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Release of <sup>108m</sup>Ag from irradiated PWR control rod absorbers under deep repository conditions

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# Release of <sup>108m</sup>Ag from irradiated PWR control rod absorbers under deep repository conditions

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Keywords: PWR, Control rod, AIC alloy, Release of 108mAg.

This report concerns a study which was conducted for Svensk Kärnbränslehantering AB (SKB). The conclusions and viewpoints presented in the report are those of the authors. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

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#### **Abstract**

In a nuclear reactor control rods are used to control the neutron flux and thereby the fission rate. In PWR reactors the control rods are grouped in assemblies of about 20 rodlets. The rodlets consist of an absorber alloy, AIC alloy with nominal composition 80 % Ag, 15 % In and 5 % Cd, surrounded by a cladding of stainless steel. PWR control rods are primarily used for startup and shutdown, while the power during an operating cycle is controlled by varying the boron content in the moderator and by burnable absorbers in the fuel.

In a future Swedish deep repository the PWR control rods are planned to be stored together with the fuel assemblies. Upon reactor operation, the composition of the control rod absorber will change due to neutron capture. The nuclides formed in these reactions may be released to ground water upon water intrusion in the deep repository. In a scenario where the barriers break at a relatively early stage (< 10 000 years), the release of <sup>108m</sup>Ag has been identified as a nuclide that may be released from the deep repository.

In this study the release of Ag from irradiated and unirradiated control rod absorbers has been studied under various experimental conditions, including the effect of external irradiation, during leaching. The radionuclide inventory of irradiated control rod absorber material has been determined.

Analysis results showed no detectable levels of <sup>108m</sup>Ag in the leaching solutions.

#### Sammanfattning

I en kärnreaktor används styrstavar för att kontrollera neutronflödet och därmed fissionshastigheten. I PWR-reaktorer består en styrstav av 20 styrstavsfingrar ihopsatta till ett knippe. Styrstavsfingrarna består av en neutronabsorberande legering, AIC, med den nominell sammansättningen 80 % Ag, 15 % In och 5 % Cd, omgiven av kapsling i rostfritt stål. I en PWR används styrstavarna främst vid uppstart och nedstängning, medan effekten kontrolleras genom variation av innehållet av bor i reaktorvattnet samt genom tillsats av absorbator i bränslet.

I ett framtida svenskt slutförvar är det tänkt att PWR-styrstavarna skall förvaras tillsammans med själva bränslet. Under användning i reaktorn ändras sammansättningen i styrstavens absorbator på grund av neutroninfångning och de bildade radionukliderna kan börja lakas ut i grundvattnet om detta tränger in i slutförvaret. I ett scenario där barriärerna har brutits vid ett relativt tidigt skede (< 10 000 år) har <sup>108m</sup>Ag identifierats som en nuklid som skulle kunna frigöras från slutförvaret.

I den här studien har frigörelse av Ag från både bestrålat och obestrålat absorbatormaterial från styrstavsfinger undersökts genom lakning vid olika experimentella förhållanden. Även effekten av extern bestrålning under lakning har studerats. Inventariet av radionuklider i det bestrålade materialet har bestämts. Analyser av laklösningarna i denna studie visar på nivåer av <sup>108m</sup>Ag under detektionsgräns.

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#### 1 Introduction

In a nuclear reactor control rods are used to control the neutron flux and thereby the fission rate. In PWR reactors the control rods are grouped in assemblies of about 20 rodlets. The rodlets consist of an absorber alloy, AIC alloy with nominal composition 80 % Ag, 15 % In and 5 % Cd, surrounded by a cladding of stainless steel. PWR control rods are primarily used for startup and shutdown, while the power during an operating cycle is controlled by varying the boron content in the moderator and by burnable absorbers in the fuel. The control rod assemblies are inserted from the top of the core. Since the rods are normally retracted with only the bottom tip facing the core, the bottom end of the control rodlets will be more heavily irradiated than the top end.

In a future Swedish deep repository, the PWR control rods are planned to be stored together with the fuel assemblies. Upon reactor operation, the composition of the control rod absorber will change due to neutron capture. The nuclides formed in these reactions may be released to ground water upon water intrusion in the deep repository. In a scenario where the barriers break at a relatively early stage (< 10 000 years), the release of <sup>108m</sup>Ag has been identified as a nuclide that may be released from the deep repository (SKB 2011). In this risk assessment immediate release of <sup>108m</sup>Ag is assumed although, the solubility of Ag is expected to be low under the reducing conditions expected to prevail in the deep repository (McNeil and Little 1992). However, to the best of our knowledge, no data on the release of <sup>108m</sup>Ag from irradiated control rods have been published in the open literature.

