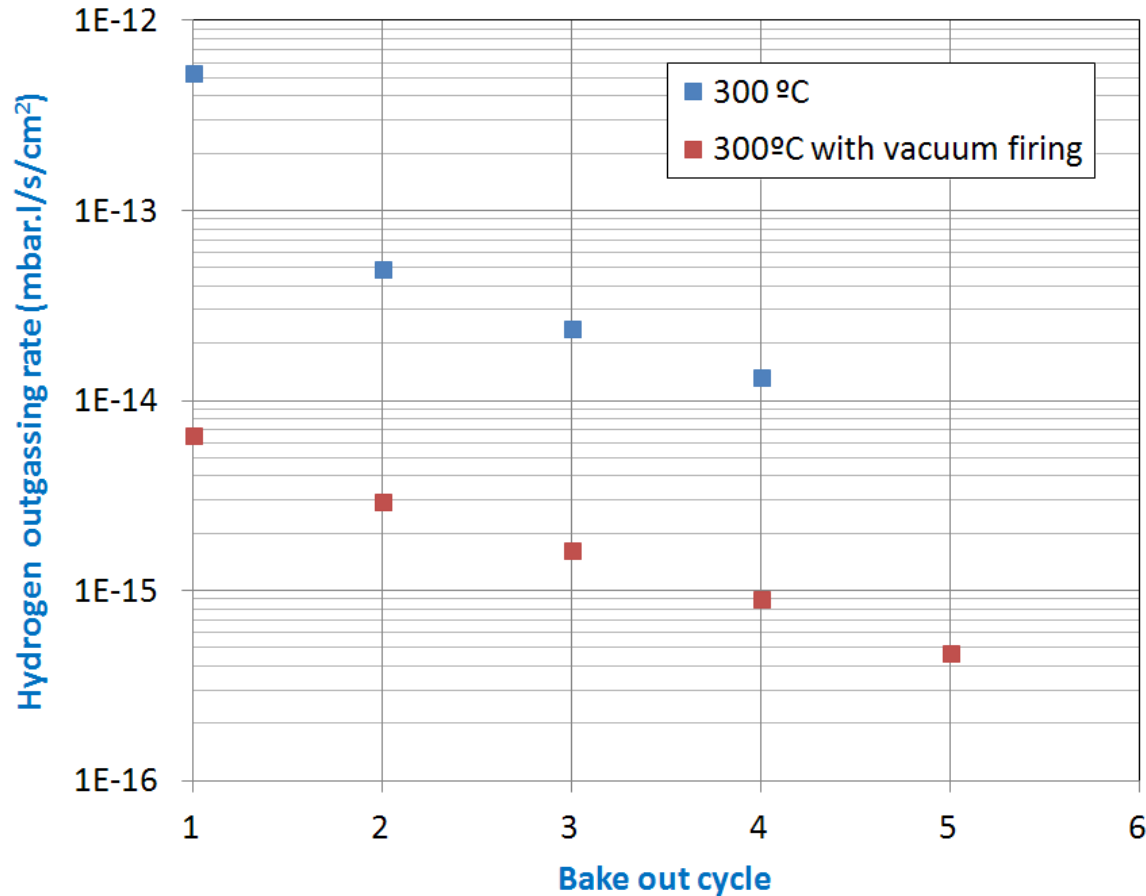
B. Versolatto, N. Hilleret, CERN Vacuum Technical Note 2002

# 2.4 Other materials

# Outgassing of plastics

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

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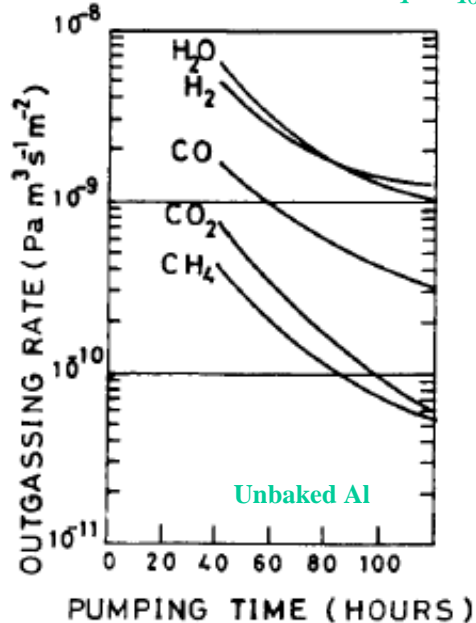
Plastic surfaces $q \sim q_0/\sqrt{t}$

**x 5 000** →



Unbaked Al

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

Lexan MR 400 (polycarbonate)
genre *Plexiglas* (polyméthacrylate de méthyle)
Er *acétal* noir (polyacétal)
*Téflon* (polytétrafluoréthylène) après 15 h d'étuvage à 100 °C
(épaisseur de 10 mm)
*Téflon* après 15 h d'étuvage à 100 °C (épaisseur de 3 mm)
*Kapton* (polyimide) (épaisseur de 125 µm)
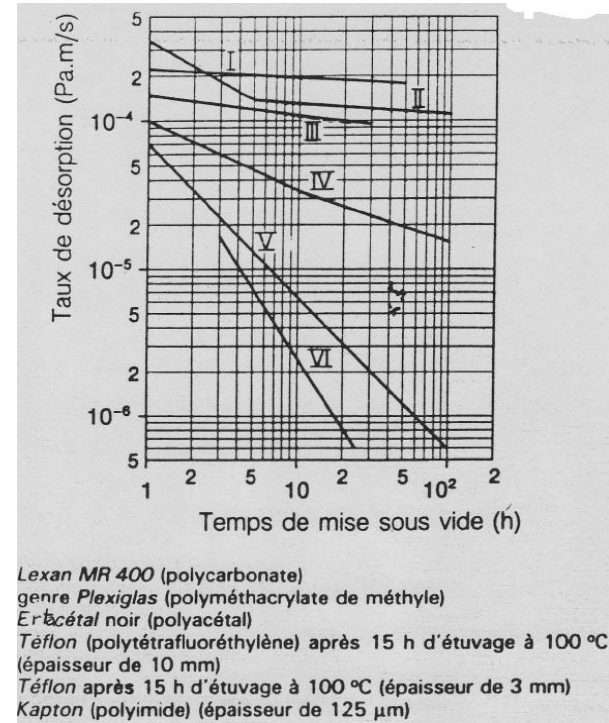
**Good Vacuum Design** :
Use ONLY metallic surfaces and reduce to ZERO the amount of plastics

# 3. Qualification of materials

# Outgassing measurement by Accumulation

• A sample is placed in an evacuated vessel and the leak valve closed

• Desorbed gas accumulates into the sample chamber

• After some accumulation time $t_{acc}$, the leak valve is opened and the mass spectra recorded

• The leak valve is closed again and the procedure repeated every 1 to 72 h
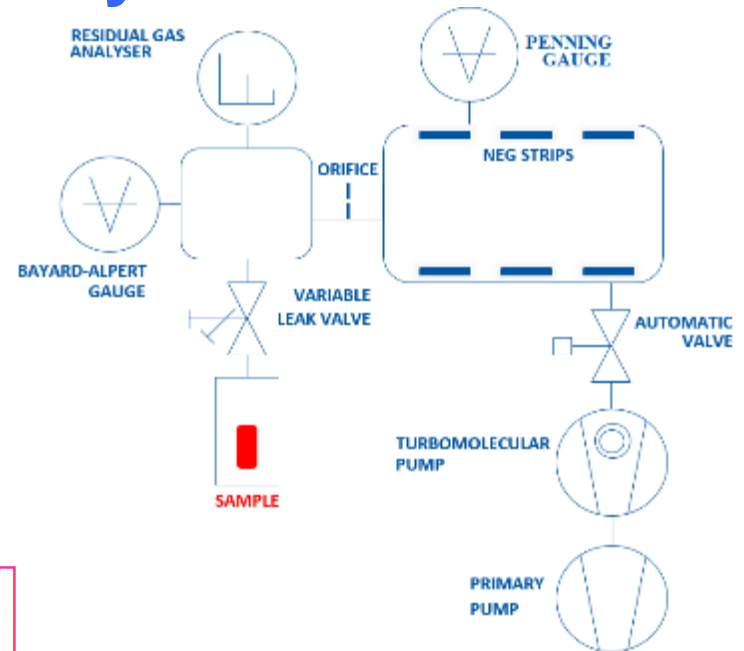
$$Q(\Delta t_{ac}) = \frac{S_i \int_0^{\Delta t} \alpha_i \, I_{RGA}(t) \, dt}{\Delta t_{ac}}$$

• 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
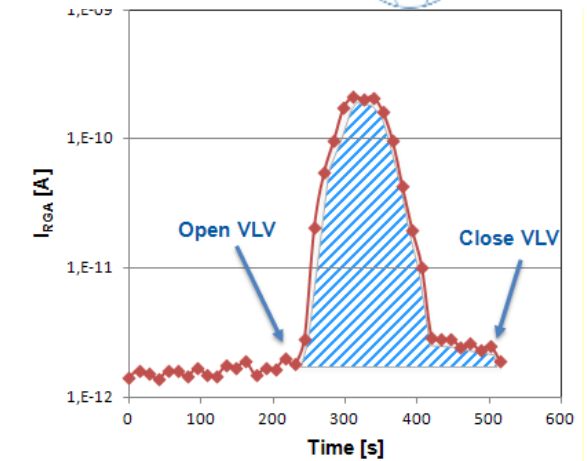
Courtesy I. Wevers, TE-VSC

