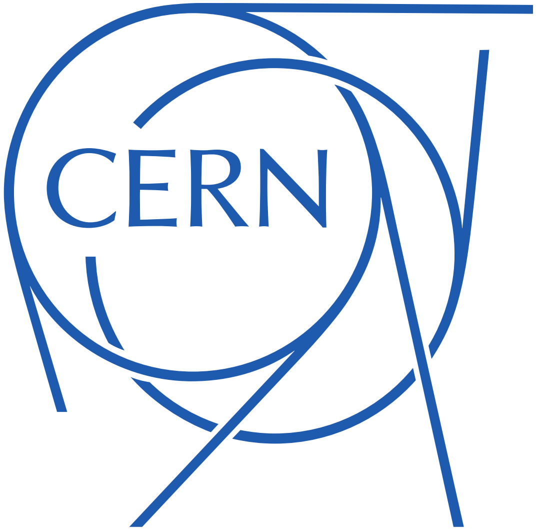
CERN

Vacuum Systems
Lecture 2

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Joint Universities Accelerator School

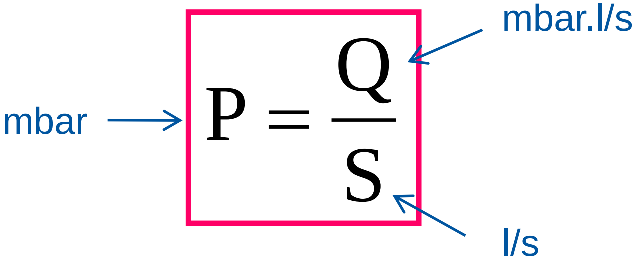
Outline

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



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

- S range from 10 to 20 000 l/s

- Q range 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 molecules/s

PV	G
1 mbar.l	4.35 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

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

Pump down of a vessel

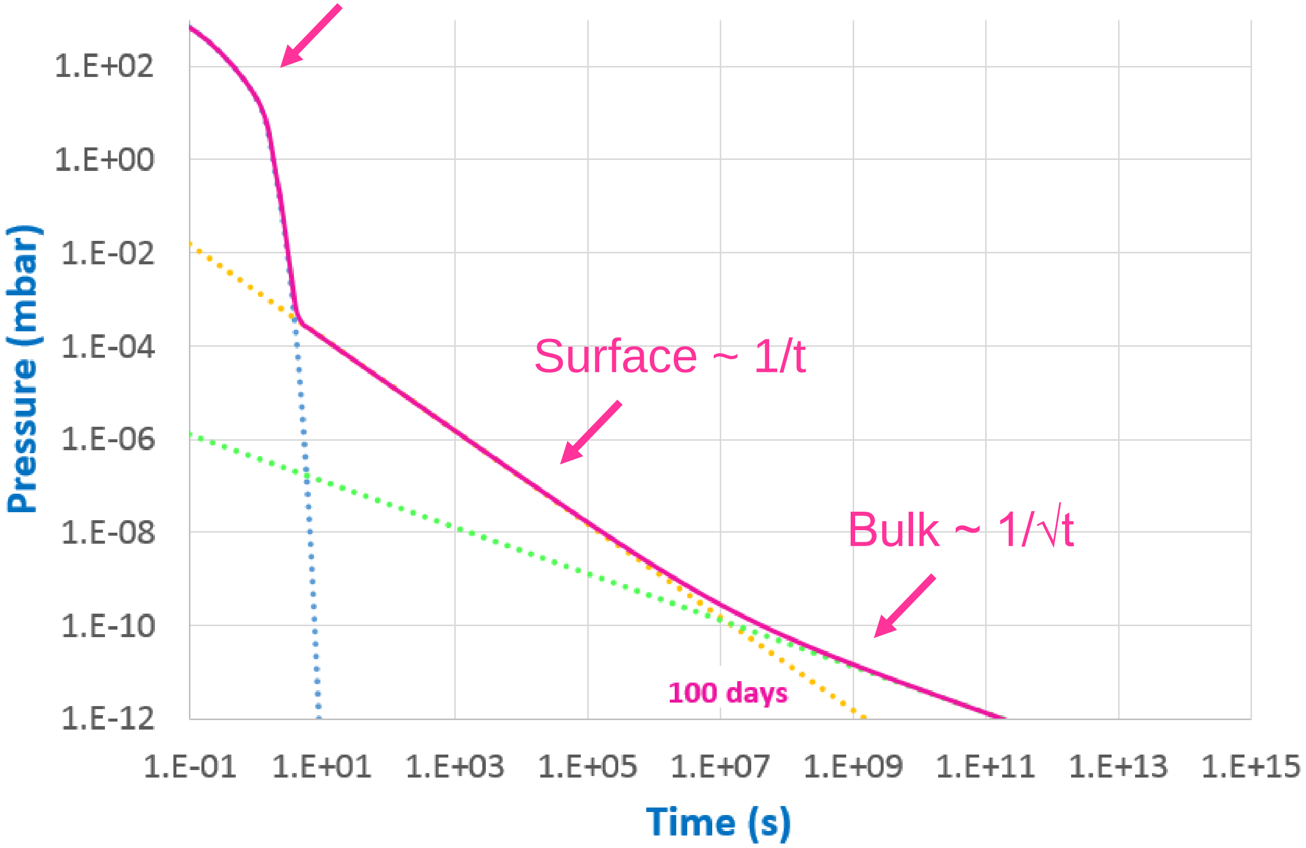
- Consider 1 m long, Ø10 cm stainless steel tube pumped by 30 l/s
- 4 regimes

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

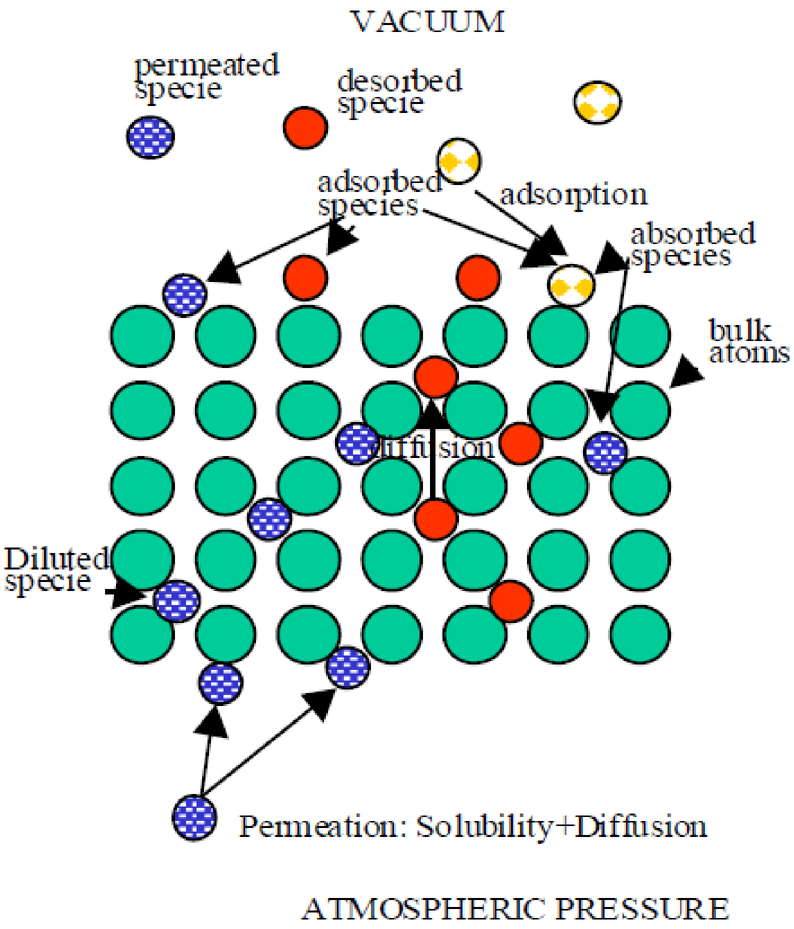


Fig. 1 Surface and bulk phenomena in vacuum.

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

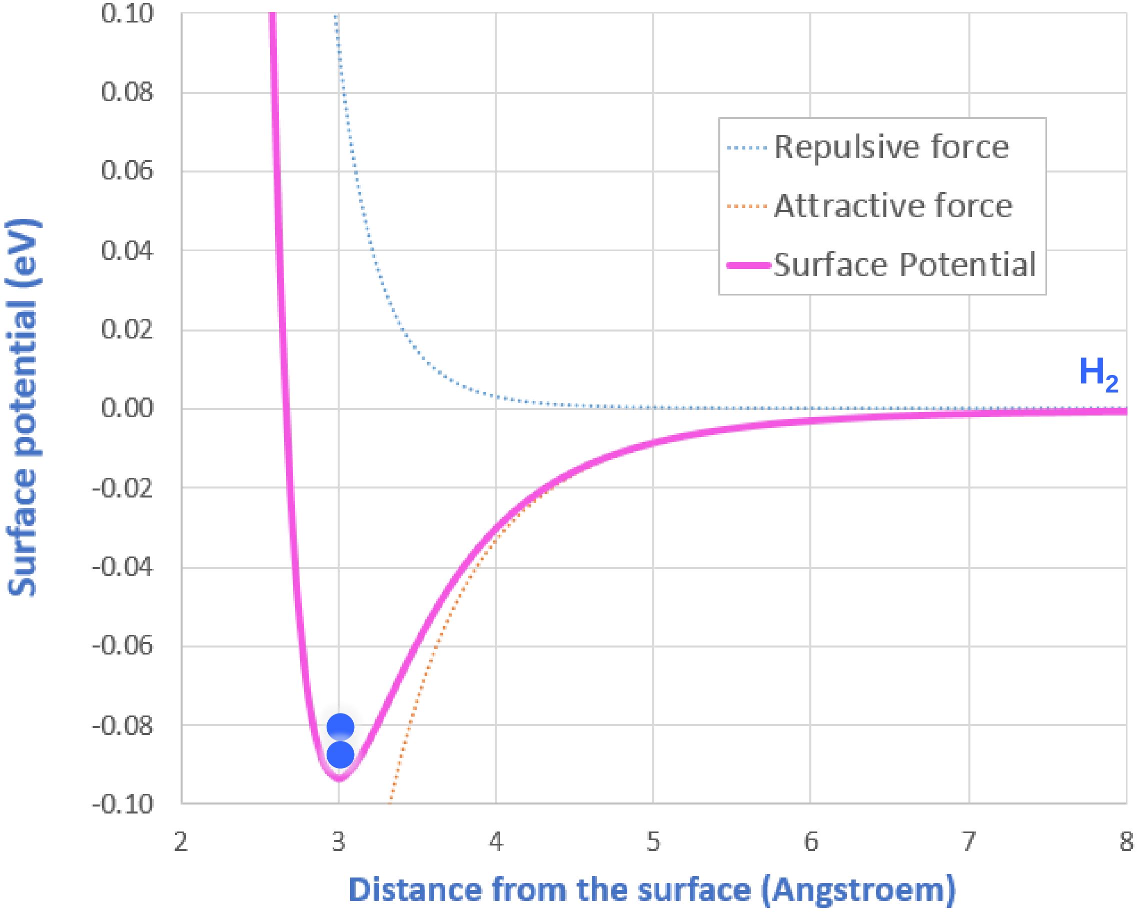
- Strong binding energy:
    - Chemical adsorption process
    - Electron sharing
    - E: 30-10000 kJ/mole or 0.3-10 eV per particle

- The surface interaction can be described by Lennard-Jones potentials, E, as a function of the distance from the surface, r.

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

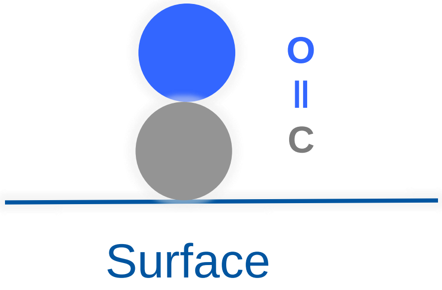
Physisorption

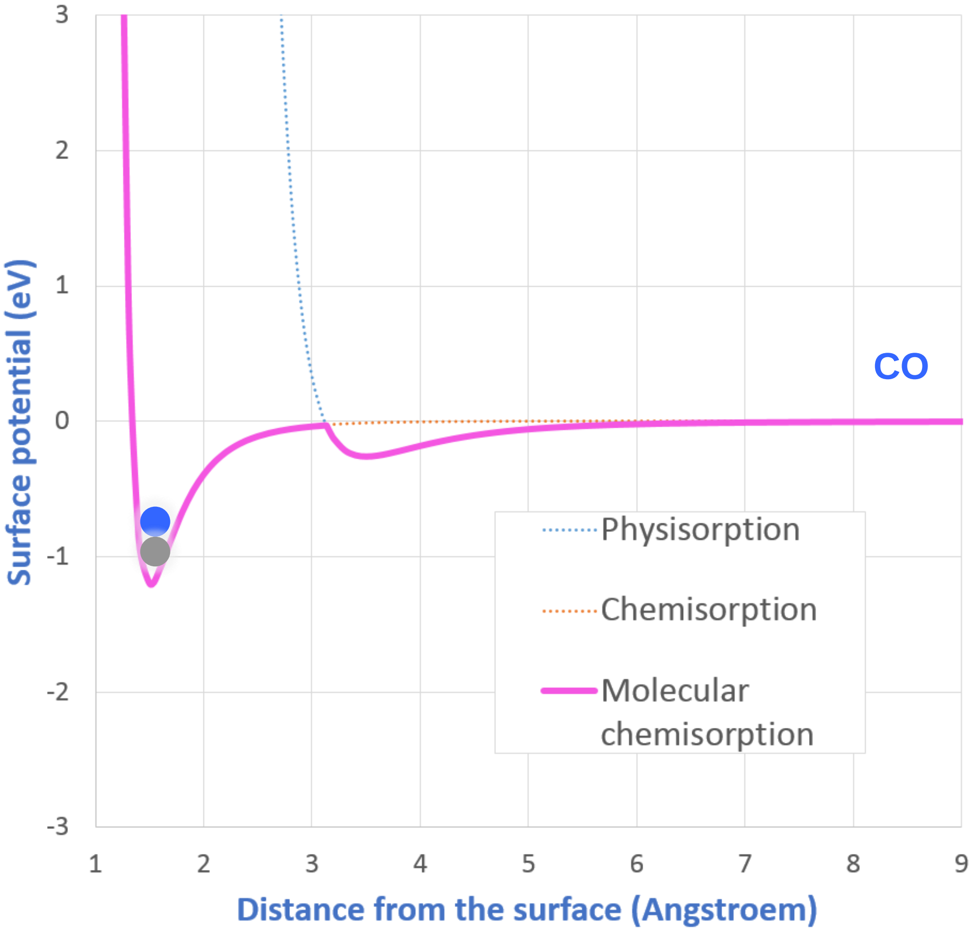
- A molecule, say H_2, approaches towards the surface
- The molecule is physisorbed onto the surface at ~ 3 Å with a “binding” (adsorption/desorption) energy of ~ 10 meV (twice the H heat of vaporization)
- Due to the nature of the physisorption process, several monolayers can be physisorbed in this 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 adsorb on the surface
- The carbon atom is oriented towards the surface



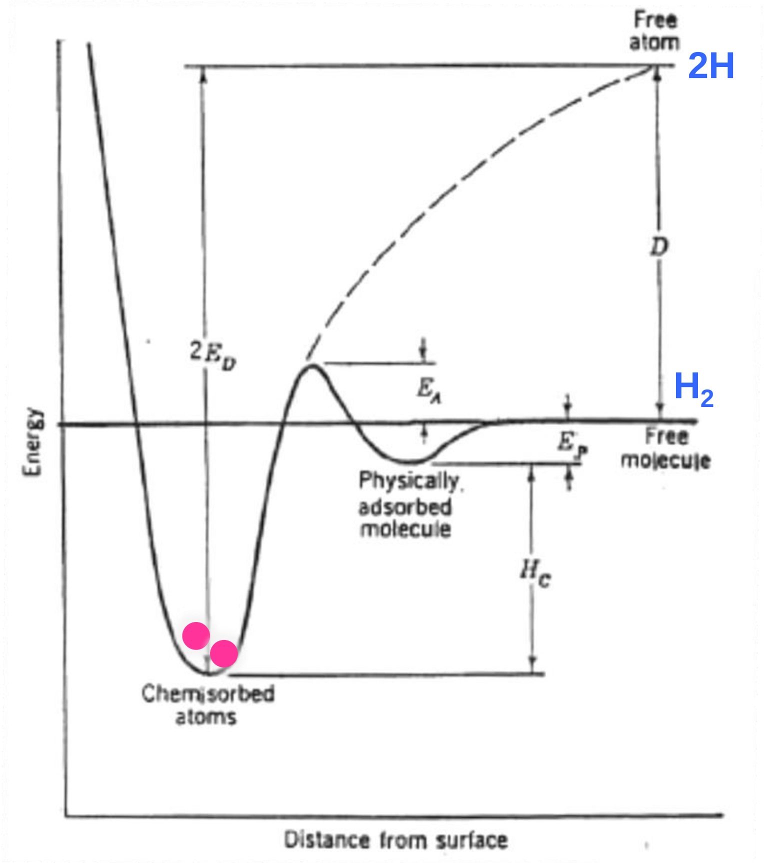


Dissociative Chemisorption

- 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~0.4 eV), the molecule is dissociate and the H atoms are chemisorbed (H-H binding energy: E_{diss} ~ 4.5 eV)
- The atoms are chemisorbed onto the surface at ~ 1.5 Å with a adsorption energy of ~ 3.7 eV
- A maximum of one monolayer can be adsorbed on the surface
- Activation energy ~ 0.4 eV

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

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



1^{st} order desorption

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

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

- θ, surface coverage, ν_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:

$$\theta(t) = Ae^{-t/_{\tau}}$$

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

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 maximum at temperature Tp 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.

