# Cleaning of failed Lead containing Zircaloy-2 Neutron Spallation Target Rods with a Dissolution Process

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## Abstract

The Paul Scherrer Institut PSI operates the spallation neutron source SINQ. SINQ is designed as a neutron source mainly for research with thermal and cold neutrons, but hosts also facilities for isotope production and neutron activation analysis. The spallation is performed with a proton beam hitting a lead target; the lead is encapsulated in Zircaloy-2 rods. The SINQ neutron spectrum resembles that of a medium flux research reactor. The Zircaloy-2 target rods have typical cross-sectional dimensions like fuel rod claddings. To avoid strong neutron moderation, heavy water is used for cooling.

On June 25, 2016, the facility was shut down because of an unexpected target failure (target with consecutive no. 11). The division hot laboratory (AHL) as well as the Laboratory for Nuclear Materials (LNM) are strongly involved in the failure investigations. Before examining the current target, similar older target rods are analyzed (target no. 9). These rods are interesting because they accumulated a high fluence but did not fail. Their investigation can help better understanding the material aging and operational impact onto the material. Foreseen and already partially performed are tests concerning micro-structure and -chemistry (EPMA), hydrides (EPMA and SIMS) and radiation embrittlement (micro hardness / metallography). Mechanical tests are planned, however, for these the rod sections need to be lead free. Some of the rods filled with lead could not be cleaned by pushing the lead out completely. Thus, chemical cleaning has been envisaged.

The first task was to find a chemical dissolution process, which does not change the hydrogen content in the samples. The hydrogen, originating from the proton deposition, is an important factor for materials degradation. After literature review, several inactive dissolution tests were made and a process was defined. We reached good results with an acetic acid mixture

For active tests we have chosen the heavily shielded and manipulator equipped dissolution box. Some of the spallation products are very exotic: e.g. polonium, mercury (Hg-194) or gold (Au-194). The amount of a possible release of gas or aerosols of these nuclides into the exhausting system had to be clarified. The use of active carbon filters has been suggested. Together with a Swiss company, specialized in nuclear industry products, the development of appropriate filter holders for existing standard filters has been started. Further, a safety report is established; in particular, personal safety equipment and a safe procedure are defined.

## 1. Introduction

The Paul Scherrer Institut operates the spallation neutron source SINQ. SINQ is designed as a continuous neutron source. It is driven by the PSI 590 MeV proton accelerator with a covered power of 1MW onto the SINQ-target. The SINQ is mainly for research with thermal and cold neutrons, but hosts also facilities for isotope production and neutron activation analysis. The spallation is performed with a proton beam hitting a lead target; the lead is encapsulated in Zircaloy-2 rods. These rods are placed in a double-walled aluminum container. Except for its different process of releasing neutrons from matter by a spallation reaction, SINQ resembles a medium flux research reactor. The Zircaloy-2 target rods have typical cross-sectional dimensions like a fuel rod cladding. To avoid strong moderation, heavy water is used for cooling. The moderator vessel contains about $4m^3$ of heavy water.
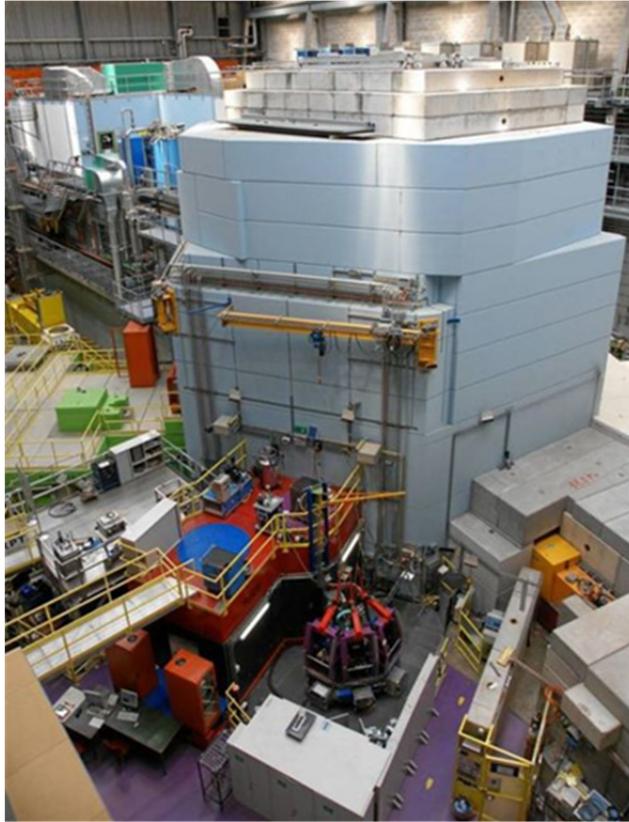
Figure 1: SINQ target Block

## 2. Target Failure and Samples Selection

On June 25th 2016 around one o' clock pm the facility was shut down because of an unexpected target failure (target with the consecutive no. 11). At that time we were running an own test at one of the SINQ beam lines. All experiments, unfortunately including our own had to be stopped and no beam was available for several months until end of October 2016.