# Outgassing measurement: throughput method

B-A gauge　Penning gauge　B-A gauge　RGA

TMP

1 $P_1$　2 $P_2$

Collimator TCS

Ion pump

Gas injection line, $H_2$, CO, $CH_4$, $CO_2$

$P_2$base ~ $3 \cdot 10^{-10}$ mbar

Conductance of 10l/s for $N_2$
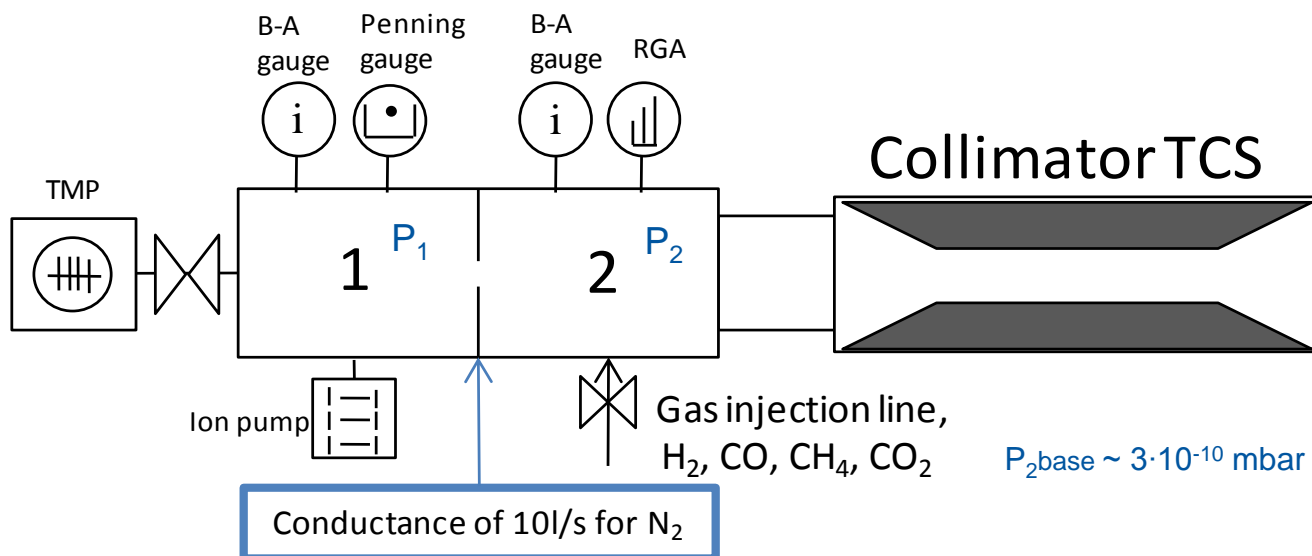
J. Kamiya *et al.*, Vacuum 85 (2011) 1178-1181

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

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

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

$$Q_{N2eq} = C \left(P_2 - P_1\right)$$

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

In $N_2$ equivalent no RGA is needed!

$\alpha$ 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



VPIAN test

NEG cartridge

BTVSS.6R8

Collimator test bench

VM NEG copper inserts

VMBGD - TDI sectorisation
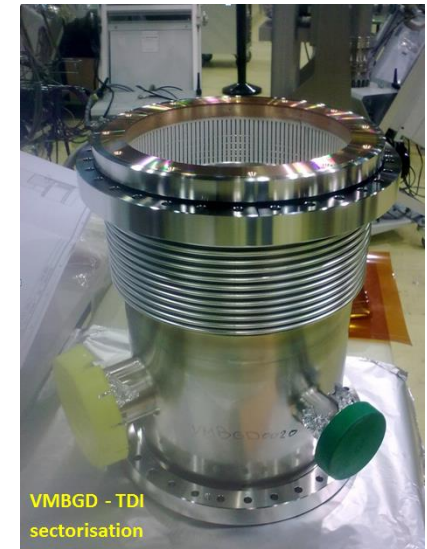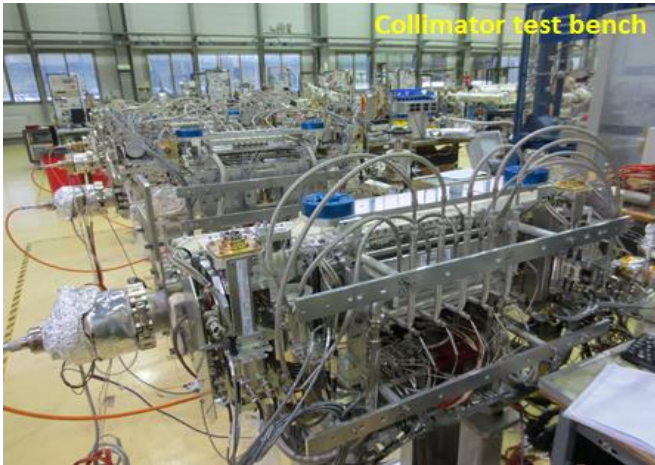
# Vacuum Acceptance Tests

- Prior to 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
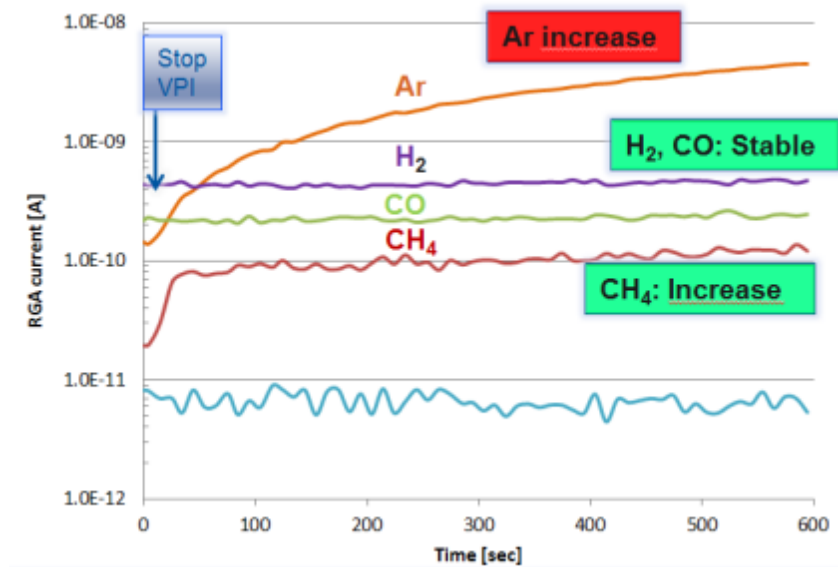


Identification of virtual leaks by accumulation test whilst pumping with NEG system
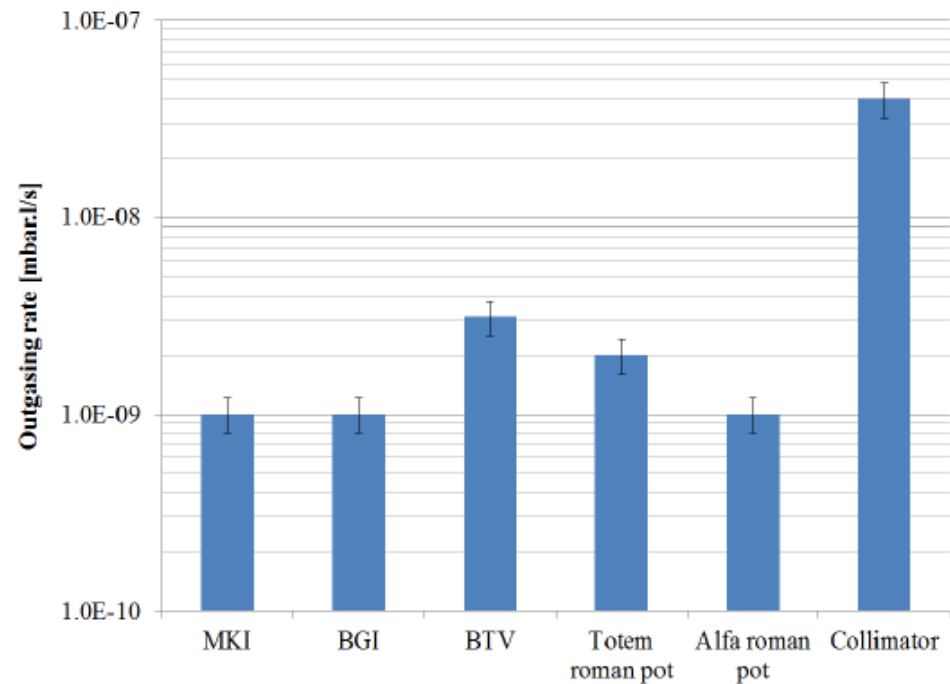


