Outgassing of vacuum materials and its reduction

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Part 1: Structure of the course

- Definition, units and methods (10’)
- General features of outgassing (20’)
- Outgassing of unbaked metals (30’)
- Break
- Outgassing of baked metals (50’)
- Break
- Outgassing and permeation of organic materials (25’)
- Induced desorption (25’)
- Break
- NEG coatings (45’)

Globe of Innovation
50th Anniversary of CERN
Outgassing is the spontaneous evolution of gas from solid or liquid.

Degassing is the deliberate removal of gas from a solid or liquid.

Desorption is the release of adsorbed chemical species from the surface of a solid or liquid.
The intrinsic outgassing rate is the quantity of gas leaving per unit time per unit of exposed geometric surface, or per unit of mass, at a specified time after the start of the evacuation.

The geometric surface is the visible surface without correction for roughness or open porosity.

The measured outgassing rate is the difference between the intrinsic outgassing rate and the rate of readsorption in the test chamber.

The readsorption rate depends on chamber and method of test.
Part 1: Units of gas quantity

The quantity of gas can be presented in:

» number of molecules

» mole

or in pressure-volume units:

» Pa m$^3$

» Torr \( \ell \)

» mbar \( \ell \)

1 mol \( = N_A \) = 6.02 \( \cdot 10^{23} \) molecules

The SI system

\[
P V = N k T \rightarrow N = \frac{P V}{k_B T}
\]

\[
k_B = 1.38 \cdot 10^{-23} \left[ \frac{N \cdot m}{K} = \frac{Pa \cdot m^3}{K} \right]
\]

\[
\frac{k_B}{k_B T} = 2.45 \cdot 10^{20} \frac{Pa \cdot m^3}{K} = 3.3 \cdot 10^{19} \frac{Torr \cdot \ell}{K} = 2.5 \cdot 10^{19} \frac{mbar \cdot \ell}{K}
\]
The outgassing rate is presented in:

\[ \frac{Pa \cdot m^3}{s \cdot m^2} = Pa \cdot \frac{m}{m} \]

\[ \frac{Torr \cdot \ell}{s \cdot cm^2} \]

\[ \frac{mbar \cdot \ell}{s \cdot cm^2} \]

\[ \frac{molecules}{s \cdot cm^2} \]

\[ \frac{mol}{s \cdot cm^2} \]

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<thead>
<tr>
<th></th>
<th>Pa m</th>
<th>Torr l</th>
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Part 1: Units of outgassing rate

Some examples

Unbaked stainless steel (10 h pumping):

\[ q = 2 \times 10^{-10} \text{ Torr } \ell \text{s}^{-1} \text{ cm}^{-2} \]
\[ q = 6.6 \times 10^9 \text{ molecules cm}^{-2} \]

Baked stainless steel (150º C x 24 h):

\[ q = 2 \times 10^{-12} \text{ Torr } \ell \text{s}^{-1} \text{ cm}^{-2} \]
\[ q = 6.6 \times 10^7 \text{ molecules s}^{-1} \text{ cm}^{-2} \]

Baked OFS Copper (200º C x 24 h):

\[ q = 2 \times 10^{-14} \text{ Torr } \ell \text{s}^{-1} \text{ cm}^{-2} \]
\[ q = 6.6 \times 10^5 \text{ molecules s}^{-1} \text{ cm}^{-2} \]

Bayard-Alpert gauges (W filaments)

\[ Q \approx 10^{-9} \text{ Torr } \ell \text{s}^{-1} \]
\[ Q \approx 3 \times 10^{10} \text{ molecules cm}^{-2} \]

Bayard-Alpert gauges (Thoria coated W filaments)

\[ Q \approx 10^{-10} \text{ Torr } \ell \text{s}^{-1} \]
\[ Q \approx 3 \times 10^{8} \text{ molecules cm}^{-2} \]

Residual gas analyzer (W filaments)

\[ Q \approx 10^{-8} \text{ Torr } \ell \text{s}^{-1} \]
\[ Q \approx 3 \times 10^{11} \text{ molecules cm}^{-2} \]
Part 1: Methods for measurement

Pressure-rise method

No external pumping during the measurement

\[
\frac{dN}{dt} = Q \quad \text{and} \quad \frac{dN}{dt} = \frac{V}{k_B T} \frac{dP}{dt} \Rightarrow \frac{dP}{dt} = \frac{k_B T}{V} Q
\]

\[
Q = A_a q_a + A_s q_s
\]

\[
\Delta P = k_B T \frac{(A_a q_a + A_s q_s)}{V} \frac{[\text{molecule}]}{[s]} \cdot [t]
\]

\[
\Delta P[\text{Torr}] = \frac{(A_a q_a + A_s q_s)}{V[l]} \frac{[\text{Torr} \cdot \text{L}]}{[\text{s}]} \cdot [t[\text{s}]]
\]

If repumping is negligible, the pressure in the system increases linearly and the total outgassing rate is obtained from the slope of the curve.

The sensitivity of the method is limited by the outgassing of the apparatus (walls, valves and gauges) and by the sensitivity of the pressure gauge.
Example: for a baked spherical system made of regular stainless steel containing the sample to be measured:

\[ V = 10 \ell \]
\[ q_a = 2 \cdot 10^{-12} \frac{\text{Torr} \cdot \ell}{s \cdot \text{cm}^2} \]
\[ \Delta P_a[\text{Torr}] = \frac{2245[\text{cm}^2] \cdot 2 \cdot 10^{-12} \frac{\text{Torr} \cdot \ell}{s \cdot \text{cm}^2}}{10[\ell]} \cdot t[s] = 4.5 \cdot 10^{-9} t \]

The signal of the sample has to be at least 25% of that of the apparatus to be significant.

\[ q_s \cdot A_s > 1.1 \cdot 10^{-9} \frac{\text{Torr} \cdot \ell}{s} \]

For a sample area of 100 cm\(^2\):

\[ q_s > 1.1 \cdot 10^{-11} \frac{\text{Torr} \cdot \ell}{s \cdot \text{cm}^2} \]

This excludes most of the metals applied in UHV. This method is used for metals when upper limits of outgassing rate are needed or when the sample is the system itself.
Part 1: Methods for measurement

Throughput method

Continuous pumping is applied during the measurement

\[
\frac{dN}{dt} = Q - \sigma \cdot A_p \left( \frac{1}{4} n \cdot v \right) \quad \text{and} \quad \frac{dN}{dt} = \frac{V}{k_B T} \frac{dP}{dt} \Rightarrow \frac{dP}{dt} = \frac{k_B T}{V} Q - \sigma \cdot A_p \left( \frac{1}{4} \right) P
\]

\[Q = A_o q_a + A_s q_s\]

\[
\frac{dP[\text{Torr}]}{dt} = Q \left[ \text{Torr} \cdot \frac{1}{s} \right] - \sigma \cdot C_a \left[ \frac{1}{s} \right] P[\text{Torr}] \quad \text{and} \quad S_{\text{eff}} \left[ \frac{l}{s} \right] = \sigma \cdot C_a \left[ \frac{1}{s} \right]
\]

\[
\Delta P = \frac{Q}{S_{\text{eff}}} \left( 1 - e^{-\frac{t}{\tau_p}} \right) \quad \tau_p = \frac{V}{S}
\]

In general \( \tau_p \) is very small compared to the time scale of the measurements, hence:

\[
\Delta P[\text{Torr}] = \frac{Q \left[ \text{Torr} \cdot \frac{1}{s} \right]}{S_{\text{eff}} \left[ \frac{l}{s} \right]} = \frac{A_o q_a + A_s q_s}{S_{\text{eff}}}
\]
Throughput method

\( \tau_p \) is the characteristic time of pumping. Typical values for \( \tau \) for test system are less than one minute.

Example: \( V=10 \ \ell \ S=10 \ \ell/s \rightarrow \tau = 1 \ s \)

This implies that the transient of \( P \) is very short and can be neglected \( \rightarrow \) the quantity of gas to built up the pressure in the volume is very small in the usual range of working pressure.

Here again, the sensitivity of the method is limited by the outgassing of the apparatus (walls, valves and gauges) and by the sensitivity of the pressure reading.

Example 1: for a baked spherical apparatus made of regular stainless steel \( (V=10 \ \ell) \) evacuated by an effective pumping speed of \( 10 \ \ell/s \).

The contribution of the system is \( \Delta P=4.5\times10^{-10} \) Torr. The detection limit of the outgassing rate is \( 1.1\times10^{-9} \) Torr \( \ell \ s^{-1} \). If the outgassing of a standard BA gauge is also taken into account the detection limit is \( 1.4\times10^{-9} \) Torr \( \ell \ s^{-1} \).
Example 2: Extreme conditions.

Same apparatus as before, but made of high temperature treated stainless steel:

\[ q \approx 10^{-14} \text{ Torr cm}^{-2} \text{ s}^{-1} \rightarrow Q_a = 2.2 \times 10^{-11} \text{ Torr cm}^{-2} \text{ s}^{-1} \]

and equipped with a very low outgassing BA gauge

\[ Q_{BA} = 1 \times 10^{-10} \text{ Torr cm}^{-2} \text{ s}^{-1} \]

The contribution of the system is \( \Delta P = 1.2 \times 10^{-11} \) Torr, dominated by the effect of the gauge.

