

ARRANGEMENTS FOR A LEACHING TEST FOR IRRADIATED ROX FUEL SAMPLES

Geert-Jan DE HAAS^a, Ron VAN DER LAAN, Frans VAN DEN BERG, Wim TAMS, Toshiyuki YAMASHITA¹, Noriko NITANI¹

Nuclear Research and consultancy Group (NRG), P.O. Box 25, 1755 ZG Petten, The Netherlands

¹Japan Atomic Energy Agency (JAEA), Tokai-mura, Japan

ABSTRACT

This paper describes the arrangements that have been made so far at NRG for the performance of leaching tests on irradiated ROX fuel samples from the OTTO experiment. An outline of the leaching procedure is presented, including the results of a study into the suitability of several Cs extracting agents to lower the dose rates of leachates and wall precipitates. Attention is paid to the preparation of the irradiated fuel samples. The design and set-up of the hotcells and the equipment is highlighted as well as the various tools, which have been constructed to guarantee smooth handling of the leaching containers.

1. INTRODUCTION

In 1998 collaboration between JAERI, PSI and NRG was started with the objective to study the incineration of plutonium in a so-called 'Once-Through-Then-Out' mode. Fuel samples for the irradiation experiment included spinel- and zirconia-based targets, also referred to as ROX fuel. Fabrication took place at PSI and NRG^[1]. The irradiation in the HFR, Petten, started in September 2000 and was completed in December 2002; PIE was concluded in March 2004.

The work done so far focussed on the first part of the OTTO fuel cycle strategy, which comprises once-through irradiation followed by final disposal of the irradiated ROX fuel samples. A well-balanced judgment about their suitability with regard to final disposal requires amongst others insight in their leaching behaviour under such conditions. At present little is known about the leaching behaviour of irradiated ROX fuels with plutonium. Therefore it was decided to perform leaching tests on samples from three different targets: one zirconia-based and two spinel-based (micro- and macrodispersion of Pu-containing particles) targets (Nr. 1, 3, and 5 in [1]). Current paper describes the arrangements for the leaching test thereby focussing on the set-up of the leach facility, the possibilities and limitations of the facility with regard to the various handling manoeuvres, the establishment of a Cs removal procedure and the preparation of the samples. Special attention will be paid to adoptions required to circumvent the lack of master-slave manipulators in the cells, in which the leaching tests will be carried out. Instead, these cells are equipped with tongs with ball joints. Not only does this necessitate, where possible, simplification of the procedure and the fabrication of tools to allow sufficient freedom of handling, it also requires attention to be paid to the design of the facility, leaving enough space for handling of the samples and repackaging.

2. OUTLINE OF THE LEACHING PROCEDURE

The leaching procedure, a static leaching test, is a slightly adapted version of ASTM C1220-92, a standard test method for static leaching of monolithic waste forms for disposal of radioactive waste. A flow chart of the procedure is depicted in Figure 1.

The leachant is deionised water. The experiments will be carried out with a sample/volume (S/V) ratio of 0.025 cm⁻¹ at a temperature of 90°C in a N₂/O₂ atmosphere. AISI 304 steel containers with 20 µm gold coating by galvanization and a volume of approximately 50 ml will be applied. Leachates will be sampled after ~ 7 days, ~30 days, ~60 days, ~120 days and ~180 days. For each interval a separate sample will be prepared. The sample series for each leaching interval will include a blanc. The 180 days experiment will be performed in duplo. After completion of the leaching experiments and removal of the samples, the pH of each leachate will be measured. Subsequently, the leachates will be pipetted out of the containers, followed by 20 µm suction filtration to remove possible fuel particles. In order to dissolve precipitates on the container wall and the sample holder, the rinsed containers will be filled with 0.1 M ultrapure HNO₃ and heated at 150°C for 1 week. The leachates and the

^a e-mail address: g.dehaas@nrg-nl.com

dissolved wall precipitates will then be analysed for their nuclide inventory by means of ICPMS analysis at PSI in Switzerland.

3. CS EXTRACTION

Safe handling of the leachates outside the hotcells, including repackaging, transport and ICPMS analysis requires that their dose rates are sufficiently low. Leaching experiments at JAERI, however, have revealed that the dose rate is in general too high and that reduction of the dose rate is inevitable^[2]. It has appeared that the dose rate is largely determined by the release of Cs from the irradiated fuel samples. An option to overcome this problem is the use of a Cs extracting agent. Preferably, any extracting agent should be highly selective towards Cs with preferably no - or hardly any - affinity for other elements. Two possibilities have been evaluated: an AMP¹ and FER² combination and (pure) CST³.