Outgassing rate of some LHC components

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

# Cleaning Methods

- Chemical cleaning is used to remove gross contamination such as grease, oil, fingerprints.
- 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

# 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
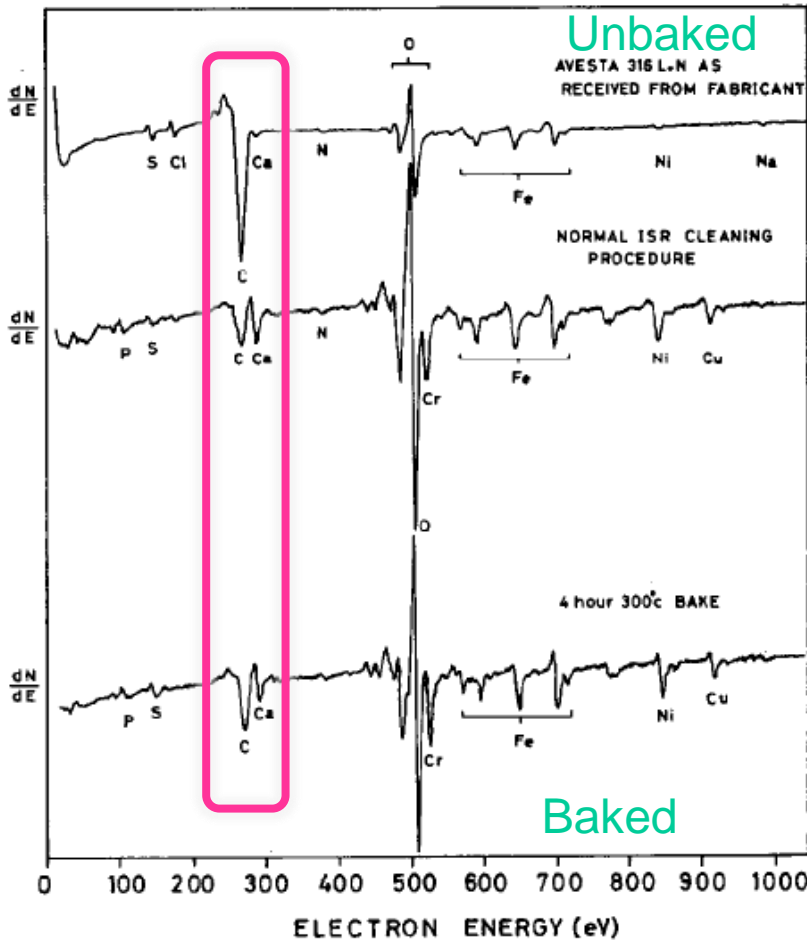


**Figure 1.** Auger spectra from a 316 L + N stainless steel specimen, as received (top) after solvent cleaning (centre) and after baking at 300°C for 4 h (bottom).
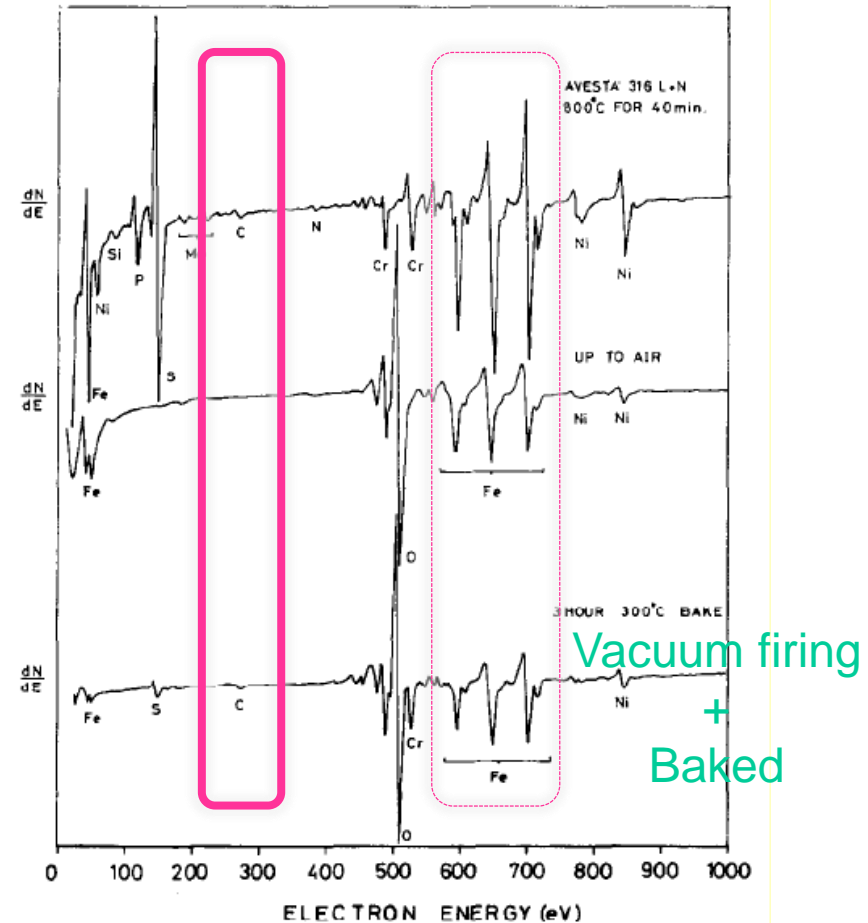
**Figure 3.** Auger spectra from a 316 L + N stainless steel specimen after heating to 800°C for 40 min *in vacuo* (top), after exposing to air (centre) and after a 3 h 300°C bake (bottom).

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

# Cleanliness evaluation by XPS

- 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



C1s

FWHM = 250 meV

BE= 284.15 eV

$\Gamma L$=130 meV
$\Gamma G$=165 meV
$\alpha$=0.093
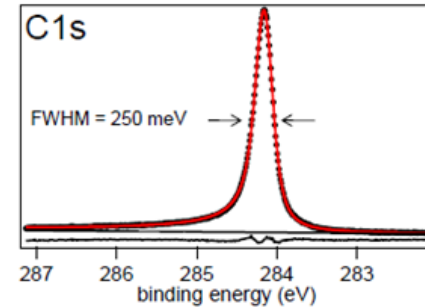


Stainless steel 316LN
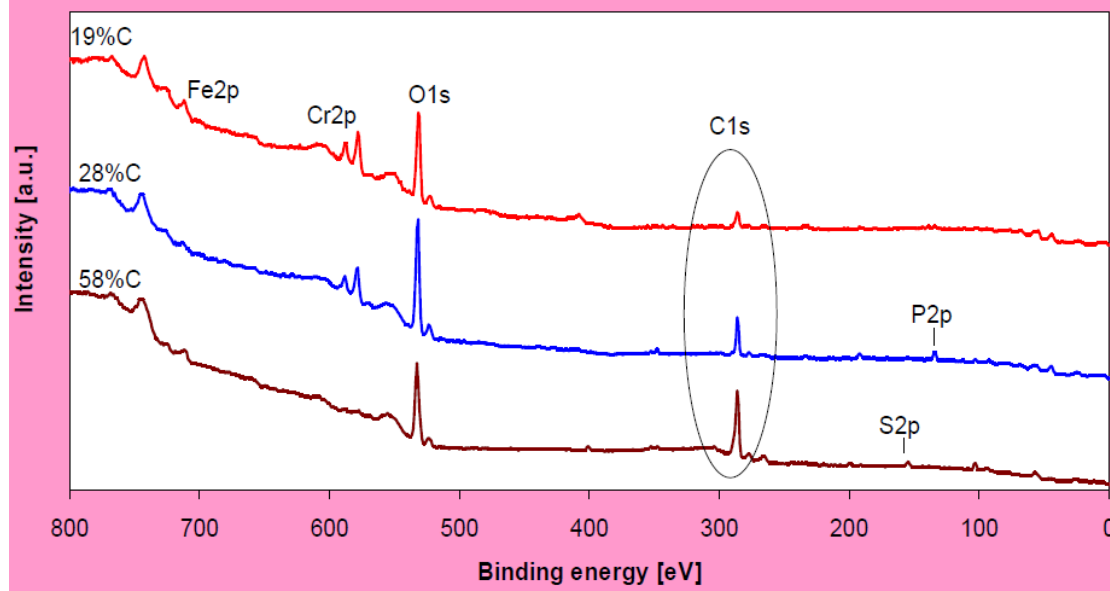


Storage of cleaned OFE copper
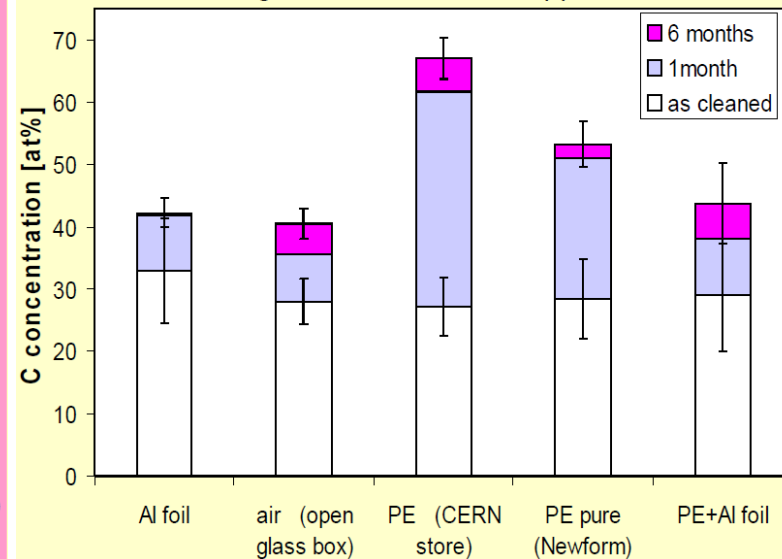
The assessment of metal surface cleanliness by XPS, C. Scheueurlein and M. Taborelli, Appl. Surf. Sci 252 (2006) 4279

