Proceedings
of the
International Topical Meeting
on

NUCLEAR AND HAZARDOUS WASTE MANAGEMENT SPECTRUM '96

August 18-23, 1996
Seattle, Washington

Sponsored by the American Nuclear Society's Eastern Washington Section
U.S. Department of Energy
International Atomic Energy Agency
European Nuclear Society
European Commission
Chinese Nuclear Society
U.S. Department of Commerce, Regional Office
Washington State Department of Community Trade and Economic Development
British Columbia Trade and Investment Office

Published by the
American Nuclear Society, Inc.
La Grange Park, Illinois 60526 USA

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LEACHING OF RADIONUCLIDES FROM MTR-FUEL ELEMENTS IN CONCENTRATED SALT BRINES

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ABSTRACT

Direct final disposal in a salt mine is being discussed in the Federal Republic of Germany as an alternative to the reprocessing of spent material test reactor fuel elements (MTR-FE). The KFA Institute for Safety Research and Reactor Technology conducts safety studies for the interim storage and final disposal of such special fuel elements. One accident scenario in long-term safety analyses is a water ingress into the salt repository. This involves the formation of brines which come into contact with the fuel elements.

Radionuclides are mobilized from the irradiated fuel element when the "meat" of the fuel element becomes accessible to the brine solution. However, it seems that most of the radionuclides are effectively trapped by the corrosion products of the cladding material aluminum. After a short leaching period, the activity concentrations in the Q-brine solution reach a constant level far below the limit of solubility with a progressing corrosion of the fuel element.

I. INTRODUCTION

Spent fuel elements from German Material Test Reactors (MTR) have been reprocessed in DOE facilities in the past. Since this was discontinued in 1988, the German authorities have been discussing direct final disposal in a rock salt repository in the deep geologic underground.

One accident scenario in long-term safety analysis is a water ingress into the repository. This involves the formation of brines which come into contact with POLLUX disposal containers. These casks are designed to resist the corrosive attack for about 500 years. After the container has failed the brine penetrates the cask wall and comes into contact with the spent fuel elements. Corrosion investigations of the fuel element cladding materials aluminum, AlMg1 and AlMg2 showed that this cladding had no barrier function /1,2/. After a short period of some months the "meat" of the fuel elements becomes accessible to the brine solution. The subject of our investigations is MTR fuel of the DIDO type, which is used in the Jülich FRJ-2 reactor. It contains 20 wt% U-Al alloy with an initial enrichment of 80 % ^{235}U. The fuel alloy plates (thickness 0.6 mm) are covered with aluminum claddings of 0.38 mm. Three plates are welded to form a concentric tube. A fuel element assembly consists of four tubes of 6, 7, 8 and 9 cm diameter, mounted onto structural elements. The tube length is about 63 cm.

The hot cell leaching experiments with fuel element parts started in August 1994 and a first phase will be finished in approximately 1998.

II. EXPERIMENTAL

A. Material and Equipment

The fuel element was discharged from the reactor on June 17, 1990. It was characterized for burn-up (45 % FIFA), residual enrichment (62.9 %), and decay heat (12 W). The inner tube of this element was sawn into pieces of 40 x 18 mm. Initially each piece carried a total calculated activity of 43 TBq (sum of actinides and fission products), 1526 days after discharge from the reactor.

Chips of cast iron (GGG40) were drilled from a solid block.

Beakers of glass, Hastelloy C4 and stainless steel 1.4541 were prepared from Pyrex glass, or from solid material of the alloys. The size of the beakers was 27 mm total height, 23 mm inner height, 25 mm total diameter, 23 mm inner diameter.

The "hot" experiments were performed in shielded (20 cm Pb) hot cells equipped with master/slave manipulators.

Separation of transuranic elements was performed by extraction chromatography on TRU®Spec columns with octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) as active phase /3, 4/.

Radioactive samples were characterized by α-spectrometry (EG&G Ortec Octête PC with ion implanted silicon surface barrier detectors) and γ-spectrometry (EG&G Ortec 919 Multichannel Analyzer with Ge-HP detector).

The compositions of the brines used for the leaching experiments are listed in table 1. All chemicals were analytical grade from "Merck".

Table 1: Brine Composition

	Brine 1 (Q-	Brine 2
Salt	Concentration (Mol/1000 Mol H_2O)	
NaCl	6.80	1.49
KCl	17.40	0.40
$MgCl_2$	77.30	97.21
$MgSO_4$	3.20	-
$CaCl_2$	-	5.68
$CaSO_4$	-	0.01
pH	3.61	3.61

B. Corrosion of spent MTR fuel

Pieces of the fuel element were weighed and immersed in 100 ml brine and stored at 90°C. The fuel element pieces were placed in a glass beaker or in a glass beaker positioned on top of a layer of GGG40 chips, or in beakers of SS 1.4541 or Hastelloy C4[a]. The total weight of the sample bottle was registered before its insertion into the oven. At intervals, varying from days to months, the pH value was measured, an aliquot of 2.5 ml was taken from the brine and filtered through a 0.45 μm membrane filter. The aliquot volume was replaced by fresh brine. In the first experiment series with Q-brine the weight loss caused by evaporation was compensated by de-ionized water whenever the aliquot sample was taken. During the second experimental series the weight loss was compensated weekly.