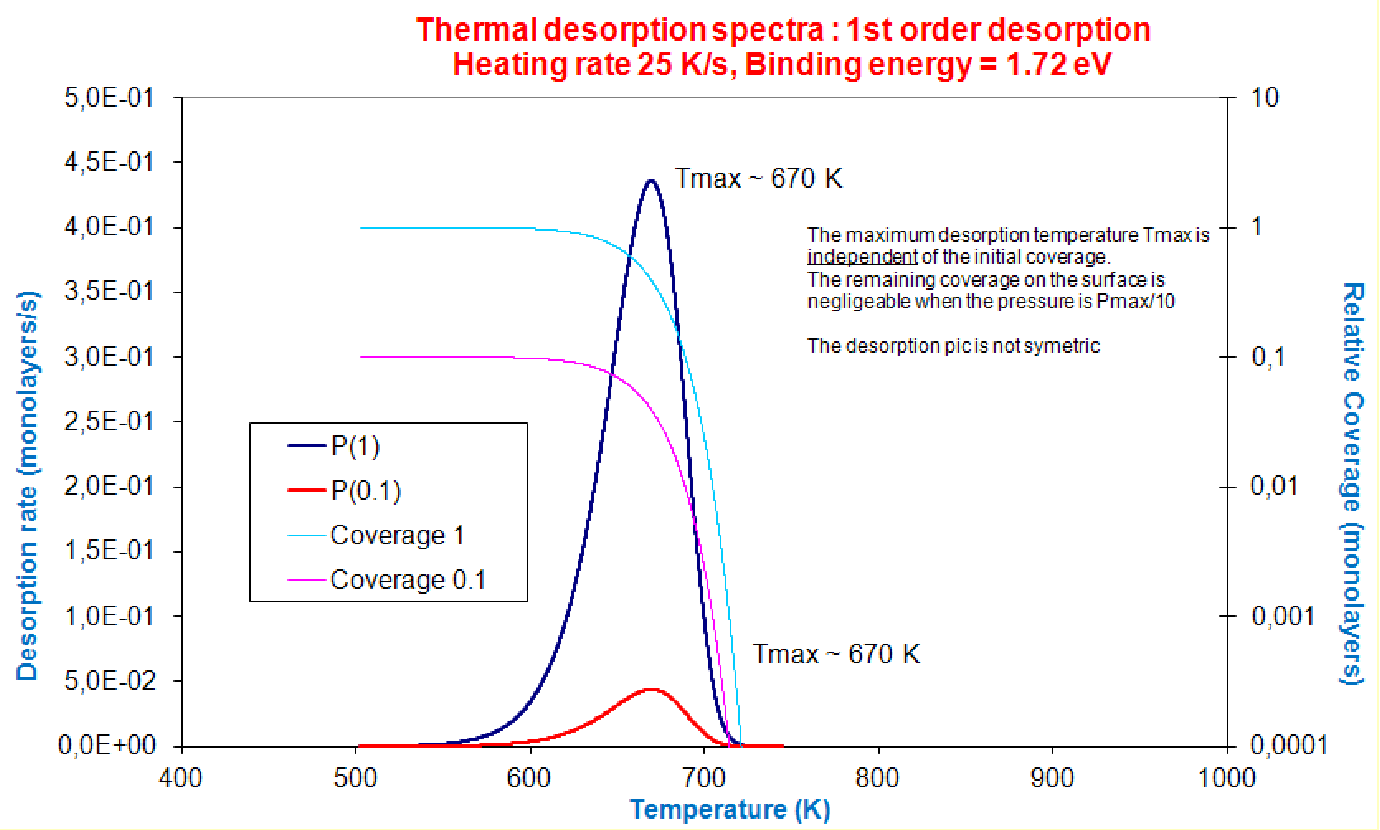
  - For second order:

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

- Solving the above equations with β and Tp as inputs give the activation energy

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



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

Evaluation of the activation energy

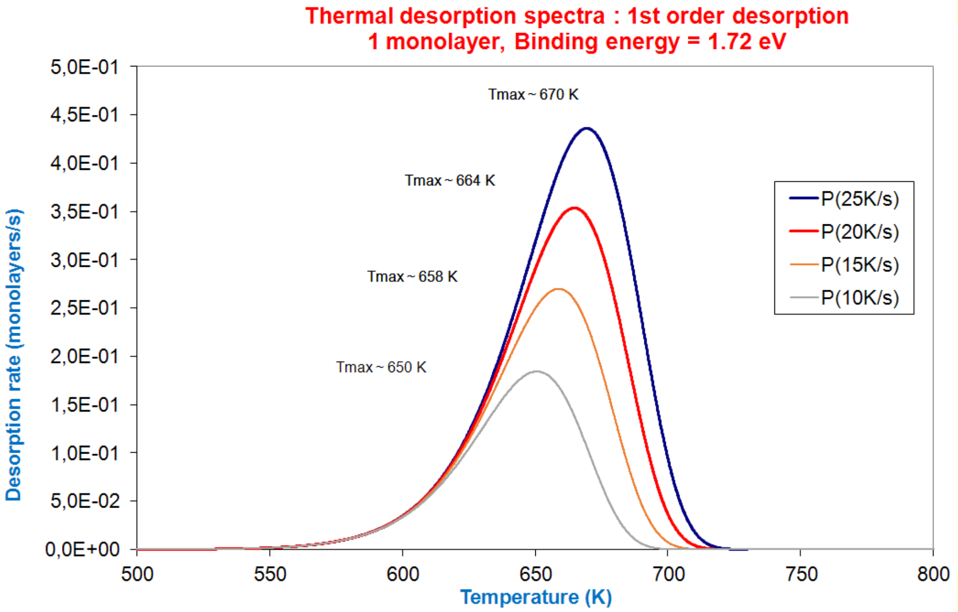
- Measure with several heating rates
- First order

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

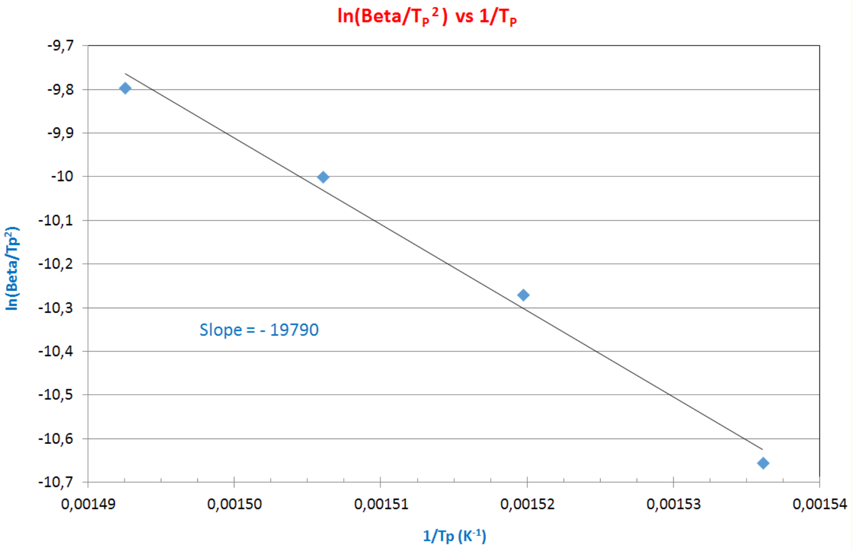
- Taking natural log and rearranging

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

- Plot ln(β/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

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:

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

- With τ0 the oscillation period of the molecules on the surface ~ 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_2O - Sojourn time

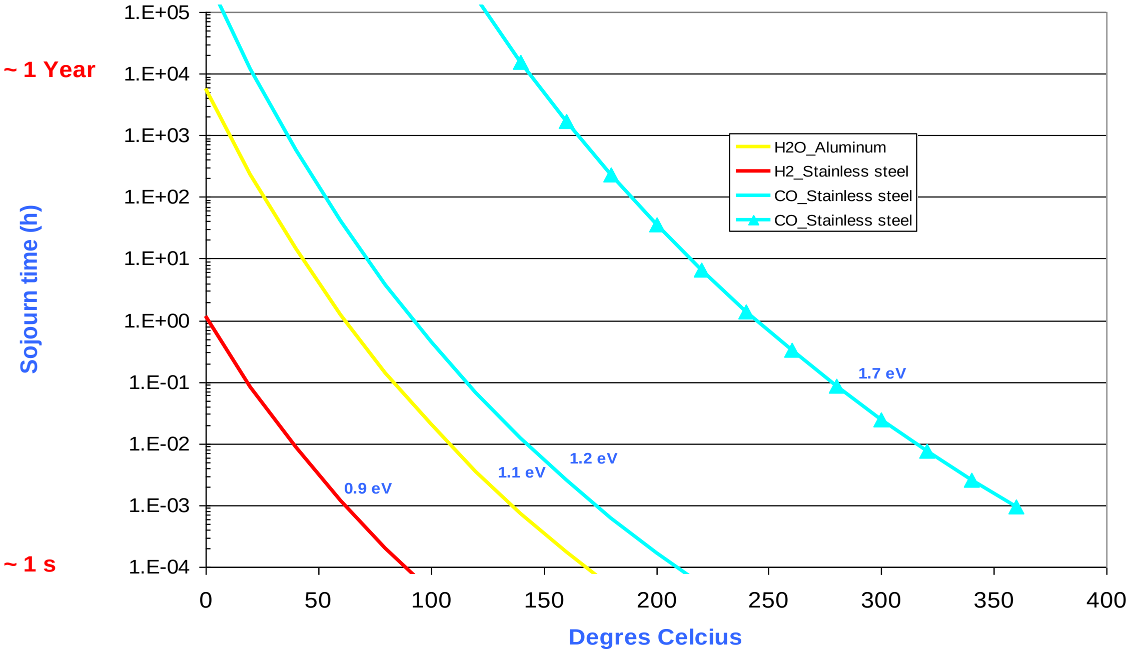
- At room temperature, the sojourn time of water on the surface is very large ~ 1 week
  - The surface coverage of water is therefore reduced by 1/e in a week

- 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



2. Outgassing

2.1 Unbaked system

Unbaked system: water outgassing

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

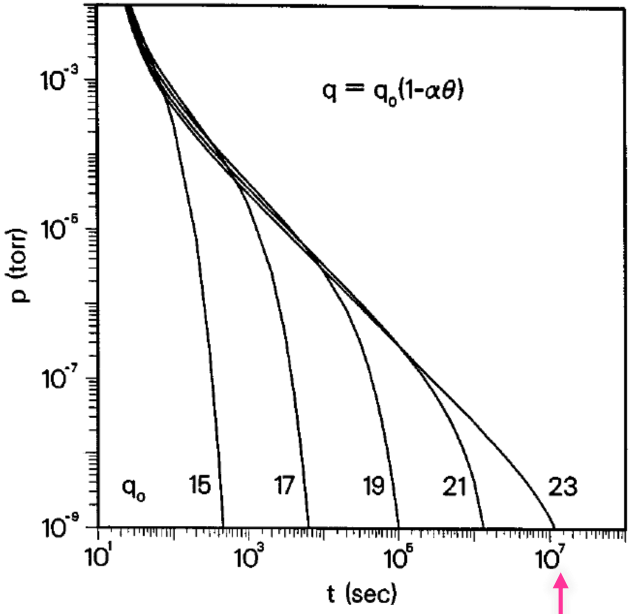
$$\boxed{q(t) = q_0\, t^{-a}}$$

- In practical units

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

- 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)

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



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

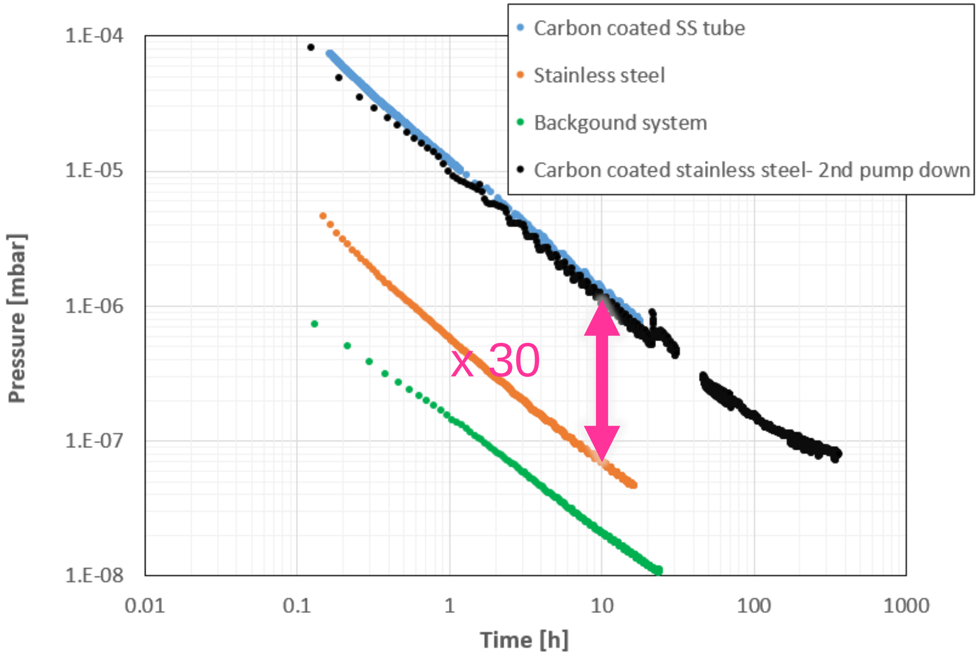
  ~ x 30 unbaked stainless steel

  2nd pump down very similar to 1st one

After 10h pumping:

Stainless steel = 2 10^{-10} mbar.l/s/cm^2

a-C coating = 6 10^{-9} mbar.l/s/cm^2



Courtesy I. Wevers

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

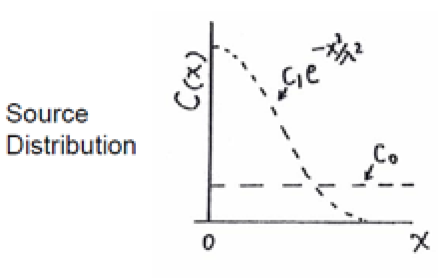
- Mechanical polishing or electropolishing are used to reduce the outgassing rate of materials

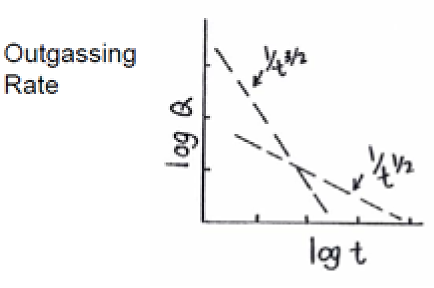
Water outgassing & exposition to water

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

- The exponent, a, varies with the quantity of water exposed:
  - large water exposure (17 ML): 1.3
  - ambiant air (8L): 1
  - 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





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

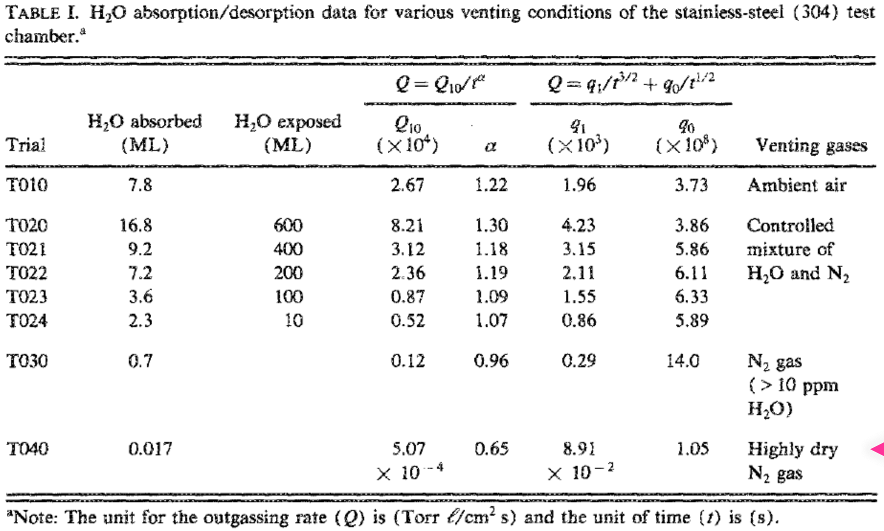


TABLE I. H_2O absorption/desorption data for various venting conditions of the stainless-steel (304) test chamber.[a]

Trial	H_2O absorbed (ML)	H_2O exposed (ML)	$Q = Q_{10}/t^\alpha$		$Q = q_1/t^{3/2} + q_0/t^{1/2}$		Venting gases
			Q_{10} ($\times 10^4$)	α	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 mixture of H_2O and N_2
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_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 ℓ/cm^2 s) and the unit of time (t) is (s).