# Lecture 2 summary

- The pressure in a vacuum vessel is determined by the outgassing of its 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 $1/\sqrt{t}$ limited by diffusion

- 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 an accelerator

# Some References

- Physics of outgassing, JL de Segovia, CAS, CERN 99-05
- Thermal outgassing, K. Jousten, CAS, CERN 99-05
- Water outgassing, H.F. Dylla, CAS Vacuum in Accelerators, May 2006
- Thermal outgassing, P. Chiggiato, CAS Vacuum in Accelerators, May 2006
- Reduction of stainless-steel outgassing in ultra-high vacuum, R. Calder, G. Lewin, Br J Appl. Phys, 18, 1967, 1459
- R.J. Elsey, Vacuum 25, 7 (1975), 299
- Making it Work, A. G. Mathewson, CAS, CERN 92-03
- Cleaning for vacuum services, CAS, CERN 99-05
- Cleaning and surface properties, M. Taborelli, CAS, CERN 2007-003
- The physical basis of ultra-high vacuum, P.A. Redhead, J.P. Hobson, E.V. Kornelsen. AVS.
- Scientific foundations of vacuum technique, S. Dushman, J.M Lafferty. J. Wiley & sons. Elsevier Science.
- Les calculs de la technique du vide, J. Delafosse, G. Mongodin, G.A. Boutry. Le vide.
- Vacuum Technology, A. Roth. Elsevier Science

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

# Complementary information

# 1. Elements of adsorption/desorption

# Conversion between energy units

|          | 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 |

# TDS spectra: 1ˢᵗ 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 $P_{max}/10$
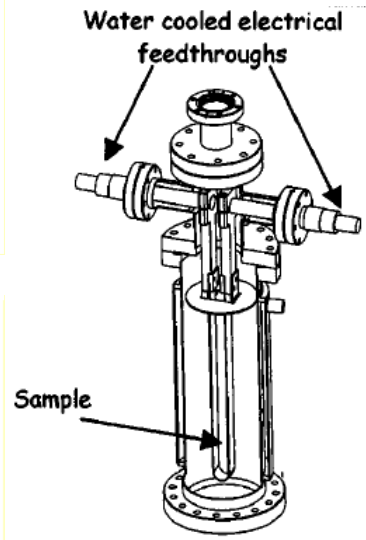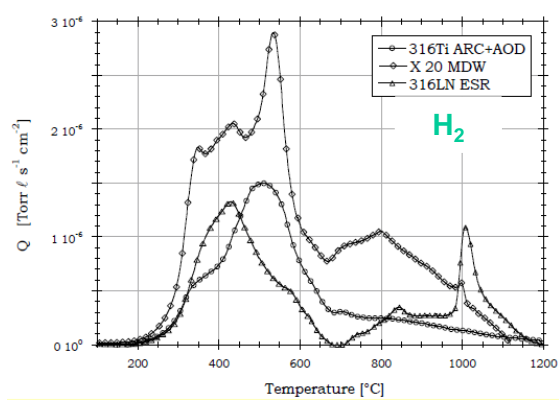
- The desorption peak is not symmetric

**Thermal desorption spectra : 1st order desorption**
**Heating rate 25 K/s, Binding energy = 1.72 eV**



Tmax ~ 670 K

The maximum desorption temperature Tmax is independent of the initial coverage.
The remaining coverage on the surface is negligeable when the pressure is Pmax/10

The desorption pic is not symetric

Tmax ~ 670 K

Legend:
- P(1)
- P(0.1)
- Coverage 1
- Coverage 0.1

X-axis: Temperature (K)
Left Y-axis: Desorption rate (monolayers/s)
Right Y-axis: Relative Coverage (monolayers)
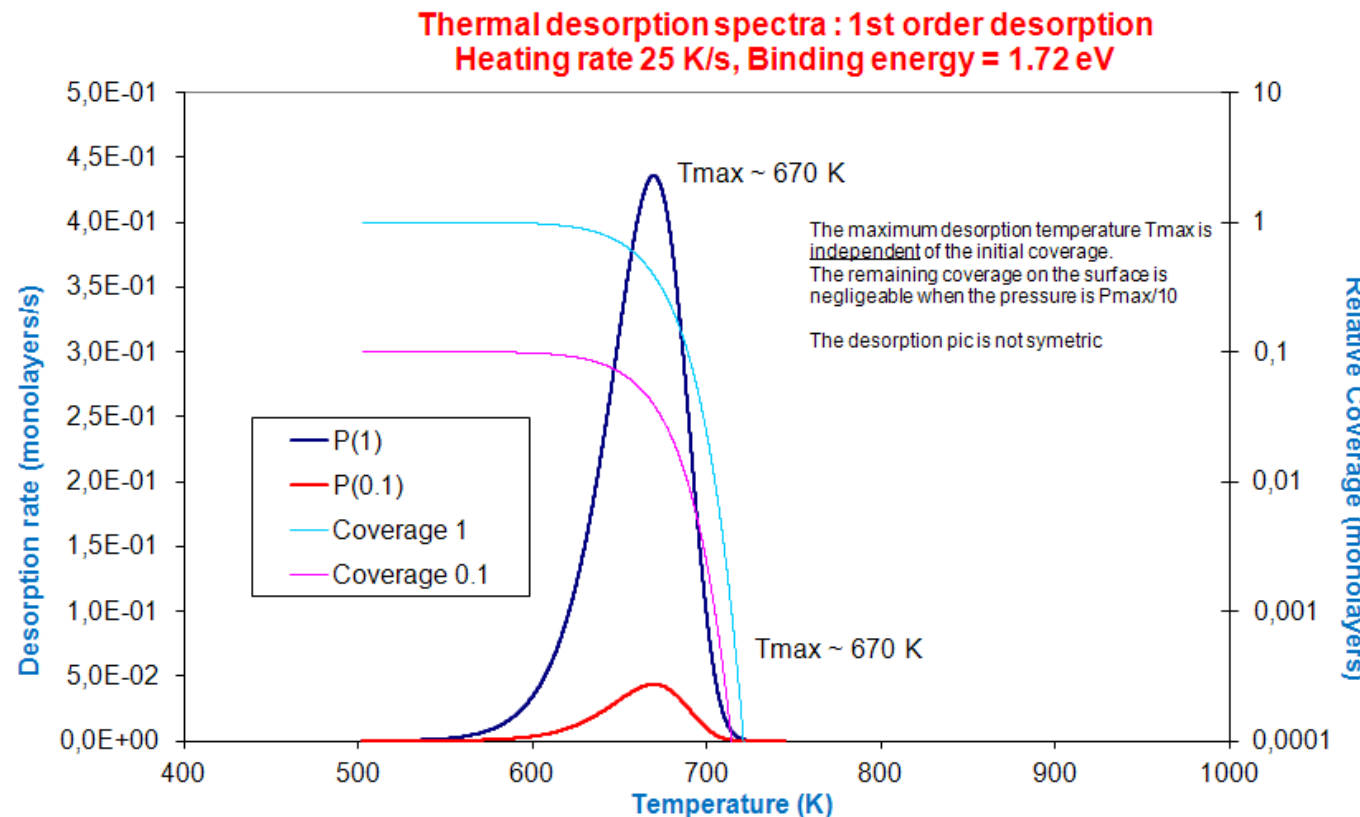
# 2<sup>nd</sup> order desorption

- For dissociatively chemisorbed molecules ($H_2$, $N_2$, $O_2$) 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 ($10^{-2}$ cm$^2$/s), $E_D$, activation energy for desorption

# TDS spectra: 2nd Order

- The maximum temperature is dependent of the initial surface coverage

- The remaining coverage on the surface is negligeable when the pressure is 0.