The division hot laboratory (AHL) as well as the Laboratory for Nuclear Materials (LNM) are strongly involved in the investigations about the reason for the target failure. The concerned rods had to stay for twelve months in the SINQ shielded storage cell, because they were too active for transportation and for the planned tests in the Hotlab. The target-11 rods are strongly damaged. There are similar older target rods in the Hotlab (target no. 9). They are of specific interest because they are less affected (despite a highly accumulated proton dose the geometry is still intact) and their investigation can help to obtain a view on the material aging and operational impact onto the material, and shall anticipate potential target failures. Foreseen and already partially performed are tests concerning micro-structure and -chemistry (EPMA), hydrides determination (EPMA and SIMS) and radiation embrittlement (micro hardness / metallography). Further, mechanical tests are planned, however, for these the rod sections need to be lead free. Some of the rods filled with lead could not be cleaned by pushing the lead out completely. Thus, chemical cleaning has been envisaged.
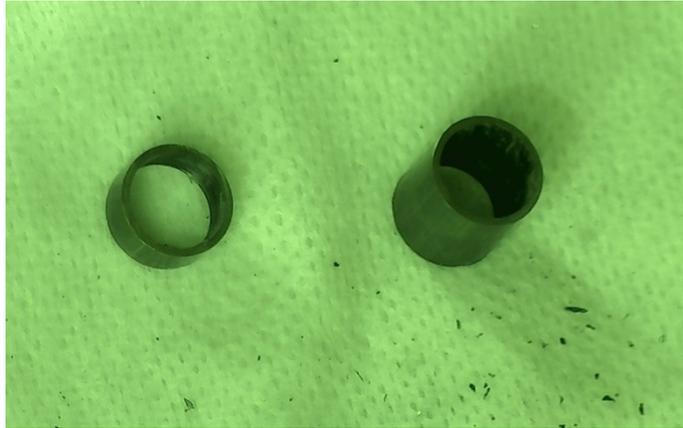
Figure 2: Target 9, cut samples

## 2.1 EPMA of Target-9 Samples

To have a fast overview what may happened, first, some of the older target-9 samples were investigated in the Electron Probe Micro Analyzer (EPMA), also using the backscatter electrons (BSE) detector to possibly visualize hydrides. Hydrides, stemming from the proton irradiation, were suspected playing a major role for material degradation. The investigations confirmed the assumption and the samples showed locally many cracks because of an enormous hydrogen loading and oriented hydrides.
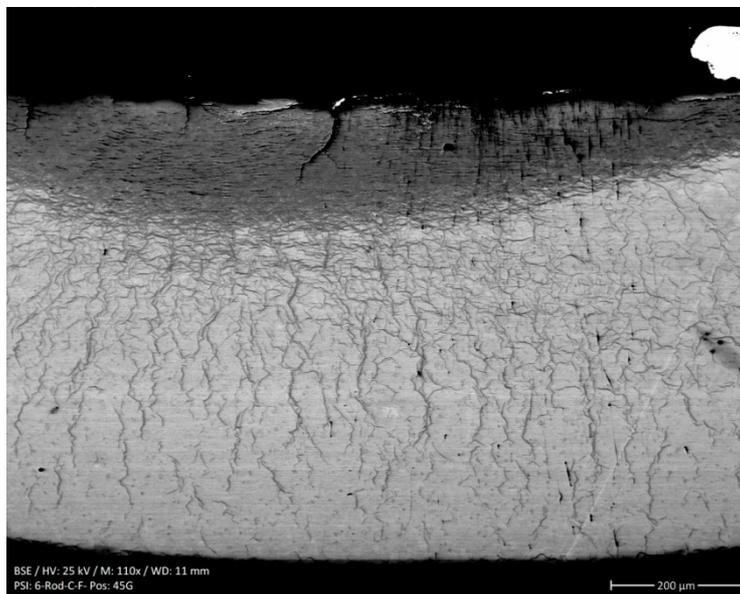


Figure 3: Target 9, EPMA (BSE detector)

An important question for further, especially mechanical, investigations was how to perform the necessary removal of the remaining Pb. For this task, we had to take into account the damage and hydrides structure adjacent to the surface and the surface chemistry. Both must not be changed during the removal procedure.

