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Additional measurement regarding corrosion of copper in oxygen free environment

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Abstract

Two experiments have been performed by Studsvik as complementary work to a previous project performed by Studsvik for The Swedish Radiation Safety Authority, aiming to examine the possibility of corrosion of copper in an oxygen free environment. The present work have been performed using the same experimental equipment: A two chamber system separated by a thin palladium membrane, which allows for hydrogen to pass through it. The first test was done to verify the equipment by performing a near repetition of one of the experiments performed in the original work. The second test was performed to test the background of the equipment and was done with both chambers evacuated. This report summarizes the results obtained during the tests, and comparisons with the previous work have been included for reasons of clarity. However, no attempts to understand, to evaluate or to discuss any similarities and/or differences (and origins of any such) between the results obtained in this work to the results obtained in the original SSM project has been included in this work.

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1 Introduction

The present additional measurements were requested and funded by SKB. The work is based upon previous work done by Studsvik Nuclear contracted by the Swedish Radiation Safety Authority (SSM) to experimentally examine the work done by Hultquist et al. on corrosion of copper in an oxygen free environment. The previous work has been published by SSM [1], and the present work was performed using the same experimental equipment.

1.1 Objective

The objective of the work is to perform complementary examinations using the same experimental equipment as was used in the previous SSM project in regards to evolution of hydrogen by copper in ultrapure water without dissolved oxygen.

2 Experimental

2.1 Equipment

The equipment used in the present experiments was the same as was used for the testing performed by Studsvik Nuclear in year 2012 [1]. The equipment is only briefly explained below, more details can be found in the original report.

Two ultrahigh vacuum chambers are connected via a palladium membrane, see Figure 1. A vacuum pump (a HighCube 80 Eco Turbo pumping station) was used to evacuate the chambers.

Figure 1
Picture of the equipment used in the present experiments.

After assembly, each chamber was continuously evacuated to remove any moisture absorbed by the parts. The integrity of the whole experimental set-up was checked by evacuating the chambers and monitoring the pressure. To make sure that a good vacuum could be achieved, the tightness between each connection was checked by measurement of the distance between the two parts using a feeler gauge.

The pressure was monitored in the lower chamber using a PTR24602 active capacitive transmitter CMR 361 (measuring range 1100 mbar to 10^{-1} mbar), and in the upper chamber using a PTR24632 active capacitive transmitter CMR 364 (measuring range 1.1 mbar to 10^{-4} mbar).

2.2 Experimental performance

2.2.1 Test one – equipment verification

The equipment verification test was performed in a similar manner as the background test in the SSM project [1] i.e. with a Pt foil immersed in ultrapure water in the lower chamber, but with the following changes:

The test was performed in two steps: An initial step where the equipment was kept at room temperature that lasted for about one week, and a second step were the equipment was kept at 60 °C (63 °C for the palladium membrane heater) that lasted for about six days. The upper chamber was evacuated in between these two steps.

The water from the glass vessel in the lower chamber was collected after the exposure together with an ultrapure reference water sample.

2.2.2 Test two – background examination

This setup of experimental parameters is new for the present project and was not performed in the SSM project. In this experiment, both chambers were evacuated to as low a pressure as possible. Evacuation of the upper chamber was performed with the temperatures already set at 63 °C. The lower chamber was empty, i.e. the glass container with water and the Pt foil was removed. The equipment was allowed to run for ten days during which time the pressures in the upper and lower chambers were monitored.

3 Results

3.1 Test one – equipment verification

3.1.1 Room temperature testing

The pressure in the lower chamber was about 34 mbar after evacuation, see Figure 2. No increase in pressure could be observed during the one week testing at room temperature, see Figure 3 (the fluctuations in pressure are attributed to fluctuations in ambient temperature).