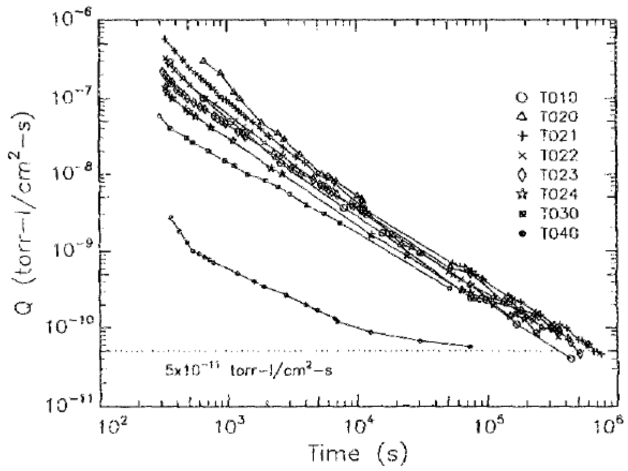


FIG. 2. Outgassing measurements for different H_2O exposures in a log (Q) vs log(t) plot. (See Table I for key to trial numbers, T010-T040.)

Venting with dry N2 reduces pump down times

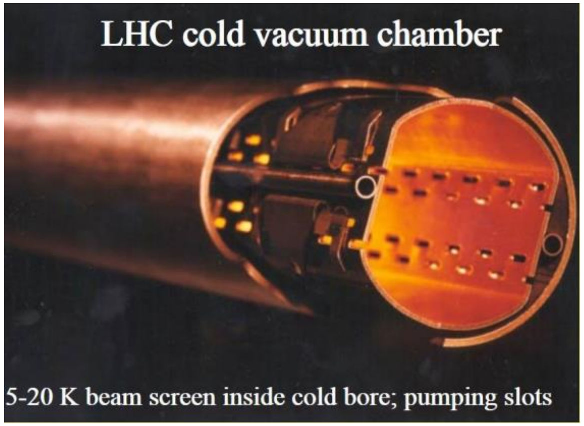
Typical design value of outgassing rates

- The outgassing rate of unbaked surfaces is dominated by $H_2$0.

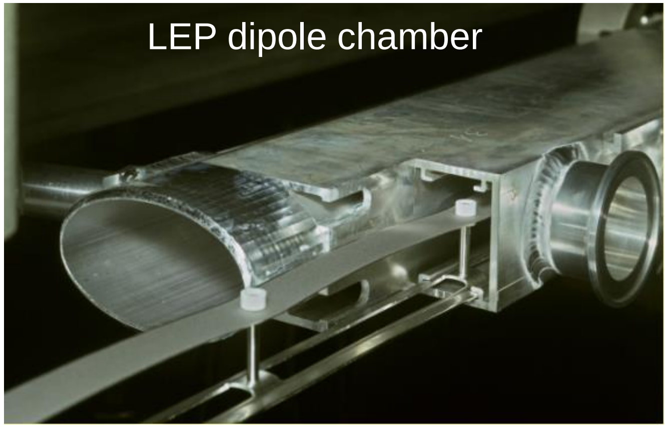
- For metallic surfaces, unbaked after 10h of pumping ($Torr.l.s^{-1}.cm^{-2}$)

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

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

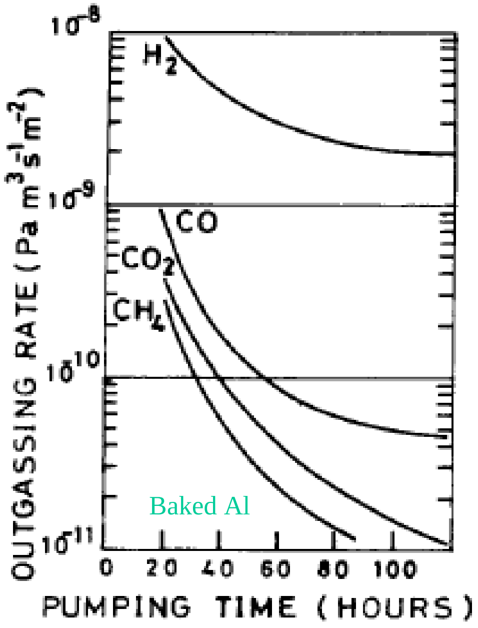
- The sojourn time decrease strongly with increasing temperature
- Heating the material allows a degassing of molecules with binding energies < 2 eV

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
  ➔ those molecules will be available for subsequent desorption by e.g. ion bombardment

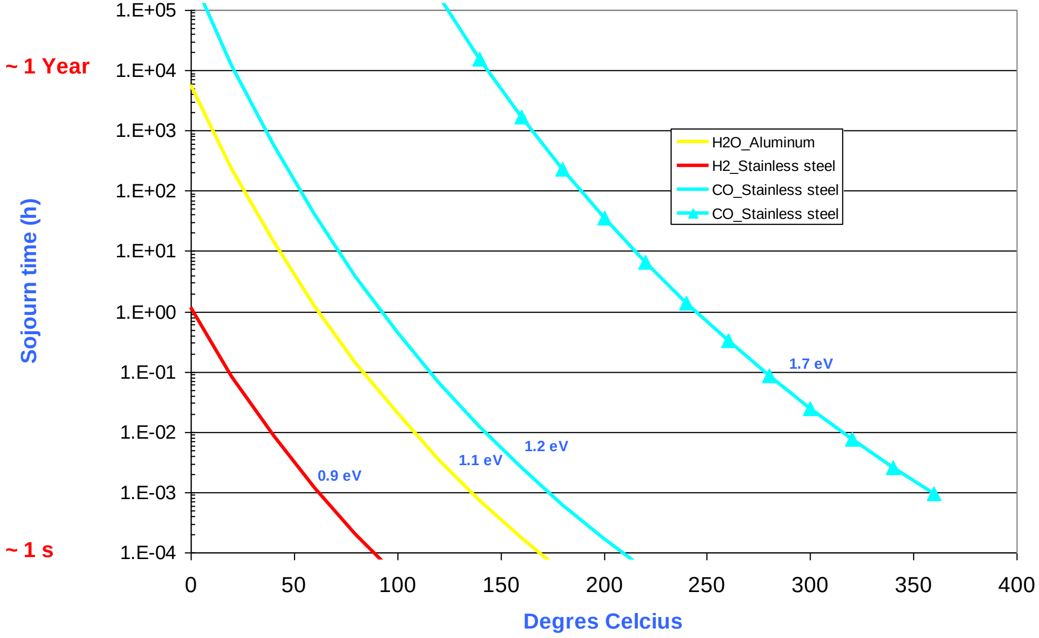
In Situ Bake Out

- A bake-out above 150 degrees increase the desorption rate of H_2O and reduce the H_2O sojourn time in such a way that H_2 become the dominant gas



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

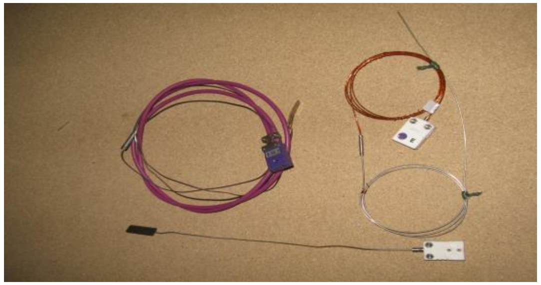
$$\tau = \frac{e^{\frac{E}{kT}}}{\nu_0}$$



Sojourn time of a molecule as a function of temperature

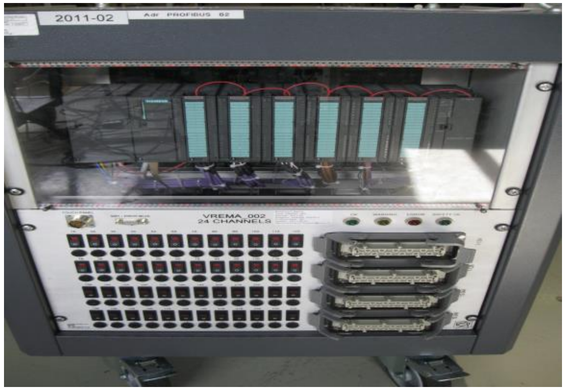
Material for bakeout

Collars



thermocouples

bakeout jackets



racks

heating tape

Storage area

Amount of gas removed after a bake-out

- After a laboratory bake-out of a stainless steel chamber at 200ºC 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:

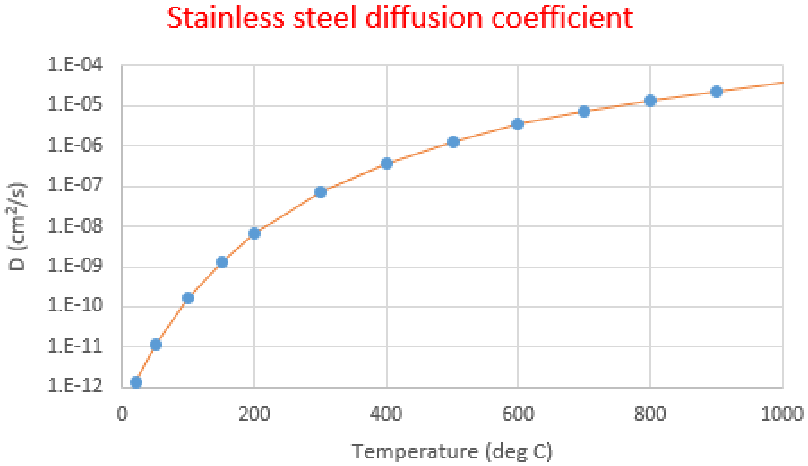
$$D(T) = D_o e^{-E_{diff}/kT}$$

- In 304L, 316L stainless steel:

T°C	20	900
D [cm²/s]	$1.4\ 10^{-12}$	$2.3\ 10^{-5}$

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

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



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

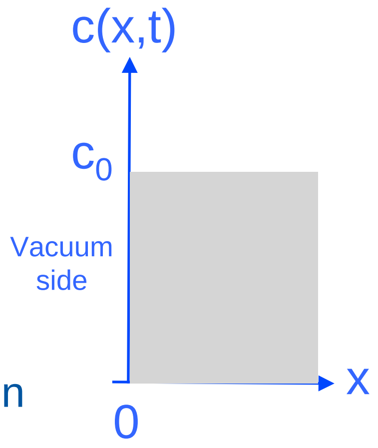
  - 1st Law: The gaseous flux, q, is equal to the production of the diffusion coefficient, D, by the gradient of hydrogen concentration

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

  - 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.* $c(0,t)=0$

- 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 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

- 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:

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

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

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

L (mm)	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

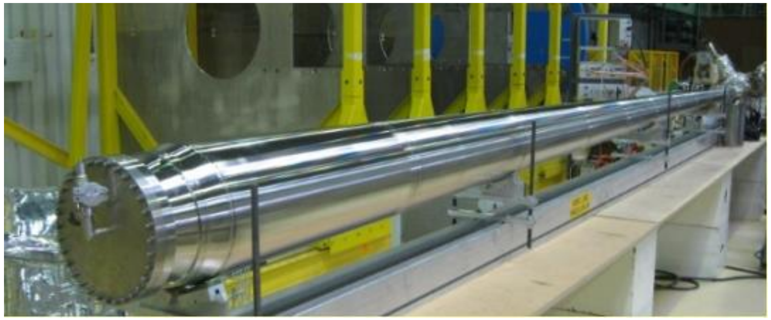
Typical design value outgassing rates

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



CMS End cap chamber

Copper tubes

Successive bakeout of a finite slab

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

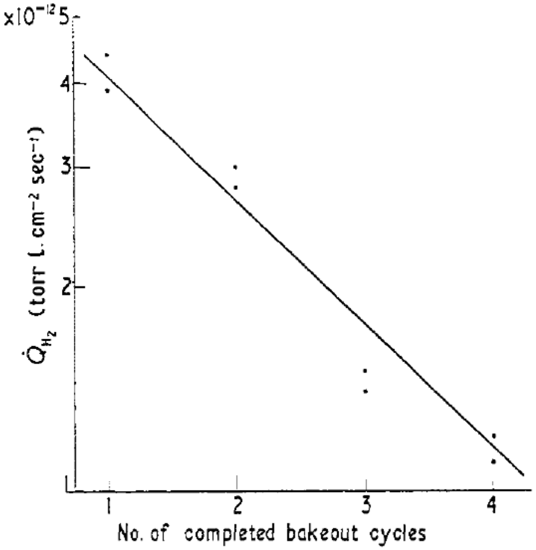
$$\boxed{q_n(t) = \frac{4\, c_o\, D(T_{RT})}{L}\, e^{-n\left(\frac{\pi}{L}\right)^2 D(T_{BO})t_{BO}}}$$

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:

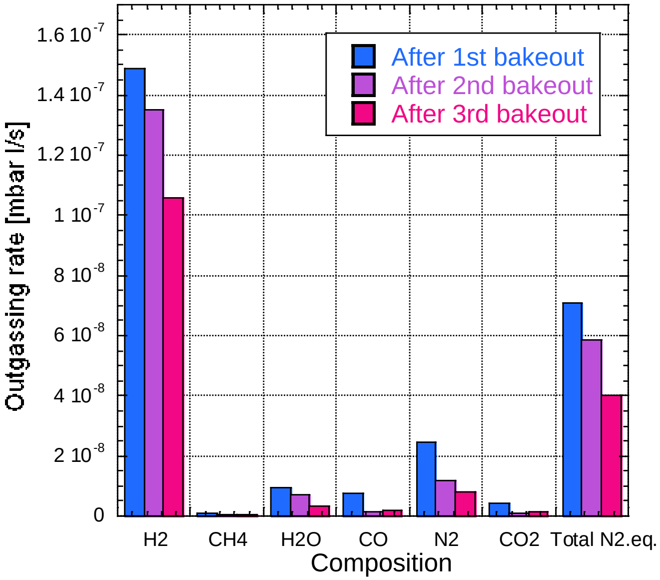
$$\boxed{\frac{q_{n+1}(t)}{q_n(t)} = e^{\left(\frac{\pi}{L}\right)^2 D(T_{BO})t_{BO}}}$$

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



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

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



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:

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

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

- Baked stainless steel:

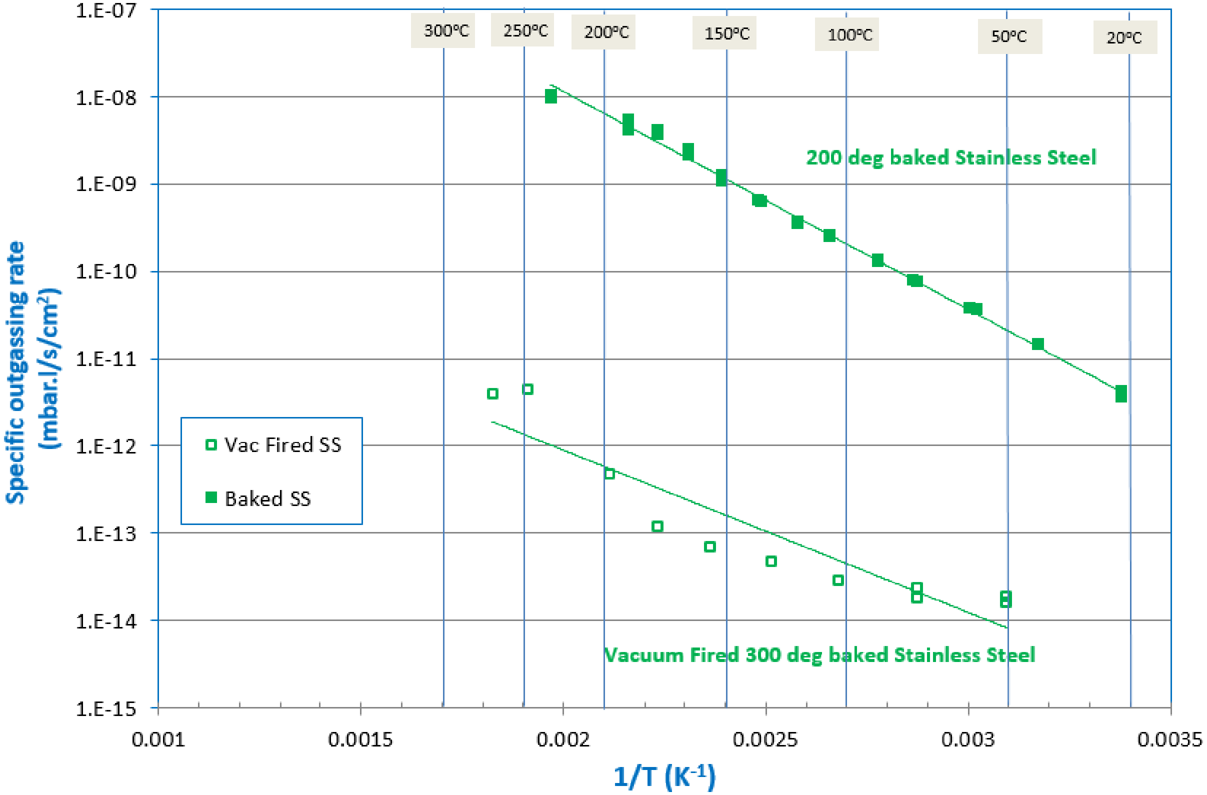
  E_a ~ 0.5 eV

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

- Vacuum fired baked s. steel:

  E_a ~ 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 the material in 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

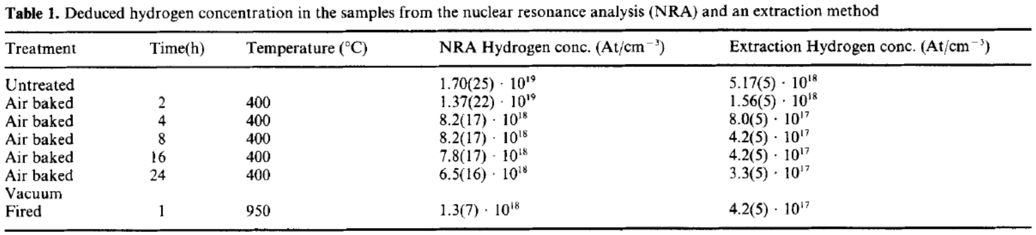


Table 1. Deduced hydrogen concentration in the samples from the nuclear resonance analysis (NRA) and an extraction method

Treatment	Time(h)	Temperature (°C)	NRA Hydrogen conc. (At/cm^{-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 ~ 2 10^{19} H/cm^3 reduced to 10^{18} H/cm^3

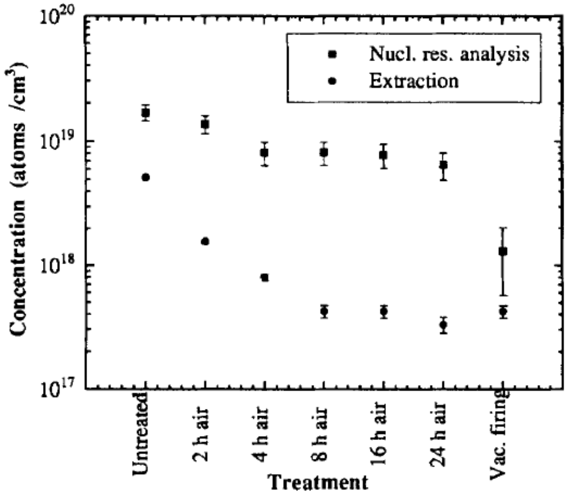


Figure 1. The average hydrogen concentration in the 0.05–0.7 μm depth range of the virgin, air baked and the vacuum fired samples. The results from the extraction method are also included.

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:

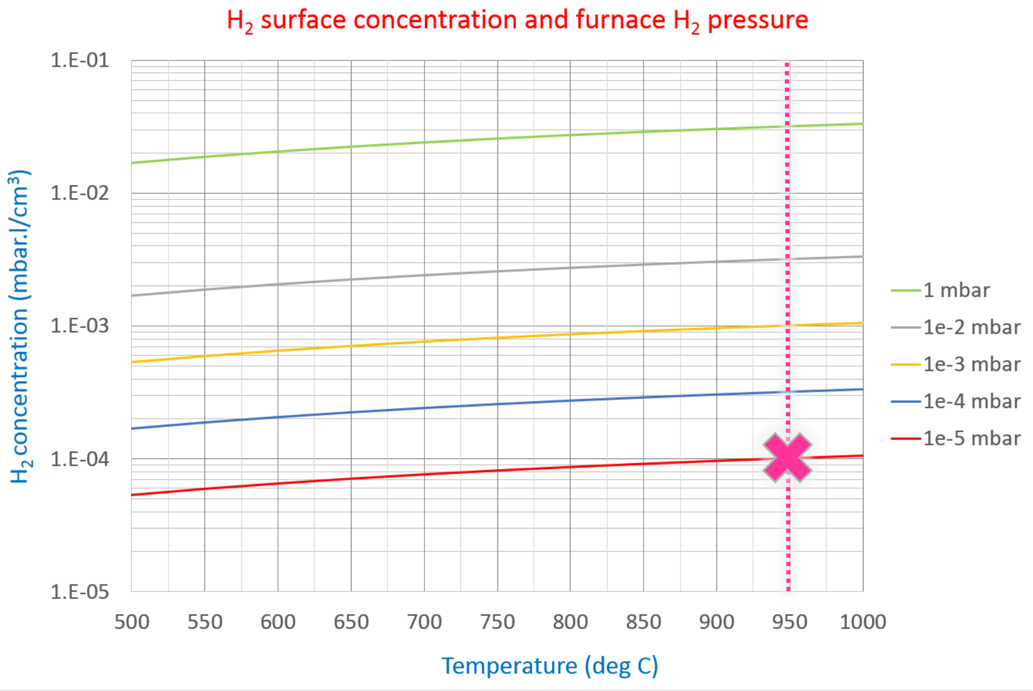
$$c_F = 3\sqrt{P}\, e^{-\frac{E_S}{k\,T}}$$

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 10^{15} H/cm^3

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



Subsequent bakeouts following vacuum firing

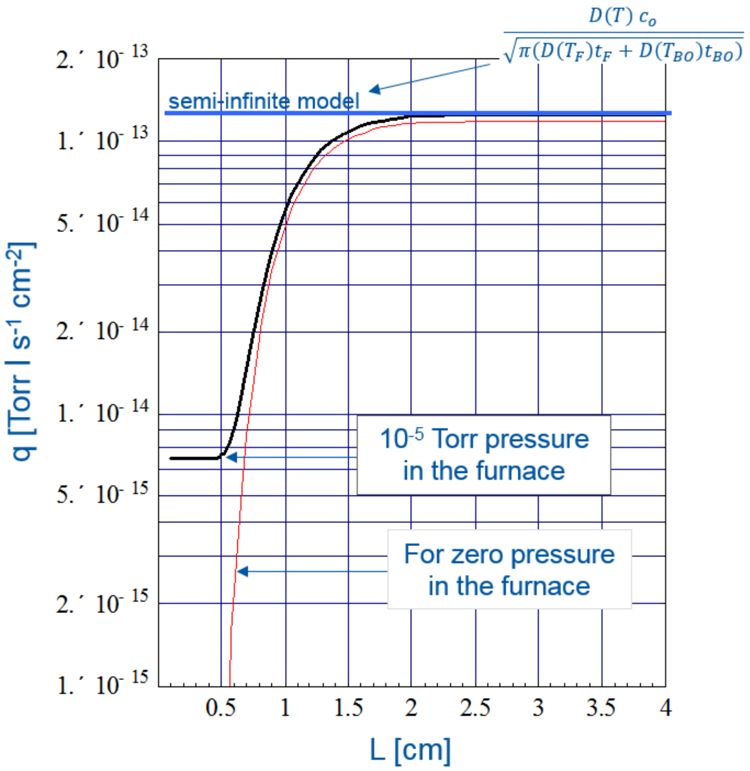
- As previously, taking into account the achieved hydrogen surface concentration following the vacuum firing, the hydrogen outgassing rate after n successive bakeout at temperature T_{BO} and duration t_{BO} is obtained from the 1st Fick Law: $q(t) = D\left(\frac{\partial c(x,t)}{\partial x}\right)_{x=0}$

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

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:
  $q \sim 5\ 10^{-15}$ mbar.l/cm²

- For thick slab, the pressure in the furnace as limited influence:
  $q \sim 10^{-13}$ mbar.l/cm²

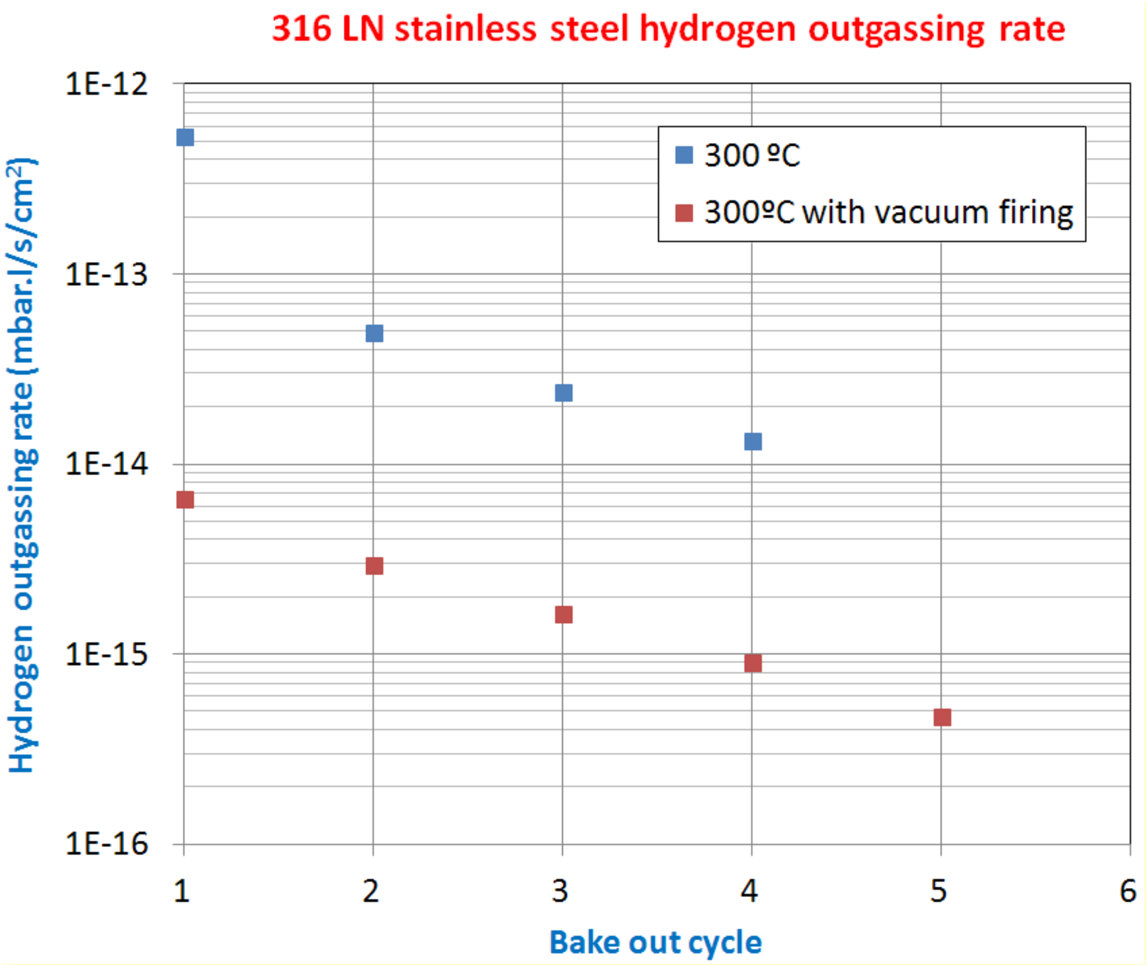


$$\frac{D(T)\, c_o}{\sqrt{\pi(D(T_F)t_F + D(T_{BO})t_{BO})}}$$

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



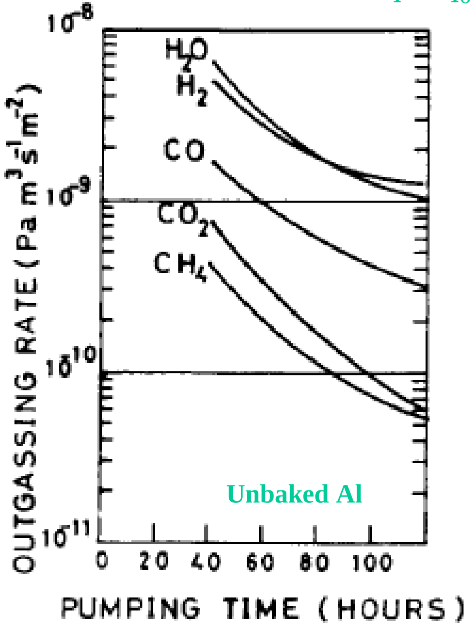
B. Versolatto, N. Hilleret, CERN Vacuum Technical Note 2002

2.4 Other materials

Outgassing of plastics

- Plastic material are highly porous and contains much more water than metalic 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

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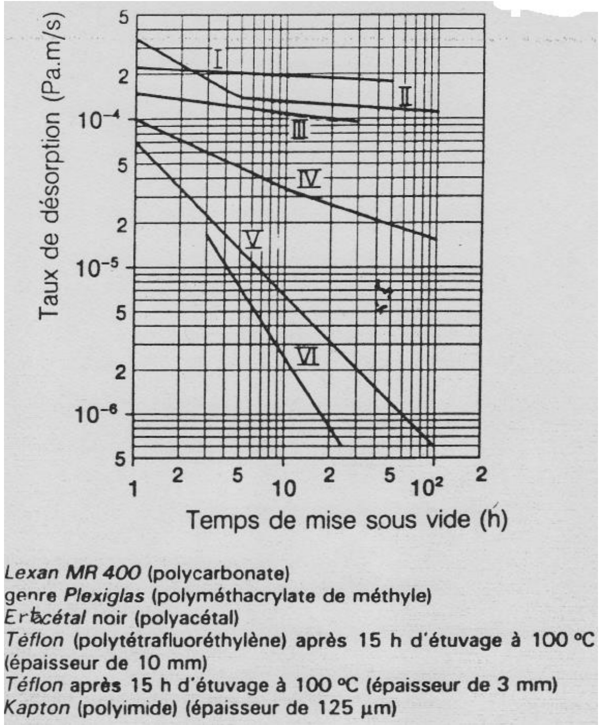
Plastic surfaces $q \sim q_0/\sqrt{t}$



Lexan MR 400 (polycarbonate)
genre *Plexiglas* (polyméthacrylate de méthyle)
Ertacétal 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

