

DISPOSAL OF BERYLLIUM AND CADMIUM FROM RESEARCH REACTORS

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ABSTRACT

The status of an ongoing R&D project is presented which is related to the decommissioning of German research reactors and to the disposal of irradiated beryllium and cadmium. The aim of the project is to identify a practicable way for the disposal of materials consisting of Be and Cd. Whereas the activity of irradiated Cd is mainly determined by activated Co impurities, irradiated Be carries significant amounts of tritium which must be held back efficiently during an intermediate storage. In addition to their radiological properties, both metals show a high chemotoxicity making their handling and storage more difficult.

INTRODUCTION

Beryllium and cadmium mostly occur in metal form as radioactive special materials during the decommissioning of research reactors. Beryllium is usually used in these reactors as a neutron reflector and moderator, while cadmium acts above all as a neutron absorber. Both metals together have a high chemotoxicity as well as an inventory of radionuclides which has not been closely characterised up to now. A high tritium content is to be expected, particularly in the case of beryllium; this tritium is due to the reaction of the metal with thermal reactor neutrons in particular. However, other nuclides which may be formed by neutron capture from impurities also contribute to the activity inventory. Up to now there is no qualified process for proper treatment, conditioning and intermediate and final repository in Germany. A plan supported by the Federal Ministry of Education and Research is to:

- define the disposal requirements for neutron irradiated beryllium and cadmium in Germany,
- estimate the inventory of radionuclides expected,
- measure the radionuclide inventory using of actual materials from the Garching research reactor (FRM),
- experimentally determine the release of tritium from irradiated beryllium under given temperature conditions,
- develop a handling and conditioning concept,
- investigate materials for containing and holding back tritium and
- select suitable casks, if necessary, appropriately equipped and tested.

In this process, release scenarios for radioactive substances under various boundary conditions (handling as defined, "fire" incident) are to be considered and investigated by experiment. In particular, containment of the volatile tritium is to be achieved by special cask design and validated by realistic measurements.

The entire project is to lead to a disposal method which can be approved using the critical accompaniment of an experienced expert.

RADIONUCLIDES PRODUCED BY NEUTRON IRRADIATION OF BE AND CD

Radionuclides can be produced during the neutron irradiation of beryllium and cadmium in several ways. On one hand there are the nuclear reactions with the bulk metal. In the case of cadmium which in nature consists of eight isotopes with masses from 106 to 116 one has to expect radioactive Cd isotopes which are produced by the following reactions with thermal neutrons:



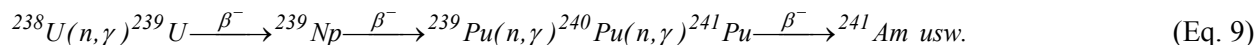
In the case of beryllium which exists in nature as Be-9 only, several reactions not only with thermal but also with fast neutrons and even high energy gamma quanta have to be considered:



Whereas Eq. 4 leads to the long-lived and therefore barely radioactive isotope Be-10, significant amounts of Tritium (H-3) are produced via Eq. 3. Be-8 which is formed via Eqs. 5 and 6 spontaneously decays into two alpha particles and contributes to a formation of He gas which can lead to a swelling of the beryllium. Impurities in beryllium and cadmium can contribute to the activity inventory through neutron bombardment. The classical example is the formation of Co-60 according to Eq. 7. But other nuclides may be produced as well (cf. Eq. 8).



If there are traces of natural uranium present, the higher actinides Np, Pu, Am and Cm can be produced by multiple neutron absorption of U-238 (Eq. 9). By fission of U-235 a number of fission products like Cs-137 may be formed (Eq. 10).