The detection limit of the outgassing rate is \( 3 \times 10^{-11} \) Torr cm\(^{-2}\) s\(^{-1}\). This limit can be attained by increasing the surface area of the sample (whenever possible) or by coupling the accumulation and the throughput methods.
Coupled method

The sample is isolated by a valve in a separated vessel where the gas is accumulated for a time $t_a$. Then the valve is opened and the accumulated gas is recorded in the measuring dome.

$$Q = S_{eff} \cdot \int_{t_a}^{t_a+\Delta t} P(t)dt$$

This method can be applied only if the outgassing rate is constant in the time of accumulation and repumping is negligible.

The detection limit is defined by the outgassing of the accumulation system and by the sensitivity of the pressure reading.

The advantages of this method are two:

- no effects of gauge on the quantity of gas accumulated
- $t_a$ can be long enough to attain gauge sensitivity
Part 1: Methods for measurement

Weight loss

This method is used for high outgassing rate materials only, namely organics.

The test consists in measuring the weight loss of a sample following a defined thermal cycle in vacuum (TML total mass loss) and the weight gain of a collector cooled at room temperature and placed in front of the sample (CVCM Collected Volatile Condensable Material).

The set-up and procedure are described in the ASTM E595-93 standard.

If the throughput method is applied in the same apparatus, data are obtained about the evolution of the outgassing rate at room temperature and at the temperature of the treatment.

This method is used largely in space applications and a wide database is available via NASA.
Part 1: Methods for measurement

Effect of readsorption

The gas released by the sample, instead of being evacuated by the pumping system, can be adsorbed by the system wall, pumped by the gauge, or eventually reabsorbed by the sample itself.

Let’s call $S_{add}$ the resulting additional pumping speed:

$$Q_{\text{int}} = P(S_{add} + S_{eff}) = PS_{eff}\left(1 + \frac{S_{add}}{S_{eff}}\right) \Rightarrow \frac{Q_{\text{int}}}{Q_m} = 1 + \frac{S_{add}}{S_{eff}}$$

Example: for a 10 l spherical chamber, supposing a sticking probability of $10^{-3}$ for water on the system wall and a sample surface area of 100 cm$^2$:

$$\frac{Q_{\text{int}}}{Q_m} \approx 3$$

Ion gauges remove molecules from the gas phase through two mechanisms:
- Cracking on the hot filaments (does not affect monoatomic molecules like rare gases). Order of magnitude $\approx 1 \text{ l/s}$ for W filaments
- Ionization by electrons (affects all gases). Order of magnitude $\approx 10^{-2} \text{ l/s}$
Exercise
The molecules outgassed in vacuum are stored on the surface or in the bulk of materials.

- Those coming from the surface have to overcome an energy barrier before being released.

- Those from the bulk in addition have to diffuse along the material lattice before encountering the surface.
Part 2: General features of outgassing

Single desorption energy: mean stay time

The mean stay time (sojourn time) is given by:

\[ \tau_d = \tau_0 e^{E_d/k_B T} \]

where the value of \( \tau_0 \) is usually assumed to be \( 10^{-13} \) s.

<table>
<thead>
<tr>
<th>( E_d ) [Kcal/mole]</th>
<th>Cases</th>
<th>( \tau_d ) [s]</th>
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<tbody>
<tr>
<td>0.1</td>
<td>Helium</td>
<td>1.2\times10^{-13}</td>
</tr>
<tr>
<td>1.5</td>
<td>H\textsubscript{2} physisorption</td>
<td>1.3\times10^{-13}</td>
</tr>
<tr>
<td>3-4</td>
<td>Ar, CO, N\textsubscript{2}, CO physisorption</td>
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<tr>
<td>10-15</td>
<td>Weak chemisorption</td>
<td>3\times10^{-6}</td>
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<tr>
<td>20</td>
<td>H\textsubscript{2} chemisorption</td>
<td>100</td>
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<tr>
<td>25</td>
<td></td>
<td>6\times10^{5} one week</td>
</tr>
<tr>
<td>30</td>
<td>CO/Ni chemis.</td>
<td>4\times10^{-9} 100 years</td>
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<tr>
<td>40</td>
<td></td>
<td>1\times10^{-17} age of Earth</td>
</tr>
<tr>
<td>150</td>
<td>O/W chemis.</td>
<td>&gt; age of universe</td>
</tr>
</tbody>
</table>
Part 2: General features of outgassing

Single desorption energy: pressure evolution without repumping

\[ P(t) \approx \frac{N_s}{S \cdot \tau_d} e^{-\frac{t}{\tau_d}} \quad \text{for} \quad t > \tau_d \]

This system is simply solved and the solution is plotted for:

V=10 \, \ell, \, S=10 \, \ell /s, \, N_s=2245\times3\times10^{-5} \, \text{Torr} \, \ell

\[ \Theta = \text{fraction of sites occupied} \]

The total number of sites is assumed to be \( \approx 10^{15} \, \text{cm}^{-2} \rightarrow 3 \times 10^{-5} \, \text{Torr} \, \text{ls}^{-1} \, \text{cm}^{-2} \)
Part 2: General features of outgassing

![Graphs showing outgassing at different temperatures and energies.](image)

- **T=296K**
  - P(0)=0
  - Energetics: 0.75 eV, 0.8 eV, 0.85 eV, 0.9 eV, 0.95 eV, 1 eV

- **T=373K**
  - P(0)=0
  - Energetics: 1 eV

**Pumping Time [s]**

**P[torr]**
Part 2: General features of outgassing

In case of multiple desorption energies equally distributed:

\[ P(t) = \int_0^\infty \frac{f(E_d)}{S \cdot \tau_d} e^{-t \tau_d} dE_d \propto \frac{N_s}{S} \cdot \frac{1}{t} \]

\[ Q(t) \propto \frac{N_s}{t} \]

The convolution of many non-interacting sites gives 1/t time evolution.
Part 2: General features of outgassing

$T = 296K$
$P_0 = 1$ Torr

![Diagram showing the relationship between pumping time and pressure for different energies.](image)
Part 2: General features of outgassing

Single desorption energy: pressure evolution with repumping

\[
\begin{align*}
V \frac{dP}{dt} &= -SP + \frac{N_s \Theta}{\tau_d} - S_W P \\
\quad \frac{d\Theta}{dt} &= -\frac{\Theta}{\tau_d} + S_W P
\end{align*}
\]

The general solution exists and for the following hypothesis:

\[
\frac{\tau_p}{\tau_d} < 1 \quad \text{and} \quad \frac{S_W}{S} >> 1
\]

the pressure can be approximated to:

\[
P(t) \approx \frac{N_s}{\tau_d \cdot (S + S_W)} e^{-\frac{t}{\tau_d \left( \frac{S_W}{S} + S \right)}}
\]

It is again an exponential function.
The same result can be obtained by simple arguments:

- the probability that a molecule leaving the surface is pumped outside the system is: \( \frac{1}{\tau_d} \)
- the probability for a molecule to leave the surface in one second is: \( \frac{S}{S + S_W} \)
- therefore, the probability for a molecule to be definitively removed in one second is: \( \frac{S}{S + S_W} \cdot \frac{1}{\tau_d} \)
- the average time the molecule is in the system is: \( \frac{S + S_W}{S} \cdot \frac{1}{\tau_d} \)

The increased residence time of the molecule in the system is due to the surface readesorption and reemission.

For \( t \ll \tau_d \Rightarrow P(0) \approx \frac{N_s}{\tau_d \cdot (S + S_W)} \)

\[ P(t) \approx \frac{N_s}{\tau_d \cdot (S + S_W)} e^{-\frac{t}{\tau_d \left( \frac{S_W + S}{S} \right)}} \]
Part 2: General features of outgassing

Single desorption energy: pressure evolution with repumping

\[ E_d = 0.75 \text{ eV} \]
\[ S_w \text{ from 0 to 1000 l/s in step of 50} \]

\[ E_d = 0.85 \text{ eV} \]
\[ S_w \text{ from 0 to 1000 l/s in step of 50} \]
Part 2: General features of outgassing

Which is the $\tau_d$ that, at time “t”, gives the maximum value of $P(t)$?

$$\frac{dP(t)}{d\tau_d} \approx \frac{N_s}{\tau_d^2 \cdot (S + S_W)} e^{-\frac{t}{\tau_d \cdot \left(\frac{S_W}{S} +1\right)}} \cdot \left(1 - \frac{t}{\tau_d \cdot \left(\frac{S_W}{S} +1\right)}\right) = 0$$

$$\tau_{d,\text{max}} = \frac{t}{\left(\frac{S_W}{S} +1\right)}$$

Hence, the maximum pressure that can be obtained in a desorption process (at constant temperature) is:

$$P_{\text{MAX}}(t) \approx \frac{N_s}{S \cdot e} \cdot t^{-1}$$

In the case of one monolayer coverage $N_s=10^{15}/3.3\times10^{19}$:

$$Q_{\text{MAX}}(t) \approx \frac{N_s}{e} \cdot t^{-1} = \frac{1.1 \cdot 10^{-5}}{t[s]} = \frac{3 \cdot 10^{-9}}{t[h]} \left[\frac{\text{Torr l}}{s}\right]$$

This behavior could be that of a real system only if adsorption sites of different energy exists and they are in the worst possible combination.
The simple models presented suppose the presence of a single desorption site or the coexistence of many but completely independent desorption sites. In addition, when readsorption is considered, the pumping speed of the wall is assumed constant.