In this study the release of Ag from irradiated and unirradiated control rod absorbers has been studied under various experimental conditions including the effect of external irradiation during leaching. The radionuclide inventory of irradiated control rod absorber material has been determined.

#### 2 Experimental

Unirradiated AIC alloy was used for the inactive studies. For studies of irradiated material, a control rodlet, F9, from the control rod R035 used in Ringhals 2, was chosen. The control rod was manufactured by Westinghouse and belongs to the original set of control rods from the start of the reactor.

#### 2.1 Leaching of unirradiated material

Three series of leaching of unirradiated material were performed, where the leaching solution and atmosphere were varied according to the following list:

- I.  $10 \text{ mM NaCl} + 2 \text{ mM NaHCO}_3$ , purging with Ar  $+ 0.03 \% \text{ CO}_2$
- II. 1 mM NaCl, purging with Ar + 0.03 % CO<sub>2</sub>
- III. 10 mM NaCl + 2 mM NaHCO<sub>3</sub>, open to air

In each experiment 1 g of unirradiated Ag-In-Cd material (80 % Ag, 15 % In, 5 % Cd) was immersed in 200 mL leaching solution in a glass vessel (Figure 2-1). The experiments were performed at room temperature. Series I and II were performed in an argon glovebox in order to ensure oxygen free conditions. The leaching was conducted for 250 days, during which 5 samples à 10 mL were withdrawn at different time intervals. The samples were analyzed with ICP-MS for Ag, In, Cd, Pd and Sn. pH was measured prior to and after the experiment.

#### 2.2 Nuclide inventory in irradiated material

From the control rod R035, two 1 mm thick discs (F9-1 and F9-3) were cut from the rodlet for the inventory determination, see Figure 2-2. In Figure 2-3 the gamma profile of another rodlet (R035/A4) is shown. The A4 rodlet is from the same control rod assembly as F9 and the irradiation history are similar, for this reason the gamma profile of A4 gives an indication of the irradiation level also for the rodlet used in this study (F9).



Figure 2-1. Leaching of unirradiated AIC alloy.

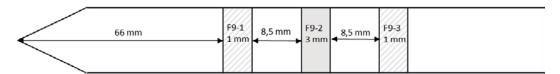


Figure 2-2. Cutting scheme of rodlet R035/F9.

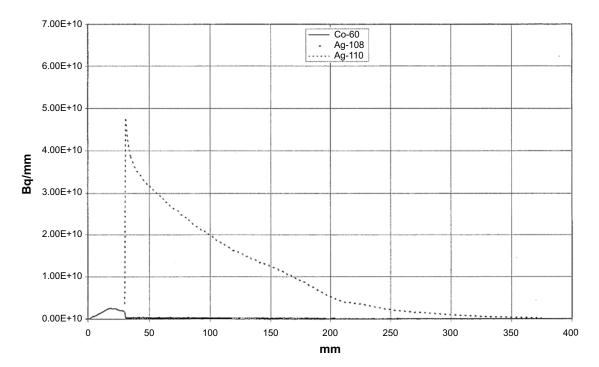


Figure 2-3. Gamma scan displaying 110 Ag distribution in rodlet R035/A4.

As the irradiation level varies significantly along the rod axis, as shown by the gamma profile in Figure 2-3, it is expected that also the radionuclide content varies in the irradiated material. In order to get a representative value for the leached sample (F9-2), the two samples used for inventory determination were taken at equidistant positions on both sides of the leached sample. The samples were weighed (0.66 and 0.72 g respectively) and dissolved in an acid mixture (12 mL supra pure 7 M nitric acid and 0.5 mL 22 M HF) after which the samples were analyzed for Ag, Cd, In, Sn and Pd using HPLC-ICP-MS. <sup>108m</sup>Ag was also analyzed by gamma spectrometry.

#### 2.3 Autoclave leaching of irradiated material

The leaching of the irradiated material was performed in an autoclave pressurized to 4 bar with  $10\% H_2$  and  $0.03\% CO_2$  in Ar. The sample disc F9-2 was cut in 4 pieces (total 1.98 g), placed in a glass basket (Figure 2-4) and immersed in 400 mL 10 mM NaCl + 2 mM NaHCO<sub>3</sub> solution. The solution was purged with  $0.03\% CO_2$  in Ar for about 2 hours prior to pressurization. The experiment was performed under stagnant conditions at room temperature.

