

# OUTGASSING OF HYDROGEN FROM A STAINLESS STEEL VACUUM CHAMBER

## RAZPLINJEVANJE VODIKA IZ NERJAVNEGA JEKLA

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Due to outgassing from the walls of vacuum calibration chambers, the generation of the calibration pressure in primary vacuum calibration systems operating below  $10^{-6}$  Pa becomes un-accurate. Austenitic stainless steel (SS) is the most common construction material for ultrahigh vacuum (UHV) and extremely high vacuum (XHV) chambers. Hydrogen is the predominant residual gas at very low pressures in SS vacuum systems, i.e., in the UHV and XHV range. Therefore, the reduction of the hydrogen outgassing rate is the most challenging problem in achieving pressures in those ranges. In this paper, a vacuum chamber with a wall thickness of 2.62 mm and made from AISI type 304 L SS was examined with the aim of mitigating the outgassing rate. The heat treatments were carried out at 250 °C for 380 h and at 350 °C for 140 h. After baking at 250 °C for 380 h (corresponding to a dimensionless time  $Fo = 3.09$ ), an outgassing rate  $q = 2.86 \times 10^{-13}$  mbar L s<sup>-1</sup> cm<sup>-2</sup> was achieved at room temperature (RT). This RT outgassing rate was further reduced to  $q = 5.7 \times 10^{-14}$  mbar L s<sup>-1</sup> cm<sup>-2</sup> after baking for another 140 h at 350 °C ( $Fo = 8.66$ , resulting in a total dimensionless time  $\Sigma Fo = 11.75$ ).

Keywords: hydrogen outgassing, stainless steel, dimensionless time, pressure-rise method, throughput method, gas-flow calibration coefficient

Zaradi razplinjevanja sten vakuumskih kalibracijskih posod postane vzpostavitev kalibracijskega tlaka v primarnih kalibracijskih vakuumskih sistemih, delujočih v tlačnem območju manjšem od  $10^{-6}$  Pa, nenatančna. Avstenitno nerjavno jeklo je najprimernejši material za gradnjo ultra visokovakuumskih (UVV) in ekstremno visokovakuumskih (EVV) posod. Pri zelo nizkih tlakih v UVV- in EVV-področju je vodik prevladujoč rezidualni plin v vakuumskih sistemih, narejenih iz nerjavnega jekla. Tako je zmanjšanje razplinjevanja vodika najpomembnejše za doseganje nizkih tlakov v naštetih področjih. V tem članku je predmet raziskav vakuumska posoda z debelino stene 2,62 mm, ki je narejena iz nerjavnega jekla AISI type 304 L. Postopki pregrevanja vakuumske posode so se izvajali pri 250 °C 380 h in pri 350 °C 140 h. Po pregrevanju pri 250 °C 380 h (kar ustreza brezdimenzijskemu času  $Fo = 3,09$ ) je bila pri sobni temperaturi dosežena gostota pretoka razplinjevanja  $q = 2,86 \times 10^{-13}$  mbar L s<sup>-1</sup> cm<sup>-2</sup>. Z nadaljnjim pregrevanjem pri 350 °C 140 h ( $Fo = 8,66$ , kar rezultira v celotni brezdimenzijski čas  $\Sigma Fo = 11,75$ ) se je gostota pretoka razplinjevanja pri sobni temperaturi zmanjšala na  $q = 5,7 \times 10^{-14}$  mbar L s<sup>-1</sup> cm<sup>-2</sup>.

Ključne besede: razplinjevanje vodika, nerjavno jeklo, brezdimenzijski čas, metoda naraščanja tlaka, pretočna metoda, kalibracijski koeficient za plinski pretok

## 1 INTRODUCTION

The development of the science and technology of ultrahigh vacuum (UHV) and extremely high vacuum (XHV) devices has been strongly coupled to the development of increasingly larger and more sophisticated devices for physics research, such as particle accelerators, magnetic fusion devices, gravity wave observatories and many surface analysis techniques. Scientific advancements in the understanding of the outgassing limits in UHV/XHV conditions are associated with these technological developments.

Outgassing refers to the spontaneous liberation of gases from the walls of a vacuum chamber or other components placed inside the vacuum chamber. This gas release results from two processes:<sup>1</sup>

- Gas diffusion from the interior of vacuum chamber walls to their inner surface. This is followed by gas desorption into the chamber volume that contributes to the vacuum system outgassing.
- Release of gases or vapours previously adsorbed onto the inner surface of the vacuum chamber walls. These

gases may have adsorbed onto the chamber inner surface while it was exposed to the environment and then slowly released as the pump removed the gas from the vacuum chamber.