Much more complicated models are needed to take into account variable pumping speed of the wall and the interdependence of the population of the different adsorption sites.

However, the essential feature of desorption are already considered by the simplest models:

1. The degassing rate of a single desorption site decreases as an exponential function of time, whose decay time is the desorption time.
2. Higher temperatures allows a faster degassing.
3. The decay time increases in case of repumping.
4. The degassing rate can have a $t^{-1}$ evolution only if simultaneous desorption from many sites is considered.
Part 2: General features of outgassing

Outgassing of molecules dissolved in the bulk of materials: solubility

Molecules A in gas phase and in solid are in thermodynamic equilibrium when:

\[ A \text{ (gas)} = A \text{ (solid)} \]

The equilibrium constant \( K \) is:

\[ K = e^{-\frac{\Delta G^0}{k_BT}} = \frac{a_A}{P_A} \]

where \( a_A \) is the activity of A in the solid. For diluted solution (ideal solution + Henry law):

\[ K = \frac{x_A}{P_A} \rightarrow x_A = K \cdot P_A \]

where \( x_A \) is the molar fraction and \( K \) the solubility of A in the solid. The temperature dependence is obtained:

\[ x_A = B \cdot e^{\frac{-\Delta H_s}{k_BT}} \cdot P_A \]

For diatomic molecules adsorption: \( A_2 \text{ (gas)} = 2 \ A \text{ (solid)} \):

\[ x_A = B \cdot e^{\frac{-\Delta H_s}{2k_BT}} \cdot \sqrt{P_A} \]

Sievert’s law
Part 2: General features of outgassing

Solubility of $H_2$ in stainless steel:

$$x_H[\text{at.ppm}] = 71.8 \cdot \sqrt{P[\text{Torr}]} \cdot e^{-\frac{0.114\,[\text{eV}]}{k_B T}}$$

The H content in standard austenitic stainless steels is about 1 ppm in weight.

After evacuation, in an isolated stainless steel vessel the hydrogen equilibrium pressure is about 10 bar!

But no humans will measure it.
Outgassing of molecules dissolved in the bulk of metals

Gas molecules are dissolved into the bulk of materials during the production processing and during their permanence in air. In vacuum, the lighter molecules diffuse and, after reaching the surface, they are released.

• In the materials of interest, except organics, only H has enough mobility to attain the surface, recombines to form H₂ and be released. In organics most of the lighter molecules are quickly diffused in the bulk and released in vacuum.
• The models that take into account all the steps in the outgassing process are quite complicated and, in general, they give only asymptotic solution for limit conditions.

Two mechanisms are considered:

1. diffusion limited outgassing \( q(t) \propto -\frac{\partial^2 c}{\partial x^2} \)

2. recombination limited outgassing \( q(t) \propto \theta^2 \)
B.M. Shipilevsky and V.G. Glebovsky have shown that, for each metal, a characteristic critical number of dissolved monolayers defines the limit between the two stages; below it, recombination becomes the controlling mechanism.

### Exothermic Metals

- Nb, Ti, Pd, Zr, ...

The recombination and desorption energy is higher than the dissolution energy. Recombination has to be taken into account in most of the problems.

### Endothermic Metals

- Fe, Ni, Cu, Mo, st. steel

The recombination and desorption energy is lower than the dissolution energy. The desorption barrier is actually transparent. Kinetics is controlled by diffusion, except when concentration is very low (much less than 1 ML dissolved, do not forget that the recombination rate is $\approx \theta^2$).
Part 2: General features of outgassing

Diffusion limited outgassing

Diffusion is a random process and in most of the cases of interest is described by the Fick’s equations:

\[
\begin{align*}
-D \frac{\partial c(x,t)}{\partial x} &= \Gamma(x,t) \\
D \frac{\partial^2 c(x,t)}{\partial x^2} &= \frac{\partial c(x,t)}{\partial t}
\end{align*}
\]

where \( c(x,t) \) is the concentration in the solid and \( \Gamma \) is the flux of molecules.

The outgassing rate is equal to the flux of molecules arriving at the surface by diffusion:

\[
q(t) = -D \frac{\partial c(x,t)}{\partial x} \bigg|_{x=\text{SURF}}
\]
Part 2: General features of outgassing

Semi-infinite solid approximation:

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

I.C. \( c(x,0) = c_0 \)

B.C. \( c(0,t) = 0 \)

\[
c(x,t) = c_0 \cdot \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)
\]

The gaussian character of the solution reflects the brownian nature of diffusion

\[
q(t) = -D \frac{\partial c(x,t)}{\partial x} \bigg|_{0} = \frac{D \cdot c_0}{\sqrt{\pi} \cdot D \cdot t} \propto t^{-0.5}
\]

The \( t^{-0.5} \) evolution holds also for solid of finite dimension \( L \) (slab) when \( L >> (Dt)^{0.5} \)

The total amount of substance \( M(t) \) which has left the solid is:

\[
M(t) = \frac{2c_0 \cdot \sqrt{D \cdot t}}{\sqrt{\pi}}
\]
Part 2: General features of outgassing

**Slab approximation**

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

**I.C.** \( c(x,0) = c_o \)

**B.C.** \( c(\pm \frac{L}{2},t) = c_w \)

\[
\frac{1}{c_w - c_o} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} (-1)^n \cos \left(\frac{(2n+1)\pi x}{L}\right) e^{-\frac{D(2n+1)^2\pi^2}{L^2}t}
\]

For \( D t > 0.05 \ L^2 \) only the first term of the series is relevant:

\[
q(t) = \frac{4(c_o - c_w) \cdot D}{L} \sum_{n=0}^{\infty} e^{-\frac{(2n+1)^2\pi^2}{L^2}Dt}
\]

For diatomic molecules

\[
q(t) \approx \frac{4(c_o - c_w) \cdot D}{L} e^{-\frac{\pi^2}{L^2}Dt}
\]

When equilibrium is assumed between gas and surface, the Sievert’s law defines the surface concentration \( c_w \):

\[
c_w = K \sqrt{P}
\]
Part 2: General features of outgassing

Slab approximation: thermal history

If the slab is heated to a temperature $T_H$ for a time $t_H$, the outgassing rate, when back at room temperature is:

$$q \approx 4 \cdot (c_0 - c_w) \cdot \frac{D}{L} \exp \left[ -\pi^2 \cdot \frac{D(T_H) \cdot t_H}{L^2} \right]$$

For an arbitrary thermal cycle it can be shown that:

$$q \approx 4 \cdot (c_0 - c_w) \cdot \frac{D}{L} \exp \left[ -\pi^2 \cdot \frac{\int_0^{t_H} D(T) \cdot dt}{L^2} \right]$$

The dimensionless number: $F_o = \frac{0}{L^2}$ is called the Fourier number

$F_o$ records the thermal history of the material and determines how much of the initial concentration is depleted.

When thermal treatment of $F_o \approx 3$ are applied the solid is actually emptied or in equilibrium with the surrounding gas phase.
Part 3: Complementary techniques for the understanding of the outgassing mechanism

**Permeation**

If the whole permeation process is considered to be dominated by diffusion through a uniform lattice, the following equation can be applied:

\[
\frac{q}{q_\infty} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-\frac{n^2 \pi^2 D t}{L^2}}
\]

Where \( q_\infty \) is the steady-state flux through the membrane. This function, its integral and its derivative give a number of characteristic points and limiting values from which the diffusion coefficient can be evaluated.

The steady-state flux is:

\[
q_\infty = \frac{c_w D}{L} = \frac{K \cdot P \cdot D}{L} = \frac{P \cdot \Pi}{L}
\]

where \( \Pi = K \cdot D = \frac{q_\infty \cdot L}{P} \) is the permeability.
Part 3: Complementary techniques for the understanding of the outgassing mechanisms

SCHEMATIC VIEW OF THE PERMEATION SYSTEM

Fig. 1

Low pressure side

High pressure side

BA gauge

RGA

Penning gauge

Capacitance gauge

Permeation cell

Penning gauge

H₂

 TMP station 260 l/s

 TMP station 70 l/s

Exhaust
Part 3: Complementary techniques for the understanding of the outgassing mechanisms
Evaluation of the diffusion coefficient: time lag

The following relation gives the asymptotic behavior of the quantity of gas permeated

$$\lim_{t \to \infty} \frac{1}{q_\infty} \int_0^t q(t) \, dt = \lim_{t \to \infty} \frac{1}{q_\infty} \left( t - \frac{l^2}{6D} \right)$$

This is a straight line (see fig. 6) that intersects the time axis at:

$$\tau_L = \frac{L^2}{6D}$$

This quantity is known as the time lag, and gives a simple method to calculate the diffusion coefficient. It is quoted in most of the literature on permeation measurements.
Evaluation of the diffusion coefficient: inflexion and breakthrough points

The inflexion time is the time at which the derivative of $q/q_\infty$ is a maximum.

$$\tau_i = \ln(16) \frac{L^2}{3\pi^2 D}$$

Similarly the breakthrough time is defined as the time at which the tangent to the normalized permeation curve at the inflexion point intersects the time axis.

$$\tau_b = 0.5 \frac{L^2}{\pi^2 D}$$
Other methods are available for the evaluation of $D$ from the permeation curve. The $D$ values obtained with the different methods should be equal. If this is not the case it means that the permeation problem does not exactly follow Fick’s law.