After 12 days of leaching, a gas sample was taken from the autoclave in order to ensure that no leakage occurred. Three liquid samples of 10 ml each were withdrawn from the autoclave at 12, 62, 133 and 913 days of leaching. The liquid samples were acidified in order to avoid sorption on the vessel walls before analysis. The gas sample was analyzed with Gas-Mass Spectrometry and the liquid samples with gamma spectrometry (108mAg) and ICP-MS (Cd, In and Sn isotopes). Release of isotopes of silver from the leached material could not be determined by ICP-MS due to interference from silver lining on the autoclave seals.



Figure 2-4. Glass basket containing sample for autoclave leaching.

#### 2.4 Irradiation of autoclave leaching

In order to investigate the effect of external irradiation on the release of <sup>108m</sup>Ag, a strong radiation source was placed near the autoclave containing the control rod material. The existing set-up described in Section 2.3 was used, and the remaining volume of the leaching solution was estimated to 300 ml. The goal was to simulate the dose rate for a PWR assembly after about 300 years (according to Table A1-48 in SKB 2000) and a 1.1 TBq <sup>137</sup>Cs source situated at Studsvik was found to be suitable.

Before start of irradiation a gas sample was taken as well as liquid samples (sampling no 4). After sampling the pressure in the autoclave were raised to 3.5 bar with Ar containing 10 %  $H_2 + 0.03$  %  $CO_2$ , resulting in a hydrogen content of 11.3 %.

The <sup>137</sup>Cs source was transported in a specially designed holder in a transport cask and docked to the lead cave containing the autoclave with the ongoing leaching, Figure 2-5. The holder with the source was pushed through a hole into the lead cave and positioned at the same level as the rodlet pieces in the autoclave and at 1 dm distance. The dose rate at the position of the rodlet pieces were calculated to 9 Sv/h.





**Figure 2-5.** Left: Transport cask docked to the lead cave. Right: Equipment for positioning the holder next to the autoclave. The hole for the <sup>137</sup>Cs source holder is plugged.

The leaching was allowed to proceed with external irradiation for 26 days. On day 13 and 34 after start of irradiation, gas and liquid sampling was performed in the same way as previous samplings, see Section 2.3. The gas sample was analyzed with Gas-Mass Spectrometry and the liquid samples with gamma spectrometry (<sup>108m</sup>Ag). With ICP-MS the intensity of masses in the range 102–124, which covers possible isotopes of Ag, Cd, In, Sn and Pd, was measured. After the final sampling the autoclave was opened, and all remaining leaching solution was collected but without centrifugation and acidification of the liquid. ICP-MS analysis was performed on the remaining solution together with the last two samplings.

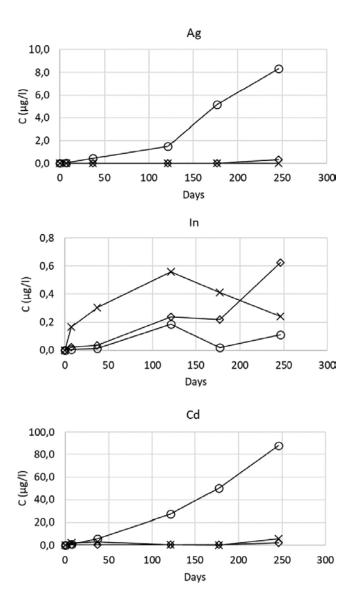
The glass basket was transferred to hot cell and photos were taken of the control rodlet pieces.

The autoclave was rinsed with water in two steps, 400 ml + 100 ml, and the two portions were merged. Then the autoclave was stripped with  $400 \text{ ml} 1 \text{M} \text{HNO}_3$  for two hours. These two solutions were measured with gamma spectrometry.

#### 3 Results

#### 3.1 Leaching of unirradiated material

The results from the three leaching experiments of unirradiated control rod alloy are presented in Figure 3-1, corresponding values in Appendix 1. Pd and Sn are not presented as they were close to or below detection limit. pH values measured corresponded to the expected values for each solution. As can be seen in Figure 3-1, the release of Ag and Cd from the alloy is significantly higher during oxidizing conditions (i.e. under air) compared to the oxygen free leaching series. The release of In on the other hand seem to be more related to the HCO<sub>3</sub><sup>-</sup> concentration. In the samples were the leaching solution contained 2 mM NaHCO<sub>3</sub>, the release of In was lower compared to the case where HCO<sub>3</sub><sup>-</sup> was introduced only by CO<sub>2</sub> purging. This can probably be explained by different pH (determined by the HCO<sub>3</sub><sup>-</sup> concentration) in the solutions.