The performance of a vacuum system is limited because it is impossible to eliminate all of the gas sources. Outgassing occurs even in the best-designed vacuum systems for UHV/XHV. The ultimate pressure in the system is related to the magnitude of the gas load; therefore, the measures taken to reduce outgassing are critical for the production of UHV/XHV. These effects extend the time required to reach UHV/XHV.

Due to the vaporisation or sublimation of atoms and molecules from some materials with a vapour pressure higher than or comparable to the residual pressure within a vacuum chamber, these materials will increase outgassing. Thus, not all types of materials can be used to build vacuum systems, and sometimes it is difficult to select appropriate materials that will fulfil the requirements of different processes. Among technical alloys, austenitic stainless steel (SS) offers several advantages compared to other alloys, and it is the most widely used

construction material for building vacuum chambers, instruments and components. SS is the most important construction material for UHV/XHV systems because of its good vacuum and mechanical properties.<sup>2</sup> It is non-magnetic, corrosion resistant and chemically inert. At room temperature (*RT*), SS exhibits negligible vapour pressure and negligible permeation of atmospheric gases.<sup>3</sup> SS is relatively cheap, and it can be machined and welded by standard procedures.

In the high-vacuum range, the predominant gas is usually water vapour resulting from the exposure of the system to humid air.<sup>4</sup> The outgassing of hydrogen from SS is the main gas load in UHV/XHV systems,<sup>5</sup> particularly in large systems (i.e., accelerators and storage rings). Thus, hydrogen outgassing is the most significant limiting factor in reaching outgassing rates below  $10^{-12}$  mbar L s<sup>-1</sup> cm<sup>-2</sup> in SS vacuum systems.<sup>6</sup> By reducing the hydrogen content in the bulk, the hydrogen outgassing rate can be reduced.

Many techniques have been reported that mitigate outgassing in vacuum systems, but reducing the outgassing rates of SS remains a challenge. These outgassing techniques include the following:

- Surface treatments to reduce surface roughness, such as electro-polishing and surface machining under special conditions<sup>3</sup>
- Surface treatments to create oxide films to act as a barrier to the diffusion of hydrogen from the bulk<sup>3</sup>
- High-temperature bake-out (vacuum firing) to reduce the amount of dissolved H (for SS as high as 1 000 °C)<sup>4,7</sup>
- Baking the vacuum system to remove water vapour, which has to be performed at 150–450 °C<sup>4</sup>
- Degreasing and chemical cleaning<sup>4</sup>
- Deposition of thin films to serve as a barrier layer on inner surfaces<sup>8</sup>
- Choosing metals with a low solubility for hydrogen (e.g., copper)<sup>4</sup>
- Reduction of hydrogen surface mobility by introducing surface trapping to reduce recombination<sup>8</sup>
- Thin-film getter coatings to serve as a pump for hydrogen diffusing from the bulk<sup>9</sup>

The typical outgassing rate of vacuum components made from SS is on the order of  $10^{-11}$  mbar L s<sup>-1</sup> cm<sup>-2</sup> without additional processing. An outgassing rate of  $10^{-13}$  mbar L s<sup>-1</sup> cm<sup>-2</sup> is "routinely" achievable with a sufficient bake-out treatment. Outgassing rates lower than  $10^{-14}$  mbar L s<sup>-1</sup> cm<sup>-2</sup> are achievable only with exceptional care, particularly in thin-wall vessels.<sup>8</sup> Until now, several reports have been published describing the reduction of SS outgassing rates by conventional bake-out or vacuum firing, but the resulting outgassing rates are not consistent: similar bake-out temperatures and times gave significantly different numerical values for the outgassing rates.

In 1967, Calder and Levin<sup>10</sup> published a paper on the reduction of outgassing of hydrogen from metals. They

proposed the diffusion-limited model (DLM), which means that the atomic hydrogen concentration at the surface is zero and the hydrogen atoms desorb and recombine as molecules as soon as hydrogen reaches the surface. However, their assumption was not correct for lower outgassing rates, whereas their assumption was reasonable for higher outgassing rates. The experimental values obtained by Calder and Levin were two orders of magnitude larger than expected according to the DLM.<sup>2</sup> Therefore, their assumption that the surface density of hydrogen when solving the diffusion equations is always zero is questionable. To overcome this problem, Moore<sup>11</sup> calculated the outgassing rate using a recombination-limited model (RLM). Moore assumed that the surface density can never be zero and that the boundary conditions must be included when solving the diffusion equation.

Nemanič, Šetina, Bogataj and Zajec<sup>12–14</sup> used very thin-wall vessels instead of using thicker materials to reduce the outgassing rate. They also introduced a Fourier number (or dimensionless time) *Fo* to describe the heat treatment intensity. They reported extremely low outgassing rates of approximately  $10^{-15}$  mbar L s<sup>-1</sup> cm<sup>-2</sup>, which were achieved using thinner materials.<sup>12</sup> Therefore, the use of thin materials is more efficient and economically suitable because shorter baking times can be used. However, the insufficient mechanical strength of very thin walls may make them unsuitable for the practical realisation of a vacuum chamber.