ESTIMATION OF THE ACTIVITY INVENTORY

An estimation of the activity A of a produced radionuclide is possible by means of Eq. 11 where the amount of the irradiated nuclide (N in atoms), neutron flux (thermal and epithermal $\Phi_{\text{therm.}}$ and Φ_{epi} , respectively) and irradiation time (t_B) as well as decay time (t_A) as important factors. These parameters are of course specific for a given plant and have to be estimated on the basis of operational records or plausible assumptions as well, whereas the other quantities in Eq. 11 are nuclear physical constants (σ : cross section for thermal neutrons, I_0 : resonance integral for epithermal neutrons, λ : decay constant of the radionuclide formed).

$$A = (\Phi_{\text{therm.}} \sigma + \Phi_{\text{epi}} I_0) N (1 - e^{-\lambda t_B}) e^{-\lambda t_A} \quad (\text{Eq. 11})$$

From realistic considerations the specific activity of tritium formed according to Eq. 3 in the Be elements of the Garching research reactor FRM is expected to be ca. $1\text{E}+9$ Bq/g. This would result in a total activity for the complete Be inventory of more than $1\text{E}+14$ Bq tritium. An estimation for nuclides which are produced from impurities according to Eqs. 7 to 10 is extremely difficult since in addition to the above mentioned flux parameters the original element or nuclide concentration has to be known. In principle that can be derived from analytical certificates of the Be and Cd producers. But often relevant elements are not specified at all or given in form as detection limits only.

DETERMINATION OF THE ACTIVITY INVENTORY IN REAL BE AND CD MATERIALS Preliminary investigations at the Garching research reactor FRM

In FRM two types of Be reflector elements were used over the years to improve and optimise the neutron balance during operation (cf. Fig. 1). 21 type I elements having almost identical dimensions as the uranium fuel elements and three type II elements with minor modifications. The bulk material of all these elements was high purity beryllium; head and bottom ends consisted of an aluminum-magnesium alloy (AlMg3).

For the shielding of beam tube F1 in the same research reactor a metallic hood was used consisting of two layers of aluminium with a layer of Cd in between like a sandwich. This hood was used for several years and showed a significant gamma dose rate but not as high as in the case of the Be elements.

For a preliminary informal measurement Be element no. 17 was taken by remote control from its storage position under water, raised to ca. one half out of the FRM pool and measured by means of a HPGe detector placed at a 5 to 6 m distance. Due to the high activity of the Be element, the detector was shielded by 10 cm of lead just viewing the element through a hole of ca. 12 mm diameter in the lead wall. Fig. 2 shows the obtained gamma spectrum in comparison to a background spectrum taken at the identical position but without the Be element.

As expected, the lines of Co-60, which was produced from impurities according to Eq. 7, were detected in the gamma spectrum. Surprising were many lines from Ta-182 indicating the presence of tantalum without any doubt. This comparably rare element may be found in Be metal because it is often produced and offered by the same companies. Obviously there are cross-contaminations of the metals which stem from the applied production process. A tiny but significant signal in Fig. 2 at ca. 662 keV could indicate the presence of small quantities of Cs-137 (cf. Eq. 10). But it can also be explained by a single escape peak of Co-60 which is nothing unusual when measuring with a thin Ge crystal (this was the case here).