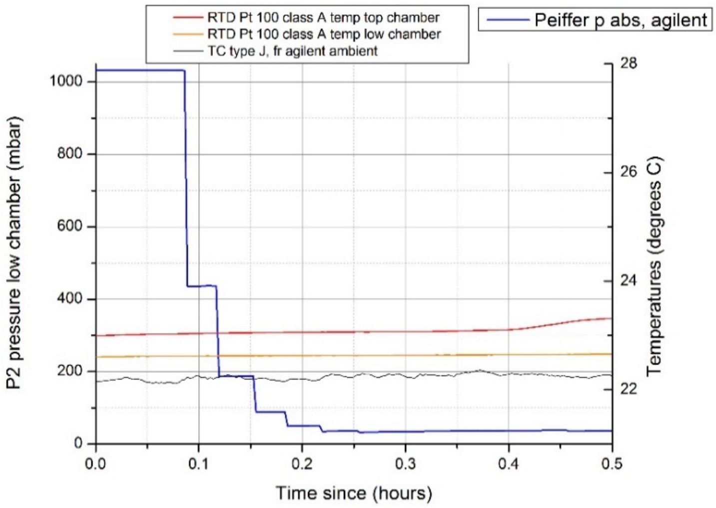

Figure 2
Stepwise decrease of the pressure in the lower chamber.

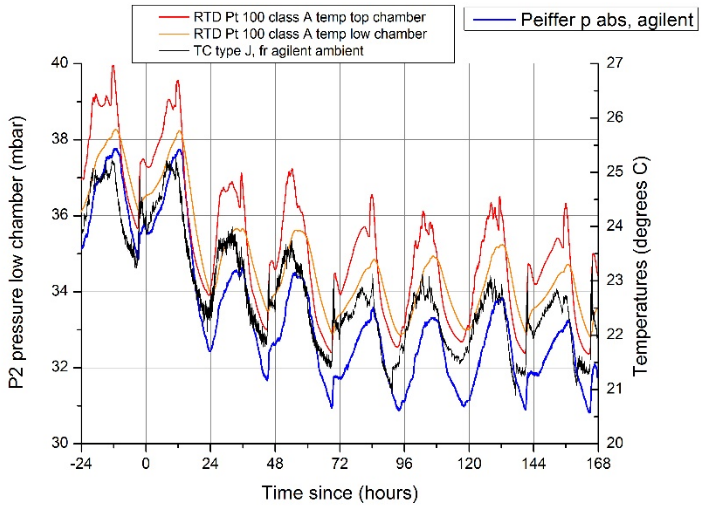

Figure 3
Pressure in the lower chamber together with temperatures in the lower heater and the heater around the palladium membrane for the test of equipment at room temperature.

The chamber above the palladium membrane had been evacuated for several days to the lower limit of the pressure sensor (< 10^{-4} mbar). The monitoring of the pressure of the chamber above the membrane after evacuation revealed a very low pressure increase, in the order of 0.0002-0.0003 mbar/24h, see Figure 4. (The negative value is a result from the measuring equipment which has a lower limit of 10^{-4} mbar. A pressure below this is given as a negative value). This result is similar to what was obtained for the platinum reference run in the previous project, see Chapter 3.3.

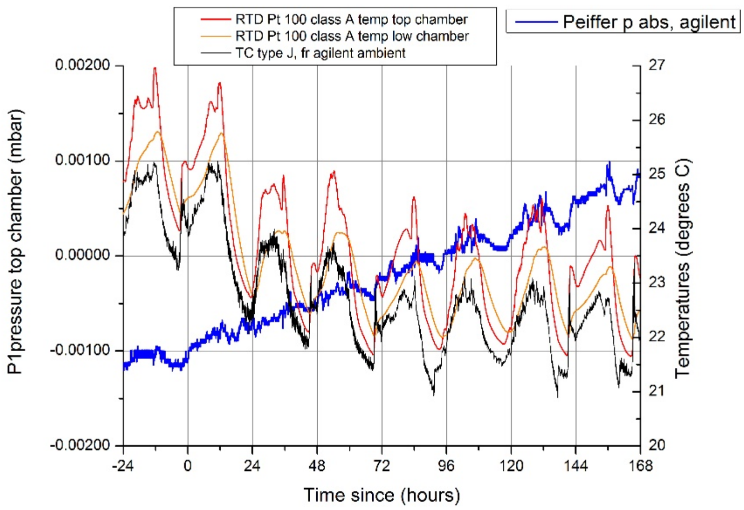

Figure 4
Pressure in the upper chamber together with temperatures in the lower heater and the heater around the palladium membrane for the test of equipment at room temperature.