### 1.1 Measuring of outgassing flux and outgassing rate

The outgassing flux of a SS sample can be measured by two general methods<sup>4</sup>. In the first method, the pressure increase is measured as a function of time in a closed vacuum chamber after its evacuation to a low pressure. This method is called the rate-of-rise (RoR) method or the gas-accumulation method. The outgassing flux *Q* is obtained as

$$Q = V \frac{dP}{dt} \quad (1)$$

where *V* is the chamber volume and *dP/dt* is the measured rate of the pressure change in a closed chamber at a constant temperature.

In the second method, the vacuum test chamber is pumped through an orifice of known conductance, and the pressure drop across the orifice is measured. This method is known as the throughput method or the orifice method. The outgassing flux *Q* is expressed as

$$Q = C\Delta P \quad (2)$$

where *C* is the conductance and  $\Delta P$  is the pressure difference.

In both methods, the outgassing rate *q* of the sample is obtained by dividing the measured outgassing flux *Q* by the surface area *A* of the sample:  $q = Q/A$ . The measured outgassing rate is the net rate of the difference

between the intrinsic outgassing rate of the surface and the readsorption rate.<sup>15</sup>

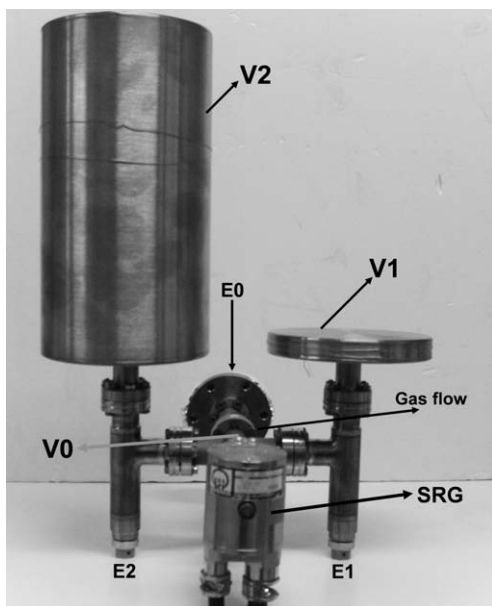
A common problem of both methods is that the test sample is placed in a vacuum measurement chamber whose walls also outgas during the measurement. Thus, the background outgassing flux of the empty chamber must be measured and subtracted from the measured outgassing flux of the sample in the chamber.

The presence of a hot cathode residual gas analyser (RGA) or ion gauge in the test chamber can cause additional outgassing, and the residual gas can react with the hot filament. Because they exhibit a certain pumping speed, RoR measurements can only be obtained with an inert vacuum gauge, such as a spinning rotor gauge (SRG).<sup>1</sup>

## 2 EXPERIMENTAL SETUP AND SAMPLE DESCRIPTION

We measured the time dependence of the outgassing rate of SS during bake-outs at 250 °C and 350 °C. Our main goal was to determine the time needed to reach the outgassing rate below  $10^{-13}$  mbar L s<sup>-1</sup> cm<sup>-2</sup> at these bake-out temperatures.

We made two simple cylindrical chambers to serve as the outgassing samples (**Figure 1**). Each chamber was assembled from a CF 16 flange and had a short connection tube with an inner diameter of 16 mm and a wall thickness of 1.5 mm. The circular end plates had a thickness of 2 mm, and the cylindrical body had an inner diameter  $d_i = 108.7$  mm and a wall thickness of 2.62 mm. The only difference between the two chambers was the cylindrical body length. The length of the body of



**Figure 1:** A photo of two SS cylindrical vacuum chambers used for the outgassing rate study

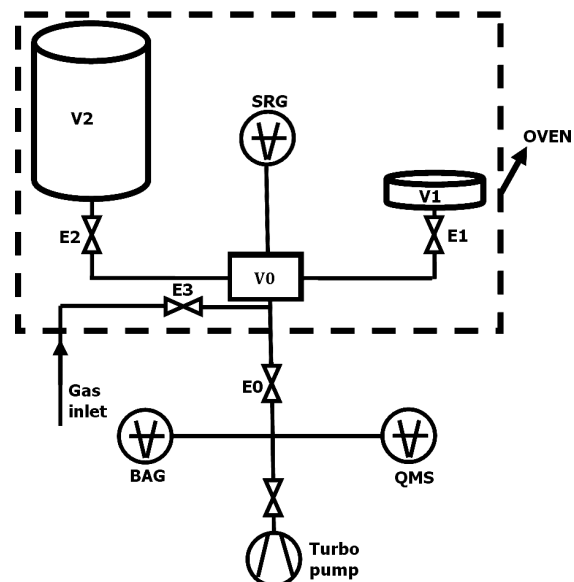
**Slika 1:** Fotografija dveh cilindričnih vakuumskih posod iz nerjavnega jekla, namenjenih za študij razplinjevanja

chamber V1 was  $l_1 = 10$  mm, and the length of the body of chamber V2 was  $l_2 = 210$  mm.