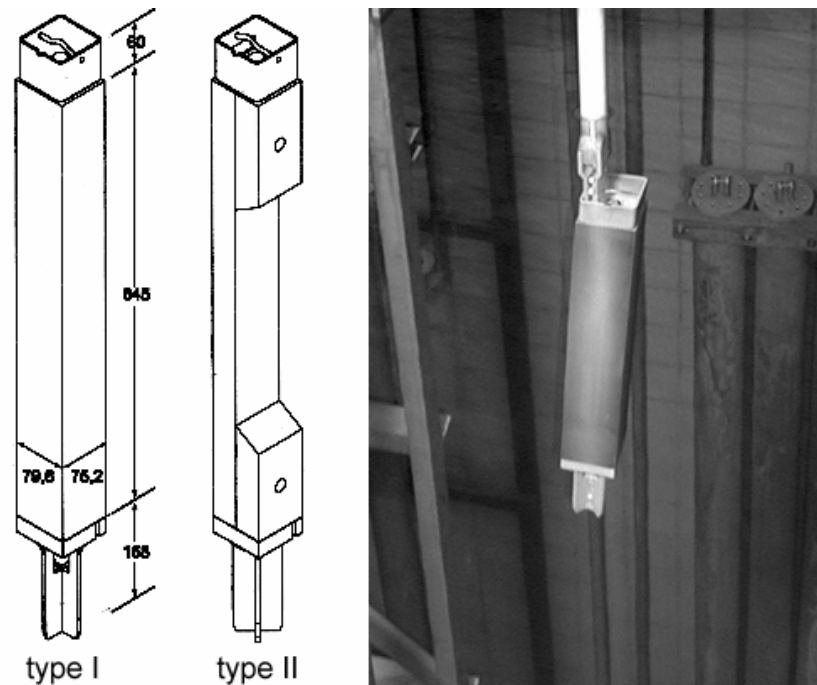


Fig. 1. Sketch of the Be elements used in the Garching research reactor FRM (left) and photo of element no. 17 (right). The type I element consists of head and bottom ends of aluminum (AlMg3) in addition to the ashlar-shaped Be block. Type II element is constructed in an analogous way but has a slot on one side. Dimensions given in mm.

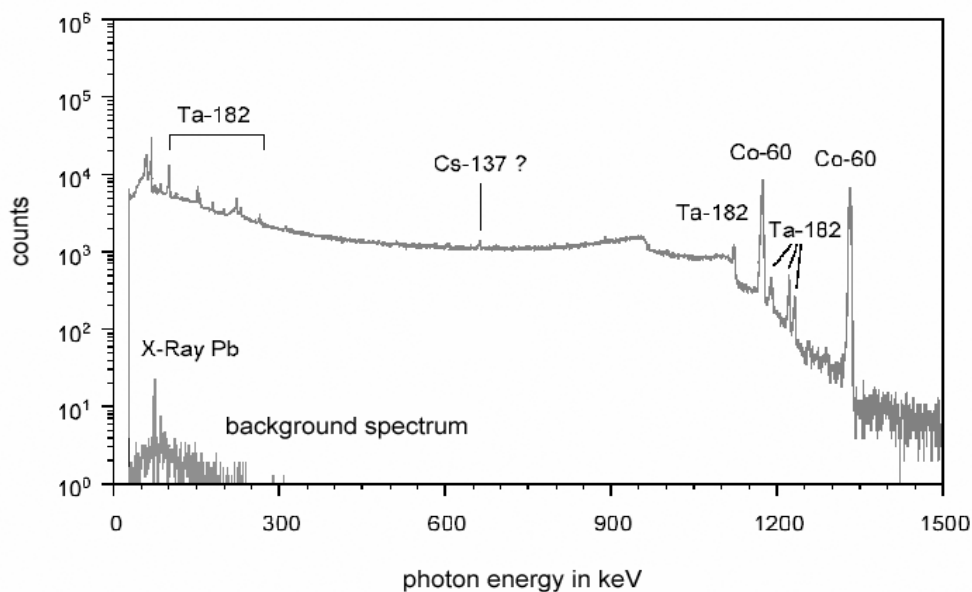


Fig. 2. Informal gamma spectrum of beryllium element no. 17 in comparison to background spectrum. The gamma dose rate at this element was ca. 20 mSv/h at ca. 2 m distance.

Due to its significantly lower gamma dose rate the Cd hood could be measured at a distance of ca. 50 cm to the unshielded detector. The resulting gamma spectrum showed the two characteristic peaks of Co-60

beside the expected lines of the two Cd isotopes Cd-109 und Cd-113m. In addition the line of Mn-54 could be identified which is well known as a typical activation product of metals.

The informal measurements of the two neutron irradiated parts showed that from a radiological point of view Be is of greater importance than Cd. The high gamma dose rate of the Be elements made necessary the utilization of a hot cell facility whereas the Cd hood could be handled in a hood with minor shielding.

Comparative gamma measurements of all Be elements at FRM

In order to obtain an overview over a possibly differing activation of the 24 Be elements of FRM they all were measured in a well defined position under water. For this, an aluminum tube (ca. 5 m long) held at a slant, closed on its down-looking end and having a stiffening girder was used as a collimator looking at the middle part of the individual Be element. The gamma detector was placed at the upper end of the tube. This way a contribution of activated head and bottom ends to the measurement results could be almost excluded. The most relevant results of the comparative measurements are compiled in Table I.