Surface recombination or internal trapping could play an important role in metals.

Strong deviation from the Fick’s law has been observed in amorphous vitreous polymers. For example linear time dependence of the flux, instead of square root, was measure; in other cases oscillations in the permeating flux were recorded.
TDS

TDS is a very useful technique to provide an insight on both the thermodynamics and the kinetics of gas-metal systems by measuring the desorbing gas spectrum obtained while heating a sample at a constant rate of temperature rise. In particular, diffusive processes may be quantified by varying the heating rate of the sample.

Uniform initial condition

\[
q(t) = \frac{4 \cdot c_0 \cdot D(t)}{L} \sum_{n=0}^{\infty} e^{-(2n+1)^2 \pi^2 \cdot F_n(t)}
\]

\[
F_n(t) = \int_0^t D(t)dt = \frac{D_0 \int_0^t e^{-\frac{E_b}{k_b T(t)}} dt}{L^2}
\]
TDS spectra could indicate the presence of multiple interactions between the gas and the solid; some of them are surface blocking and bulk trapping.

Unbaked metals

- After evacuation, the outgassing rate from typical structural metals (Cu, Al alloys, stainless steels,...) varies approximately inversely as the first power of the time for at least the first days of pumping.

- The outgassing of unbaked systems is dominated by water vapor. The remaining outgassing species for clean systems are H₂, CH₄, CO, and CO₂.

- Most of the economic effort to attain UHV condition is dedicated to reduce water outgassing.
Experimental value valid for most of the metals:

$$q(t) \approx \frac{2 \cdot 10^{-9}}{t[h]} \frac{Torr \, l}{s \, cm^2}$$

The outgassing rate of an unbaked material depends on pumping time, it is not an intrinsic value!
Part 4: Outgassing of unbaked metals

The Edwards' upper limit is very close to the experimental values. In the context of the analysis reported before, it means that water is initially adsorbed in many energy states in the worst possible combination. This is true for all the typical metals!

Other models explain the 1/t variation; they are based on diffusion from the bulk of ad hoc initial distribution, adsorption in small porosity in the oxide layer, and quasi-equilibrium approximations allowing the application of standard isotherms.
The nature of the material has only a slight influence on the outgassing rate variation.

**Edwards’ upper limit**

**Figure 4.** The total outgassing rate for a variety of materials.
The kind of post production treatment has also a slight influence on the outgassing rate variation.
The $\approx 1/t$ variation holds for pumpdown performed at temperature up to 110° C.

Fig. 1. The total outgassing rate is plotted versus the time from the end of an atmospheric exposure for various pumping speeds and system temperatures.
The total quantity of water desorbed during the pumpdown is of the order of one, two monolayer.

$3 \times 10^{15}$ molecules cm$^{-2}$
Reduction of the pumpdown time

At present there are no methods, except heating (in situ bake-out), to accelerate the pumpdown of water.

Several attempts were done, but poor results were attained.
Baked metals

- The fact that desorption rates depend exponentially on temperature allow a faster reduction of outgassing through heating (bakeout procedure). If a heat of adsorption of 15 Kcal/mol and a bakeout temperature of 150°C are assumed, the rate of gas removal will be increased by a factor of roughly 5000 relative to the value at room temperature.

- The outgassing of baked systems is dominated by H₂ diffusing out of the metallic walls. The remaining outgassing species are CH₄ and CO, which are believed to be related to the presence of H₂, and if the H₂ level is reduced, their levels will also be reduced.

- The simpler and most effective method to reduce H₂ outgassing is heating at high temperature.
Typical H$_2$ outgassing rate

Many data are reported in the literature (contradictory in some cases), and some reference values or upper limits can be drawn:

<table>
<thead>
<tr>
<th>Baking procedure</th>
<th>Stainless steel</th>
<th>Aluminum alloys</th>
<th>Copper alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>150°C x 24 h</td>
<td>$\approx 3 \times 10^{-12}$</td>
<td>$&lt; 2 \times 10^{-13}$</td>
<td>$\approx 2 \times 10^{-12}$</td>
</tr>
<tr>
<td>200°C x 24 h</td>
<td>$\approx 2 \times 10^{-12}$</td>
<td></td>
<td>$\approx 5 \times 10^{-14}$</td>
</tr>
<tr>
<td>350°C x 24 h</td>
<td>$\approx 5 \times 10^{-13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>950°C x 2 h</td>
<td>$&lt; 2 \times 10^{-13}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

After the baking procedure, the H$_2$ outgassing rate does not change significantly with time. It is an intrinsic value for materials once the thermal history is known.

Part 5: Outgassing of baked metals
Application of the diffusion model to the study of the bakeout efficiency

In the approximation of the diffusion limited model, the influence of thermal cycles on H\textsubscript{2} outgassing rate is taken into account by the Fourier number \( F_0 \).

$$ \int_0^{t_{th}} D(T) \cdot dt $$

where \( t_{th} \) is the total time of the thermal treatment. For repeated bakeout cycles the value of \( F_0 \) is very simply calculated:

$$ \frac{n \cdot D(T_{bo}) \cdot t_{bo}}{L^2} $$

for \( n \) bakeout at the temperature \( T_{bo} \) for the time \( t_{bo} \).

The outgassing rate becomes:

$$ q_n(t) = \frac{4 \cdot c_0 \cdot D(296 K)}{L} \exp\left( -\pi^2 \cdot \frac{n \cdot D(T_{bo}) \cdot t_{bo}}{L^2} \right) $$

supposing \( F_0 > 5 \times 10^{-2} \).

It comes out that:

$$ \ln(q_n) = A - B \cdot n $$

where \( A = \frac{4 \cdot c_0 \cdot D(296 K)}{L} \), \( B = \pi^2 \cdot \frac{D(T_{bo}) \cdot t_{bo}}{L^2} \).

→ Linearity in Log(q)-n plot

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

→ Each bakeout reduces the outgassing rate by the same factor.

If the external wall is impermeable \( L^2 \) becomes \( 4L^2 \).
Each bakeout reduces the outgassing rate by a factor of ≈ 1.6.

From A:

\[ D(300^\circ C) = 2.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \]

If the diffusion rate at room temperature reported in the literature is assumed, from the value of B:

\[ C_0 = 0.05 \text{ Torr l/cm}^3 = 0.75 \text{ wt. ppm} \]

This is a very reasonable quantity for austenitic stainless steels.
Another model: recombination limited outgassing

In the last 10 years several papers proposed to consider surface recombination as limiting process for outgassing. This could explain discrepancies between reported measurements and expectation based on the diffusion limited model. The essential point is that the thermal treatments should be less efficient than foreseen by diffusion model in depleting $H_2$ because the H atoms recombination slow down the release process.

In a pure recombination limited process, the concentration in the bulk is flat and the outgassing rate is given by:

$$q(t) = K_R(T) \cdot c(t)^2$$

where $K_R$ is called recombination coefficient. Recombination is an activated process and so:

$$K_R(T) = K_{R,0} \cdot e^{\frac{E_R}{k_BT}}$$
Other models: recombination limited outgassing

The recombination regime is dominant for:

\[ K_R c^2 \ll \frac{c \cdot D}{L} \rightarrow c \ll \frac{D}{K_R \cdot L} = c^* \]

Typical concentrations for as received austenitic stainless steel are about 1 wt. ppm (57 at. ppm, \(4.6 \times 10^{18}\) H atoms cm\(^{-3}\)).

\[ c^* \approx \begin{cases} \text{H atoms/cm}^3 \\ \text{at. H ppm} \\ \text{wt. ppm} \end{cases} \]

\[
\begin{array}{l|c|c|c}
T [\degree C] & 23 & 350 & 950 \\
\hline
C^* [\text{H atoms/cm}^3] & 5.3 \times 10^1 & 1.7 \times 10^1 & 3.6 \times 10^1 \\
C^* [\text{at. H ppm}] & 6.6 \times 10^{-1} & 2.2 \times 10^{-2} & 4.5 \times 10^{-3} \\
C^* [\text{wt. ppm}] & 1.1 \times 10^{-2} & 3.9 \times 10^{-4} & 7.9 \times 10^{-5} \\
\end{array}
\]

During vacuum firing, a minimum concentration of about \(6 \times 10^{15}\) atoms H cm\(^{-3}\) can be attained in industrial furnaces → recombination could become the limiting step (experimental verifications are necessary).
Application of the recombination model to the study of the bakeout efficiency

In the frame of the recombination limited model, the hydrogen concentration in the solid can be obtained in the following way:

\[ L \frac{dc(t)}{dt} = -K_R c^2 \rightarrow \frac{dc}{c^2} = -\frac{K_R}{L} dt \rightarrow \frac{1}{c(t)} - \frac{1}{c_0} = \frac{K_R t}{L} \]

\[ c(t) = \frac{c_0}{1 + \left( \frac{K_R c_0}{L} \right) \cdot t} \]