¹ ammonium phosphomolybdate; $(\text{NH}_4)_3\text{PO}_4(12\text{MoO}_3) \cdot n\text{H}_2\text{O}$

² potassium hexacyanocobalt(II)-ferrate(II); $\text{K}_2[\text{CoFe}(\text{CN})_6]$

³ crystalline silicotitanate

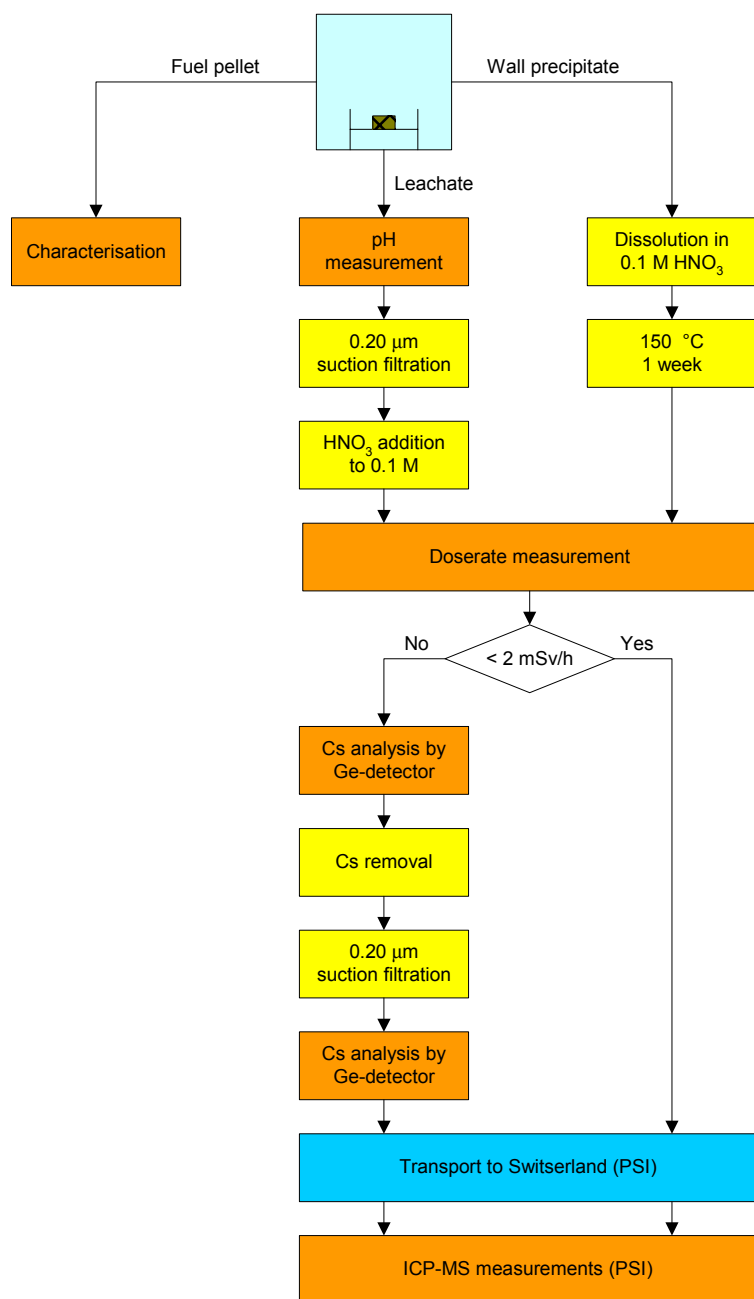


Figure 1. Flow chart of the leaching procedure.

The AMP/FERO combination assumes two parallel sample series, one of which is treated with AMP and the other with FERO as both agents extract (small) amounts of other elements as well^[2]. Analysis of the two sample series should give a complete overview of the nuclide inventory of the leachates. Application of CST only involves one removal step, which is obviously an advantage.