If possible, the filtered sample solutions were directly removed from the hot cell and further treated in the laboratory. If the dose rate of a sample was too high for non-shielded handling, an aliquot of the original sample solution was diluted with nitric acid in the hot cell, and a fractional amount was removed to the laboratory.

For α-spectrometry, a redox and chemical separation procedure was applied. Typically, standard solutions of ^{236}U, ^{236}Pu and ^{243}Am and 2 ml 2 M HNO_3 were added to an aliquot of 0.3 ml original solution, followed by 50 μl freshly prepared 2.5 M hydroxylamine hydrochloride solution and 100 μl 0.1 N Fe(II)-sulfamate solution. After 10 min 50 μl 0.8 M ascorbic acid solution were added, after 10 min 100 μl 1 M $Al(NO_3)_3$ and 200 μl 2.5 M freshly prepared $NaNO_2$ solution were added, after 20 min this mixture was passed through a TRU-Spec® column, washed with 10 ml 2 M HNO_3, eluted with 10 ml 4 M HCl (Am, Cm), and with 15 ml 0.5 M oxalic acid (U, Pu). The HCl fraction was evaporated to near dryness in a PTFE beaker, diluted with 500 μl 2 M HNO_3 and completely transferred to the electrodeposition chamber. The oxalic acid fraction was evaporated to near dryness, then fumed off several times with 7 M HNO_3/30 % H_2O_2, diluted with 500 μl 2 M HNO_3 and also electrodeposited. The electrodeposition was performed from 1 M NH_4Cl solution on polished, Ni-coated brass platelets on an area of 20 mm diameter.

In an alternative procedure an unspiked sample solution was separated on TRU-Spec®, the eluate fraction containing U and Pu was electrodeposited, and the relation of the $^{239/240}Pu$ and ^{238}Pu peaks was determined by a-spectrometry. As this relation is constant for the whole set of fuel samples, it could be used for the calculation of the ^{241}Am fraction present in the overlapping peak with ^{238}Pu. This procedure avoids the necessity of separating each individual sample, although it introduces an increased statistical scatter into the (calculated) ^{241}Am peak area.

γ-Spectrometry was used for the determination of ^{137}Cs in aliquots of the original sample solution. $^{106}Ru/Rh$, ^{125}Sb, ^{144}Ce, ^{144}Pr, ^{154}Eu and ^{60}Co were measured after separation from the interfering high activity of Cs with ammonium phosphomolybdate. After γ-spectrometry 1 ml of this solution was used for the determination of ^{90}Sr. 100 μl of a 1000 ppm $SrNO_3$ solution were added as a tracer and if necessary conc. HNO_3 to increase the NO_3^- concentration to 8 mol/l. This mixture was passed through a Sr-Spec® column, washed with 10 ml 8 M HNO_3 and eluted with 0.05 M HNO_3. ^{90}Sr was measured by liquid scintillation counting (LSC) and to determine the recovery rate the concentration of natural Sr was analyzed with ICP-OES.

III. RESULTS

A. pH values

The pH value of brine 1 decreased from an initial pH of 4.6 to 3.5. In brine 2 the pH dropped to 2.0 - 2.6 during the first four days and increased to pH values between 3.1 and 3.5. A pH drop of about 1 at the start of the leaching experiments in brine 1 also occurs in the presence of metallic additives.

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[a] Wall material of the storage casks

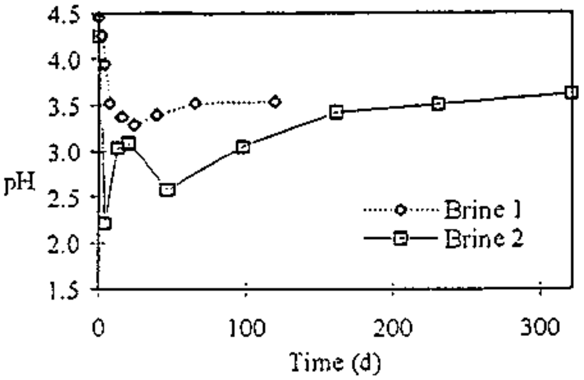

Figure 1: pH value of the plain leachates (temperature corrected for 25°C)

B. Mobilization of γ-emitters

1. Brine 1. After a prompt appearance in the leachates of both experimental series, the activity A of γ-emitters in brine 1 in the absence of iron remained almost unchanged; in the case of Ce, Eu, Ru and Pr the activity decreased by more than one order of magnitude (Figure 2). The mobilization of γ-emitters from MTR fuel in brine 1 in direct contact with Hastelloy C4 or SS 1.4541 showed no significant difference from the leaching experiments with plain brine. In the presence of GGG40 the corrosion of the fuel pieces is much faster compared to the other samples and therefore the radionuclide release is higher by about four orders of magnitude. Figure 3 shows this influence of the different metallic additives on release of ^{137}Cs.