**Figure 3-1.** Release of Ag, Cd and In from leaching of unirradiated control rod alloy under varying experimental conditions. Note there is different scale at y-axis.

- ( $\Diamond$ ) I. 10 mM NaCl + 2 mM NaHCO<sub>3</sub>, purging with Ar + 0.03 % CO<sub>2</sub>.
- (×) II. 1 mM NaCl, purging with  $Ar + 0.03 \% CO_2$ .
- (o) III. 10 mM NaCl + 2 mM NaHCO<sub>3</sub>, air.

#### 3.2 Nuclide inventory of irradiated material

During irradiation of the control rod material upon reactor operation the composition will change. The major neutron absorption reactions taking place are listed below:

| opes          | After irradiation (T1/2)                                |  | After decay     |
|---------------|---|--|-----------------|
| $\rightarrow$ | 108m Ag (438 y)   | $\rightarrow$  | 108 Pd (stable) |
| $\rightarrow$ | 108 Ag (2.4 min)  | $\rightarrow$  | 108 Cd (stable) |
| $\rightarrow$ | 110 Ag (249 d)  | $\rightarrow$  | 110 Cd (stable) |
| $\rightarrow$ | 113m Cd (14 y)  | $\rightarrow$  | 113 In (stable) |
| $\rightarrow$ | 114 Cd (stable)   |  |                 |
| $\rightarrow$ | 115 Cd (45 d)   | $\rightarrow$  | 115 In (stable) |
| $\rightarrow$ | 116 Cd (stable)   |  |                 |
| $\rightarrow$ | 117 Cd (h) $\rightarrow$ 117 In (h)                     | $\rightarrow$  | 117 Sn (stable) |
| $\rightarrow$ | 116 In (min)  | $\rightarrow$  | 116 Sn (stable) |
|               | $\begin{array}{ccc}                                   $ | <ul> <li>→ 108 Ag (2.4 min)</li> <li>→ 110 Ag (249 d)</li> <li>→ 113m Cd (14 y)</li> <li>→ 114 Cd (stable)</li> <li>→ 115 Cd (45 d)</li> <li>→ 116 Cd (stable)</li> <li>→ 117 Cd (h) → 117 In (h)</li> </ul> |                 |

The elemental and isotopic composition of the two samples from the irradiated control rod are shown in Figures 3-2 and 3-3, corresponding values in Appendix 2. The values presented here are from ICP-MS analysis, except for <sup>108m</sup>Ag which could not be measured with ICP-MS due to chromatographic issues caused by the specific Ag isotopic composition and hence was analyzed with gamma spectrometry.

In Roth et al. (2015) and in Appendix 2 the  $^{108m}$ Ag content of sample F9-1 and F9-3 are reported to be 670 µg/g and 560 µg/g respectively. Later review of the gamma spectra on which those numbers are based, indicate that these values need to be corrected for drift in the energy calibration of the gamma detector. Such a correction gives values around 1 000 µg/g (979 µg/g for F9-1 and 797 µg/g for F9-3).

As can be seen in Figure 3-2, the largest change in composition compared to the nominal values are seen in sample F9-1.<sup>1</sup> This is expected since this sample was taken closer to the bottom end of the control rod (i.e. the part closest to the reactor core) and hence has experienced a stronger radiation field during operation. Pd was below detection limit.

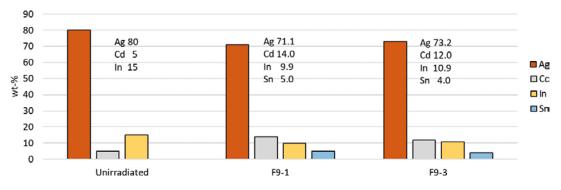


Figure 3-2. Composition of irradiated samples compared to nominal composition.

<sup>&</sup>lt;sup>1</sup> The data in the figure differs slightly from that presented in Roth et al. (2015). A small calculation error in the datafile has been corrected for the current report.