## 3. Inactive Tests of Chemical Solution

The first task was to find an optimal dissolution process and an appropriate acid, respectively. We also had to make sure, that there was no change of the hydrogen content in the samples during the boiling with the acid. Concerning the solubility of lead we found some hints in a work description of a former project [1] and in the literature. Corresponding to the former project a mixture of acetic acid, hydrogen peroxide and ethyl alcohol (1:1:1) is suitable for dissolving lead residues. After further internet searches, we decided to use 30% acetic acid, 40% hydrogen peroxide and absolute ethyl alcohol. We also wanted to clarify with inactive tests whether the alcohol can be omitted. In these inactive trials, a conservative lead amount was calculated and all tests went well. Thus, we generally refrain from the use of alcohol, but reserve the possibility to use it in case of need.

Table of inactive Zircaloy-2 pre-tests

| H conc. [ppm] | Hydrogen loading | Lead filling | Chemical treatment |
|---|---|---|---|
| 15.2 | no | without | untreated |
| 14.4 | no | without | in 100 ml acetic acid 30%/$H_2O_2$ (1:1) boiled; optimization test |
| 13.6 | no | with | in 120 ml alcohol/acetic acid 30%/$H_2O_2$ (1:1:1) |
| 13.7 | no | with | in 120 ml acetic acid 30%/$H_2O_2$ (1:1) boiled |
| 261.3 | yes | without | untreated |
| 262.8 | yes | with | in 120 ml acetic acid 30%/$H_2O_2$ (1:1) boiled |



Figure 4: Inactive dissolution equipment

The reflux temperature is about 98° C without alcohol. The maximum treatment time is limited to 6 hours per day; due to hotlab time restrictions the treatments had to end in any case at 4 pm, taking shutdown times and transition to safe conditions into account. Further, the operator has to be present in the laboratory, apart from prescribed breaks. The amount of the total mixture should be about 100 ml. It was clearly shown, that neither the hydrogen content nor the sample surface change during the treatment.

## 4. Preparation of Tests for Active Samples

For active tests, we have chosen the heavily lead shielded dissolution box, which is equipped with manipulators. The box is constructed like a standard glove box. It has a stainless steel frame, floor, ceiling, walls and acrylic glass windows. A 15 cm thick wall made of lead and 20 cm thick lead glass windows are used for the shielding. Four compartments are connected to each other in the middle by a rotary lock. The partition of the box ensures that not the entire inner space can be heavily contaminated. The dissolution of samples is carried out only in one compartment.

It is relevant to mention that, in contrast to the envisaged lead dissolution process, in this box, usually concentrated nitric acid is used to dissolve irradiated fuel and, in some cases, additional hydrofluoric acid is added. The samples are boiled in the acid under reflux in a round-bottomed flask with the aid of a hemispherical heating mantle and an intensive condenser. No measurable gaseous nuclides occur when dissolving irradiated fuel. The intensive cooler is connected to a cryostat (mini-chiller). This keeps the cooling circuit closed.



Figure 5: Active shielded dissolution box

Before starting the procedure for the active material, a safety consideration had to be formulated. Despite the fact that a box made for fuel and fuel-contaminated specimens is used, some of the present spallation products are very exotic from a nuclear fuels point of view and pose a challenge: e.g. polonium, mercury (Hg-194) or gold (Au-194). The amount of a possible gaseous release as well as aerosols of these nuclides into the exhausting system had to be clarified. Emission limits have to be met by using additional activated carbon filters.

## 4.1 Calculations of the possible nuclides inventory

Contaminations in the exhaust system are hold back by a filter system. Remaining amounts, if present at all, are controlled and released via a tall chimney according to the respective rules. In the past, when cutting samples with irradiated lead in the hot cells, we could detect an increased level of spallation nuclides in the exhaust system, untypical for the standard work (fuel, structural materials). Thus, a potential release of nuclides from the chemical dissolution process had to be considered, too.

### Hg-194 / Au-194

After cutting the target-9 lead containing samples, an increased activity of Hg-194 or its subsequent product Au-194 was measured. In the week after the Pb-containing tube was cut, the limits of the exhaust gas were not reached. These findings lead to the approach to compare the cutting losses with the potential amount of chemically dissolved lead.

For a rough assessment of potential release from the cutting process, we firstly assumed that the tube is completely filled with lead and its lead release volume is equal to the inner tube volume during cutting loss. This was 393 mm$^3$ for 13 cuts, a cutting width of 0.45 mm and a nominal inner diameter of the tubes of 9.25 mm.

For the chemical process, we based the amount of lead to be considered on the photos from the tubes after the lead had been pushed out. The lead residual quantity was estimated with a thickness of 0.1 mm on 10% of the inner wall surface with 4 of 5 sample tubes of approximately 12 mm length. For one tube, more residual lead appears to be present and the residual quantity is estimated with a thickness of 0.15 mm on the entire inner wall. The total volume is then equal to 65 mm$^3$.