After one bakeout at the temperature \( T_{bo} \) for a duration \( t_{bo} \) the outgassing rate should be:

\[ q_1 = K[T_{RT}] \cdot \left( \frac{c_0}{1 + B \cdot c_0} \right)^2 \text{ where } B = \frac{K_R \cdot t_{bo}}{L} \]

It can be shown that after \( n \) identical bakeout:

\[ q_1 = K[T_{RT}] \cdot \left( \frac{c_0}{1 + n \cdot B \cdot c_0} \right)^2 \propto n^{-2} \]

There is no experimental evidence for this theoretical expectation.
Methods for the reduction of H$_2$ outgassing from stainless steels

- Ex situ heating at high temperature in vacuum furnaces (vacuum firing)
- Heating in air (air bakeout)
- Passive coatings: BN, TiN.
- Active coating: Non Evaporable Getter coatings
Production of austenitic stainless steels for UHV applications

Melting in electric Arc furnace (ARC) + AOD

Refinement: Electro-Slag Remelting (ESR):
Final ingot

Thermo-Mechanical treatments

Rolling

Forging

Thermal mechanics treatments

Thickness ≥ 5mm: Hot-rolling

Thickness < 5mm: Cold-rolling

Sheets (vacuum chambers)

Plates (for flanges)

Solution annealing (1050-1100°C) + water quenching

Acid pickling (HNO₃ solution)

Skin-passing (for very thin sheets)
Before any application in UHV environment stainless steel components undergo

- **surface cleaning** → to remove surface contamination (organic contaminants, mineral oils, etc...)

Then one of the following treatments can be applied:

- **acid pickling** → to remove thick oxide layers or carbonized contaminants
- **electropolishing** → to reduce the specific surface area.
- **air or vacuum firing** → **to reduce H$_2$ outgassing**

Finally in-situ bakeout is applied, mainly to reduce water vapor outgassing.
Vacuum firing allows the residual H content to be reduced. At CERN it is performed at 950°C for about 2 hours.

Lower temperatures could result in carbide precipitation and in a less effective H depletion for thick sheets.

Higher temperatures are detrimental for the mechanical properties of stainless steel.
Vacuum firing

- $T < 500^\circ C$
  diffusion is too slow

- $500^\circ C < T < 900^\circ C$ (depending on the steel grade)
  carbide and carbo-nitride precipitation
  residual $\delta$-ferrite transformation into $\sigma$- phase (very brittle)

- $T > 1050^\circ C$
  Solution annealing, abnormal grain growth, recristallisation, excessive nitrogen loss
Part 6: Methods for the reduction of $\text{H}_2$ outgassing

Vacuum firing

$$L_{\text{dif}} = \sqrt{D(T) \cdot t_T}$$
CERN large furnace

- **Length:** 6 m
- **Diameter:** 1 m
- **Maximum charge weight:** 1000 Kg
- **Ultimate pressure:** $8 \times 10^{-8}$ Torr
- **Pressure at the end of the treatment:** order of $10^{-6}$ Torr
The outgassing rate after the vacuum firing treatment can be calculated in the frame of the diffusion limited model.

Two asymptotic values are identified.

For **thin sheets** the initial gas content is fully emptied. In this case the $H_2$ pressure in the furnace can’t be neglected: it defines the final concentration through the Sievert’s law.

\[
c \left[ \frac{\text{Torr} (H_2)}{\text{cm}^3} \right] = 8.21 \cdot 10^{-2} \sqrt{P[\text{Torr}]} \cdot e^{\frac{2650}{1.99T[\text{K}]}}
\]

An ultimate minimum concentration of about $6 \times 10^{15}$ atoms $H$ cm$^{-3}$ could be attained after the treatment when the pressure in the furnace about $10^{-5}$ Torr.

For **thick slab**, the model has to converge to the semi-infinite solid approximation. Actually, in this case the pressure in the furnace has a very limited influence.
Part 6: Methods for the reduction of H$_2$ outgassing

Vacuum firing

After firing the concentration in the solid is given by:

$$c(x,t) = c_w + (c_o - c_w) \sum_{n=0}^{\infty} \frac{(-1)^n}{2n-1} \cos \frac{(2n+1)\pi \cdot x}{L} e^{-\frac{(2n+1)^2 \pi^2 F_o(T_f, t_f)^2}{L}}$$

In the consecutive bakeout it evolves as the concentration in a sheet with uniform concentration $c_w$ at time zero and zero surface concentration.

In the consecutive bakeout the Fourier number is increased accordingly.

$$F_o(T_f, t_f) = \frac{D(T_f) \cdot t_f}{L^2}$$

$$q(t) = \frac{4 \cdot c_w \cdot D(T)}{L} \sum_{n=0}^{\infty} e^{-\frac{(2n+1)^2 \pi^2 F_o(T_{bo}, t_{bo})}{L}} + \frac{4 \cdot (c_0 - c_w) \cdot D(T)}{L} \sum_{n=0}^{\infty} e^{-\frac{(2n+1)^2 \pi^2 [F_o(T_f, t_f) + F_o(T_{bo}, t_{bo})]}{L}}$$

where $T$ is the temperature of the measurement.
Part 6: Methods for the reduction of $\text{H}_2$ outgassing

Vacuum firing

Calculation performed for 1 wt. initial concentration and in-situ bakeout at 150° C for 24 h.

Values for diffusivity and solubility taken from P. Tison, Thesis Université Pierre et Marie Curie, Paris 6 CEA-R-5240(1) 1984

Outgassing rates in the $10^{-15}$ Torr $\ell$ s$^{-1}$ cm$^{-2}$ range are expected. For thick plates (flanges) the rate is 20 times larger.
Measurement of the outgassing rate of vacuum fired austenitic stainless steels


In 1967, R. Calder and G. Lewin reported several data for vacuum fired stainless steels (1000° C for 3 h in 2x10^{-6} Torr residual H\textsubscript{2} pressure, 1.1x10\textsuperscript{3} cm\textsuperscript{2} of 2 mm thick vacuum chamber + 10\textsuperscript{4} cm\textsuperscript{2} of 0.25 mm thick strip). Their main results, obtained by the throughput method, were:

1. the measured outgassing rates at room temperature of fired and in-situ baked stainless steels were between 6.9x10^{-15} and 1.3x10^{-14} Torr l s\textsuperscript{-1} cm\textsuperscript{-2}.

2. the outgassing rates do not increase by heating the sample up to 100° C, and a small increase can be record only at 200° C (1.9x10^{-14}). Their explained this unexpected behavior by arguing that the untreated section of the system (1.4% of the total area) could be responsible for all the H\textsubscript{2} observed up to 100° C.

The implication of the results is that “the specimen outgassing rate was very much less than 10^{-14} Torr l s\textsuperscript{-1} cm\textsuperscript{-2} “.

Calculations performed with the diffusion model show that the outgassing rate should be lower than 10^{-16} Torr l s\textsuperscript{-1} cm\textsuperscript{-2}
Measurement of the outgassing rate of vacuum fired austenitic stainless steels


G. Grosse and G. Messer measured the outgassing rate of several materials by accumulation and selective molecular beam methods. The detection limit of such a method was extremely low: \(10^{-17} \text{Torr l s}^{-1} \text{cm}^{-2}\).

Stainless steel was heated at 550° C for 3 days in an excellent vacuum of \(10^{-8} \text{Torr}\). The accumulated \(F_0\) was very high (7.9) and the final in-situ bakeout was done at 280° C for 24 h. From the diffusion limited model:

\[
q = \frac{4 \cdot (1.6 \cdot 10^{-6}) \cdot 1.9 \cdot 10^{-12}}{0.3^2} \exp\left(-\pi^2 \cdot \frac{2.6 \cdot 10^{-8} \cdot 3600 \cdot 24}{0.3}\right) \approx 3 \cdot 10^{-17} \frac{\text{Torr} \cdot \text{l}}{\text{s} \cdot \text{cm}^2} \approx 1000 \frac{\text{H}_2 \text{ molecules}}{\text{s} \cdot \text{cm}^2}
\]

The lowest value reported by the authors is \(9 \times 10^{-17} \text{Torr l s}^{-1} \text{cm}^{-2}\).