3.1.2 Elevated temperature testing

For the continued test of the equipment at 60 °C, the heater on the palladium foil was set to 63°C using a heating rate of 10 °C/h. This resulted in a rapid increase in pressure in the upper chamber, leading to a decision to evacuate the upper chamber. As a stable background level was observed after this evacuation, the heater of the lower chamber was then set to 60 °C using a heating rate of 10 °C/h.

The pressure of the lower chamber increased with the temperature increase most likely due to an increase of the vapour pressure of the water. The final pressure of the lower chamber was around 160 mbar at 60°C, see Figure 5.

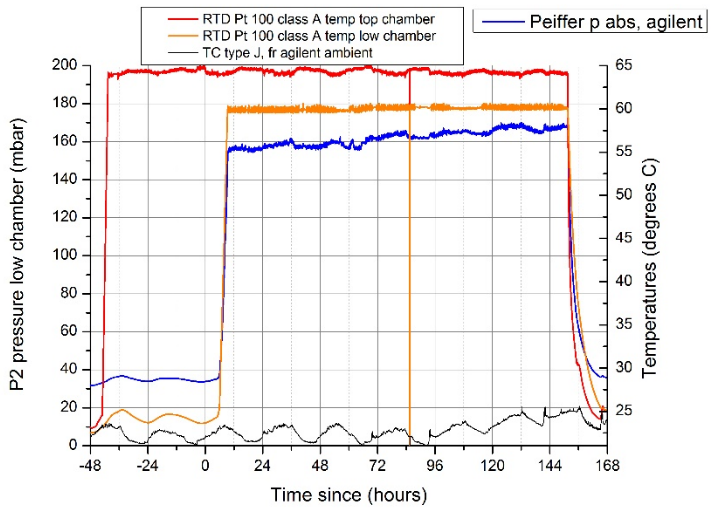

Figure 5
Pressure in the lower chamber together with temperatures in the lower heater and the heater around the palladium membrane for the test of equipment at 60 °C.

The pressure of the upper chamber increased after the evacuation of the upper chamber, see Figure 6. This result diverge from what was obtained for the platinum reference run in the previous project, see Chapter 3.3. No attempt to seek an explanation to the cause of this pressure increase was done within this project.

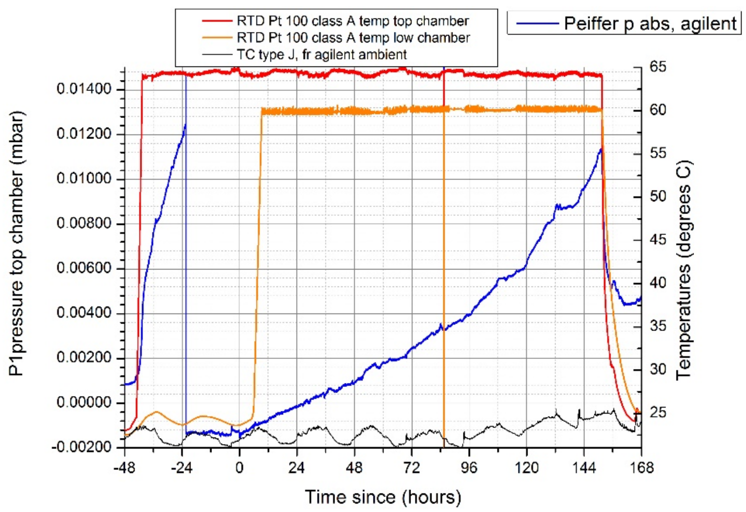

Figure 6
Pressure in the upper chamber together with temperatures in the lower heater and the heater around the palladium membrane for the test of equipment at 60 °C.