- The desorption peak is symmetric
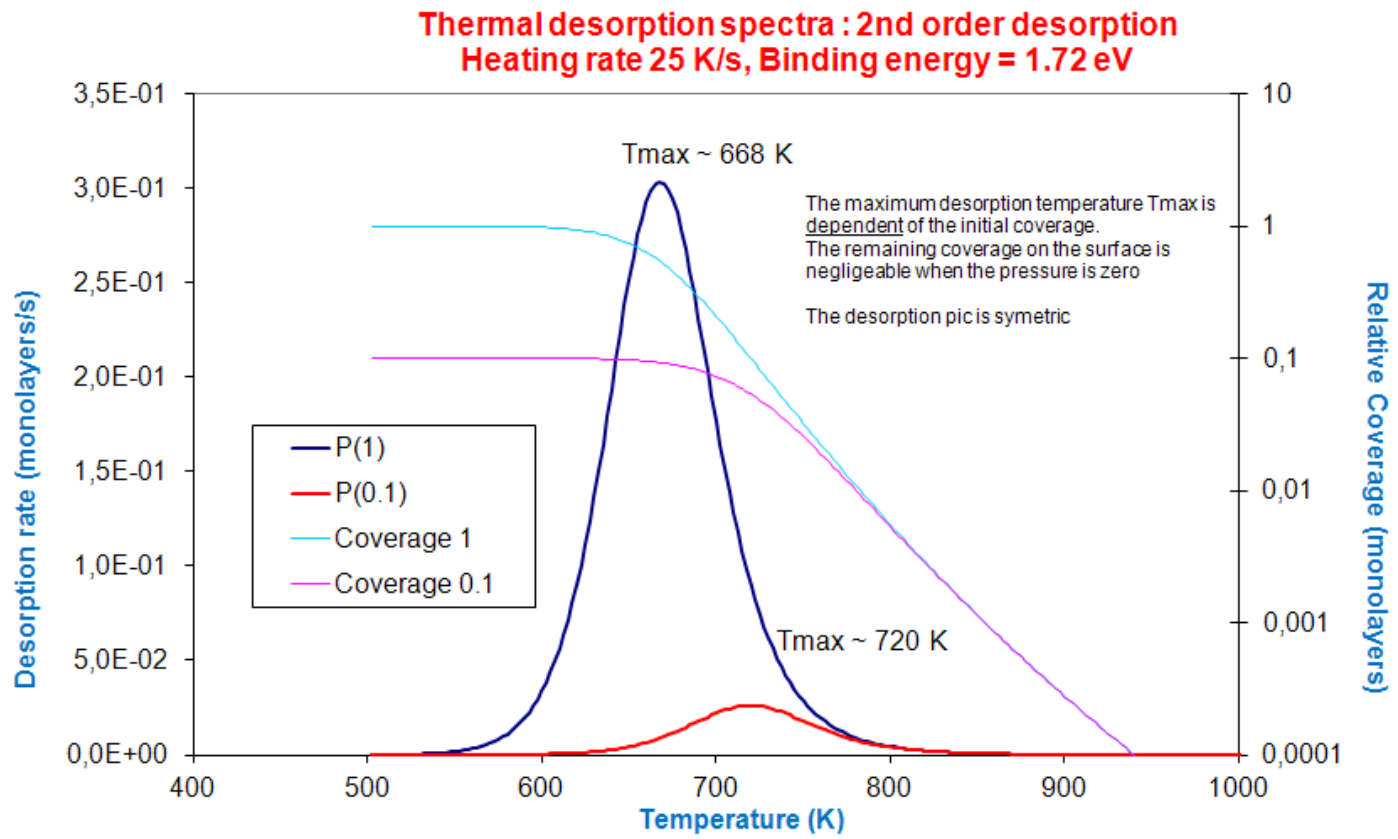


**Thermal desorption spectra : 2nd order desorption**
**Heating rate 25 K/s, Binding energy = 1.72 eV**

Tmax ~ 668 K

The maximum desorption temperature Tmax is dependent of the initial coverage.
The remaining coverage on the surface is negligeable when the pressure is zero

The desorption pic is symetric

Tmax ~ 720 K

- P(1)
- P(0.1)
- Coverage 1
- Coverage 0.1

Desorption rate (monolayers/s)

Relative Coverage (monolayers)

Temperature (K)

# TDS spectra: 3rd 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 not symmetric and exhibit a tail



**Thermal desorption spectra : 3rd order desorption**
**Heating rate 25 K/s, Binding energy = 1.72 eV**

Tmax ~ 667 K

The maximum desorption temperature Tmax is depandant of the initial coverage.
The remaining coverage on the surface is negligeable when the pressure is zero. The cleanning efficiency is less than smaller orders

The desorption pic is not symetric and exhibit a tail

Tmax ~ 779 K

Legend:
- P(1)
- P(0.1)
- Coverage 1
- Coverage 0.1

x-axis: Temperature (K)
left y-axis: Desorption rate (monolayers/s)
right y-axis: Relative Coverage (monolayers)

# 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
- $H_2$ is desorbed at different temperature
- $H_2O$ is still present
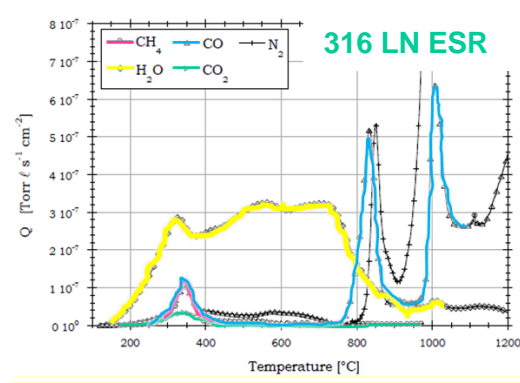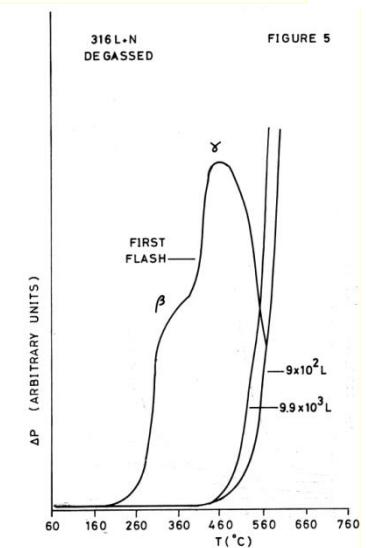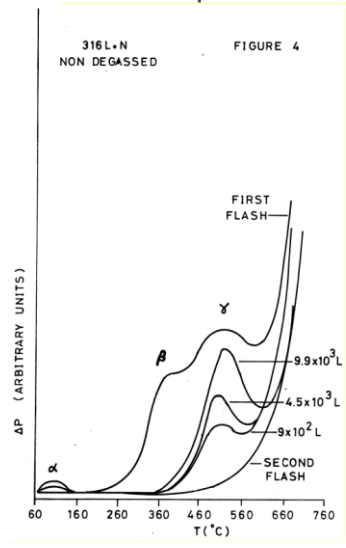