The implication of this result is that the diffusion limited model can provide estimation of the outgassing rate for concentration as low as 1 at. H ppb.
Unpublished results obtained at CERN

Material: 316LN
Wall thickness: 0.2 mm
Vacuum firing: 950°C x 2 h, 10^{-5} Torr H₂

The room temperature value for the fired samples is lower than the apparatus sensitivity. It can be obtained by extrapolating the line fit

![Graph showing H₂ outgassing vs. 1/T]
Modification of Mechanical and Metallurgical properties after vacuum firing

Cu ConFlat gasket

Hardness HB (ISO 6506)

<table>
<thead>
<tr>
<th></th>
<th>As received</th>
<th>Fired 950° C</th>
<th>Fired 1050° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>304L</td>
<td>150</td>
<td>128</td>
<td>126</td>
</tr>
<tr>
<td>316L</td>
<td>130</td>
<td>121</td>
<td>109</td>
</tr>
<tr>
<td>316LN</td>
<td>155</td>
<td>151</td>
<td>139</td>
</tr>
</tbody>
</table>

No additional precipitates have been detected after vacuum firing at 950° C

No significant variation of ”rupture strength” and “stretch at break”: less than 5%
Modification of the surface roughness induced by vacuum firing

Vacuum firing

Recrystallization
Part 6: Methods for the reduction of $\text{H}_2$ outgassing

Sublimation of metallic elements during vacuum firing

Diffusion coefficients at 950°C in austenite:
[A.F. Smith, R. Hales, Metals Science Journal, 9(1975)181]

\[
\begin{align*}
D_{\text{Cr}} &= 7 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1} \\
D_{\text{Mn}} &= 6 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1} \\
D_{\text{Fe}} &= 2 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1} \\
D_{\text{Ni}} &= 5 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}
\end{align*}
\]

Because of the higher sublimation rate of Cr, the surface of stainless steels is expected to be enriched with Fe after firing.
After vacuum firing the oxide layer is strongly enriched with Fe: Cr/Fe = 0.33 for 316L and 0.22 for 304L (0.75 for cleaned); oxide thickness as for cleaned.

Cr\textsuperscript{2p}\textsuperscript{3/2} and O1s lines indicate the presence of less hydroxides than on cleaned samples (Cr\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3}).
Not baked fired samples: Fe$_2$O$_3$ and some metallic Fe, Cr$_2$O$_3$

After 350° C 1h: FeO + metallic Fe; shift of O1s due partly to FeO, but a slight shift of Cr2p might indicate formation of Cr(OH)$_3$

Same results for 304L and 316LN
BN surface segregation during vacuum firing

- At temperature higher than 700°C, boron segregates to the surface and, in N added stainless steels (316LN), can form h-BN. Heating temperatures higher than 1150°C are needed to dissolve the h-BN layer.
- BN does not form for B concentration lower than 9 ppm.
- When the concentration is equal or larger than 9 ppm BN forms only when B is free to move, namely not blocked in BN precipitates already existing in the steel bulk.
- The BN layer strongly reduces the surface wettability and may produce peel-off of thin film coatings.
- The BN layer can be effectively removed by electropolishing.
The H₂ desorption is effectively reduced by the firing treatment. A significant fraction of the remaining hydrogen is released at 320°C and the rest at about 700°C (peaks related to the surface oxide!)
To check the validity of the Sievert’s law for the specific case of vacuum firing, a dedicated experiment has been performed in the TDS system. Vacuum firing at different D$_2$ pressures has been performed. The D$_2$ content in the samples after firing and without air venting has been measured by TDS.

The H (D) content depends on the square root of the pressure during the treatment.

The absolute values are in good agreement with data reported in the literature.
Deep **trapping sites** as carbides and nitride play a very **important role** in the kinetics of H depletion during vacuum firing.

Trapping sites should be at least partially emptied during the treatment. During cooling they should act as **powerful sinks for the residual H**. A significant reduction of the hydrogen outgassing rate at room temperature might be expected.

TDS measurement after vacuum firing of an austenitic stainless steel (Nb stabilized) containing many Nb carbide and nitride precipitates.

---

M-P Reinert, Ph.D Thesis, Université Paris-Sud, 1996
Air bakeout

This method, originally proposed by Petermann (French Patent, No 1, 405, 264), consist in forming a thick oxide layer on the metal by heating in air.

D.G. Bills, J. Vac. Sci. Technol. 6, 166 (1969):

“Such processing is reported to decrease the hydrogen diffusion rate [he means outgassing rate] by $10^3$ times if the oxidized surface is not subsequently baked above about 200° C”
Some recent data:

V. Brisson et al., Vacuum 60(2001)9. and

After air bakeout at 450° C for 38 h and in-situ bakeout at 150° C for 7 days:

\[ q \approx 10^{-15} \text{ Torr l s}^{-1} \text{ cm}^{-2} \]

The result confirm the indication given by the Bills’ paper.

It would be worthwhile to understand whether the benefit of the treatment is due to hydrogen depletion or not.

A dedicated experiment was performed at CERN by programmed thermal desorption. The 0.1 mm thick 316 LN samples were air-baked at 450°C for 24 h and 100 h. The in-situ baking was at 200°C for 12 h. The heating ramp was 5 K/min.
Part 6: Methods for the reduction of $H_2$ outgassing

Air bakeout

Temperature [°C]

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

- 24 h air bakeout
- 100 h air bakeout
- no air bakeout

50% remaining
80% remaining
The quantity of hydrogen extracted from air baked samples is of the same order of that from untreated stainless steels.

Consequence: **air bakeout decreases the outgassing rate without depleting the residual hydrogen significantly.**

However, the main hydrogen peak is shifted to higher temperatures (650°C).

Consequence: **hydrogen is blocked or trapped by the thick oxide layer.**

How thick is the oxide?

Which is the nature of this oxide?
The oxide layer of air baked austenitic stainless steels

- Cr/Fe = 0.01 (0.75 for cleaned) → very high Fe concentration
- Oxide thickness 10 times larger than cleaned
Reduction by passive barrier
Polymers

The term polymer was introduced by Berzelius in 1830. Its etymology is from Greek πολλαί—many μέρος—parts. Actually polymers are made of basic unit (monomer) repeated to form chain. The degree of polymerization is the number of monomers in the polymeric chain.
In a **cross linked polymer** the constitutional units form a three-dimensional network.

A useful classification of polymer is the following:

**Thermoplastics**: they can be repeatedly softened by an increase in the temperature and hardened by a decrease in temperature.

**Thermosets**: when cured, they change into substantially infusible and insoluble product.

**Elastomers**: they can be stretched repeatedly to at least twice their original length and, upon immediate release of the stress, will return with force to their approximate original length.

A rubber is a polymer that can be, or already is, vulcanized to an elastomeric state.
The polymer structure can be:

**Crystalline**: the macromolecules form three-dimensionally ordered arrays.

**Amorphous**: no long-range order. Spaghetti like material

**Semicrystalline**: mixing of crystalline and amorphous regions.

Only amorphous and semicrystalline polymers will be considered.
Part 7: Outgassing of polymers

**T<sub>g</sub> and excess volume**

Glass-Transition temperature T<sub>g</sub> is defined as the temperature below which thermally induced molecular motion is frozen-in (second order transition).

Above this temperature there is sufficient thermal energy to permit motion and undulation in the chain. In amorphous polymer this chain motion is associated with softness and plastic or elastic characteristics. In crystalline polymer chain motion is hindered by the crystalline forces.

Below T<sub>g</sub>, amorphous polymers are stiff, hard and often brittle.

Generally, the level of T<sub>g</sub> is associated with the relative flexibility of the polymer chain.

In the glassy state the macromolecules are not free to move in an “equilibrium position”. This generates stable empty space called excess volume.
Transport of gas in polymers

In the rubbery state the gas molecules are dragged by the thermal movement of the chain.

In the glassy state the gas molecules diffuse through the volume of the polymer and also through the excess volume.

The diffusion process in amorphous or semicrystalline polymers is not always well described by Fick’s law. This is attributed to deformation and relaxation of the polymer chains induced by the solute gas molecules (swelling). The different diffusion process can be distinguished by evaluating the **Deborah number** (dimensionless):

\[ D_e = \frac{\tau}{\nu} \]

where \( \tau \) is the polymer-penetrating molecule relaxation time, and \( \nu = \frac{L^2}{D} \) is the characteristic time for diffusion.

For \( De >> 1 \) the time for diffusion is shorter than the time for relaxation, the diffusing molecules does not record change in the polymer structure → Fick’s law is valid.

For \( De << 1 \) the penetrating molecules swell the polymer and hence allow the adsorption of additional molecules. → non fickian process.
Part 7: Outgassing of polymers

Outgassing rate of polymers is known to be much higher than that of metals. Two reasons explain this phenomenon: polymer contains much more gases than metals, and the gas mobility in polymer is orders of magnitude larger than in metals.

Example

Water solubility:
0.1 to 0.5 wt.% (4.4 to 22x10^{19} molecules/cm³)

10 to 50 times larger than the H total content in as produced austenitic stainless steel

Water diffusivity at RT:
5 x 10^{-9} cm² s^{-1}

2000 times larger than that reported for H in austenitic stainless steel.

Outgassing of Elastomers

In elastomers the molecular chains are reticulated by vulcanization. The process of vulcanization was developed by Goodyear and Hancock (1844) by heating natural rubber with sulfur. Chemical bonds are formed by chains of sulfur atoms which reacts with the unsaturated bonds of the primary macromolecules. Modern elastomers utilize a wide variety of chemicals to produce the permanent network.

Fluorocarbon rubbers are prepared by crosslinking a copolymer of tetrafluoro-ethylene and hexafluoro-propylene. These rubbers are thermally stable and have very low coefficient of friction.