A series of extraction experiments with CST and the AMP/FERO combination and simulated waste solutions has been conducted. For the Cs extraction experiments two different solutions were prepared: a 0.1M HNO₃ solution with 0.2 g Cs/l and a 0.1M HNO₃ simulated HLLW (high level liquid waste) solution, to which an extra amount of Cs (0.12 g/l) had been added. Variable amounts of CST, AMP and FERO were added to 15 ml of each of these solutions, to which 150 Bq Cs-137 tracer had been mixed in. The remaining Cs activities after extraction and filtration were detected by NaI (0.1M HNO₃) and Ge[HP] (0.1M simulated waste) detectors. The results of the Cs extraction experiments, executed with a 0.1M HNO₃ solution with 0.2 g Cs/l, favour the use of AMP/FERO combination. The extraction curve of especially AMP indicates effective extraction of Cs after addition of relatively small amounts AMP (Figure 2). Nearly complete (>99%) removal is also achieved with CST, although CST is apparently less effective. CST pre-treated with HNO₃ appears to be more effective than CST pre-treated with H₂O.

Experiments to determine extraction of elements by CST other than Cs were performed with (diluted) 0.1M and 3M (undiluted) simulated waste solutions. Extraction of Tc and Am by the CST was monitored by adding 335 Bq Tc-99 tracer and 250 Bq Am-241 tracer. The remaining Tc-99 and Am-241 activities were analysed by a Ge[HP] detector and LSC, respectively. Extraction of other elements was checked by ICP-AES analysis of digested CST. The results were compared with the composition of non-exposed, as-received CST and the results for AMP/FERO as previously obtained at JAERI.

It appears that for some elements extraction properties of CST, AMP/FERO are rather similar: Tc, Am, Zr (significant extraction), Sr, Y (hardly extracted), and lanthanides (no extraction). CST does not extract Rb and Sn whereas Se data indicate significant extraction by CST. Ba, Te, Mo and Ru are hardly extracted by CST. CST seems to have slightly more favourable properties. It is important to note, that elements such as Am or Zr can easily be measured by gamma spectrometry. Tc- and Se-concentrations will be more difficult to determine. From a practical point of view, the use of CST is favoured as well. CST is made up by small grains, which makes it easy to handle; contrastingly, AMP is sticky, making handling and weighing procedures complicated. In addition the use of AMP/FERO doubles the number of steps/actions in the cells and the number of ICPMS analyses.

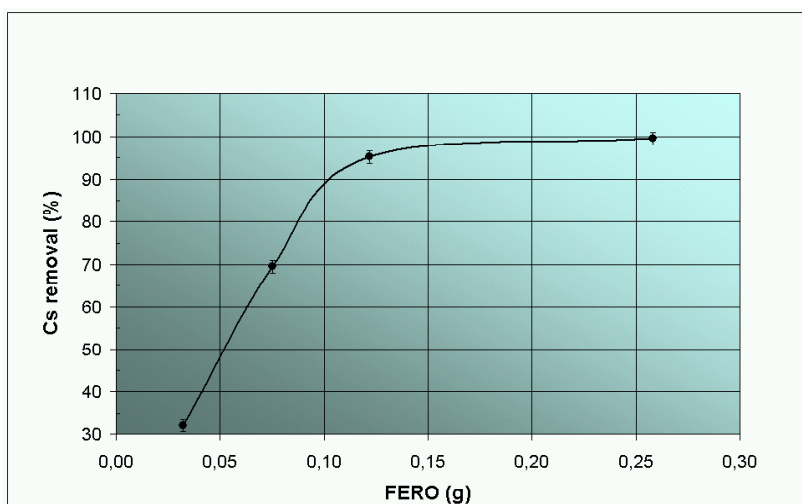
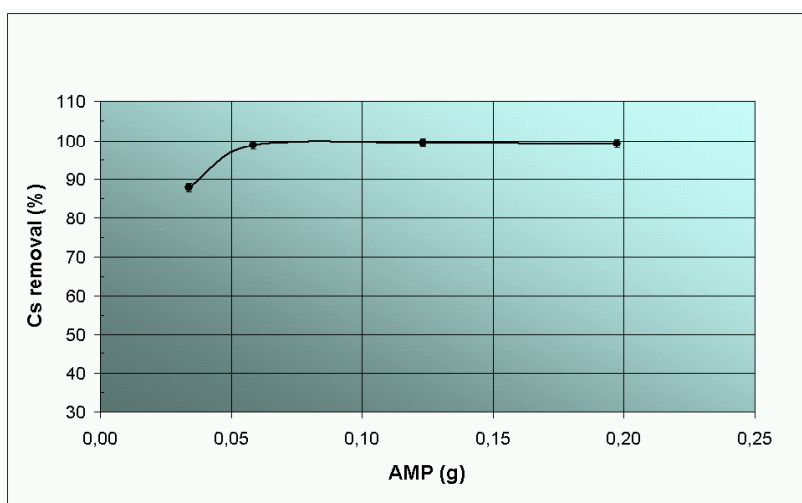
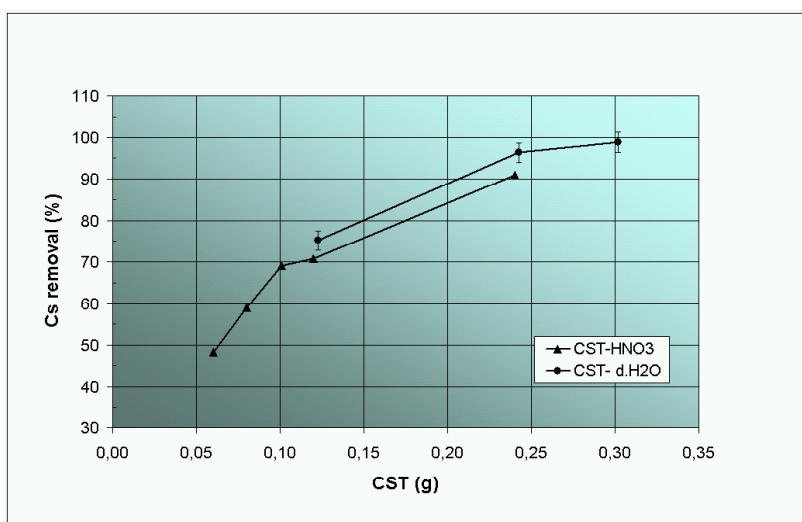