The chambers were connected to a vacuum measurement system, as shown in **Figure 2**. The system was pumped by a turbomolecular pump and was equipped with a quadrupole mass spectrometer (QMS), a Bayard-Alpert gauge (BAG) and an SRG. The SRG was connected to a small chamber V0 that was made of a standard CF16 4-way cross and a CF16 T-piece. The chamber V0 can be isolated from the pump by a valve (E0). The chambers V1 and V2 were symmetrically connected to V0 through the bake-proof CF16 all-metal valves E1 and E2, respectively. The calibration gas was introduced into V0 through valve E3.

For the modelling of the outgassing behaviour of SS by DLM and RLM, the thickness of the sample is an important parameter. The same reduction in the outgassing rate of a plane sheet takes 4 times longer time if the sample is 2 times thicker. The entire measurement sample chamber was constructed from AISI type 304 L SS, but we were unable to make the whole chamber from the same sheet of SS. Additionally, each part had a different thickness. However, the measurement procedure was designed so that we could easily calculate the outgassing rate of the cylindrical body (which has a well-defined thickness) from the separate measurements of the outgassing flux of each chamber.

The chambers V0, V1 and V2 were placed in an oven where they could be uniformly heated up to 350 °C. Additional vacuum measurement instruments (BAG and QMS) were mounted outside the oven due to the



**Figure 2:** A schematic of the outgassing measurement system: QMS – quadrupole mass spectrometer; SRG – spinning rotor gauge; BAG – Bayard-Alpert gauge; E0, E1, E2 and E3 – bake-proof vacuum valves; V0, V1 and V2 – measuring volumes

**Slika 2:** Shema vakuumskega sistema za meritve razplinjevanja: QMS – kvadropolni masni spektrometer; SRG – viskoznostni merilnik z lebdečo kroglico; BAG – Bayard-Alpertova trioda; E0, E1, E2 in E3 – pregrevni vakuumski ventili; V0, V1 in V2 – merilni volumni

limitation of their operational temperature. During the bake-out, the SRG suspension head was removed, and only a thimble with a rotor was baked with the other parts.

The outgassing flux measurements at ambient temperature were performed using the RoR method. The outgassing flux measurements while baking the vacuum system (at temperatures of either 250 °C or 350 °C) were performed using the throughput method, which is described in Section 2.2.

### 2.1 Measuring of outgassing flux using the RoR method

By closing valves E0, E2 and E3 and opening valve E1, we measured the pressure increase in chambers V0 + V1 with the SRG and used this reading to calculate the outgassing flux  $Q_1 = Q_{V0} + Q_{V1}$ . With the same SRG, we also measured the pressure increase in chambers V0 + V2 when valve E1 was closed and E2 was opened. This measurement gave  $Q_2 = Q_{V0} + Q_{V2}$ . In both cases,  $Q_{V0}$  was the same because of the symmetrical configuration of the connection with V1 and V2. By subtracting the two measured outgassing fluxes, the outgassing flux of V0 can be eliminated:  $Q_2 - Q_1 = Q_{V2} - Q_{V1}$ . The difference is equal to the outgassing flux from the major part of the cylindrical body of chamber V2 having a surface area  $A = \pi d_i \times (l_2 - l_1)$ .

To calculate the outgassing flux by the RoR method following Equation 1, we need to know the volume of the measurement system. The volumes V1 and V2 can be calculated from geometrical measurement because they are composed of simple cylindrical parts. The volume V0 has a more complicated geometrical shape because it includes the inner volume of the CF16 valves. Its volume can be determined by the static gas-expansion method. The calculated surface areas of V1 and V2 are accurate. However, we can only estimate the surface area of V0. The volumes and the surface areas for the 3 parts of the vacuum system are given in **Table 1**.