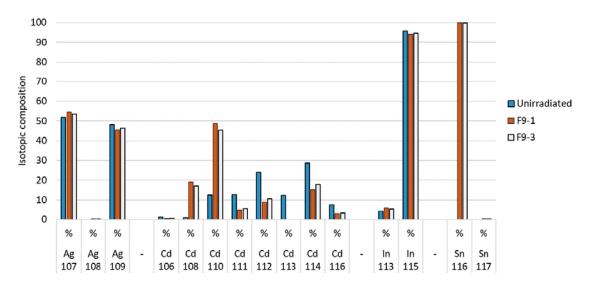


Figure 3-3. Isotopic composition of irradiated samples compared to nominal composition given in weight-%.

#### 3.3 Autoclave leaching of irradiated material

Due to possible leaching of the autoclave vessel and other components, such as the lining on the autoclave seals containing silver, natural Ag isotopes could not be used for measuring the Ag release from the control rod during leaching. For this reason, gamma analysis of <sup>108m</sup>Ag is used to assess the Ag release, whereas ICP-MS is used for other elements.

The gas sample taken from the autoclave at 12 days leaching showed no signs of air intrusion. The Cd, In and Sn content in the samples taken at 12 and 62 days leaching was close to detection limit for the ICP-MS. The results from the analysis of  $^{108m}$ Ag by gamma spectrometry showed results below the detection limit. For gamma analysis the detection limit is largely dependent on the measuring time. In this case the samples were measured for around 65 hours resulting in a detection limit around  $1 \times 10^{-12}$  mol/l for  $^{108m}$ Ag.

The third and fourth samples taken at 133 and 913 days leaching, also showed <sup>108m</sup>Ag levels below detection limit, as well as for In and Sn, whereas trace levels of Cd now could be detected with ICP-MS. The measured release of Cd<sup>2+</sup> can be delayed by sorption on the autoclave inner walls, which could explain why no Cd was detected at 12 and 62 days.

#### 3.4 Irradiation of autoclave leaching

The pressure and the  $H_2$ -content in the autoclave are presented in Table 3-1 together with the analysis results from gamma measurement of  $^{108m}$ Ag.

The hydrogen content has increased during the first leaching period (2.5 years without external irradiation) from 10 % to 15.6 %. When pressurizing the autoclave at set-up for external irradiation it resulted in a hydrogen content of 11.3 %, i.e somewhat higher than at the beginning of leaching. After 4 weeks of irradiation the hydrogen content had again increased, now to 14.4 %.

<sup>108m</sup>Ag is still below detection limit.

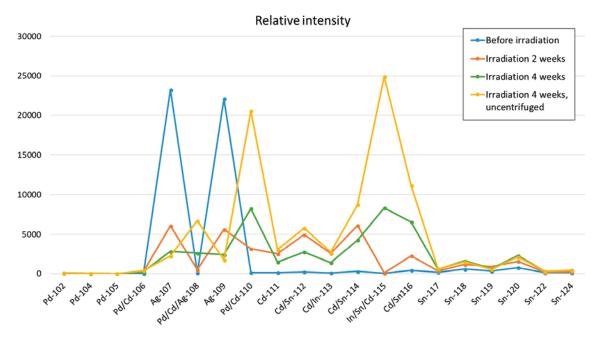
Tabell 3-1. Pressure, H<sub>2</sub> and <sup>108m</sup>Ag.

|  | Pressure<br>(bar) | H <sub>2</sub> from gas-MS analysis (%) | <sup>108m</sup> Ag<br>(mol/l) |
|--|-------------------|---|-------------------------------|
| Before irradiation and pressurizing          | 2.04              | 15.6                                    | < 1.3 × 10 <sup>-12</sup>     |
| Before irradiation but after pressurizing    | 3.54              | 11.3                                    | n.a.                          |
| After 2 weeks of irradiation, at sampling    | 3.44              | 13.7                                    | < 1.2 × 10 <sup>-12</sup>     |
| After 2 weeks of irradiation, after sampling | 2.79              | n.a.                                    | n.a.                          |
| After 4 weeks of irradiation, at sampling    | 2.69              | 14.4                                    | < 1.2 × 10 <sup>-12</sup>     |

It is not possible to evaluate the actual concentration in the solution of all Ag, Cd, In, and Sn isotopes with an ICP-MS scanning of the mass range. Instead the intensity (counts per second) is plotted for selected masses from 102 to 124 as shown in Figure 3-4, (values presented in Appendix 3). Thus, trends in the isotopic content can be observed.