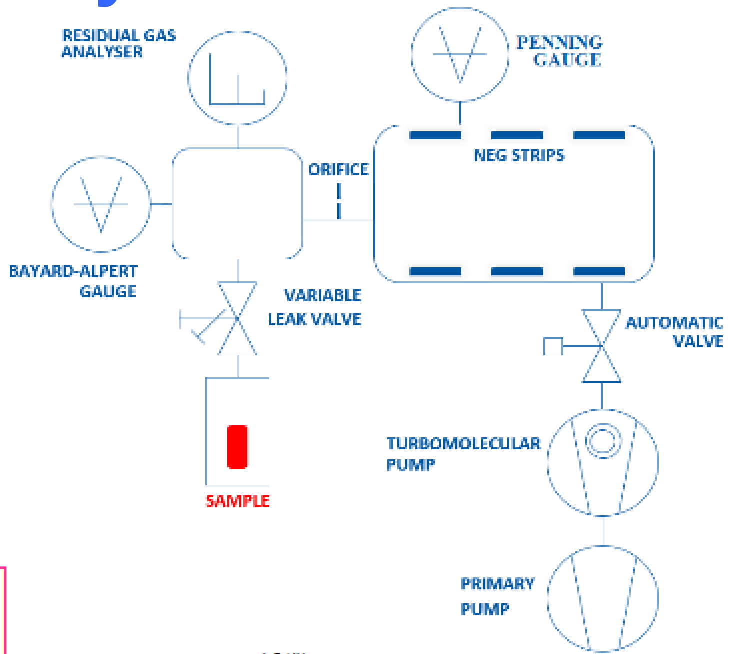
Outgassing measurement by Accumulation

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

- Gas accumulates into the sample chamber

- After some accumulation time t_{acc}, the leak valve is opened and the mass spectra measured

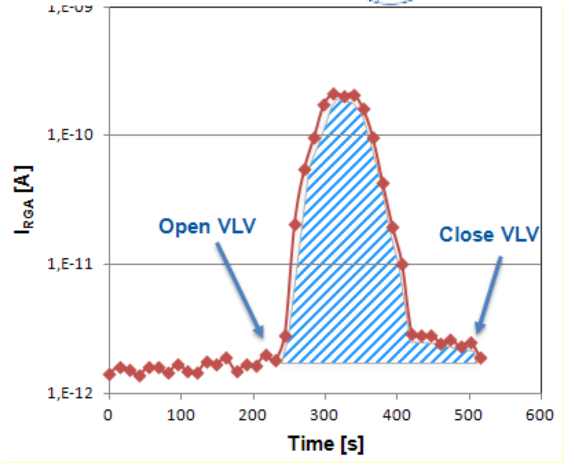
- The leak valve is closed again and the procedure repeated every 1 to 72 h



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

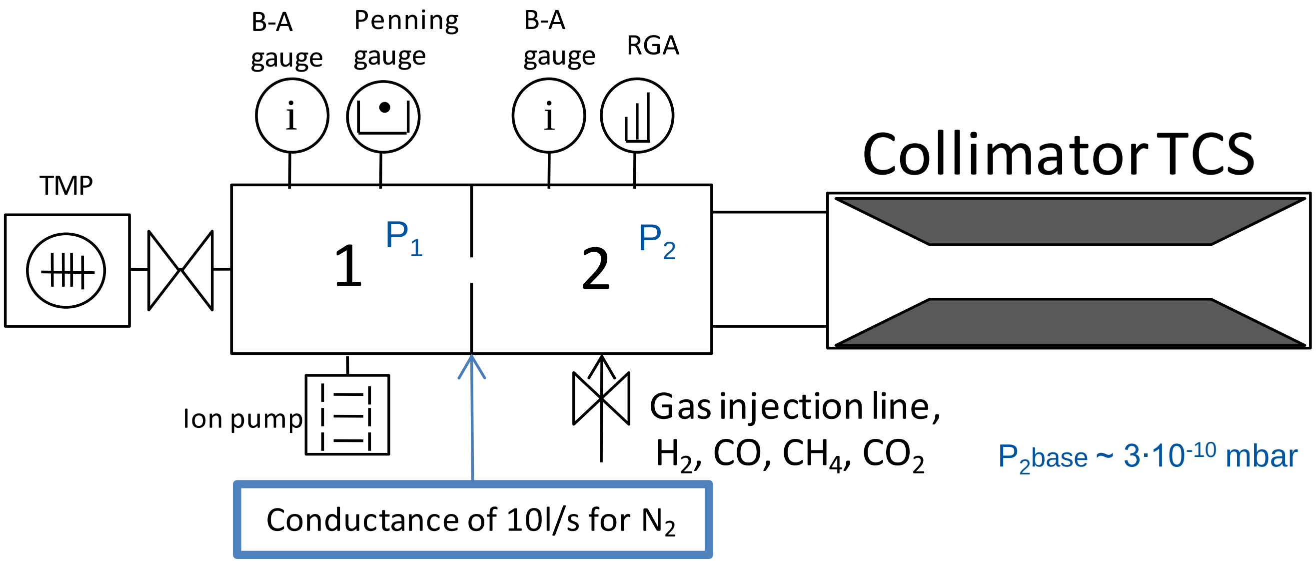
- With:
  - S_i the pumping speed for gas, i
  - α the RGA calibration factor for gas, i
  - I_{RGA} the current recorded during the leak valve opening
  - Δt the RGA recording duration
  - Δt_{ac} the accumulation time

- Sensitive measurement



Courtesy I. Wevers

Outgassing measurement - Throughput



P_2base ~ $3\cdot10^{-10}$ mbar

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

$$\boxed{Q_{N2eq} = C\,(P_2 - P_1)}$$

In N_2 equivalent no RGA is needed!

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

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

↓

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

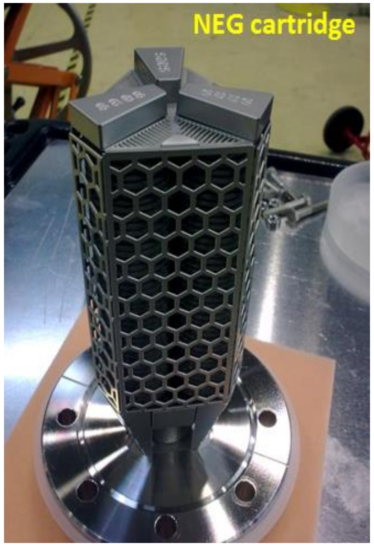
α the RGA calibration factor for gas, i

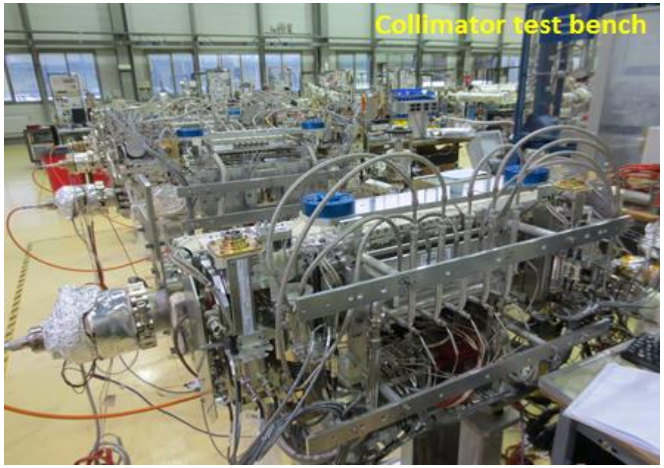
I_i the RGA current for gas I

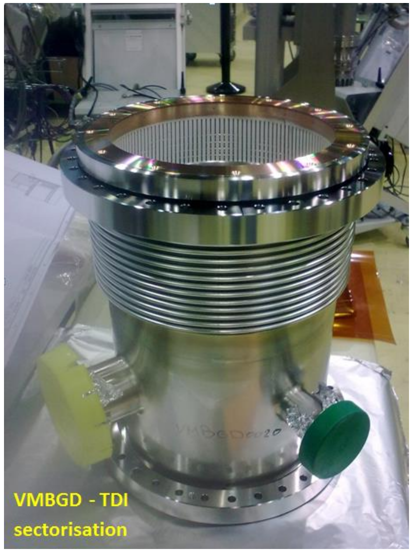
c_i the conductance for gas i

Vacuum Acceptance Test Laboratory

Example of tested parts

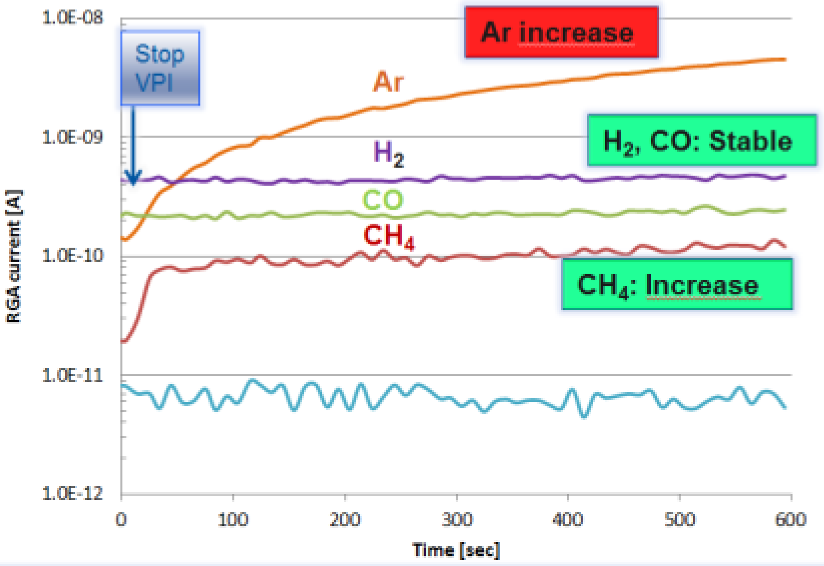




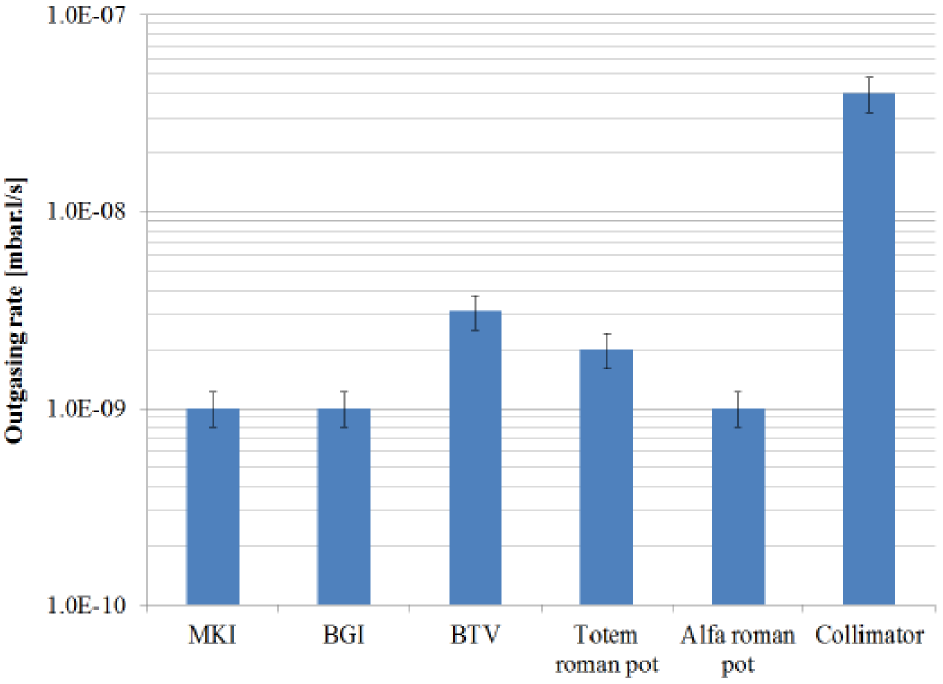


Vacuum Acceptance Tests

- 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 whilst pumping with NEG system



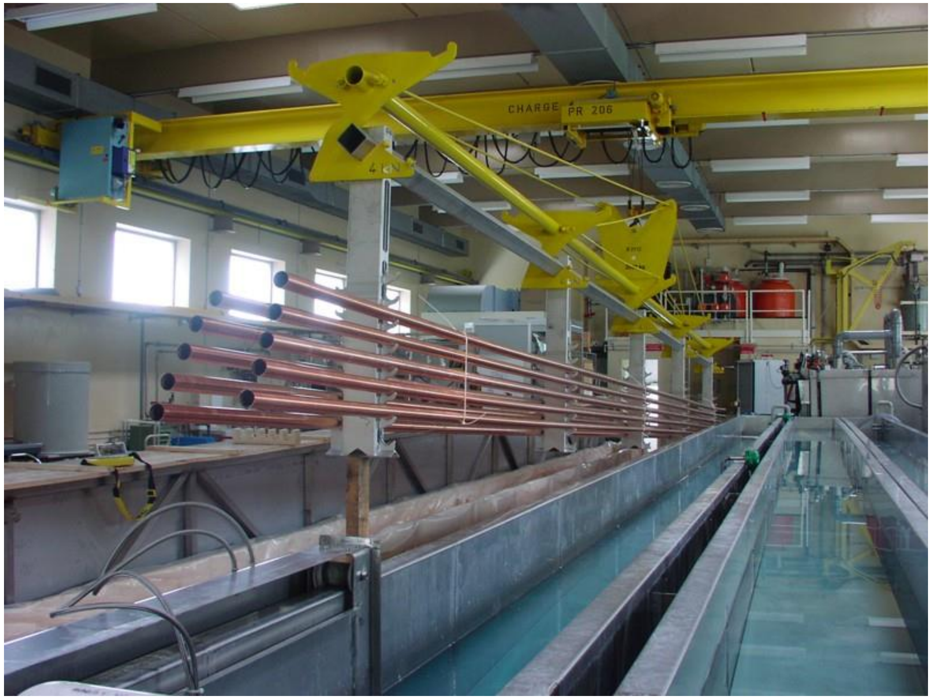
Outgassing rate of some LHC components

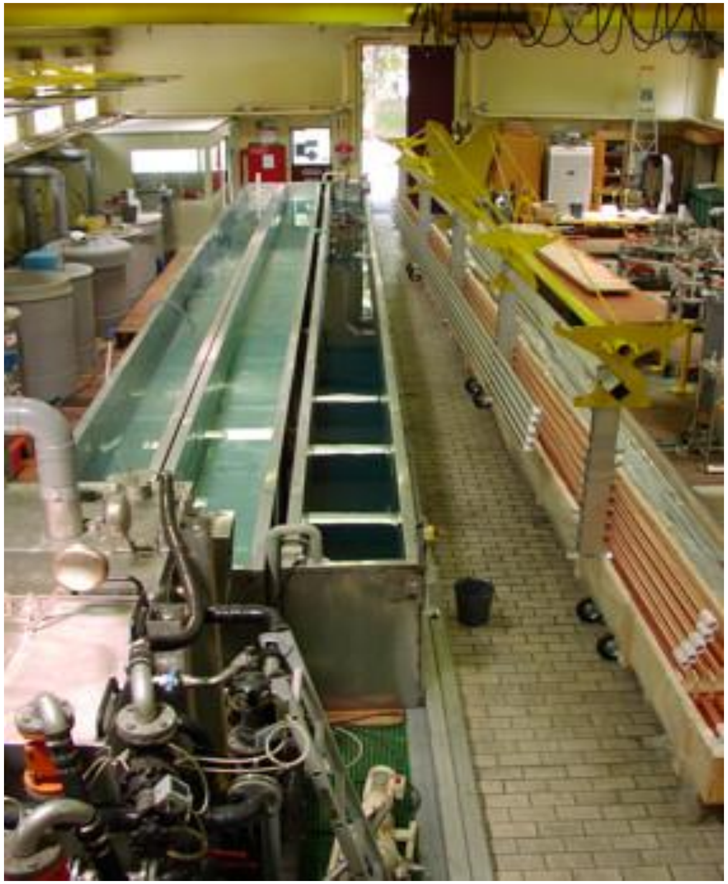
G. Cattenoz *et al.* , Proceeding of IPAC'14, Dresden, Germany