3.1.3 Summary of test one

Figure 7 below shows the pressure in the upper chamber from both the room temperature and the 60 °C experiments along a common x-axis. The first section at room temperature revealed a pressure increase of 0.00028 mbar/24h, in the same order as was detected in the original SSM work. The pressure increase after the temperature increase and subsequent evacuation of the upper chamber is 0.00202 mbar/24h, about a factor of 7 larger. No attempts to divulge the origin of this pressure increase has been performed within this project.

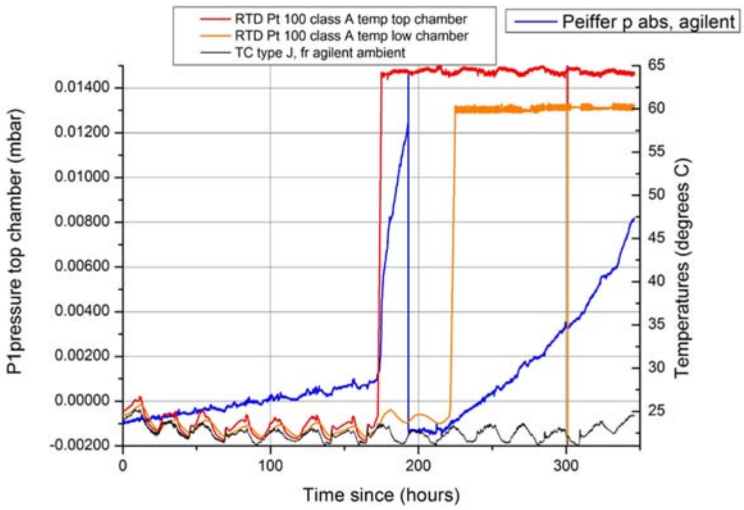

Figure 7
Pressure in the upper chamber together with temperatures in the lower heater and the heater around the palladium membrane for the test of equipment at room temperature and at 60 °C.

3.2 Test two – background examination

The pressure of the lower chamber was low and stable throughout the ten day monitoring period (see Figure 8). Note that the pressure sensor used in the lower chamber has a measuring limit of 10^{-1} mbar.

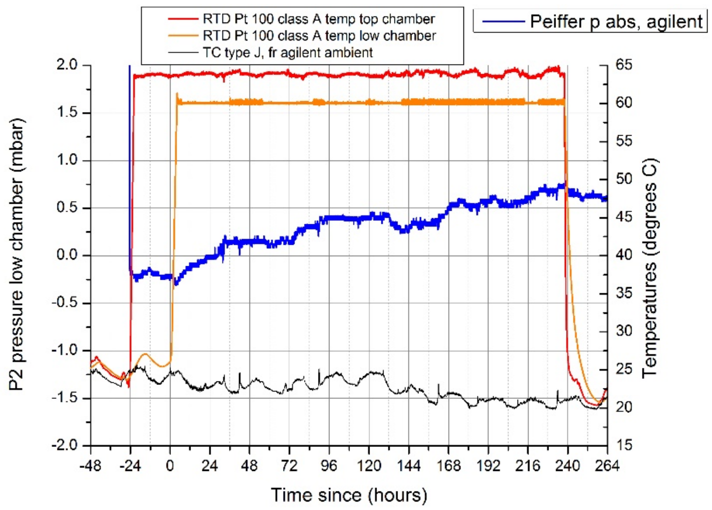

Figure 8
Pressure in the lower chamber together with temperatures in the lower heater and the heater around the palladium membrane for the test of background.

The pressure of the upper chamber increased during the ten day monitoring period, see Figure 9. The pressure increase was found to be about 0.00109 mbar/24h, see Chapter 3.3.