From the diagram in Figure 3-4 it is noted that the Ag-content in the leaching solution seems to decrease during the irradiation experiment, compared to the last sampling just before start of irradiation. The content of Cd and In, on the other hand, seem to increase. When comparing the last sampling with and without centrifugation there is no significant difference in the Ag-content, however the Cd and In shows further increase.

The water and acid solutions from rinsing of the autoclave did not show any detectable levels of <sup>108m</sup>Ag. The rinse water contained a fine gray powder which sedimented quickly and was included in the gamma measurement as the whole batch were measured.



**Figure 3-4.** Comparison of the relative intensity of analyzed masses in leaching solution samples before, during and after the irradiation period.

#### 4 Discussion and conclusions

The first part of the work was designed to find out how different parameters affect leaching of Ag from the AIC alloy and the results can be seen in Figure 3-1. It is clear that the release of Ag and Cd is strongly dependent on the redox conditions. All three elements are oxidized by  $O_2$ . However, since  $In(OH)_3$  is not soluble except under highly acidic conditions, the oxidation of In will not result in measurable amounts of In in solution. This explains why Ag and Cd are released at significant rates under aerated conditions, whereas the release of In seems more related to the pH of the solution. Since both  $Cl^-$  and  $HCO_3^-$  are present in the systems, the release of Ag and Cd is limited by the formation of AgCl(s) and  $CdCO_3(s)$  (Roth et al. 2015), though this point is not reached during the experiment.

Determination of the nuclide inventory of the irradiated material was needed for calculation of the release fraction of Ag. The two pieces (taken from each side of the leached irradiated sample) showed reasonable values where the largest change in composition compared to the nominal values are seen in the most irradiated sample.

In the following experiment a piece of irradiated control rod was leached in 10 mM NaCl + 2 mM NaHCO<sub>3</sub> in an autoclave pressurized to 4 bar with 10 %  $H_2$  and 0.03 %  $CO_2$  in Ar, giving initially reducing conditions. Under these conditions, Ag should be stable in its metallic form and In stable as In(OH)<sub>3</sub>, according to simulation with MEDUSA (KTH 2013). Cd however, can be released as  $Cd^{2+}$  unless the dissolution is limited by the formation of  $CdCO_3(s)$  (KTH 2013). The inherent radioactivity of the irradiated material will lead to the production of oxidizing water radiolysis products such as  $H_2O_2$  and  $O_2$ . However, the results up to the third sampling (after 4 months leaching) indicates that the inherent radiation of the alloy is not sufficient to cause significant dissolution of the material (Roth et al. 2015). Even after 30 months of leaching no significant levels of  $^{108m}Ag$  could be detected. The radiation field in this part of the study originates from the alloy alone and is significantly weaker than the radiation field from the spent fuel which will dominate in a future deep repository.

In order to investigate the influence of a stronger radiation field an external <sup>137</sup>Cs source was used, giving a radiation environment comparable to that expected in the deep repository. The results showed that the external irradiation did not give a detectable increase of the level of <sup>108m</sup>Ag release. No detectable levels of <sup>108m</sup>Ag could be recorded in the leaching solution after 4 weeks of leaching under external irradiation. The high Ag content in the sampling before start of irradiation, i.e. after 2.5 years of leaching, as seen in Figure 3-4, is considered to be due to the Ag silver lining on the autoclave seals. The autoclave seals were supposed to be corrosion free and the presence of silver in the lining was not known at the beginning of the experiments. The silver from the lining affects the samples taken, especially when there is a large interval to the previous sampling. There was no use in evaluating the Ag-content.

In conclusion, assuming a release of  $1.2 \times 10^{-12}$  M  $^{108m}$ Ag over a time period of 2.5 years (based on the detection limit and the duration of the experiment), using the average Ag content in the material of 74 weight-% and the average isotopic composition of 614 ppm<sup>2</sup>  $^{108m}$ Ag, the release fraction of  $^{108m}$ Ag is calculated to be in the order of  $1.7 \times 10^{-8}$  year<sup>-1</sup>.

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<sup>&</sup>lt;sup>2</sup> Using this value is a conservative approach since the average <sup>108m</sup>Ag composition may be higher as explained in Section 3.2.