Cleaning Methods

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

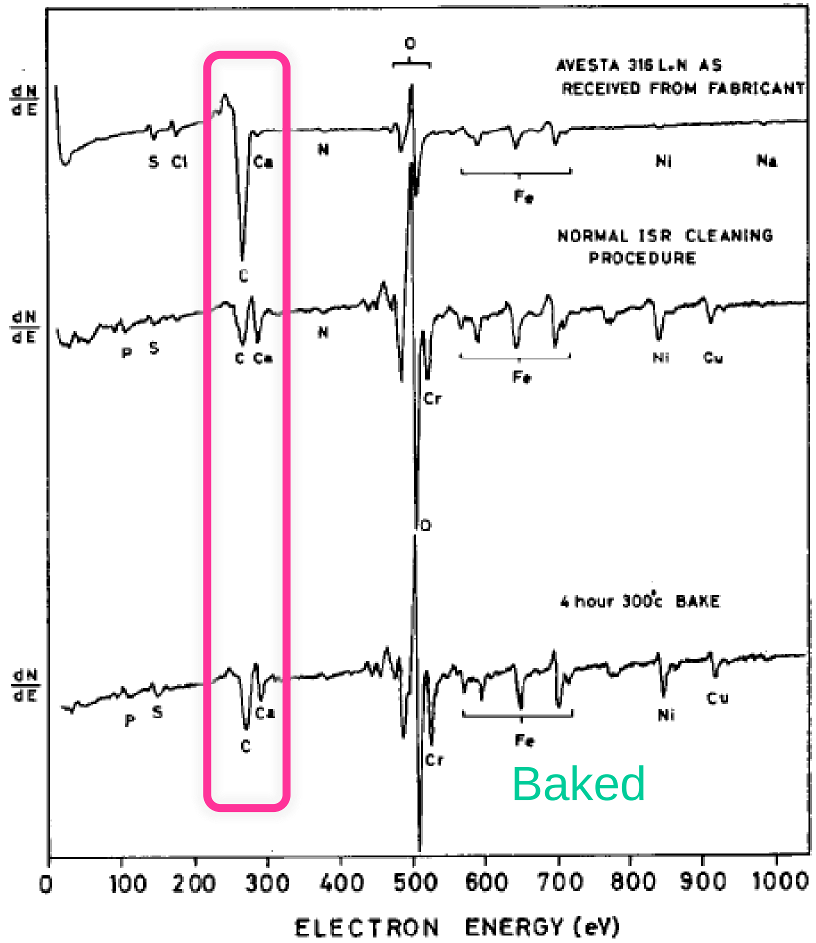
- Example of CERN LHC beam screens :
  - Degreasing with an alkaline detergent at 50°C in an ultrasonic bath
  - Running tap water rinse
  - Cold demineralised water rinse by immersion
  - Rinse with alcohol
  - Dry with ambient air





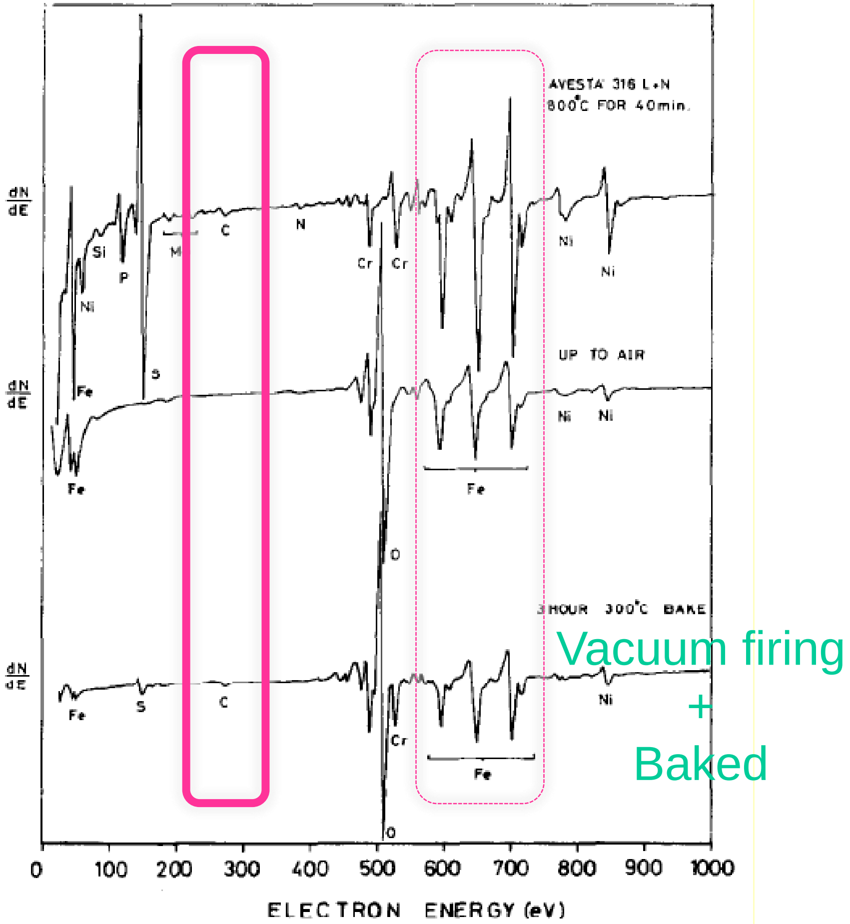
C content after chemical cleaning and vacuum firing

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



Baked

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).



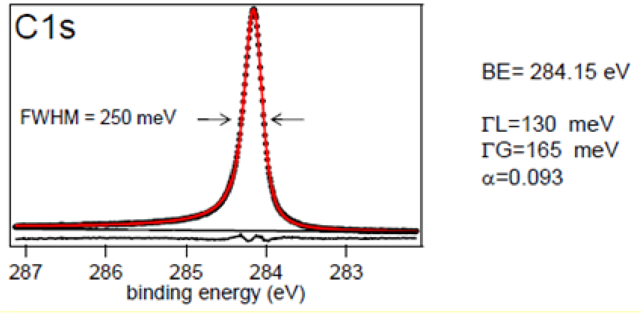
Vacuum firing
+
Baked

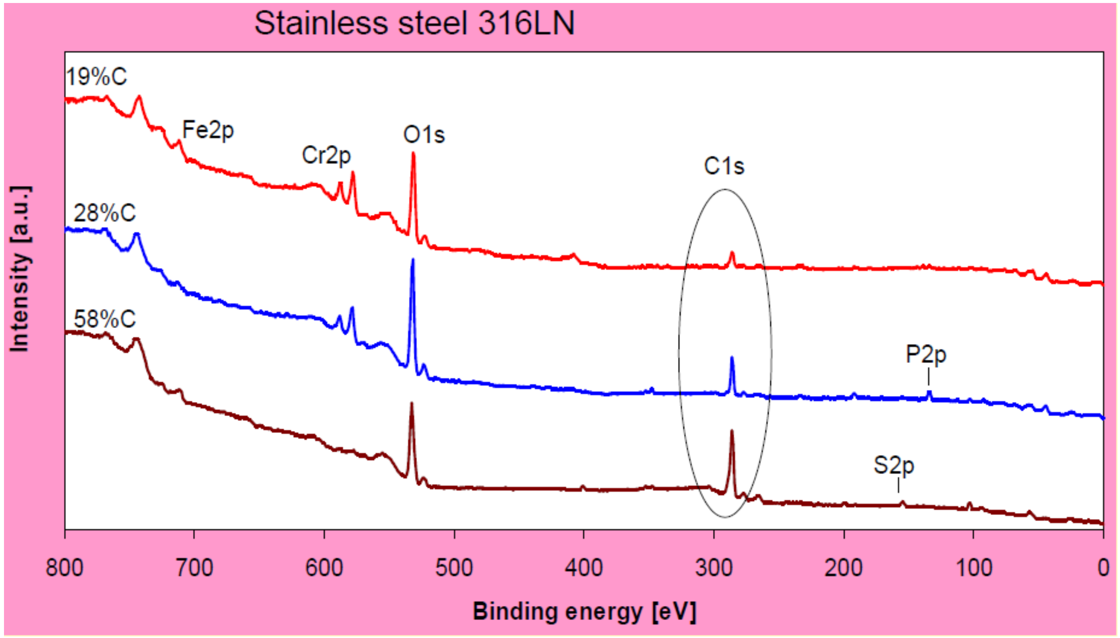
Figure 3. Auger spectra from a 316 L + N stainless steel specimen after heating to 800°C for 40 min *in vacuo* (top), after exposing to air (centre) and after a 3 h 300°C bake (bottom).

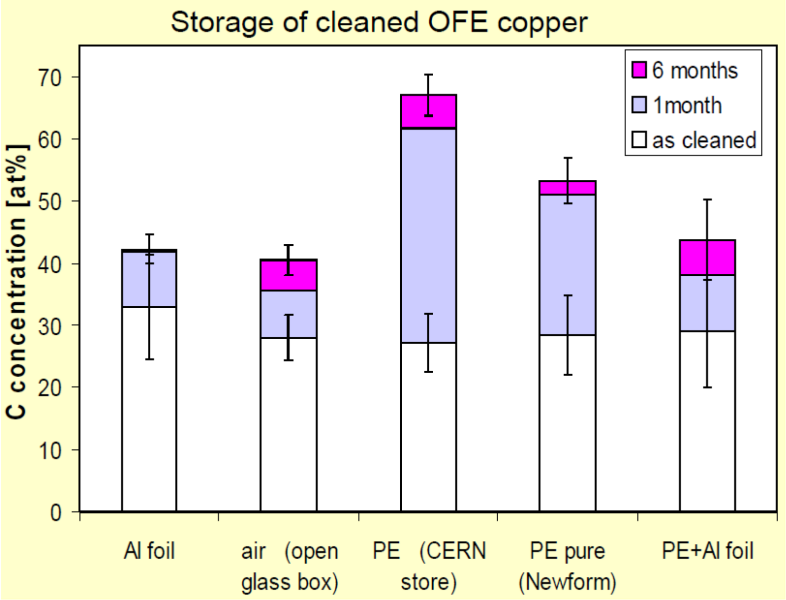
The surface cleanliness of 316 LN stainless steel studied by SIMS and AES, A. G. Mathewson, Vacuum 24 (1974) 505

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







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 biding 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

- 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
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- 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 !!!

CERN

Complementary information

1. Elements of adsorption/desorption

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

2nd order desorption

Complementary information

- 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:

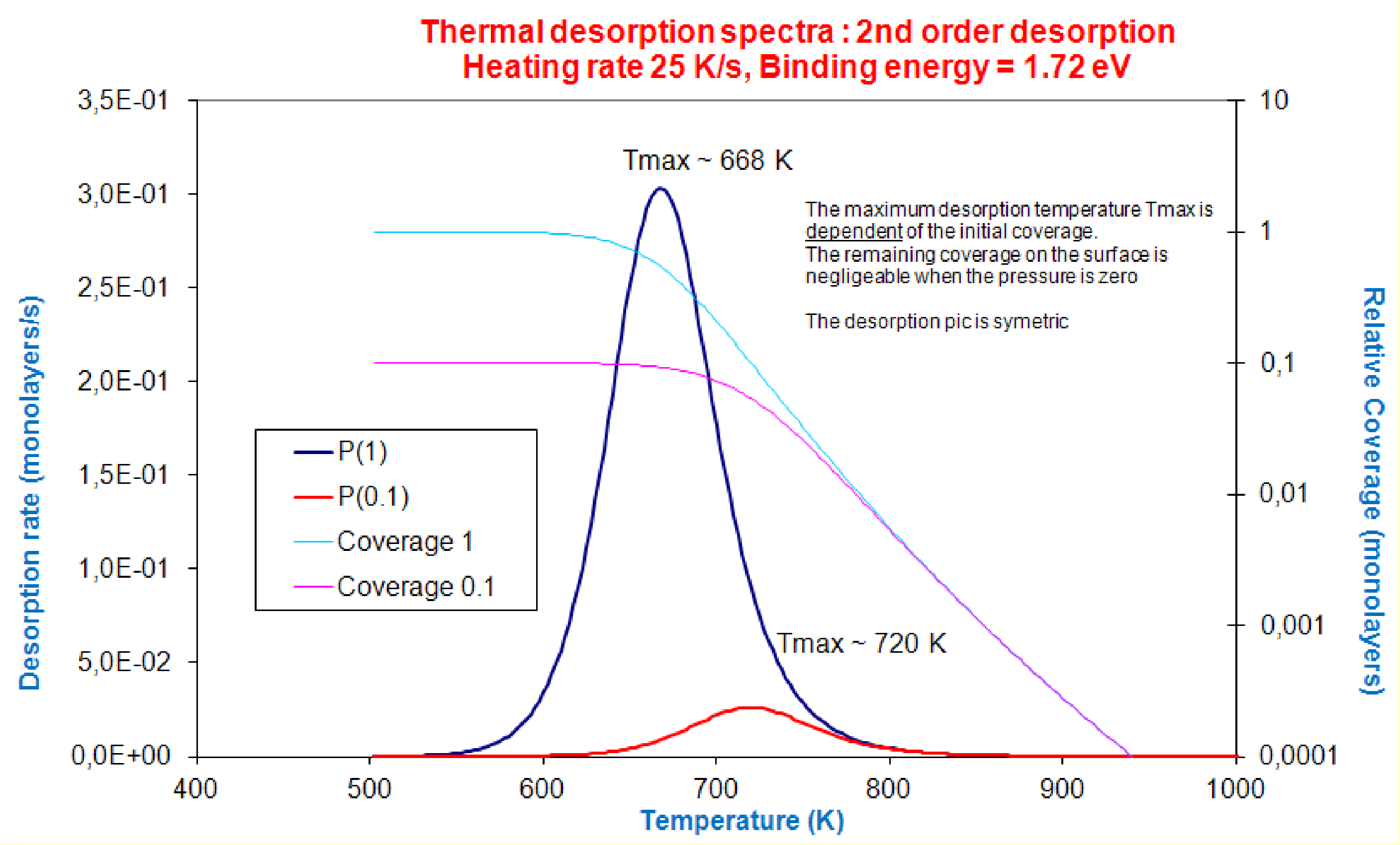
$$-\frac{d\theta}{dt} = \upsilon_2 \theta^2 e^{-E_D/kT}$$

- θ, surface coverage, v_2, second order rate desorption constant (10^{-2} cm^2/s), E_D, activation energy for desorption

TDS spectra: 2nd Order

Complementary information

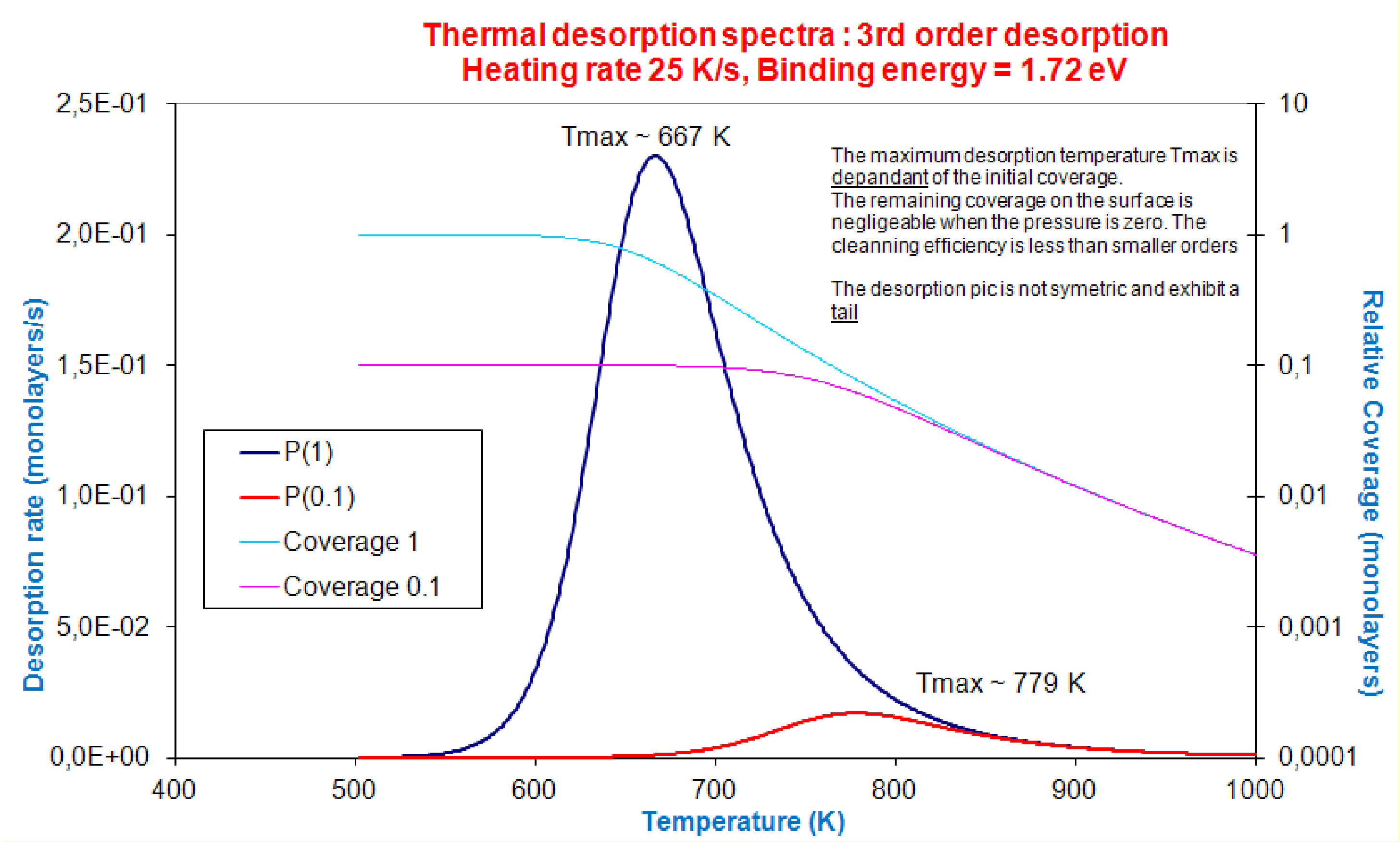
- The maximum temperature is dependent of the initial surface coverage
- The remaining coverage on the surface is negligeable when the pressure is 0.
- The desorption peak is symmetric