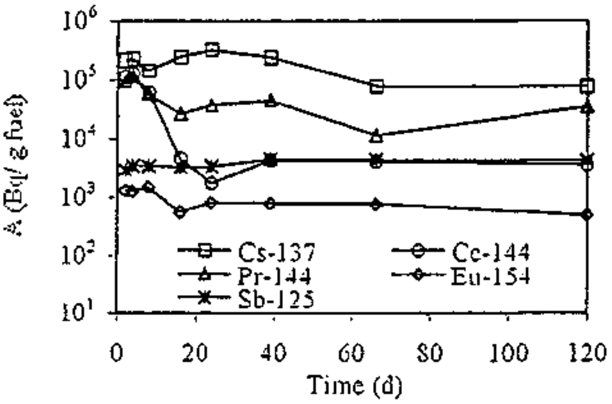

Figure 2: Mobilization of γ-emitters from MTR fuel in brine 1 at 90°C

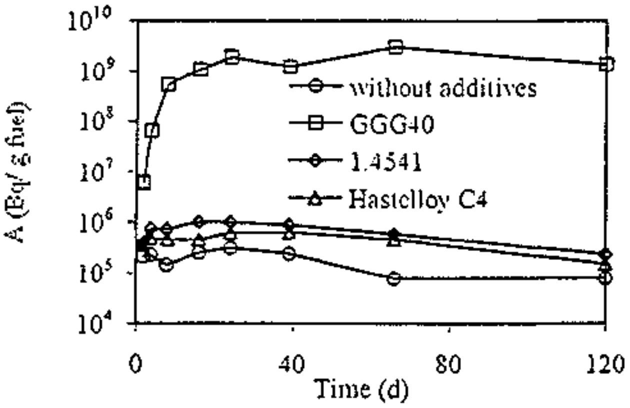

Figure 3: Influence of metallic additives on the release of ^{137}Cs in brine 1

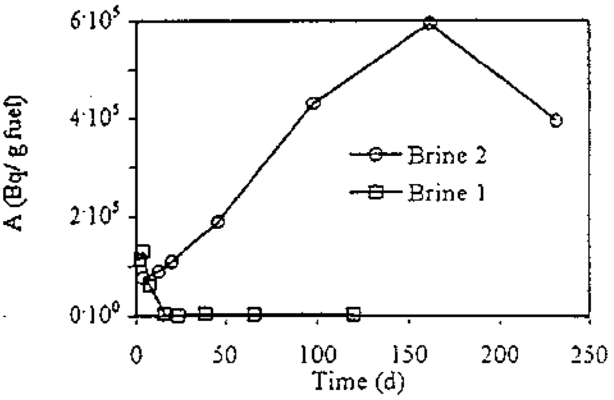

Figure 4: Leaching of ^{144}Ce in plain brine 1 and brine 2

2. Brine 2. The activity of γ-emitters is about one order of magnitude higher and a constant or decreasing activity occurs much later in the leaching experiments with brine 2, as compared to the leaching rates obtained with brine 1. Figure 4 shows the leaching of ^{144}Ce in plain brine as an example. The shape of the release curves of the other γ-emitters is similar.

An activity decrease occurred after about 150 days together with precipitation of the corrosion products from the cladding material. An explanation for the later occurrence of precipitates in brine 2 could be the higher

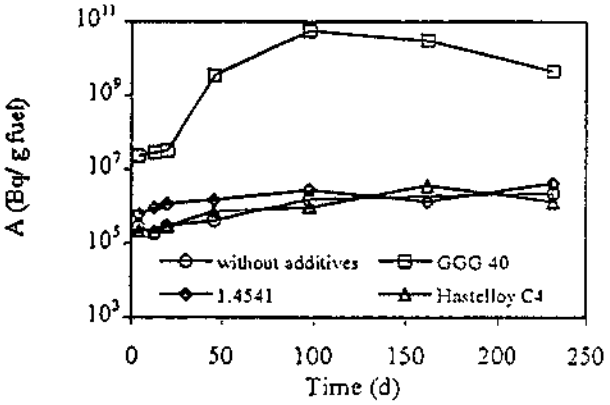

Figure 5: Influence of metallic additives on the release of ^{137}Cs in brine 2

pH value at the beginning of leaching. The activity decrease in the presence of GGG40 after about 100 days is caused by an earlier precipitation of corrosion products in comparison to the plain brine. The influence of metallic additives on the leaching rates is shown in Figure 5 on the example of ^{137}Cs. The absolute leaching rates are much higher than with brine 1 but the influence of the metallic additives show the same tendency. The presence of GGG40 leads to an increase of the leaching rate of about four orders of magnitude. The other metallic additives have no significant influence on the activity release.