Figure 2. Removal percentages for Cs extraction experiments with (a) HNO_3 and H_2O pre-treated CST (b) AMP and (c) FERRO in a 15 ml 0.1 M HNO_3 solution with a Cs concentration of 0.2 g/l.

4. SAMPLE PREPARATION

An important aspect concerns the exposed surface of the samples in relation to the amount (volume) of leachant. Any meaningful comparison of the results for the various samples requires a fixed S(urface)/V(olume) ratio. It is therefore important to prepare samples in such a way that the exposed surface can be determined with great accuracy. Part of the irradiated ROX pellets had been fallen apart whereas some were stuck in the cladding. Therefore the pellets and their enveloping cladding have been cast in Hysol resin. After hardening disks has been sawn dry. The initial thickness of the samples (including the cladding) amounted to approximately 3 mm. The samples were then placed in specially designed sample holders facilitating grinding of the sample down to a thickness of at first 2.5 mm and, after turning the sample, to a final thickness of 2.2 mm.

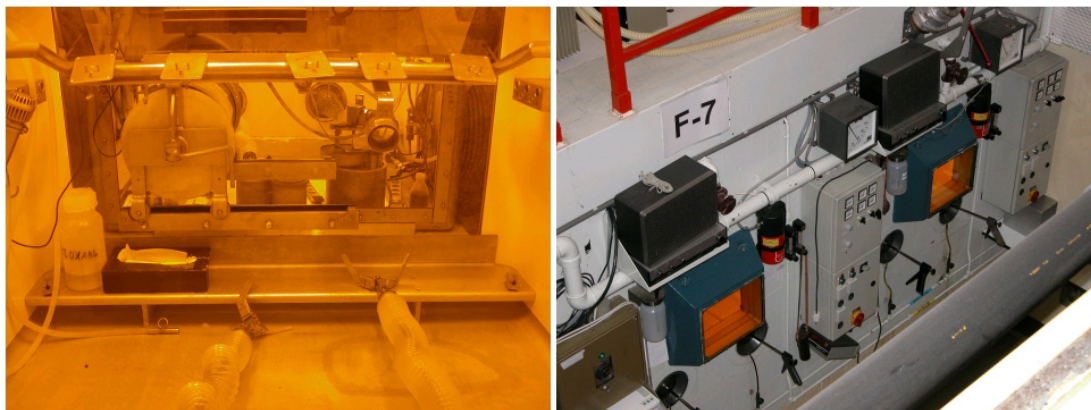


Figure 3. Interior and front of F7 cell (F8 cell is located to the right of F7).