TDS spectra: 3rd 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



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

Tmax ~ 667 K

Tmax ~ 779 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

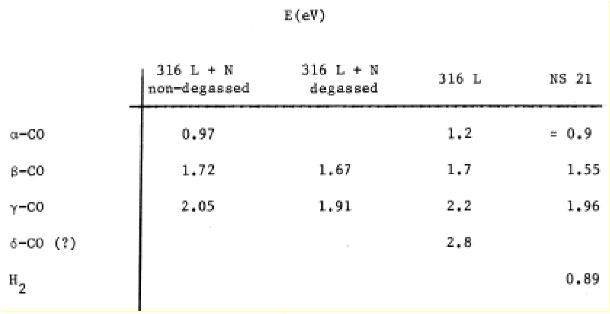
The desorption pic is not symetric and exhibit a tail

Some results of TDS

Complementary information

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

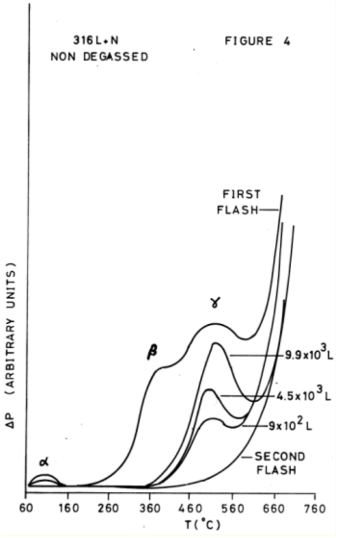
- 200°C bakeout
- H_2 is desorbed at different temperature
- H_2O is still present

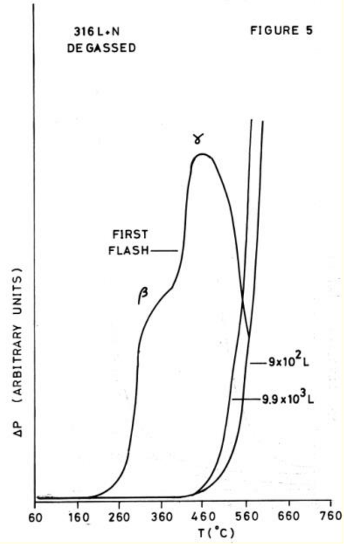


E(eV)

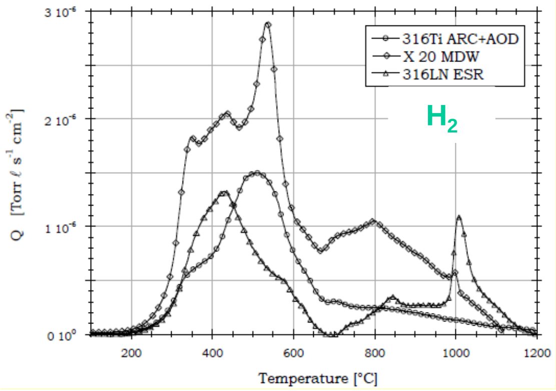
	316 L + N non-degassed	316 L + N degassed	316 L	NS 21
α-CO	0.97		1.2	≃ 0.9
β-CO	1.72	1.67	1.7	1.55
γ-CO	2.05	1.91	2.2	1.96
δ-CO (?)			2.8	
H_2				0.89

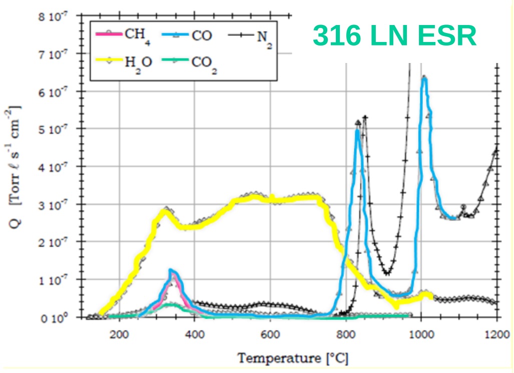
25 K/s

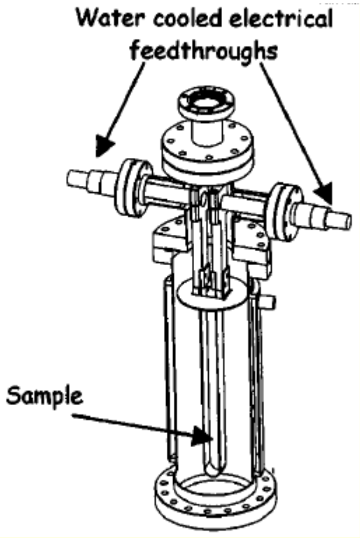




A.G. Mathewson *et al*, Proc. 7th Int. Vac. Congr, Vienna, 1977







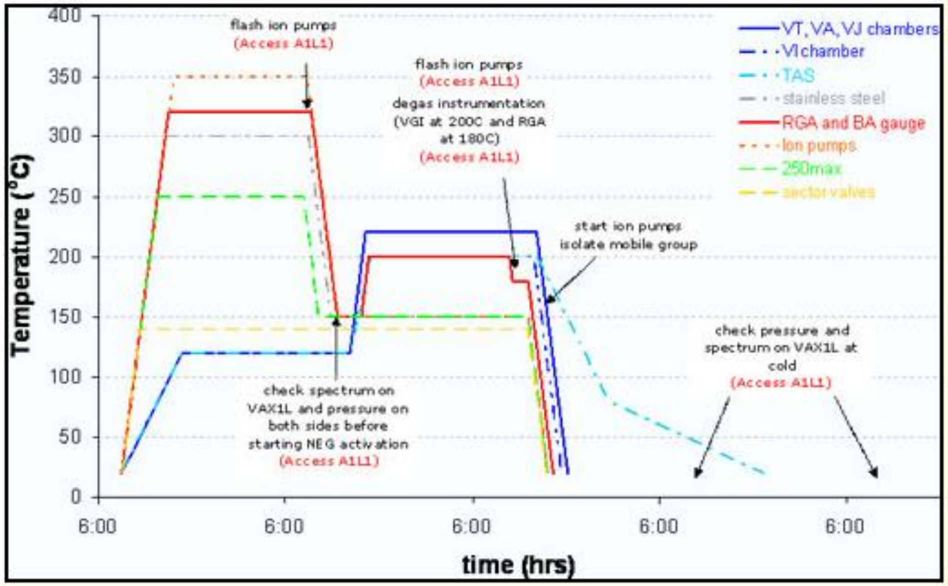
5 K/s

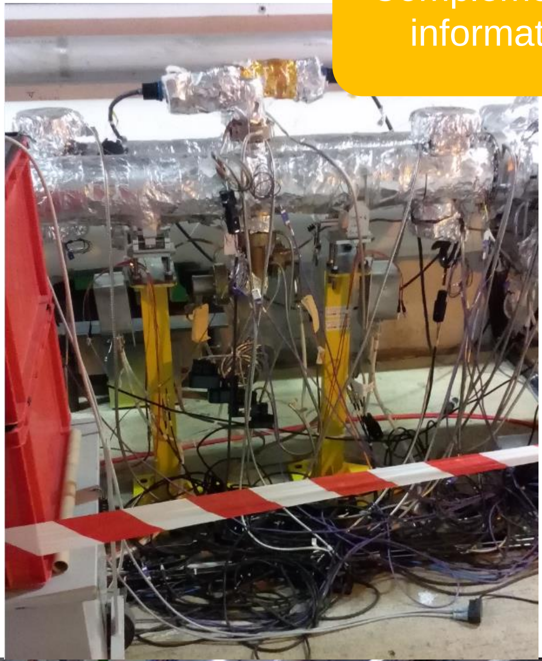
JP Bacher *et al*, JVSTA 21 Jan/Feb 2003, 167

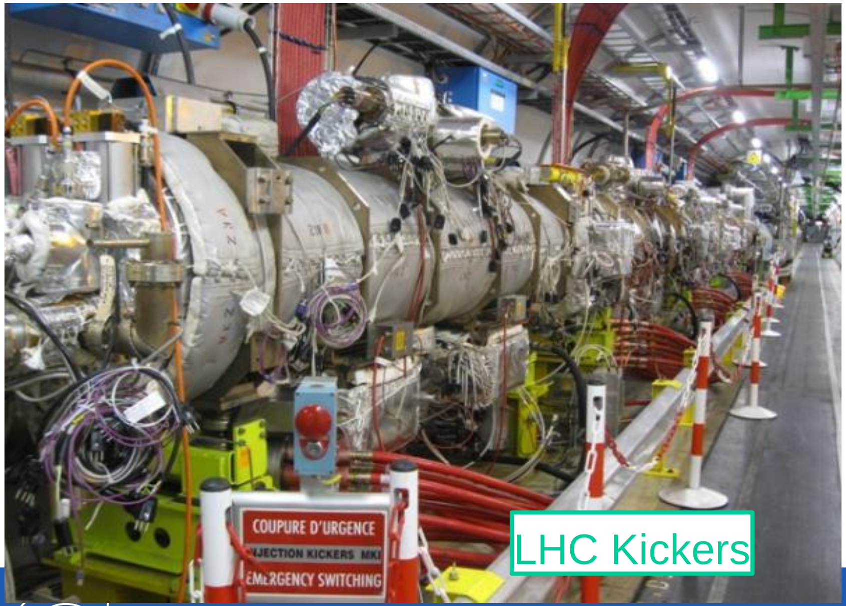
2.2 Baked system

Bakeout systems

Complementary information







LHC Kickers

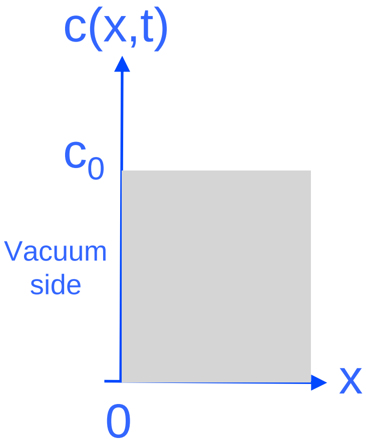
"Combined" sector
Both beams circulates in the same beam pipe

Diffusion in a semi-infinite slab

Complementary information

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

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

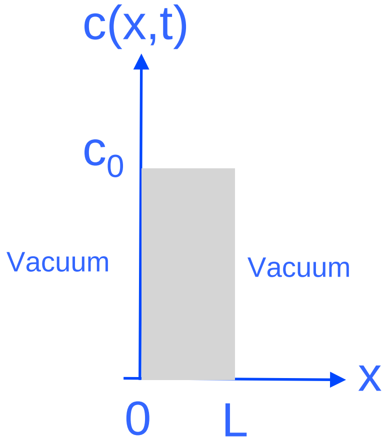


R.J. Elsey, Vacuum 25, 7 (1975), 299

Diffusion in a finite slab

Complementary information

- 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:

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

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

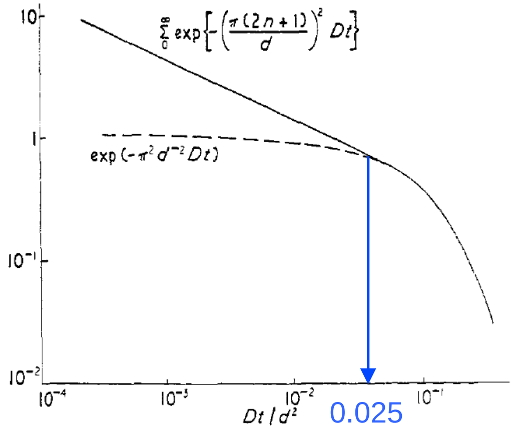
$$q(t) = 2\,D\left(\frac{\partial c(x,t)}{\partial x}\right)_{x=0} = \frac{8\,c_o\,D}{L} \sum_{n=0}^{\infty} e^{-\left(\frac{\pi(2n+1)}{L}\right)^2 Dt}$$

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

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

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

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



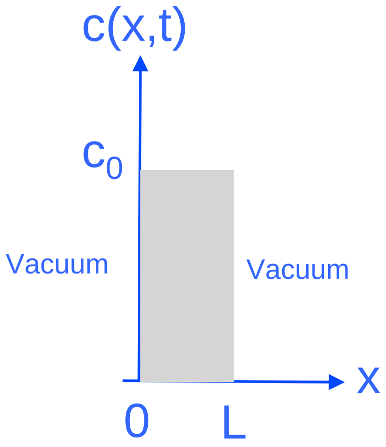
R. Calder, G. Lewin,
Br J Appl. Phys, 18, 1967, 1459

Diffusion in a finite slab

Complementary information

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

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

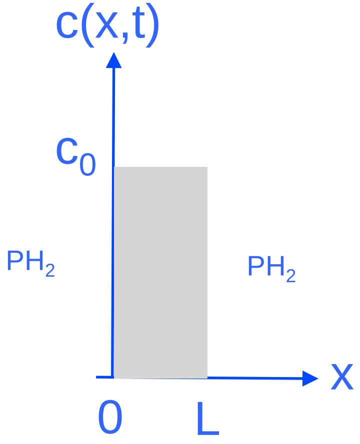


R.J. Elsey, Vacuum 25, 7 (1975), 299

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 2nd Fick law with these boundary conditions gives:

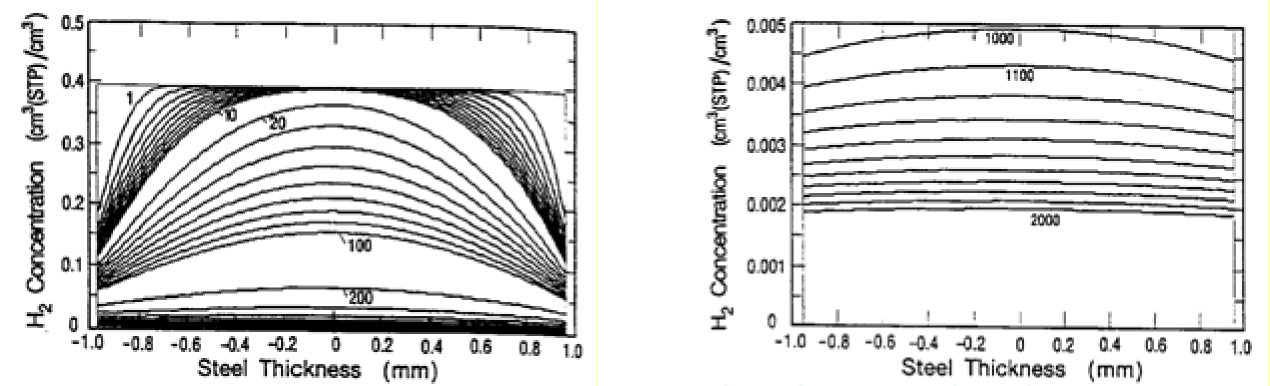
$$c(x,t) \approx c_F + (c_o - c_F)\,\frac{4}{\pi}\,sin\left(\frac{1}{L}\,\pi x\right)e^{-\left(\frac{\pi}{L}\right)^2 Dt}$$

- 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

Diffusion barrier: air baking

Complementary information

- 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!