C. Mobilization of α-emitters

The mobilization of α-emitters has so far only been evaluated for the leaching test with brine 1. First measurements of samples with brine 2, however, show, that the release rate is one up to two orders of magnitude bigger.

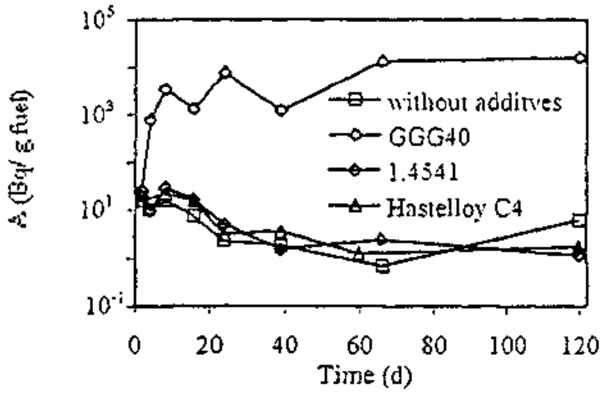

Figure 6: Mobilization of $^{239/240}$Pu from MTR fuel in brine 1 at 90°C

The shapes of the leaching curves for the α-nuclides are quite similar to those obtained for the γ-emitters, as shown in Figure 6. In the presence of GGG40, where the highest leaching rates were achieved, only 6.8 MBq of actinides had been released, corresponding to about 0.007 % of the total inventory. This low release rate probably results from co-precipitation with the corrosion products. It is interesting that Cm could not be detected in leachates formed in the presence of GGG40. This may be due to a specific sorption mechanism of Cm in the presence of iron ions.

IV. CONCLUSIONS

Radionuclides from spent MTR fuel will be mobilized into concentrated salt brines after the brines have penetrated the storage casks. The corrosion of the fuel is accelerated by iron respectively by iron ions which arise from the corrosion of the storage container.

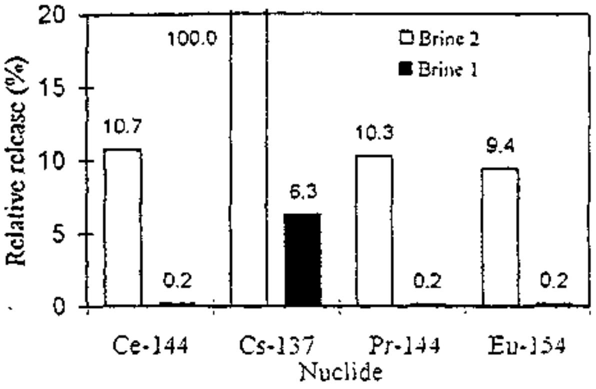

Figure 7: Maximum relative release related to the total amount in presence of GGG40

Only a small percentage of the radionuclides are mobilized into the brine (except Cs in brine 2, Figure 7) and as far as may be concluded from these short-time observations, initially released radionuclides seem to be co-precipitated with the formed iron and aluminum hydroxides and thus immobilized.

The experiments will be continued with variation of the leaching parameter set (different brine compositions), investigation of the hydrogen gas formation and release of volatile radionuclides.

ACKNOWLEDMENTS

This project is sponsored by the Federal Ministry of Education, Science, Research and Technology, reference number 02 E86547.

REFERENCES

/1/ B.-G. Brodda, J. Fachinger, „Corrosion Behavior of Spent MTR Fuel Elements in a Drowned Salt Mine Repository," Mat. Res. Soc. Symp. Proc., 353, 593 (1995)

/2/ H. Rainer, I. Syuhada, J. Fachinger, „Effects of a Hypothetical Water Ingress into a Salt Dome Repository on the Aluminum Cladding of Directly Stored Material Test Reactor Fuel Elements," Proceeding of Waste Management '96, (1996)
(only on CD-ROM available)

/3/ E.P. Horwitz, R. Chiarizia, M.L. Dietz, H. Diamond, D.M. Nelson, Analytica Chimica Acta 281, 361, (1993).

/4/ E.P. Horwitz, M.L. Dietz, D.E. Fisher, Solvent Extr. Ion Exch. Vol. 8 Issues 4 and 5 (1990); Vol. 9 Issue 1 (1991).