25 K/s

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



$H_2$

316 LN ESR

5 K/s

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

# 2.2 Baked system

# Bakeout systems

LHC Kickers
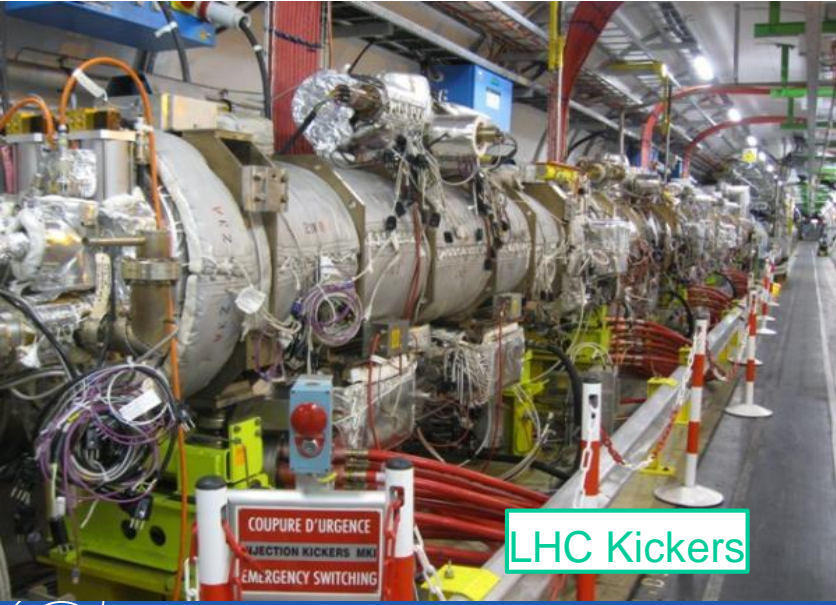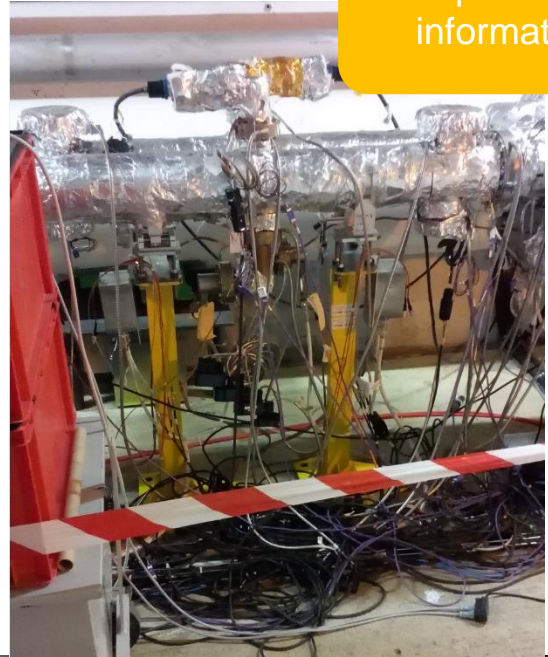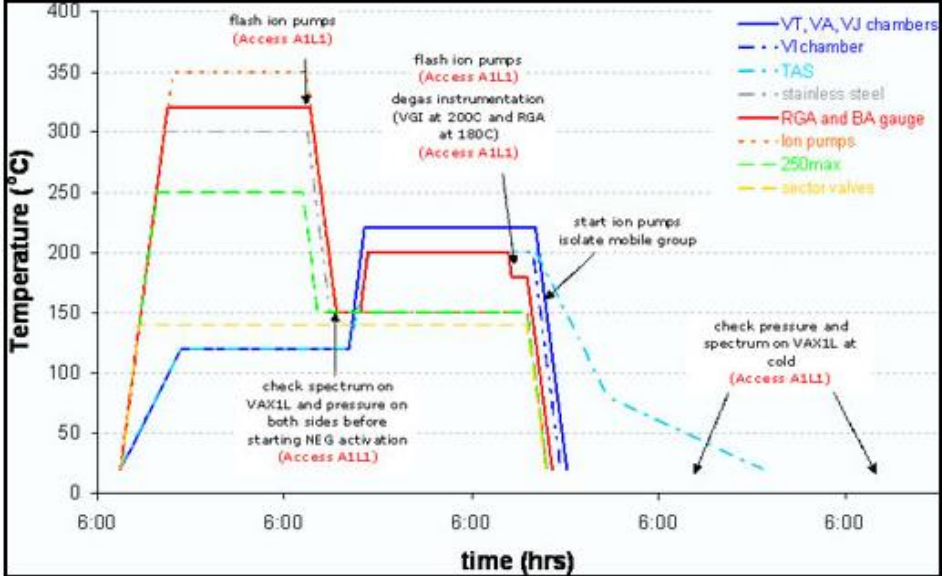

"Combined" sector
Both beams circulates in the same beam pipe

# Diffusion in a semi-infinite slab

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

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

c(x,t)

$c_0$

Vacuum
side

x

0
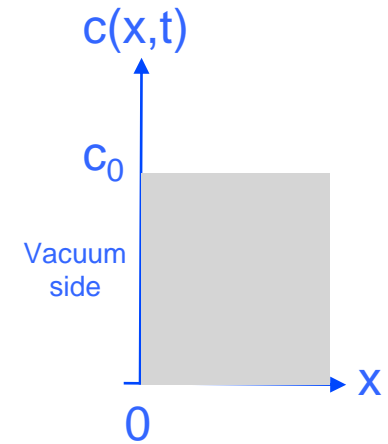
R.J. Elsey, Vacuum 25, 7 (1975), 299

# 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
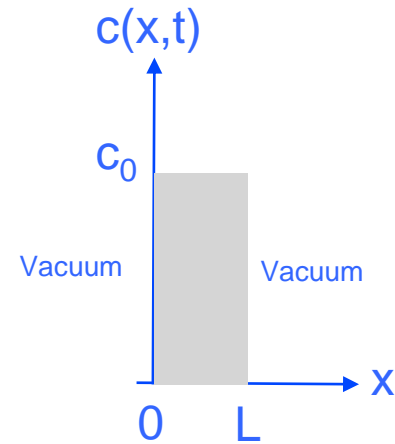
- Solving the 2nd Fick law with these boundary conditions gives:

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



$c(x,t)$

$c_0$

Vacuum        Vacuum

0      L      x

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

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



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

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

$$q(t) = \frac{8 c_o D}{L} e^{-\left(\frac{\pi}{L}\right)^2 Dt}$$
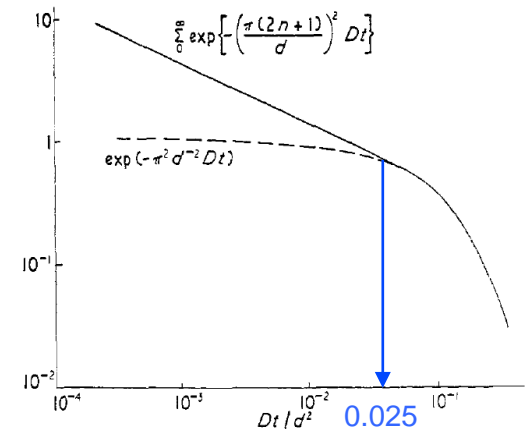
R.J. Elsey, Vacuum 25, 7 (1975), 299

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

# Diffusion in a finite slab

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

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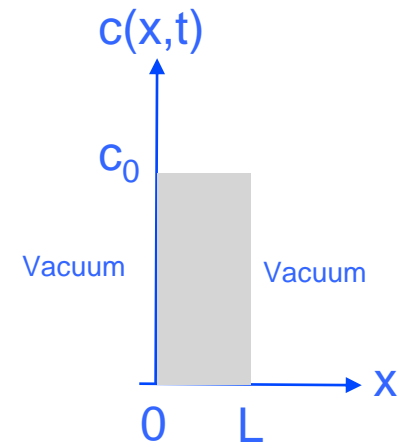


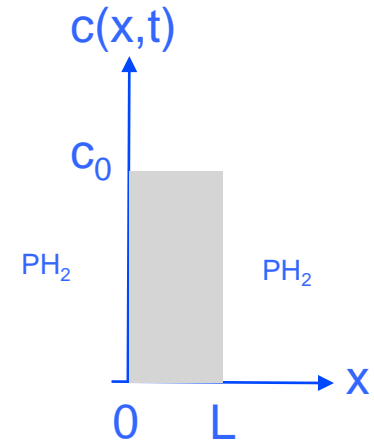R.J. Elsey, Vacuum 25, 7 (1975), 299

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

# 2.3 Hydrogen reduction

# Diffusion in a finite slab with residual H$_2$ 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$^{nd}$ Fick law with these boundary conditions gives:

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

c(x,t)

c$_0$

PH$_2$        PH$_2$

0    L

x

- 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

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

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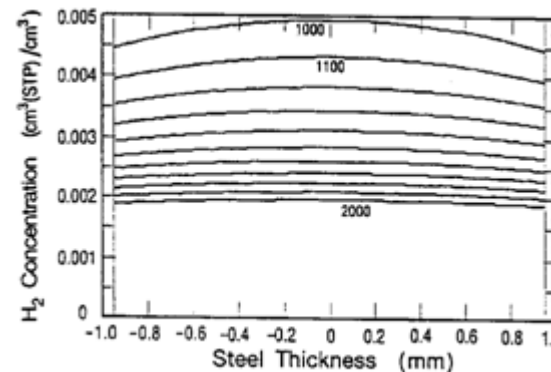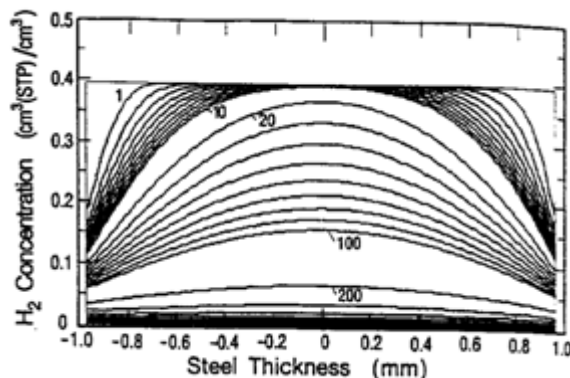


B.C. Moore, J. Vac. Sci. Technol. A 13 (1995), 545.