**Table 1:** The geometrical surface areas and volumes of particular parts of the vacuum measurement system, including their ratios

**Tabela 1:** Geometrijska površina  $A$  in volumen  $V$  posameznih delov vakuumskega merilnega sistema, vključujoč njihovo razmerje

|                  | Geometrical surface area<br>$A$ (cm <sup>2</sup> ) | Volume<br>$V$ (L) | Ratio ( $V/A$ )<br>(L cm <sup>-2</sup> ) |
|------------------|--|-------------------|--|
| V0               | 475 (rough estimate)                               | 0.1206            | $2.54 \times 10^{-4}$                    |
| V1               | 247  | 0.1046            | $4.23 \times 10^{-4}$                    |
| V2               | 931  | 1.962             | $2.11 \times 10^{-3}$                    |
| V <sub>tot</sub> | 1653   | 2.1872            | $1.32 \times 10^{-3}$                    |

### 2.2 Measuring of outgassing flux using throughput method

To measure the outgassing flux of the test chambers during baking, the use of the SRG is not possible because the operating temperature for the measuring head of the SRG only ranges from 10 °C to 50 °C.<sup>16</sup> As a

consequence, the RoR method cannot be used. Therefore, an adapted throughput measurement method that differs from the orifice method was used.

The steady-state outgassing flux from chamber V1 can be calculated by measuring the pressure difference  $\Delta P_1$ , as measured by the BAG or QMS while opening and closing valve E1. By knowing the effective pumping speed  $S$  at the point where the BAG or QMS are connected to the vacuum system, we can calculate the corresponding outgassing flux  $Q_1 = S \times \Delta P_1$ . Similarly, by opening and closing E2, we can determine  $\Delta P_2$ , and the outgassing flux  $Q_2 = S \times \Delta P_2$ . Also, the difference between the two fluxes is the outgassing flux from the major part of the cylindrical body of chamber V2, which has a surface area  $A = \pi d_i \times (l_2 - l_1)$ , as in the case of RoR measurements.

We were primarily interested in the outgassing of hydrogen from SS, so we used a QMS tuned to the mass number 2 (H<sub>2</sub> peak) for the  $\Delta P$  measurements. The basic output signal of the QMS is an ion current of a particular gas. The ion current  $I_i^+$  as a function of the partial gas pressure  $P_i$  is given by  $I_i^+ = g_i \times P_i$ , where  $g_i$  is the sensitivity coefficient, which depends on the gas type, the QMS geometry and the settings of various operational parameters. For accurate measurements,  $g_i$  must be determined experimentally (calibrated *in situ*) for each instrument and each gas. Therefore, to measure the outgassing flux of hydrogen, the sensitivity coefficient of the QMS  $g_{H_2}$  and the effective pumping speed  $S_{H_2}$  had to be determined. For hydrogen, the outgassing flux  $Q$  equals

$$Q = \frac{S_{H_2} \Delta I_{H_2}^+}{g_{H_2}} \quad (3)$$

To more easily determine the outgassing rate  $q = Q/A$ , we combined the effective pumping speed and the sensitivity coefficient into a single calibration coefficient  $K_{H_2}$ :

$$K_{H_2} = S_{H_2} / g_{H_2} \quad (4)$$

The calibration coefficient  $K_{H_2}$  can be determined experimentally in a straightforward manner and is described in the following section.

### 2.3 Determination of calibration coefficient

We can introduce a known flow of a calibration gas through valve E3, which is an adjustable leak valve. By closing valves E0, E1 and E2, the flow rate of the calibration gas  $Q_{cal}$  into the volume V0 can be measured by the RoR method using the same SRG as for the outgassing flux measurement. After the flow of calibration gas is determined, we can measure the difference in the hydrogen ion current  $\Delta I_{H_2}^+$  by opening valve E0. Because the calibration gas flow was introduced to the QMS from the same direction as the outgassing flux from the measuring chambers, the calibration coefficients for the calibration gas flow and the outgassing flux



have similar values. The calibration coefficient can be calculated by rearranging Equation 3:

$$K_{H_2} = \frac{Q_{cal}}{\Delta I_{H_2}^+} \quad (5)$$

The measurements of  $\Delta I_{H_2}^+$  have been performed for a wide range of calibration gas flows  $Q_{cal}$ . **Figure 3** shows that when the  $Q_{cal}$  (measured by the SRG) increases, the  $\Delta I_{H_2}^+$  (measured by the QMS) increases proportionally.

From the data in **Figure 3** and with Equation 5, we have calculated the calibration coefficient. The calculated values are given in **Table 2**. The mean value of the calibration coefficient  $K$  of the QMS for hydrogen was  $1.12 \times 10^5$  mbar L A<sup>-1</sup> s<sup>-1</sup>, and the relative standard deviation was  $\sigma(K)/K = 3.61$  %.