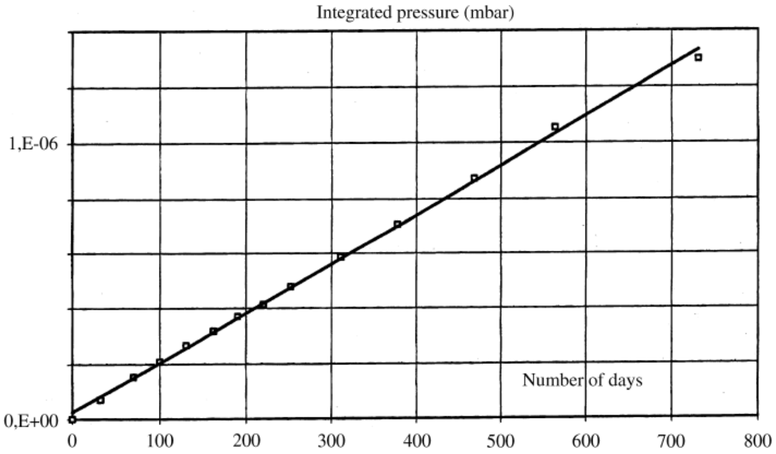


Fig. 1. Hydrogen accumulation over a long period of time in the Orsay corrugated prototype tube for VIRGO.

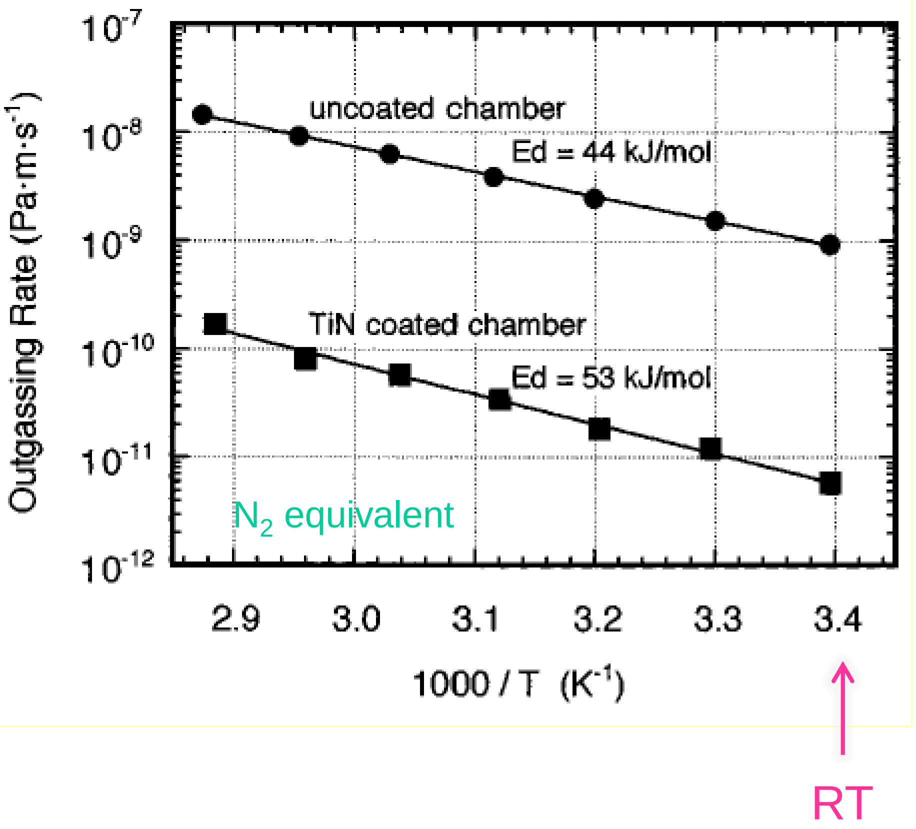
Outgassing performance of an industrial prototype tube for the Virgo antenna, P. Marin *et al.* , Vacuum 49 (1998) 309

Diffusion barrier: coating ?

Complementary information

- 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

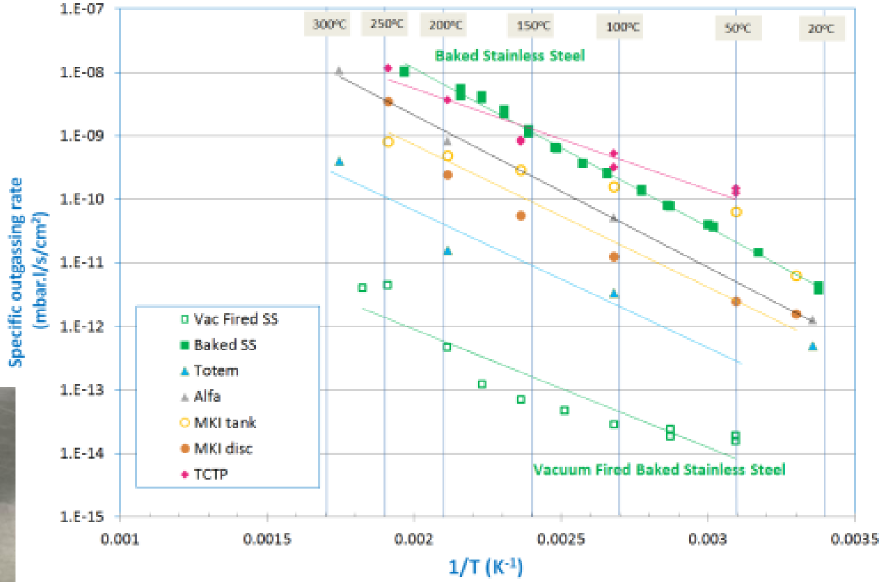
2.4 Other materials

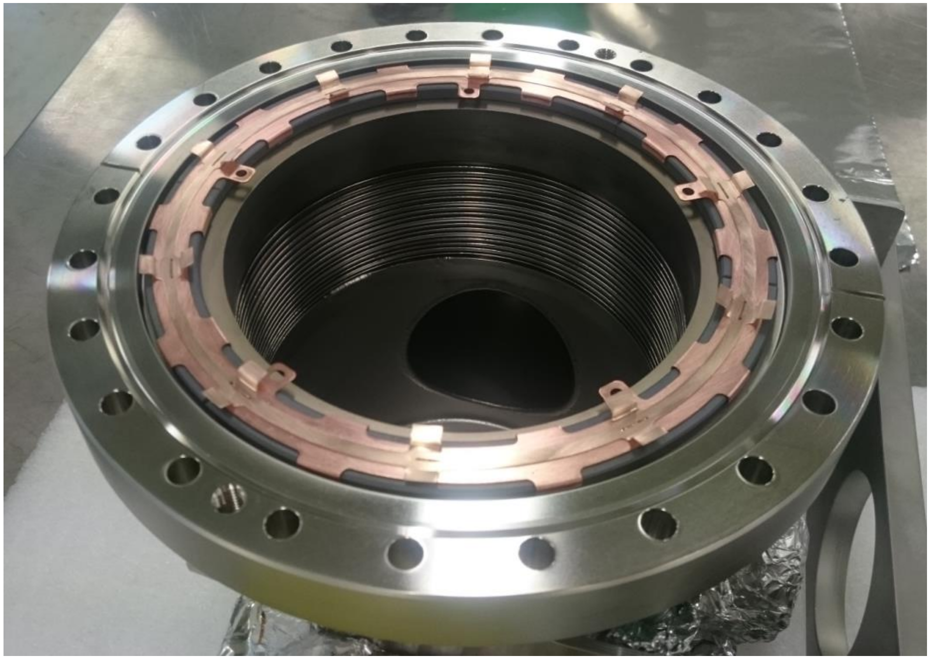
Outgassing of ferrites

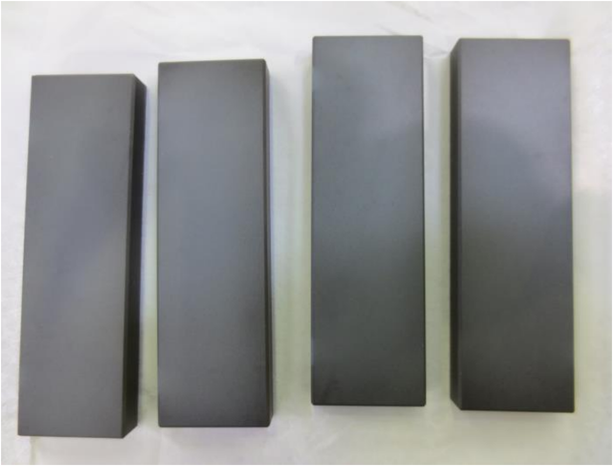
Complementary information

- 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

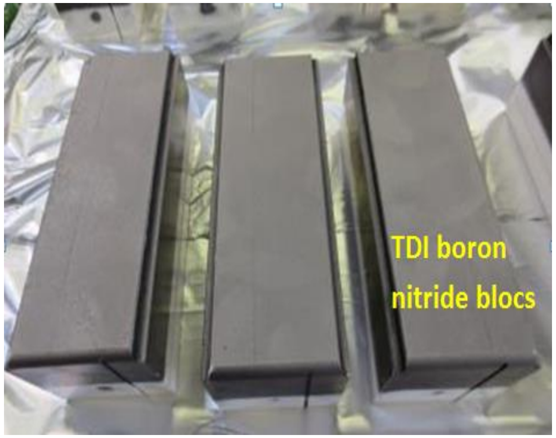


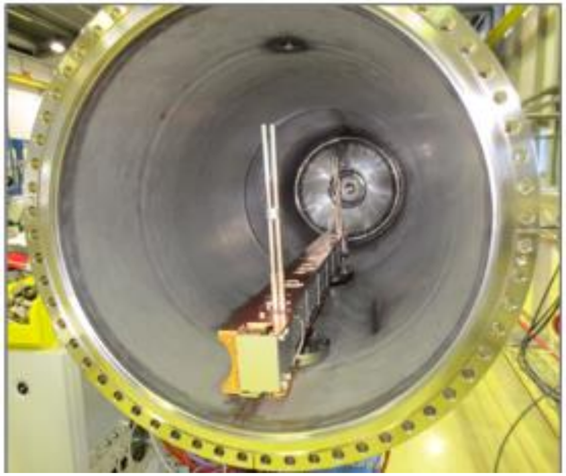


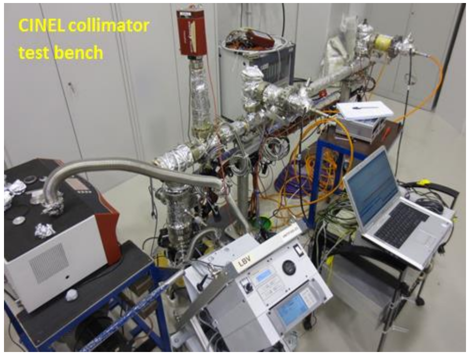


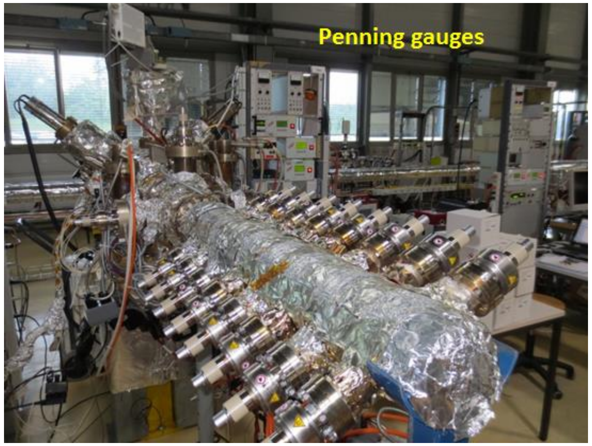
3. Qualification of materials

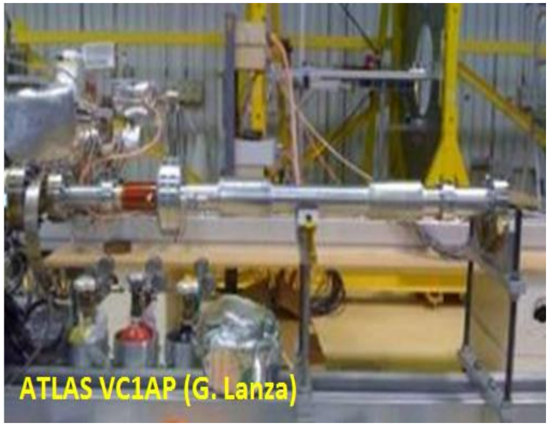
Example of tested parts











Surface characterisation – AES

Complementary information

- Auger Electron Spectroscopy is surface sensitive (nm ?)
- Hydrogen and helium are not detected

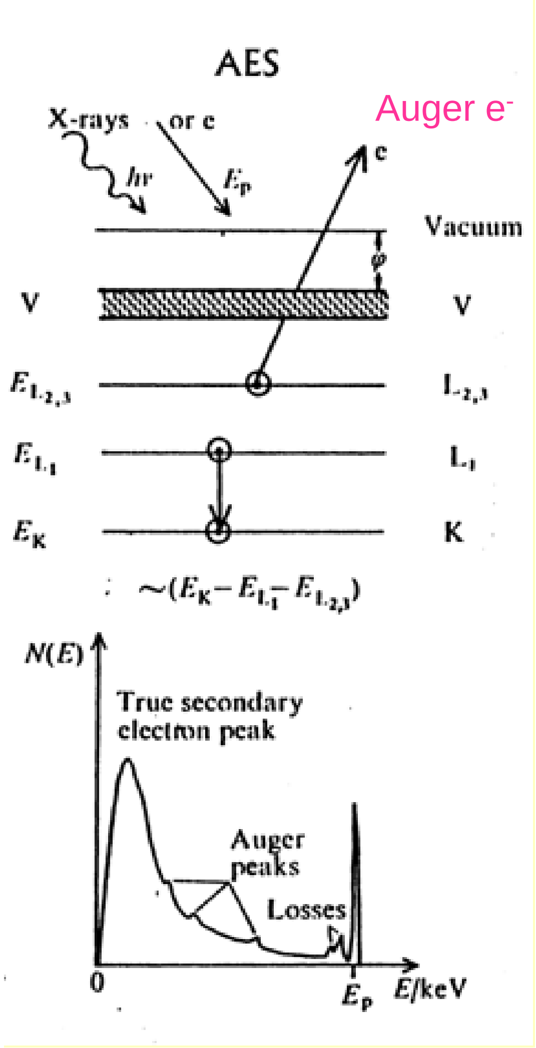
- An incoming electron/photon eject an electron from a core level of an atom to create a hole

- This hole is filled by an electron falling from an higher energy level

- The energy released is transferred to a 3rd 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

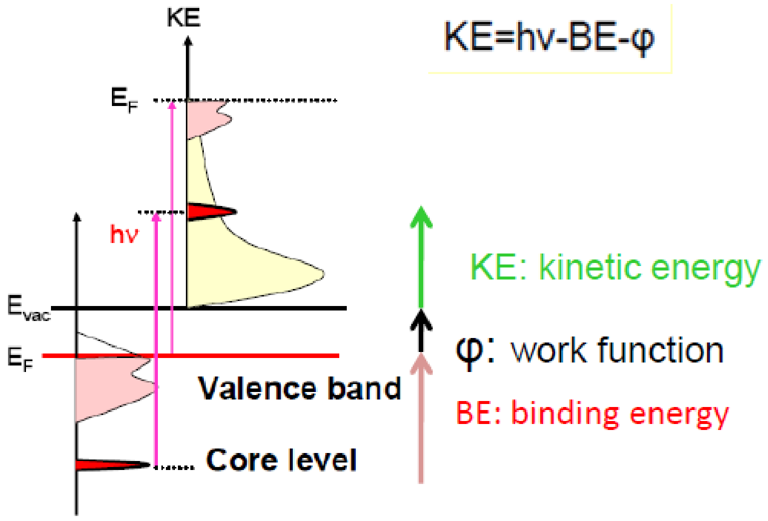


Surface characterisation – XPS

Complementary information

- 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



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