**Viton®**

Viton is a fluorocarbon rubber typically employed for O-ring in vacuum technology. Typical elements of the Viton composition are:

- Viton resin 100 parts by wt.
- Carbon black 25 //
- MgO 15 //
- curing agent 1.5 //
Outgassing of Elastomers

The MgO is added as an acid acceptor to remove small amount of HF which results from the curing of the resin. The reaction is:

\[ \text{MgO} + \text{HF} \rightarrow \text{MgF}_2 + \text{H}_2\text{O} \]

Therefore, Viton is created with a built-in source of water.

Three simple warnings:

1. Viton should never be cleaned with solvents, because the solvent is dissolved in the material and its outgassing could remain for long time.

2. Ozone can cause cracking of O-rings.

3. Pre-baking of O-ring gaskets at 200°C for some hours in air or vacuum is a necessary operation when possible contaminants needs to be removed.
The outgassing rate reported in the literature have a large spread. This could be due to:

1. The large spreading in the composition and the source of the resin
2. Different history of the samples
3. The relative humidity of the laboratory

In case of seals, the benefit of the baking is hindered by atmospheric gas permeation.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Unbaked, 1 h pumping</th>
<th>Baked, ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoroelastomer</td>
<td>$4 \times 10^{-7}$</td>
<td>$3 \times 10^{-11}$–$2 \times 10^{-9}$</td>
</tr>
<tr>
<td>Buna-N</td>
<td>$2 \times 10^{-7}$–$3 \times 10^{-6}$</td>
<td>—</td>
</tr>
<tr>
<td>Neoprene</td>
<td>$5 \times 10^{-5}$–$3 \times 10^{-4}$</td>
<td>—</td>
</tr>
<tr>
<td>Butyl</td>
<td>$2 \times 10^{-6}$–$1 \times 10^{-5}$</td>
<td>—</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>$5 \times 10^{-7}$</td>
<td>—</td>
</tr>
<tr>
<td>Silicone</td>
<td>$3 \times 10^{-6}$–$2 \times 10^{-5}$</td>
<td>—</td>
</tr>
<tr>
<td>Perfluoroelastomer</td>
<td>$3 \times 10^{-9}$</td>
<td>$3 \times 10^{-11}$–$3 \times 10^{-10}$</td>
</tr>
<tr>
<td>Teflon</td>
<td>$2 \times 10^{-8}$–$4 \times 10^{-6}$</td>
<td>—</td>
</tr>
<tr>
<td>KEL-F</td>
<td>$4 \times 10^{-8}$</td>
<td>$3.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>Polyimide</td>
<td>$8 \times 10^{-7}$</td>
<td>$3 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Permeability of elastomers

The permeation flux of atmospheric water through a Viton O-ring, 5 mm cross section diameter, 6 cm torus diameter is $10^{-7}$ Torr l s$^{-1}$. The stationary condition (ultimate outgassing) will be attained after about two months.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Helium ($K \times 10^8$)</th>
<th>Nitrogen ($K \times 10^8$)</th>
<th>Oxygen ($K \times 10^8$)</th>
<th>Carbon dioxide ($K \times 10^8$)</th>
<th>Water ($K \times 10^8$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoroelastomer</td>
<td>9–16</td>
<td>0.05–0.3</td>
<td>1.0–1.1</td>
<td>5.8–6.0</td>
<td>40</td>
</tr>
<tr>
<td>Buna-N</td>
<td>5.2–6</td>
<td>0.2–2.0</td>
<td>0.7–6.0</td>
<td>5.7–48</td>
<td>760</td>
</tr>
<tr>
<td>Buna-S</td>
<td>18</td>
<td>4.8–5</td>
<td>13</td>
<td>94</td>
<td>1800</td>
</tr>
<tr>
<td>Neoprene</td>
<td>10–11</td>
<td>0.8–1.2</td>
<td>3–4</td>
<td>19–20</td>
<td>1400</td>
</tr>
<tr>
<td>Butyl</td>
<td>5.2–8</td>
<td>0.24–0.35</td>
<td>1.0–1.3</td>
<td>4–5.2</td>
<td>30–150</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>—</td>
<td>0.4–1.1</td>
<td>1.1–3.6</td>
<td>10–30</td>
<td>260–9500</td>
</tr>
<tr>
<td>Propyl</td>
<td>—</td>
<td>7</td>
<td>20</td>
<td>90</td>
<td>—</td>
</tr>
<tr>
<td>Silicone</td>
<td>—</td>
<td>—</td>
<td>76–460</td>
<td>460–2300</td>
<td>8000</td>
</tr>
<tr>
<td>TEFLOM</td>
<td>—</td>
<td>0.14</td>
<td>0.04</td>
<td>0.12</td>
<td>27</td>
</tr>
<tr>
<td>KEL-F</td>
<td>—</td>
<td>0.004–0.3</td>
<td>0.02–0.7</td>
<td>0.04–1</td>
<td>—</td>
</tr>
<tr>
<td>Polyimide</td>
<td>1.9</td>
<td>0.03</td>
<td>0.1</td>
<td>0.2</td>
<td>—</td>
</tr>
</tbody>
</table>

Part 7: Outgassing of polymers


Table VII. Gas permeabilities for several polymers and for vitreous silica.

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>Gas</th>
<th>T(°C)</th>
<th>(\Phi K^*) kcal/mole</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viton</td>
<td>Air</td>
<td>24</td>
<td>0.1</td>
<td>De Pont brochure</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>24</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N(_2)</td>
<td>24</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO(_2)</td>
<td>30</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(_2)</td>
<td>30</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Kapton</td>
<td>H(_2)</td>
<td>23</td>
<td>1.1</td>
<td>George</td>
</tr>
<tr>
<td></td>
<td>He</td>
<td>23</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(_2)</td>
<td>23</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N(_2)</td>
<td>23</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO(_2)</td>
<td>23</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Kei-F</td>
<td>O(_2)</td>
<td>24</td>
<td>0.7</td>
<td>Thorne</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>He</td>
<td>30</td>
<td>5.8</td>
<td>Ash, Barrer, and Palmer</td>
</tr>
<tr>
<td></td>
<td>Ne</td>
<td>30</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ar</td>
<td>30</td>
<td>3.3</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>H(_2)</td>
<td>30</td>
<td>9.1</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>N(_2)</td>
<td>30</td>
<td>0.9</td>
<td>11.3</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>H(_2)</td>
<td>25</td>
<td>0.10</td>
<td>Pasternak, Christensen, and Heller</td>
</tr>
<tr>
<td></td>
<td>N(_2)</td>
<td>25</td>
<td>0.01</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>O(_2)</td>
<td>25</td>
<td>0.04</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>CO(_2)</td>
<td>25</td>
<td>0.12</td>
<td>3.3</td>
</tr>
<tr>
<td>Vitreous Silica</td>
<td>He</td>
<td>24</td>
<td>0.04</td>
<td>Perkins and Begeal</td>
</tr>
</tbody>
</table>

* Units of \(\Phi\) are cm\(^3\) (STP) sec\(^{-1}\) cm\(^{-1}\) atm\(^{-1}\).
Application of polymers in UHV technology is hindered by the **huge outgassing and permeability**.

This drawback has been partially overcome in other technological domains (i.e. packaging) by **coating polymers with metals** or metal oxides (more recently also with a:C-H).

How effective are coatings in reducing outgassing and permeation rate?
In materials made of several layers the total permeability depends on the permeability and thickness of each layer through the equation:

\[
\frac{L_{TOT}}{\Pi_{TOT}} = \frac{L_1}{\Pi_1} + \frac{L_2}{\Pi_2} + \frac{L_3}{\Pi_3} + \ldots
\]

Since the permeability of metals is negligible for all gases (except hydrogen), metallic coatings should entirely block the polymer outgassing and permeation.

Despite this expectation, experimental results show that only a partial reduction of the flux is attained.

This is attributed to defects on the coating (pinholes or scratches) that cause discontinuity on the surface coverage.

Pinholes are produced during the deposition process and they are presumably due to atmospheric dust particles.
Examples of pinholes on Al coating deposited on PEEK
Transmitted light optical microscopy has been used to detect uncoated surfaces on metals films, showing that they mainly consist of pinholes of different diameters.

Counts in the scanned area
Diameter of the pinholes [μm]
Scanned area = 40 mm²

Normalised uncoated surface areas of the order of $10^{-4}$ are measured
However, experiments have shown that the permeability is reduced much less than expected from the uncoated fraction.

Example:
Al/PEEK(0.125 mm thick)
The uncoated fraction is $10^{-4}$, but the permeability of He is $10^{-2}$ of that of the uncoated polymer.
This apparent inconsistency can be justified considering that the pinhole gas throughput is enhanced by lateral diffusion.

\[ \rho = \text{Normalised permeability} \rightarrow \text{order of } 10^{-2} \]

\[ \Theta = \text{Normalised uncoated area} \rightarrow \text{order of } 10^{-4} \]

For \( L/R_0 > 0.3 \):

\[ \rho = \Theta \times \left( 1 + 1.18 \frac{L}{R_0} \right) \]

Amplification factor

Part 7: Outgassing of polymers
Part 7: Outgassing of polymers

In the literature the barrier efficiency is called “barrier improvement factor” or BIF. It is the inverse of normalized permeability.