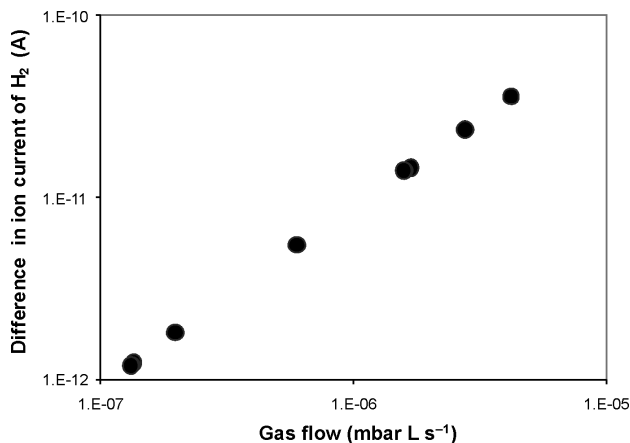
**Table 2:** The calibration coefficients of QMS for hydrogen while measuring outgassing flux by the throughput method

**Tabela 2:** Kalibracijski koeficient QMS pri merjenju pretoka razplinjevanja vodika s pretočno metodo

| $I^+$ (A)              | $K_{H_2}$ (mbar L A <sup>-1</sup> s <sup>-1</sup> ) |
|------------------------|---|
| $1.21 \times 10^{-10}$ | 116998  |
| $1.10 \times 10^{-10}$ | 118505  |
| $3.63 \times 10^{-11}$ | 114295  |
| $2.37 \times 10^{-11}$ | 115234  |
| $1.47 \times 10^{-11}$ | 113737  |
| $1.42 \times 10^{-11}$ | 110694  |
| $1.41 \times 10^{-11}$ | 110739  |
| $5.54 \times 10^{-12}$ | 106750  |
| $1.83 \times 10^{-12}$ | 107483  |
| $1.24 \times 10^{-12}$ | 107763  |
| $1.21 \times 10^{-12}$ | 108467  |
| $1.20 \times 10^{-12}$ | 108439  |

The final equation to calculate the outgassing rate is

$$q = \frac{K}{A} (\Delta I_{V_2} - \Delta I_{V_1}) \quad (6)$$



**Figure 3:** The difference in the hydrogen ion current, measured by QMS (using the throughput method), as a function of the hydrogen gas flow, measured by SRG (using the RoR method)

**Slika 3:** Razlika v ionskem toku vodika (ki je bil izmerjen s pretočno metodo in uporabo QMS) v odvisnosti od pretoka vodika (izmerjenega z metodo hitrosti naraščanja tlaka in uporabo SRG)

where  $\Delta I_{V_1}$  and  $\Delta I_{V_2}$  are the changes in the hydrogen ion current when closing valves E1 and E2, respectively.

### 3 RESULTS AND DISCUSSION

#### 3.1 Time dependence of H<sub>2</sub> outgassing rate during bake-out at 250 °C

The measuring chambers were first baked at 250 °C for 380 h. The bake-out temperature was increased to 350 °C, and baking continued for an additional 140 h. The chambers were baked by keeping the outer side of the chamber wall in air while the inner side was under vacuum.

During the bake-out at 250 °C, we performed several measurements of the outgassing rate at the bake-out temperature using the throughput method. The heat treatment intensity expressed as a Fourier number, the baking time of the system and the outgassing rates during the heat treatment are given in **Table 3**.

**Table 3:** The measured hydrogen outgassing rate of the SS vacuum chamber during the bake-out. All of the outgassing rates were measured at a temperature of 250 °C.

**Tabela 3:** Izmerjena gostota pretoka razplinjevanja vodika vakuumske komore iz nerjavnega jekla med pregrevanjem pri 250 °C

| $\Sigma Fo$ | $t$ (h) at 250 °C | $q$ (mbar l s <sup>-1</sup> cm <sup>-2</sup> ) |
|-------------|-------------------|--|
| 0.20        | 24                | $2.6 \times 10^{-8}$                           |
| 0.77        | 95                | $1.10 \times 10^{-8}$                          |
| 0.77        | 95.2              | $1.12 \times 10^{-8}$                          |
| 0.78        | 96                | $1.19 \times 10^{-8}$                          |
| 0.88        | 108               | $8.20 \times 10^{-9}$                          |
| 0.89        | 110               | $8.40 \times 10^{-9}$                          |
| 0.91        | 112               | $8.80 \times 10^{-9}$                          |
| 1.54        | 190               | $4.20 \times 10^{-9}$                          |
| 1.59        | 196               | $3.90 \times 10^{-9}$                          |
| 1.71        | 211               | $2.90 \times 10^{-9}$                          |
| 1.72        | 211.5             | $2.95 \times 10^{-9}$                          |
| 1.72        | 212               | $3.00 \times 10^{-9}$                          |
| 1.84        | 227               | $2.50 \times 10^{-9}$                          |
| 1.86        | 228.5             | $2.40 \times 10^{-9}$                          |
| 1.87        | 230               | $2.30 \times 10^{-9}$                          |
| 2.06        | 254               | $2.00 \times 10^{-9}$                          |
| 2.07        | 255               | $2.05 \times 10^{-9}$                          |
| 2.08        | 256               | $2.08 \times 10^{-9}$                          |
| 2.26        | 278               | $1.80 \times 10^{-9}$                          |
| 2.27        | 279               | $1.85 \times 10^{-9}$                          |
| 2.84        | 350               | $1.00 \times 10^{-9}$                          |
| 2.85        | 351               | $1.05 \times 10^{-9}$                          |
| 3.06        | 376               | $6.90 \times 10^{-10}$                         |
| 3.07        | 378               | $7.30 \times 10^{-10}$                         |