Complementary information

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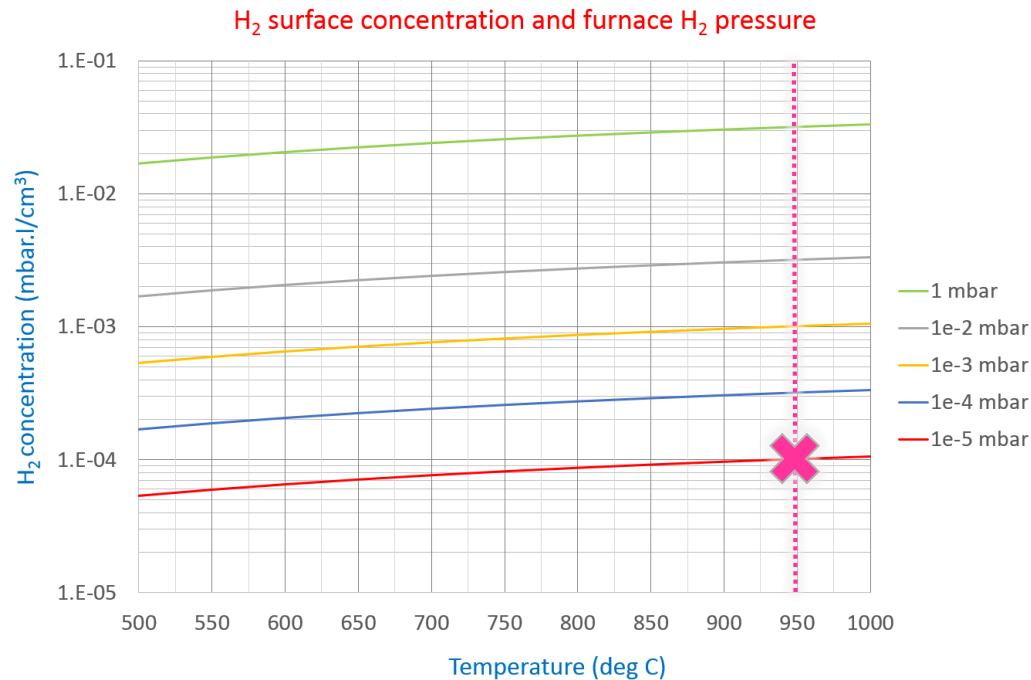
$$c_F = 3 \sqrt{P} \, e^{-\frac{E_S}{kT}}$$

With $E_s$ = 0.115 eV, P in bar and $c_F$ in mbar.l/cm$^3$

• A furnace pressure < 1 mbar is needed to reduce the "natural" H surface concentration

• At $10^{-5}$ mbar and 950ºC, the minimum $H_2$ concentration is $10^{-4}$ mbar.l/cm$^3$ *i.e.* ~ $5 \cdot 10^{15}$ H/cm$^3$

• 3 to 4 order magnitude less than in "natural" stainless steel !



H$_2$ surface concentration and furnace H$_2$ pressure

A low pressure in the furnace during the vacuum firing is of primary importance

# 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$^2$

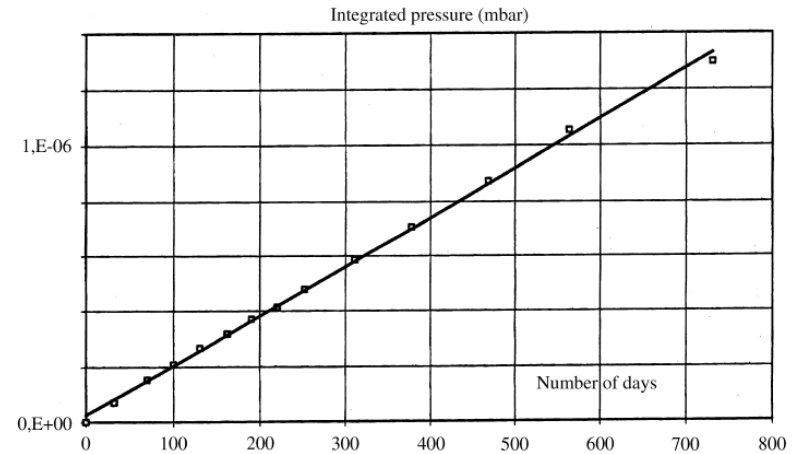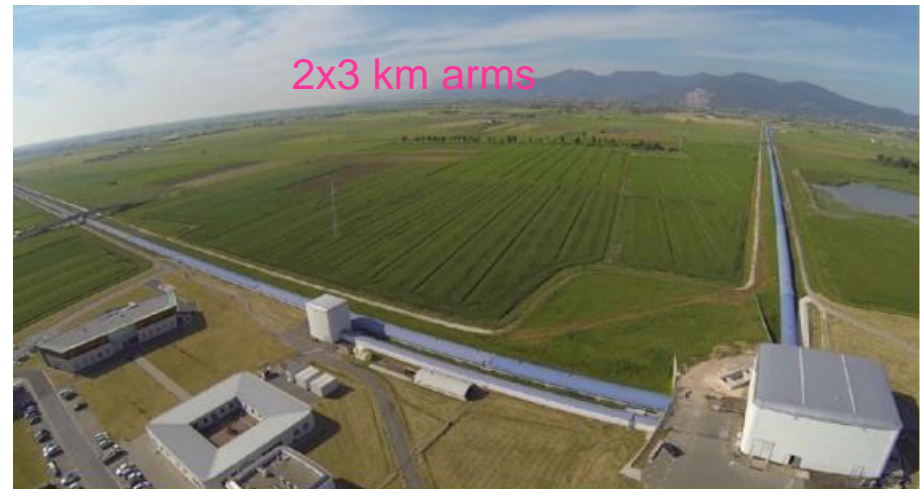- Diffusion energy increased from 0.5 to 0.6 eV

- 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



2x3 km arms

# Diffusion barrier: coating ?

- The hydrogen diffusion is reduced by a diffusion barrier created by a coating e.g. TiN