Table I Compilation of relevant results of the comparative gamma measurements of the 24 Be elements of FRM. Elements no. 22 to 24 were the ones with the slot on one side (cf. Fig. 1) and were only used in the last 5 years of reactor operation. Elements no. 4, 5 and 6 were not used during the last 5 years. Since measurements were not carried out in a calibrated geometry but under identical conditions, the count rates can not be attributed to activity directly. In Table I counts in the peaks at 100.11 keV (Ta-182), 604.70 keV (Cs-134), 661.6 keV (Cs-137) and 1173.2 keV (Co-60) are listed. The peak which is attributed to Cs-137 also contains single escape events of the Co-60 1173.2 keV line.

Be element no.	deadtime in %	counts in selected peak of			
		Ta-182	Cs-134	Cs-137	Co-60
1	9.11	2151	403	961	47605
2	7.91	1192	-	630	41499
3	9.23	1682	603	1281	48428
4	6.34	-	-	1232	33924
5	6.47	-	-	1246	35621
6	6.21	-	-	961	33831
7	7.53	1797	-	882	39185
8	8.66	2336	-	1012	45139
9	10.16	2103	439	992	53403
10	10.60	1667	-	993	56316
11	10.63	2407	649	1071	56616
12	10.00	2059	-	1068	53354
13	9.69	2608	-	1396	53127
14	7.67	2208	-	998	40820
15	8.21	1327	-	1091	42848
16	8.26	2241	-	811	43146
17	9.91	3197	587	881	54990
18	10.17	2252	-	1182	53821
19	11.84	2751	723	1422	65910
20	11.65	2484	609	1112	64775
21	11.43	3461	1115	1373	63367
22	3.18	1508	-	175	15875
23	2.98	1649	-	292	14474
24	2.12	1942	-	-	9649

It was evident that this time Cs-134 could be detected putting more weight on the attribution of the 661.6 keV peak to Cs-137. That peak was much bigger than under the unfavourable geometric conditions during the informal measurement (cf. Fig. 2). Although not all Be elements showed exactly the same count rates for individual nuclides, the bandwidth of the results was comparably small with respect to the differing operation times of the elements. So, a single Be element was considered to be sufficient for the further investigations.

Further investigations on a selected Be element

Due to the fact that in element no. 21 all expected and identified gamma emitters were detected with sufficiently high count rates this element was selected for all subsequent investigations and transported into the RCM hot cell facility. For transportation purpose a lead container of ca. 1900 kg was used as it was utilized for handling irradiated FRM fuel elements. All working steps for the introduction into the hot cell facility were tested before by means of an inactive dummy element, in order to guarantee a smooth operation. Gamma dose rate on the outside of the transport container was ca. 60 $\mu\text{Sv/h}$.

In the hot cell the Be element was gamma scanned by means of the same HPGe detector which was used for all preliminary measurements at FRM described above. The element was fixed on a remote controlled positioning system whereas the detector was placed outside the hot cell. A 10 mm hole through a hot cell wall worked as a 100 cm long collimator. The scanning with a lateral resolution of 20 mm showed that all detectable gamma emitters were not distributed uniformly in the element. The maximum activity - Co-60 was taken as a key nuclide - was found to be in the middle whereas the aluminium end parts showed low counts rates only.

For a good and reliable activity determination of the gamma emitters present, for further radiochemical analyses (H-3, C-14 etc.) and for the intended experimental studies of the tritium release under certain conditions, a ca. 7 mm thick slice was cut out of the Be element at a well defined position. A low-speed diamond saw (cf. Fig. 3) was installed in the hot cell and successfully applied for this purpose.



Fig. 3. Installation of a low-speed diamond saw in the RCM hot cell facility for the destructive sampling of the selected beryllium element no. 21.