The Fourier number (or dimensionless time)  $Fo = 4Dtd^{-2}$  is a characteristic quantity for describing and modelling diffusion. It was used to compare the outgassing rates for different experiments.<sup>17</sup> To determine the dimensionless time  $Fo$ , the following must be known: the diffusion constant  $D$  for hydrogen at temperature  $T$ , the processing time  $t$  and the wall thickness  $d$ .

The parameters  $t$  and  $d$  are measured directly. The temperature dependence of  $D$  is given by

$$D = D_0 \exp\left(\frac{-E_a}{kT}\right) \quad (7)$$

Typical values for the diffusion pre-exponential factor ( $D_0 = 0.012 \text{ cm}^2 \text{ s}^{-1}$ ) and the activation energy ( $E_a = 0.57 \text{ eV}$ )<sup>18</sup> were used to calculate the  $Fo$  values.

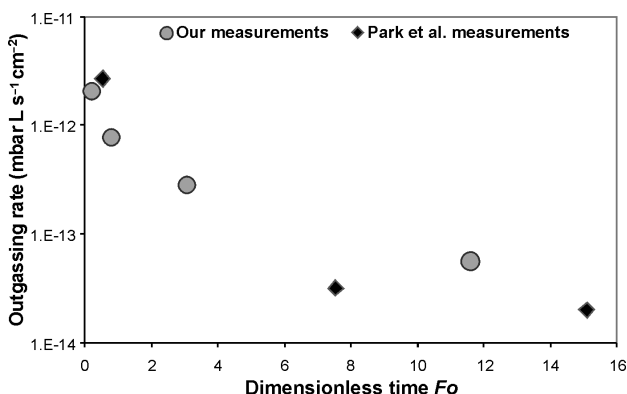
The bake-out at 250 °C was interrupted a few times to cool the chambers and to measure the outgassing rates at RT. The time course was as follows: bake-out at 250 °C for 24 h, interrupt baking for the RT measurement, bake-out at 250 °C for 73 h, interrupt baking for the RT measurement and bake-out at 250 °C for 284 h followed by an RT measurement. The temperature was then raised to 350 °C, and baking was performed for additional 140 h. The system was then cooled again, and the last RT measurement was performed. The results of the hydrogen outgassing rate measurements at RT, which were performed using the RoR method, are summarised in **Table 4**.

**Table 4:** The hydrogen RT outgassing rates of SS after the indicated bake-out treatment

**Tabela 4:** Gostota pretoka razplinjevanja vodika iz nerjavnega jekla pri sobni temperaturi po navedenem postopku pregrevanja

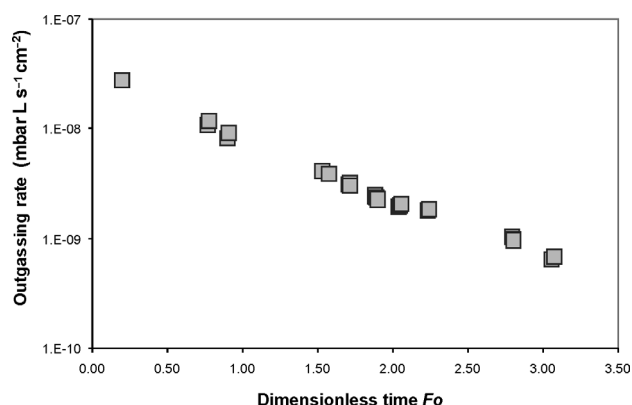
| $T$ (°C) | Incremental time $\Delta t$ (h) | $Fo$ ( $\Delta t$ ) | $\Sigma Fo$ | $q$ ( $\text{mbar L s}^{-1} \text{ cm}^{-2}$ ) |
|----------|---------------------------------|---------------------|-------------|--|
| 250      | 24                              | 0.19                | 0.19        | $2.10 \times 10^{-12}$                         |
| 250      | 73                              | 0.59                | 0.78        |  |
| 250      | 284                             | 2.31                | 3.09        |  |
| 350      | 140                             | 8.66                | 11.75       |  |

A comparison of our results of the RT outgassing rate with the results obtained by Park et al.<sup>19</sup> is shown in **Figure 4**. The Fourier numbers for the data from Park et al. were recalculated using our activation energy for the diffusion  $E_a = 0.57 \text{ eV}$  (instead of  $E_a = 14.5 \text{ kcal mol}^{-1} \approx 0.622 \text{ eV}$ , which was used by Park et al.). Our results