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### Results from leaching of unirradiated control rod alloy

Table A1-1. The results from the three leaching experiments with unirradiated control rod alloy.

| Sample     | Cd<br>(mol/l)            | Ag<br>(mol/l)                   | In<br>(mol/l)                      |
|------------|--------------------------|---------------------------------|------------------------------------|
| Series I   | 10 mM NaCl + 2           | mM NaHCO <sub>3</sub> , purging | g with Ar + 0.03 % CO <sub>2</sub> |
| Sampling 1 | $5.40 \times 10^{-09}$   | $2.78 \times 10^{-11}$          | 1.96 × 10 <sup>-10</sup>           |
| Sampling 2 | $3.79 \times 10^{-09}$   | $6.53 \times 10^{-11}$          | $3.17 \times 10^{-10}$             |
| Sampling 3 | $3.37 \times 10^{-09}$   | $9.17 \times 10^{-11}$          | 2.08 × 10 <sup>-09</sup>           |
| Sampling 4 | $4.21 \times 10^{-09}$   | $1.10 \times 10^{-10}$          | 1.91 × 10 <sup>-09</sup>           |
| Sampling 5 | $1.80 \times 10^{-08}$   | $3.23 \times 10^{-09}$          | 5.43 × 10 <sup>-09</sup>           |
| Series II  | 1 mM NaCl, pur           | ging with Ar + 0.03 %           | CO <sub>2</sub>                    |
| Sampling 1 | $1.78 \times 10^{-08}$   | 1.88 × 10 <sup>-11</sup>        | 1.45 × 10 <sup>-09</sup>           |
| Sampling 2 | $2.50 \times 10^{-08}$   | $9.03 \times 10^{-12}$          | $2.47 \times 10^{-09}$             |
| Sampling 3 | $6.18 \times 10^{-09}$   | $1.88 \times 10^{-11}$          | $4.87 \times 10^{-09}$             |
| Sampling 4 | $7.02 \times 10^{-10}$   | $1.88 \times 10^{-11}$          | $3.59 \times 10^{-09}$             |
| Sampling 5 | $5.04 \times 10^{-08}$   | 1.88 × 10 <sup>-11</sup>        | $2.10 \times 10^{-09}$             |
| Series III | 10 mM NaCl + 2           | mM NaHCO <sub>3</sub> , open to | air                                |
| Sampling 1 | $8.07 \times 10^{-09}$   | $3.28 \times 10^{-10}$          | 5.02 × 10 <sup>-11</sup>           |
| Sampling 2 | $5.24 \times 10^{-08}$   | $4.20 \times 10^{-09}$          | $9.96 \times 10^{-11}$             |
| Sampling 3 | $2.43 \times 10^{-07}$   | 1.41 × 10 <sup>-08</sup>        | $1.62 \times 10^{-09}$             |
| Sampling 4 | 4.45 × 10 <sup>-07</sup> | $4.81 \times 10^{-08}$          | $1.72 \times 10^{-10}$             |
| Sampling 5 | $7.82 \times 10^{-07}$   | $7.73 \times 10^{-08}$          | 9.46 × 10 <sup>-10</sup>           |

# Elemental and isotopic composition of irradiated control rod

Table A2-1. Elemental composition of irradiated control rod.

| Element<br>Sample | Ag<br>Wt-% | Cd<br>Wt-% | In<br>Wt-% | Sn<br>Wt-% |
|-------------------|------------|------------|------------|------------|
| Unirradiated      | 80         | 5          | 15         | 0          |
| F9-1              | 71.12      | 13.98      | 9.93       | 4.97       |
| F9-3              | 73.17      | 11.97      | 10.89      | 3.96       |

Table A2-2. Isotopic composition of irradiated control rod.