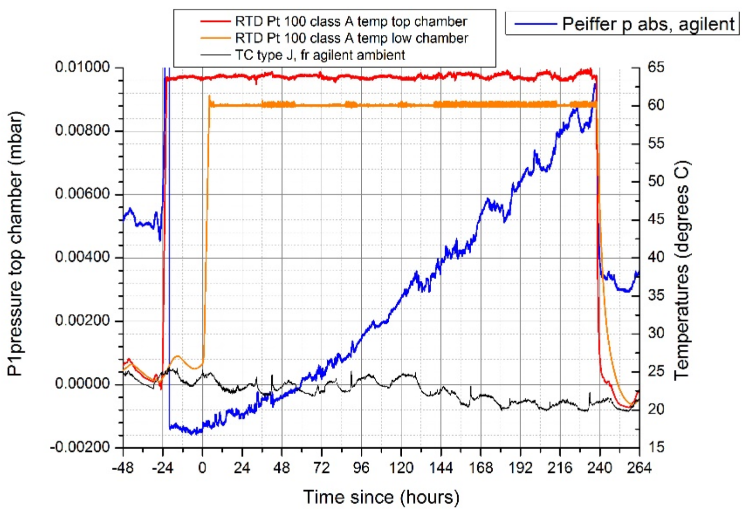

Figure 9
Pressure in the upper chamber together with temperatures in the lower heater and the heater around the palladium membrane for the test of background.

3.3 Comparison of results to the previous SSM project

Figure 10 below shows the results from the pressure measurements of the previous SSM work with the results from this work. Figures of the pressure increase rate is presented in Figure 10.

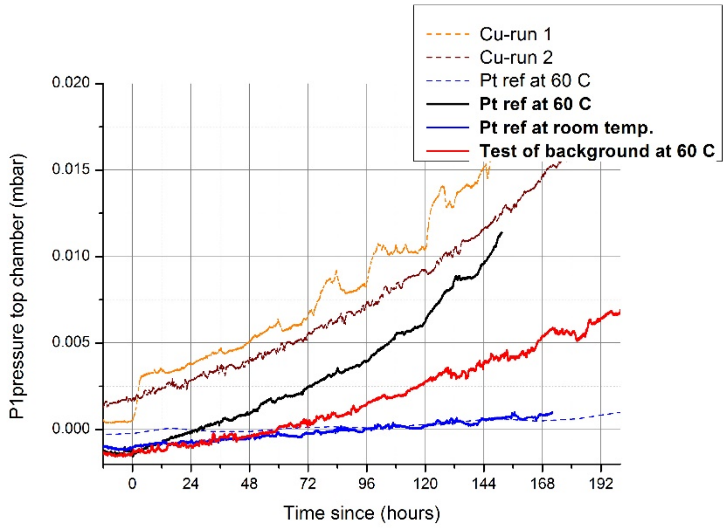

Figure 10
Comparison of results in the present project (bold text and lines) to results obtained in the previous SSM project (dotted lines) [1].

Table 1
Pressure increase rates for the experiments in the previous and the present project, respectively.

	Measurement	**Range of data evaluation (hours)**	**Pressure increase rate (mbar/24h)**
Previous SSM project	Cu-run 1	0-300	0.00534
	Cu-run 2	0-300	0.00312
	Pt ref at 60 °C	0-300	0.00016
Present project	Pt ref at 60 °C	0-151	0.00202
	Pt ref at room temp.	0-168	0.00028
	Test of background at 60 °C	0-238	0.00109

No attempts to understand, to evaluate or to discuss any similarities and/or differences (and origins of any such) between the results obtained in this work to the results obtained in the original SSM project has been included in this work.

4 Acknowledgments

Riitta Johansson, the Studsvik lead technician who performed most of the experimental work, is greatly acknowledged for her contribution to this work.

Richard Becker, Studsvik Nuclear, is acknowledged for his experience and discussions regarding the previous work performed by Studsvik.

Allan Hedin, SKB, is acknowledged for fruitful discussions throughout this work.

5 References

[1] Richard Becker and Hans-Peter Hermansson. **Evolution of hydrogen by copper in ultrapure water without dissolved oxygen**. *The Swedish Radiaion Safety Authority (SSM): Report number: 2011:34 ISSN: 2000-0456*, Available at: www.stralsakerhetsmyndigheten.se