**Figure 4:** A comparison of the hydrogen outgassing rates between our measurements and the measurements of Park et al.<sup>17</sup>, which were performed after the system was cooled to RT

**Slika 4:** Primerjava gostote pretoka razplinjevanja vodika iz nerjavnega jekla med našimi meritvami in meritvami Parka et al.<sup>17</sup>, ki so bile izvedene po ohladitvi sistema na sobno temperaturo



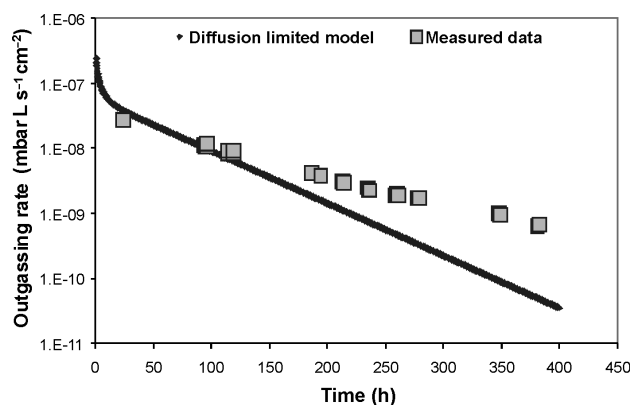
**Figure 5:** The hydrogen outgassing rate of SS as a function of the dimensionless time  $Fo$  during the heat treatment at 250 °C

**Slika 5:** Gostota pretoka razplinjevanja vodika iz nerjavnega jekla v odvisnosti od brezdimenzijskega časa  $Fo$  med postopkom pregrevanja pri 250 °C

agree and are within a factor 3 to 4 of the results of Park et al.

A graphical representation of the results (taken from **Table 3**) of the outgassing rates measured at 250 °C as a function of dimensionless time  $Fo$  is shown in **Figure 5**.

In **Figure 6**, the same measured outgassing rates as a function of the bake-out time are presented and compared with the calculations based on the DLM.<sup>1,6</sup> The outgassing rate predicted by diffusion theory for  $t = 380 \text{ h}$  is  $q = 5 \times 10^{-11} \text{ mbar L s}^{-1} \text{ cm}^{-2}$ , which is 15 times lower than the measured value  $q = 7 \times 10^{-10} \text{ mbar L s}^{-1} \text{ cm}^{-2}$ . In the early stage of bake-out, until approximately 100 h at 250 °C, the predicted curve according to the DLM and the measured data agree. However, discrepancies start to emerge after 100 h. For  $Fo > 0.8$ , the atomic hydrogen recombination on the SS surface is assumed to become a rate-limiting step. When a hydrogen atom has moved from the bulk to the surface/vacuum interface, it needs to find another hydrogen atom on the surface to recombine.



**Figure 6:** A comparison of the DLM-predicted hydrogen outgassing rate of SS and the measured data during the heat treatment at 250 °C as a function of the bake-out time

**Slika 6:** Primerjava gostote pretoka razplinjevanja vodika iz nerjavnega jekla, predvidenega na osnovi modela DLM, z merilnimi rezultati v odvisnosti od časa pregrevanja pri 250 °C

As the number of freely diffusing hydrogen surface atoms is reduced, recombination becomes less likely. Thus, when the diffusion of hydrogen atoms to the surface become small, the recombination of the hydrogen atoms might be the rate-limiting step, i.e., outgassing from the surface is described by the rate at which the hydrogen atoms can be recombined, not the bulk diffusion rate.

#### 4 CONCLUSIONS

The determination of the calibration coefficient  $K$  for the BAG and QMS allowed us to measure the outgassing rate during the heat treatment without stopping the heating process. The DLM governs the initial removal of hydrogen from SS, and it is assumed that hydrogen surface recombination plays an important role in the outgassing rate at lower hydrogen concentrations. To compare the different outgassing treatments, the  $Fo$  number appears to be a good choice because it can be accurately calculated for any processing time and temperature. The  $Fo$  number is a parameter that shows the level of heat treatment of SS, and it is related to the diffusion of hydrogen atoms in SS.

An outgassing rate  $q = 2.86 \times 10^{-13}$  mbar L s<sup>-1</sup> cm<sup>-2</sup> at RT was achieved for AISI type 304 L SS after baking the system at 250 °C for 380 h (conversion to dimensionless time gives  $Fo = 3.09$ ). This outgassing rate was further reduced to  $q = 5.7 \times 10^{-14}$  mbar L s<sup>-1</sup> cm<sup>-2</sup> by baking for another 140 h at  $T = 350$  °C ( $Fo = 8.66$ , total dimensionless time  $\Sigma Fo = 11.75$ ).

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