In principle, the remaining lead is not uniformly distributed; in the center is more than at the edge of the target tubes. The error made in the calculation should be approximately the same in both cases: cutting loss and adhering residual quantities.

Conclusion: The amount of lead in the dissolution box is less than 1/6$^{th}$ of that of cutting. Therefore, a contamination below the limits is expected.

### Other gaseous radionuclides

According to a dissertation about spallation products at the SINQ [2, Tobias Lorenz], Cl-36 and J-129 are further relevant. Since these are produced with a factor of approx. 10E6 less than Hg-194 / Au-194, they should not play any role.

### Non-gaseous radionuclides

Polonium nuclides were calculated by SINQ colleagues to the following amounts (in lead, tube position row 6 in target, irradiation time for target-9, Pb volume 65 mm$^3$, mass 0.74 g):

Po-208 – 7.99765E+04 Bq/g ⇨ 5.92 E4 Bq
Po-209 – 8.10781E+02 Bq/g ⇨ 6.00 E2 Bq
Po-210 – 2.22016E+03 Bq/g ⇨ 1.64 E3 Bq

The activities on the right side correspond to a mass of 0.74 g for the abovementioned volume. Since the cutting of Po has not been found to be critical in the exhaust air, a comparatively small quantity is emitted during the dissolution.

### Gd-148

According to [2, Tobias Lorenz], Gd-148 has to be considered as an alpha-emitter. It is produced in a similar quantity as Po. The activity limit is of a comparable level or even slightly higher than for Po. It can therefore be considered as similar to Po. Consequence: due to the experience of cutting SINQ target-9 tubes, the exhaust air limits are not exceeded.

Besides performing calculations, we have to assure technically that radionuclides are kept back by filters. Therefore we tried to find an industrial filter or filter system, which is capable to

hold back gaseous Hg-194/Au-194 and Po aerosols at the same time. However, this task turned out to be quiet difficult: suppliers for filters for the nuclear industry are specialized in filtering α-particles and iodine. For gaseous mercury, we found only filters for personal breathing masks.

## 4.2 New Filter System

After consultation of radiochemistry specialists at PSI, active carbon filters have been identified as best solution for holding back the respective gaseous nuclides.

Together with the Swiss company PEDI Zürich AG (Oberentfelden), specialized in nuclear industry products, appropriate filter holders for existing active carbon standard filters could successfully be developed. The filters are designed in a way that they can be used inside the dissolution box as well as the interface to the exhaust system.

## 4.3 Liquid Waste and Safety Implications

An attempt is made to keep the amount of waste solutions as low as possible. All waste solutions are collected until they can be delivered to the hotlab group 'post-processing radioactive materials NRM' for solidification. It is to be noted that the solutions outgas and therefor the plastic containers should not be completely closed during storage to avoid overpressure. When the waste solutions are removed, consequently respiratory protection masks with activated carbon filter have to be worn. For processing the waste solution, we have to consider that it contains organic acid and salts (acetic acid, lead acetate). Since acetic acid has been diluted, it is not combustible.

## 4.4 Safety report

A safety report has been established [3], in particular, personal safety equipment and a safe procedure were defined. For example, in the event of a ventilation failure or any incident involving the release of nuclides, especially polonium, immediately a respiratory mask has to be placed and an alarm to be given. All work in the particular laboratory must be stopped and the systems must be put into safe conditions. Then, the particular laboratory must be left immediately.

## 5. Outlook

A comprehensive material damage assessment will be performed for the samples of target-9. This comprises EPMA for micro-structural and -chemical analyses, especially with respect to the accumulation of hydrogen/hydrides and for detection of any potential corrosion relevant nuclides. In the subsequent metallography, the distribution of hydrides shall be further elucidated. In addition, the irradiation-induced embrittlement shall be clarified, at areas where hydrides are found and areas where no hydrides are present. Secondary Ion Mass Spectrometry (SIMS) shall be used to try to differentiate between hydrides stemming from protons (irradiation) and from deuterons (heavy water cooling).

Finally and after removal of the remaining lead, mechanical tests shall be performed. Depending on the results of the other investigations, the focus will be more on ring tensile or compression tests, or fracture toughness tests or tests to check the susceptibility for Delayed Hydride Cracking (DHC).

The results shall then be used to optimize the investigations of target-11 rods.

**Acknowledgment**

**References**

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[3]    R. Zubler, J. Bertsch, internal work description AA-LNM-03, *Sicherheitsbetrachtung für Bleirückstandsauflösung in OHLA/027*, 2017.