The Be slice was gamma scanned as well but with a somewhat better lateral resolution. Again, the gamma emitters were found to be inhomogeneously distributed in the material reflecting the neutron field the Be element has experienced during the reactor operation. In a calibrated geometry where the detector was placed at a distance of more than 3.5 m from the sample, the Co-60 activity in the slice could be determined gamma spectrometrically to be $1.2\text{E}+9$ Bq. Taking into account the inhomogeneous distribution in the element a total Co-60 activity of ca. $2.4\text{E}+11$ Bq was calculated.

INVESTIGATION OF HYDROGEN CONTAINMENT

The basis for the containment technology is the long-known ability of some metals such as palladium or platinum (e.g. as PtH_x , PdH_x) and transition metal alloys (e.g. $\text{Zr}_n\text{Fe}_m\text{H}_x$, FeTiH_{2-x} , MgNiH_{2-x} , $\text{LaNi}_5\text{H}_{6-x}$) to store hydrogen. Recently, carbon nanotubes have also come under discussion as a hydrogen storage medium.

The scope of the work included containment experiments initially with light hydrogen carried out with the aim of achieving optimum conditions for long-term storage. The most important criterion is the release temperature in addition to the storage capacity. This release temperature is the temperature at which detectable amounts of hydrogen are released from the storage medium. In the case of final repository conditions, the optimisation goal is the highest possible release temperature to ensure the long-term binding of tritium.

The quantitative representation of the release scenario was conducted on selected metal hydrides using thermogravimetry and differential scanning calorimetry. Subsequently the determination of the degradation or decomposition stages of various metallic and salt hydrides as well as deuterides was carried out. Furthermore, the decomposition temperatures with various heating regimes were determined.

Thermal decomposition of the metal hydrides investigated always took place in a multi-stage process. In the case of magnesium hydride, the first decomposition stage can be detected as the main decomposition stage, which is the stage where the maximum amount of hydrogen is released. Aspects relevant to both kinetics and crystal structure may be responsible for the multi-stage process observed. If the heating rate is increased, a shift in the thermal decomposition to higher temperatures can be observed. This effect is of a purely kinetic nature. The thermodynamic instability of the hydride is shifted to higher temperatures due to the kinetic inertia of the system.

Furthermore, investigations on hydrogen release and quantitative detection of the hydrogen content via a hydrogen analyser (a process mass spectrometer) were carried out. The decomposition of e.g. lithium deuteride ranges in a temperature interval from $520\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$. The maximum of decomposition is at $664\text{ }^\circ\text{C}$.

The hydrides MgH_2 , CaH_2 , TiH_2 , ZrH_2 and the deuteride LiD were tested for their thermal degradation mechanisms and decomposition temperatures in the investigations on hydrogen containment. Table II lists the maximum temperatures of the first degradation stage of the substances used. This clearly shows that the decomposition temperature increases in the order $\text{CaH}_2 < \text{MgH}_2 < \text{TiH}_2 < \text{ZrH}_2 < \text{LiD}$, thus the stability of the hydride or deuteride also increases. The qualification as a containment material must be interpreted correspondingly. Plans also include an investigation to determine the physically optimum form of the solid storage medium. Approaches include powder beds, open-pored blocks (foams) and also porous thermal sprayed layers.

Table II Maximum decomposition temperatures of the first degradation stage of selected deuterides and hydrides

hydride/deuteride	maximum decomposition temperature
LiD	664 °C
CaH ₂	306 °C
MgH ₂	400 °C
TiH ₂	514 °C
ZrH ₂	518 °C

CONSIDERATIONS ON CASK SELECTION

Various casks are suitable to take beryllium elements, from 200 L drums as type A packaging through various steel plate and cast iron casks to MOSAIK[®] casks. The geometric dimensions of the elements to be packaged, activities, nuclides and any gas release are relevant to the selection of casks. The shielding required for the packaging of the beryllium elements over and above the expected radiological inventory is to be determined from a radiological point of view.

The cask type MOSAIK[®] from GNS offers universal properties for the requirements. Any shielding can be integrated into the MOSAIK[®] cask as lead lining. A suitable basket is to be developed specifically for the task to facilitate adjustment and fixation of the beryllium elements.

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