| Isotope<br>Sample | <sup>107</sup> Ag<br>% | <sup>108</sup> Ag<br>% | <sup>109</sup> Ag<br>% |                   |                   |                   |                   |       |
|-------------------|------------------------|------------------------|------------------------|-------------------|-------------------|-------------------|-------------------|-------|
| Unirradiated      | 51.8                   | 0                      | 48.2                   | _                 |                   |                   |                   |       |
| F9-1              | 54.51                  | 0.0668                 | 45.42                  |                   |                   |                   |                   |       |
| F9-3              | 53.55                  | 0.0556                 | 46.40                  |                   |                   |                   |                   |       |
| Isotope           | <sup>106</sup> Cd      | <sup>108</sup> Cd      | <sup>110</sup> Cd      | <sup>111</sup> Cd | <sup>112</sup> Cd | <sup>113</sup> Cd | <sup>114</sup> Cd | 116Cd |
| Sample            | %                      | %                      | %                      | %                 | %                 | %                 | %                 | %     |
| Unirradiated      | 1.2                    | 0.9                    | 12.4                   | 12.8              | 24                | 12.3              | 28.8              | 7.6   |
| F9-1              | 0.43                   | 19.02                  | 48.77                  | 4.84              | 8.98              | 0.00              | 15.19             | 2.77  |
| F9-3              | 0.52                   | 16.96                  | 45.25                  | 5.56              | 10.53             | 0.00              | 17.90             | 3.28  |
| Isotope           | <sup>113</sup> In      | <sup>115</sup> In      |                        |                   |                   |                   |                   |       |
| Sample            | %                      | %                      |                        |                   |                   |                   |                   |       |
| Unirradiated      | 4.3                    | 95.7                   | _                      |                   |                   |                   |                   |       |
| F9-1              | 5.85                   | 94.15                  |                        |                   |                   |                   |                   |       |
| F9-3              | 5.38                   | 94.62                  |                        |                   |                   |                   |                   |       |
| Isotope           | <sup>116</sup> Sn      | <sup>117</sup> Sn      |                        |                   |                   |                   |                   |       |
| Sample            | %                      | %                      |                        |                   |                   |                   |                   |       |
| Unirradiated      | 0                      | 0                      | _                      |                   |                   |                   |                   |       |
| F9-1              | 99.81                  | 0.19                   |                        |                   |                   |                   |                   |       |
|                   |                        |                        |                        |                   |                   |                   |                   |       |

# ICP-MS measurements of leaching solutions before, during and after external irradiation

Table A3-1. The relative intensity of analyzed masses in leaching solution samples before, during and after the irradiation period.

|         |              | Blank | Before<br>irradiation | Irradiation<br>2 weeks | Irradiation<br>4 weeks | Irradiation<br>4 weeks,<br>uncentrifuged |  |
|---------|--------------|-------|-----------------------|------------------------|------------------------|--|--|
| Element | mass         | (cps) | (cps)                 | (cps)                  | (cps)                  | (cps)                                    |  |
| Pd      | Pd-102       | 7     | 71                    | 87                     | 109                    | 110                                      |  |
| Pd      | Pd-104       | 17    | 31                    | 35                     | 31                     | 67                                       |  |
| Pd      | Pd-105       | 18    | 23                    | 18                     | 21                     | 15                                       |  |
| Pd/Cd   | Pd/Cd-106    | 17    | 27                    | 268                    | 238                    | 401                                      |  |
| Ag      | Ag-107       | 56    | 23232                 | 6077                   | 2807                   | 2231                                     |  |
| Pd/Cd   | Pd/Cd/Ag-108 | 38    | 116                   | 488                    | 2616                   | 6706                                     |  |
| Ag      | Ag-109       | 47    | 22084                 | 5636                   | 2406                   | 1735                                     |  |
| Pd/Cd   | Pd/Cd-110    | 49    | 153                   | 3 159                  | 8 2 5 9                | 20563                                    |  |
| Cd      | Cd-111       | 36    | 134                   | 2535                   | 1479                   | 3080                                     |  |
| Cd/Sn   | Cd/Sn-112    | 91    | 234                   | 4966                   | 2761                   | 5800                                     |  |
| Cd/In   | Cd/In-113    | 45    | 110                   | 2588                   | 1390                   | 2742                                     |  |
| Cd/Sn   | Cd/Sn-114    | 107   | 280                   | 6125                   | 4277                   | 8749                                     |  |
| In/Sn   | In/Sn/Cd-115 | 55    | 70                    | 92                     | 8350                   | 24891                                    |  |
| Cd/Sn   | Cd/Sn116     | 241   | 424                   | 2264                   | 6564                   | 11 154                                   |  |
| Sn      | Sn-117       | 93    | 191                   | 355                    | 531                    | 590                                      |  |
| Sn      | Sn-118       | 316   | 571                   | 1157                   | 1624                   | 1493                                     |  |
| Sn      | Sn-119       | 119   | 321                   | 876                    | 645                    | 556                                      |  |
| Sn      | Sn-120       | 415   | 771                   | 1543                   | 2284                   | 2106                                     |  |
| Sn      | Sn-122       | 59    | 120                   | 215                    | 319                    | 299                                      |  |
| Sn      | Sn-124       | 89    | 129                   | 277                    | 429                    | 405                                      |  |
| Int.std | Rh-103       | 55925 | 50857                 | 50920                  | 50763                  | 48 959                                   |  |
| Int.std | Ir-193       | 32984 | 30 906                | 30495                  | 30 760                 | 30 071                                   |  |

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