Normalized permeability:

$$\rho = \Theta \times \left( 1 + 1.18 \frac{L}{R_0} \right)$$

Barrier improvement factor:

$$BIF = \frac{1}{\rho} = \frac{1}{\Theta \times \left( 1 + 1.18 \frac{L}{R_0} \right)}$$

The fact that $\rho$ depends on $L$ means that for $L>10R$ the flux value does not depend on the polymer thickness. In other terms, all the concentration gradient is localized near the pin-hole.

It follows also that, for similar coating, the improvement due to the coating is less significant for thicker polymer substrates.
Part 7: Outgassing of polymers

The BIF for Al coated PEEK. For thickness larger than 5 mm, the coating is useless.
Part 8: Induced desorption

The impingement of electrons and photons, of energy higher than some eV, on solid surfaces can result in ions and neutral molecules desorption.

The first observation of induced desorption are very old and they go back to the origin of modern vacuum technology.

- In 1918, Dempster observed ion desorption from electron bombarded salts (Phys. Rev. 11, 323)
Part 8: Induced desorption

Millikan reported the first evidence of photon induced desorption in 1909 during the measurement of the photoelectric current of metals exposed to ultraviolet radiation. The first interpretation is given by Winch in 1930 (Phys. Rev. 36, 601).

Winch was the first to see the implication of photoelectrons on photon induced desorption.

While attempting to study the photoelectric emission from the two sides of an unbacked film of gold, 2×10^{-8} cm thick, it was found that the emission did not hold constant but increased with exposure to ultraviolet. With 360 hours of exposure of the film to ultraviolet the photo-current from the side where the light was incident increased 136 fold and at the same time the long wave limit shifted from 2000A to 2537A.

The emission from the unexposed face increased, in the first 50 hours, about one tenth as much as from the exposed face. It was found that the film was transmitting down to a wave-length of 2259A but only about 10 percent of the energy in the lines below 2537A was being transmitted. On exposure of the second face to the direct radiation of the arc its emission increased as in the case of the first face.

It was found that with the film charged positively, so that the electrons returned to the film after being ejected, the increase in emission was more rapid and the long wave limit shift was greater than when the film was charged negatively. In either case, when the film was exposed through a filter which absorbed all wave-lengths below 2800A but transmitted 55 percent of the total energy of the arc, there was no increase in emission.

A plate of solid gold was treated in like fashion and showed a similar increase in photo-current, which took place much more slowly, accompanied by a shift in long wave limit from about 2000A to 2482A.

At intervals during the exposure of the specimen to ultraviolet fatigue curves, taken by leaving the specimen in a vacuum of 10^{-7} mm of Hg unexposed, showed during the first stage a rapid decrease in photocurrent with time of standing, but, after 360 hours of exposure for the film and 160 hours for the solid gold, the photo-current from the former held constant for 3 hours, and from the latter 1½ hours. This seemed to indicate that a fairly stable equilibrium had been reached, and the subsequent fatigue was consistent with the idea that it was due to return of gas to the surface.

The experiment was repeated, using a silver filament approximately 0.025 mm thick, and an increase in emission comparable to that for the gold film was obtained.

The probable explanation is that photoelectrons, both when ejected and returned to the surface by a reverse field, remove adsorbed gas from the surface.

Millikan noted an increase in photoelectric emission on exposure of certain metals to ultraviolet, but did not note the corresponding change in long wave-length limit or that the photoelectrons themselves apparently play an important part in the outgassing.

Work is being carried forward testing this explanation and obtaining more data on photoelectric properties of thin films.

RALPH P. WINCH

Laboratory of Physics,
University of Wisconsin,
Madison, Wisconsin,
July 15, 1930.

Part 8: Induced desorption

The first ESD theory

- In the range of the electron current typically used (~$10^{13} - 10^{14}$ electrons cm$^{-2}$ s$^{-1}$) the probability for an adparticle to interact simultaneously with more than one primary electron is small $\Rightarrow$ ESD = isolated electron adsorbate interactions

- When considering collisions between an incident low-energy particle (E$_i$ ~ 500 eV) of mass m and a free particle of mass M, one can estimate the order of magnitude of the maximum energy transferred ($\Delta E$) during the process with classical kinematics. For hard-sphere scattering the elementary result is:

$$\frac{\Delta E}{E_i} \sim 2 \frac{m}{M}$$

For electrons impinging on atoms: m $<<$ M. So the energy transfer is of the order of 2/1840 $\sim$ 0.001 for electron atomic hydrogen collisions, implying that less than 0.5 eV would be moved to the H atom in this case.

- However, ESD experiments often observe desorbing molecules, ions and molecular fragments with mass greater than 1 amu and with kinetic energies in the range from 2-10 eV. This indicates that direct momentum transfer is not usually dominant in electron adsorbate collisions, and that electronic energy transfer must be considered
One of the earliest and general models to explain ESD from surfaces was introduced independently by Menzel, Gomer, and Redhead in 1964. The acronym MGR is applied to this model. It incorporates adiabatic approximations and a semi classical description of possible excitations of an adsorbate-substrate system. The mechanism proposed is based on the Franck-Condon principle.

Neutral desorption is much more likely than ion desorption.
The initiating step in the process is the ionization or excitation of an adsorbed molecule by electron impact.

This excitation process results in a charged or excited adspecies, whose interaction energy curve with the solid may be very different from that of the ground state neutral species. The excited species may have a shallow attractive potential well or no attractive region at all.

After the excitation process, the system will relax by the excited species moving away from the surface, thus reducing the system potential energy and imparting equivalent kinetic energy to the excited species.

If no further processes occur, then the ion or excited neutral will appear in the gas phase with a defined kinetic energy.
Desorption yield

- The number of molecules desorbed per impinging electron is called desorption yield and it is usually indicated as “$\eta$”.

- $\eta$ depends on the nature of the molecule adsorbed, on the substrate material, and on the energy of the impinging particle. Typical values for traditional baked vacuum materials vary between $10^{-1}$ and $10^{-3}$ molecules per electron at 500 eV. For impinging photon the $\eta$ is in general two order of magnitude lower,

- $\eta$ saturates for energy higher than 500 eV
Part 8: Induced desorption

- For any baked material, $\eta$ is the highest for $H_2$: this reflects the Franck-Condon nature of the process, where lighter excited molecules have a higher probability to escape from the surface without decaying into the ground state.

- The other desorbed gases are CO, CO$_2$ and CH$_4$.

- $\eta$, except for H$_2$O, has a power law dependence on the dose D of bombarding particles:

$$\eta = \eta_o \cdot D^{-\alpha}$$

where $\alpha$ is found to vary between 0.6 and 1.

J. Gomez-Goñi and A. G. Mathewson

The samples were baked at 150 C for 24 h and at 300 C for 2 h
1ML = 2 x 10^{15} \text{ molecules/cm}^2

The samples were baked at 150 \degree C for 24 h and at 300 \degree C for 2 h.

The total quantity of gas desorbed exceed by far one monolayer.

In order to explain the huge quantity of gas desorbed, some authors considered stimulated gas diffusion from the oxide layer.
Part 8: Induced desorption

Synchrotron radiation induced desorption

- In modern circular accelerators, relativistic particles emit intense electromagnetic radiation in a forward-directed narrow cone (synchrotron radiation). This energetic photon flux produces strong outgassing from the vacuum system and thus a large dynamic pressure increase, which limit the beam lifetime.

- Bernardini and Malter [J. Vac. Sci. Technol. 2, 130 (1965)] were the first to study in detail the role of synchrotron radiation in the dynamic vacuum of accelerators.

- Apart from the total number of photon hitting the inner wall of the vacuum chambers, the other important parameter required to evaluate the effect of synchrotron light is its critical energy $\varepsilon_c$:

$$\varepsilon_c (eV) = \frac{3 \cdot 10^{-7}}{R} \left( \frac{E_B}{E_o} \right)^3$$

$E_o = 0.94$ GeV for proton, $5 \cdot 10^{-4}$ GeV for electron

$E_B$ is the energy of the beam, $R$ the bending radius

It is the energy at which half of the total power is emitted.
For common vacuum materials, the synchrotron desorption yields are almost linear with critical energy.
The photon desorption yield does not vary significantly up to doses of about $5 \times 10^{20}$ photons/m.

For higher doses, the decrease is similar to that of electron induced desorption.
Part 8: Induced desorption

Methods for the reduction of electron and photon induced desorption

Traditional methods for the reduction of outgassing were applied to reduce induced desorption:

- In situ bakeout is effective but the reduction of the desorption yields is less than a factor of 10.

- The effect of vacuum firing and of electropolishing, if any, is negligible.

- Air bakeout has a positive effect, but at best the reduction is of a factor of 3.

The only traditional method that reduce drastically induced desorption is discharge cleaning.
Electropolishing does not influence the desorption yield of H\textsubscript{2}. Very small variations are recorded for the other gasses.
The desorption yields of vacuum fired stainless steels are similar to those of cleaned only samples $\Rightarrow$ vacuum firing does not reduce electron stimulated desorption.
Electron induced desorption yields of an air baked sample (400°Cx24h) normalized to those of the cleaned only samples:
The slight benefit of air bakeout is not lost after high dose bombardment.

Air baked at 400°C for 24h

Cleaned only

Part 8: Induced desorption
Discharge cleaning