5. DESIGN AND SET-UP OF THE CELLS

The leaching tests will be executed in the lead cells F7 and F8 of the Hot Cell Laboratories at NRG (Figure 3). A series of activities and arrangements have been undertaken to make these cells suitable for performance of the leaching tests. Special attention has been paid to the design of the cells, more specific the allocation of the various activities and pieces of equipment like oven, balances and a facility for liquid handling activities like pH measurement and filtration, over the two cells. From a practical point of view it has been decided to place the oven, the balance for determining the weight of the container before and after the leaching experiments, and the tools for opening/closing the containers in the F8 cell. The balance for weighing the pellets, equipment for chemical/analytical activities like extraction and pH measurement are located in the F7 cell. This arrangement assures a minimum number of transport steps between the two cells, while maintaining sufficient space for handling. A transport mechanism consisting of a rail-like track on which a holder for the container has been mounted has been developed for transfer of the containers between the F7 and F8 cell (Figure 4a).

Before every session the calibration of the balances will be checked. The balances are equipped with internal calibration weights. In addition, a set of external calibration weights has been purchased. For reasons of convenience, portions of the Cs-extracting agent CST will be weighed in advance outside the cell.

A special designed oven with a separate control unit has been constructed. It offers place to 16 containers at one time (Figure 4b). The oven has been designed for continuous heating at a temperature of 150°C. The control unit of the oven is situated outside the cell. Special attention has been paid to security devices in order to prevent the oven from high temperature excursions. Apart from the temperature control unit equipped with a thermocouple, the oven is provided with an additional alarm unit with a separate thermocouple in case the control unit or primary thermocouple fails. Finally, a bi-metal switch tuned at a slightly higher temperature than the alarm unit, has been mounted on the oven, in case both the electronic devices fail.

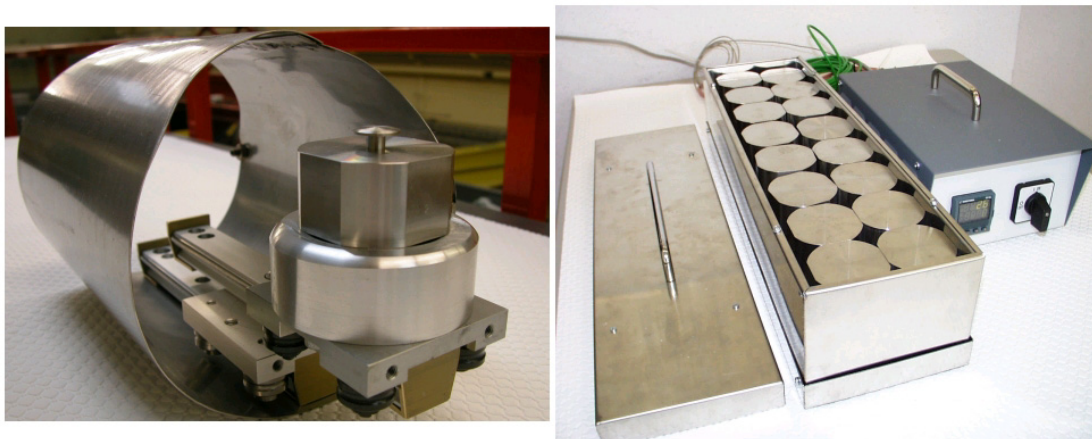


Figure 4. a) transport mechanism for transfer of containers between F7 and F8 cells; b) oven loaded with 16 containers.

6. TRIAL EXPERIMENTS AND TOOLS

To get acquainted with the various handling manoeuvres and to experience the limitations of the facility and to encounter - and to resolve - possible problems, trial experiments have been executed with a dummy test facility equipped with two tongs with ball joints. A series of specially designed tools have been constructed to compensate for the lack of master-slave manipulators and to guarantee smooth handling of the containers. An important aspect concerns the transfer and handling, including opening/closing, of the relatively heavy containers. In order to facilitate accurate positioning of the containers in the oven, the lids have been equipped with a knob (Figure 5a); brace-like constructions have been mounted on the tong for within-cell transfer of the containers (Figure 5b). Figure 6 depicts amongst others equipment to remove/screw the lid firmly onto the container. For removing the lid, the container is placed in the circular base; a clamp with an outline identical to that of the lid will then be put over the lid. The lid is loosened by gently pushing the lever (not depicted) in clockwise direction. For screwing the lid onto the container, the lever is moved in opposite direction. In addition, a separate device for opening and closing the filtration tubes has been constructed (Figure 6). The filtration tubes will also be used for the extraction of Cs from the leachates and - if necessary - the dissolved wall precipitates.