- At least 1 µm film thickness

- The film reduce the hydrogen permeation

- Extrapolation from coupons measurements predicts $10^{-14}$ Pa.m s$^{-1}$ ($10^{-17}$ mbar.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: $10^{-10}$ mbar.l/s/cm$^2$
  - TiN coated chamber: 7 $10^{-13}$ mbar.l/s/cm$^2$
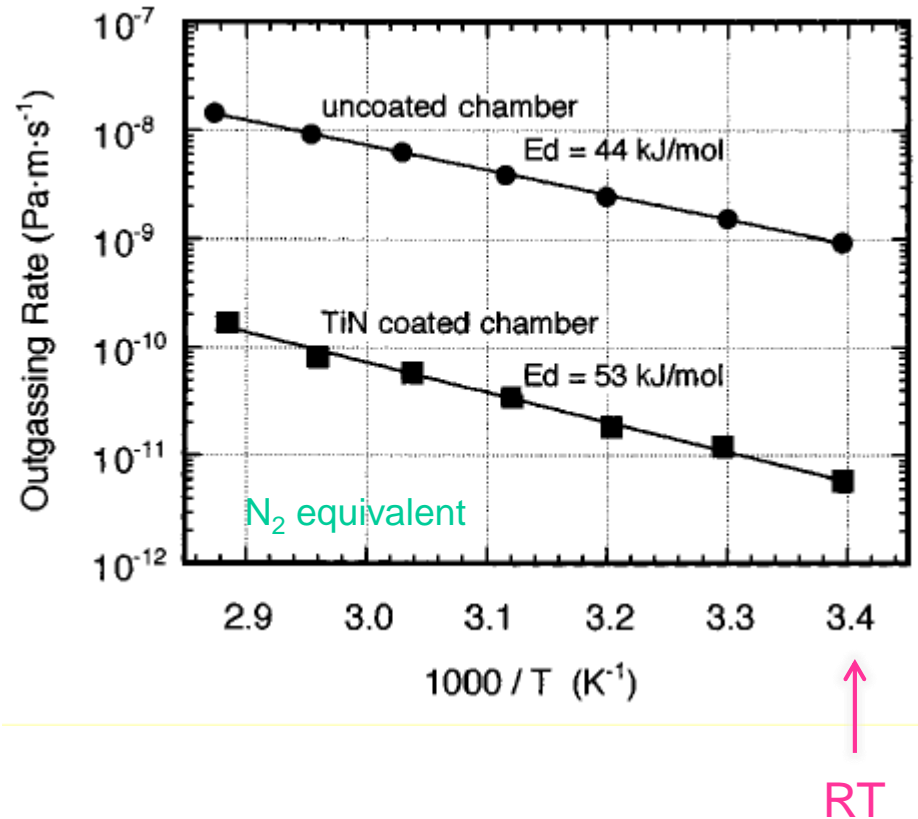
TiN thin film on stainless steel for extremely high vacuum material, K. Saito *et al.* , J. Vac. Sci. Technol. A 13(3) May/Jun 1995, 556
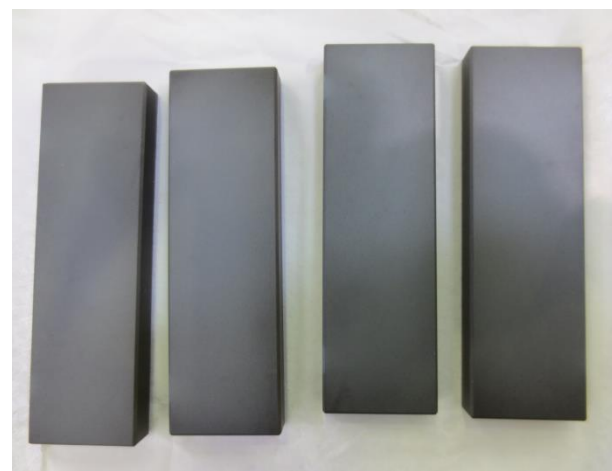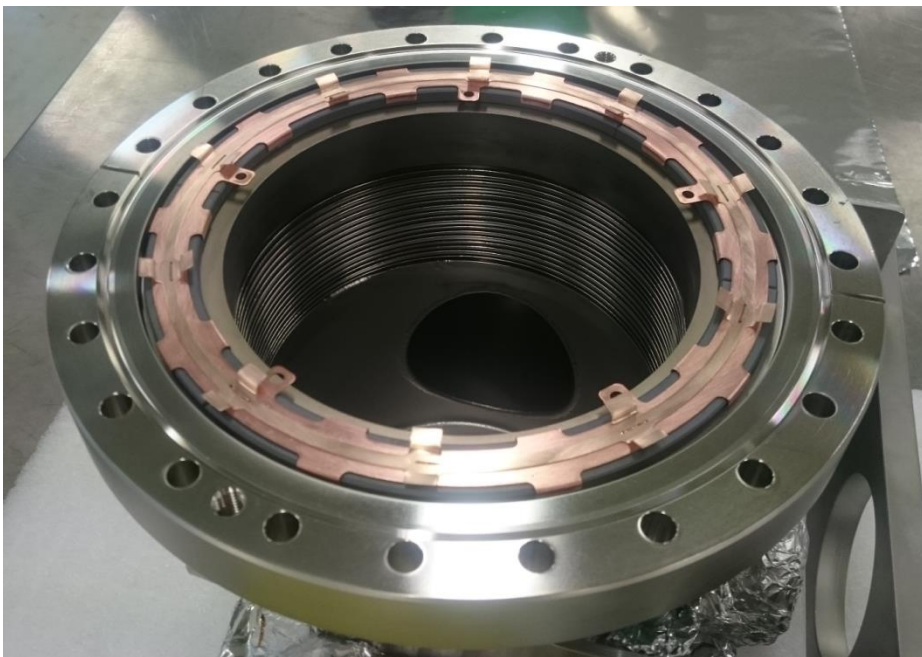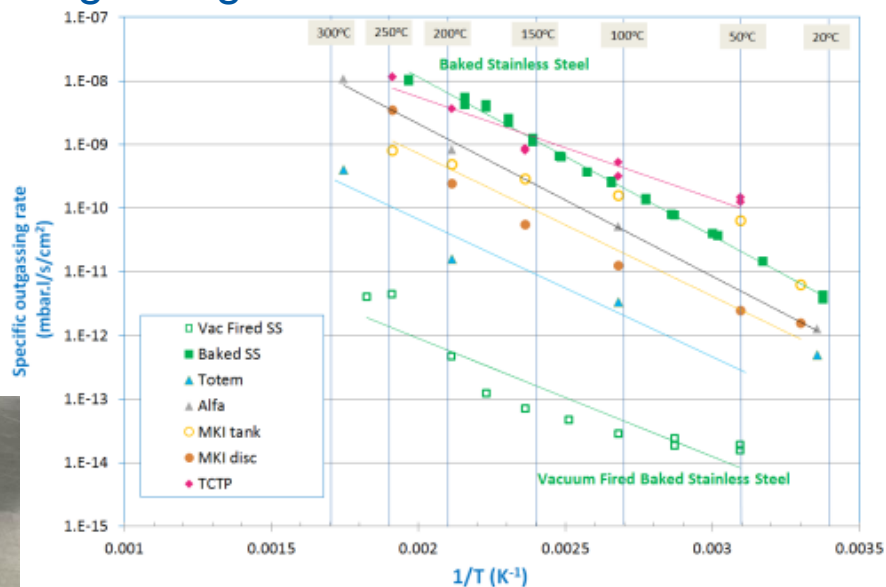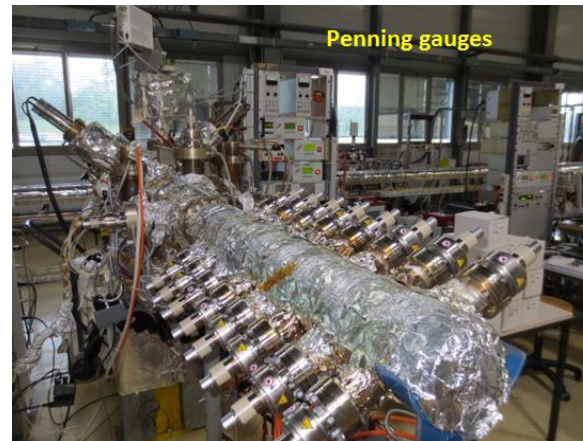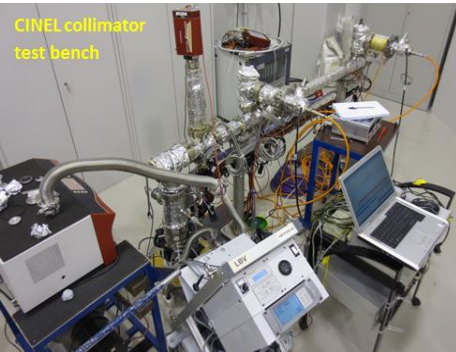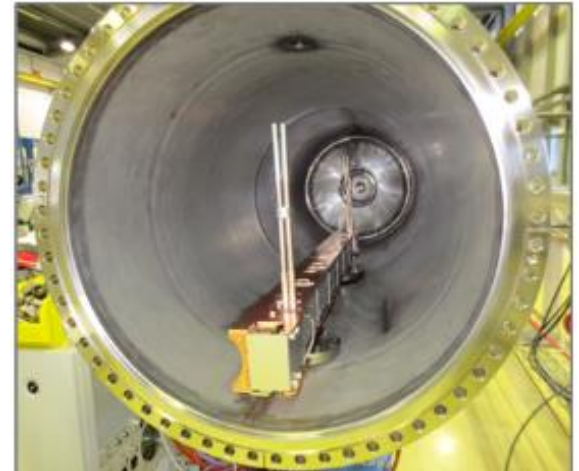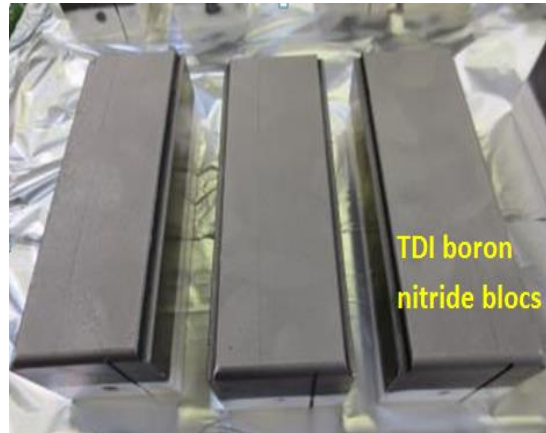
# 2.4 Other materials

# Outgassing of ferrites

- 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 |
|---|---|---|---|---|
| $\dfrac{q}{q_{RT}}$ | 5 | 40 | 150 | 600 |

# 3. Qualification of materials

# Example of tested parts



MKI Oven test facility B.867



TDI boron nitride blocs





CINEL collimator test bench



Penning gauges



ATLAS VC1AP (G. Lanza)

# 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$^{rd}$ 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$^-$ gun source might induce surface modification
• Auger lines might overlap
• spot: 0.01x0.01 to 0.1x0.1 mm$^2$
• Detection limit ~$10^{14}$ atoms/cm$^2$
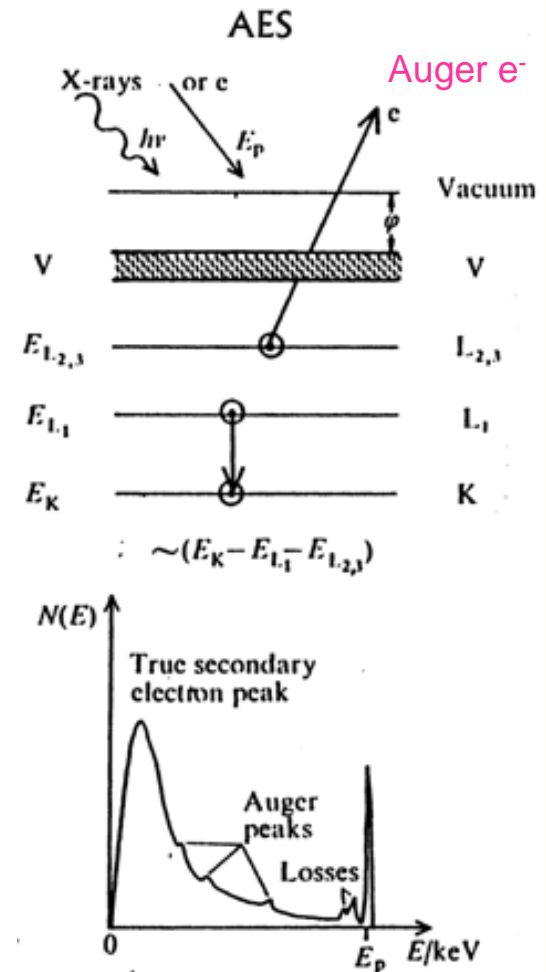
# Surface characterisation – XPS

- 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 ~$10^{14}$ atoms/cm$^2$

$$KE = h\nu - BE - \varphi$$

KE: kinetic energy

$\varphi$: work function

BE: binding energy

**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$^2$

**Synchrotron radiation based X-Ray Sources:**
- Monochromatic photon energy
- From IR to hard X-rays
- High flux