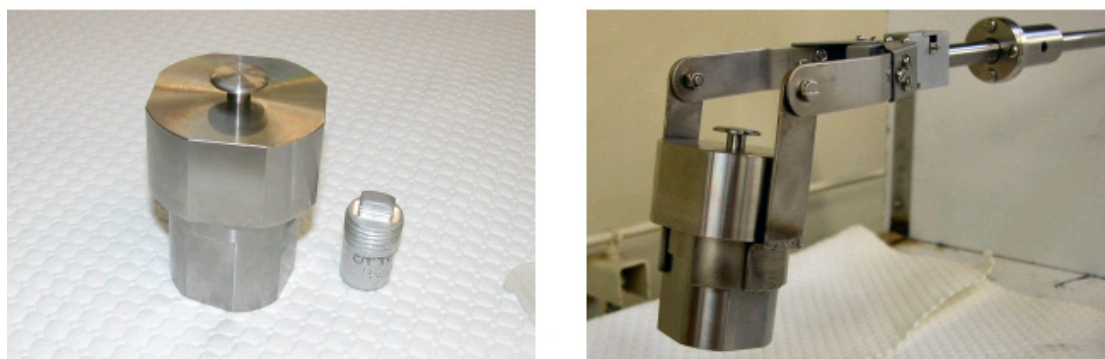


Figure 5. a) containers for the leaching experiments have been equipped with a knob to facilitate their positioning with the tongs in the oven; the lids of the containers in which the samples are stored prior to leaching, have also been restyled to ease opening and removal of the lid; b) brace-like constructions have been mounted on the tong for transfer purposes within the cell.

An automated dispensing system, equipped with a mechanism for automatic tip ejection, will be applied; the volume of any liquid to be pipetted/dispensed is entered via the control unit in steps ranging from 0.1 ml up to 50 ml, depending on the volume of the tip; the control unit will be located outside the cell. In addition a carousel for filtration equipment and the automated dispenser has been constructed (Figure 6). It has been extended with additional positions for:

- stock solutions of HNO_3 and H_2O (large square screw-top beakers),
- square screw-top beakers for storage of the final leachate samples (back),
- a sample holder for putting the container in a slant position to easen dilution and sampling of the leachants (front),
- filtration tubes.



Figure 6. Devices for opening and closing the filtration tubes (left) and leaching containers (right; lever not depicted), and equipment for liquid handling activities (centre); the dispenser can be moved in up- and downward direction along the stand; the upper half of the base, which can be rotated in both clockwise and anti-clockwise direction, is provided with positions for stock solutions, beakers in which the treated leachates and wall precipitates are collected and stored, a sample holder for putting the container in a slant position, and a position for the filtration tubes; the latter position is connected to a vacuum pump for liquid extraction purposes.

7. CONCLUDING REMARKS

Experiences so far have demonstrated the technical feasibility of the leaching experiments in the F7 and F8 cells. The trial experiments with the dummy test facility play a key role in the preparatory stages: they form part of a continuous process of improvement during which tools and instrumentation are adjusted according to the experiences acquired during testing, followed by renewed testing. Special attention is paid to the ergonomics of the set-up for safe operation of the leaching facility, i.e. good overview, maximum degree of flexibility, easy access, and maintenance thus minimizing the risk of (sample) spillage and accidents.

The cells are currently equipped with connectors for electric wiring and electronic data transfer. The wiring of the electrical components and equipment has therefore to be adjusted and extended. The start of the leaching experiments is planned for spring 2006.

8. REFERENCES

- [1] Schram et al. (2003), J. Nuc. Mat. 319, 118-125.
- [2] Dr. K. Kuramoto, pers. com. October 2004.
- [3] T. Tomasberger et al. (2001), Radiochimica Acta 89, 145-19