FORMATION OF HYDROGEN AND RADIOACTIVE GASES IN WASTE PACKAGES WITH CEMENTED INTERMEDIATE LEVEL WASTE

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ABSTRACT

Six 200 l waste packages from the German pilot reprocessing plant WAK with fuel hardware, cladding hulls and dissolver sludge cemented in place were examined with respect to their radiolytic formation of hydrogen and their mobilization of volatile radio-nuclides. Hydrogen was found to be formed by the radiolytic disintergration of water contained in the matrix material. The specific formation rates of hydrogen partly disagree with predictions from the radio-lysis of cement. Considerable amounts of Kr-85 were found to be released from waste packages with cladding hulls and dissolver sluge fixed in a cemen-titious matrix. The experimental results are presented and compared to theoreti-cal expectations.

INTRODUCTION

In the Federal Republic of Germany, it is planned to dispose of intermediate level waste packages with non-negligible heat production (so-called heat-generating ILW) in deep vertical boreholes in the salt dome repository at the Gorleben site.

These ILW packages contain certain types of reprocessing wastes such as fuel hardware (FH) and cladding hulls (CH) from LWR fuel elements, dissolver sludges (DS) from the clarification of the fuel solution and spent HTR fuel elements from the two German High-Temperature Reactors.

The borehole disposal technique for these waste packages is being developed and tested in an R&D project at the Jülich Research Centre (KFA) (1,2).

According to practice in the German pilot reprocessing plant at Karlsruhe (WAK), the above mentioned reprocessing wastes are embedded in cement grout as a conditioning method for final dis-posal. In compliance with the reprocessing contracts between German power companies and the reprocessing companies COGEMA and BNFL, the wastes originating from German fuel elements reprocessed abroad will be returned and have to be disposed of in the German final repository. The conditioning concepts of COGEMA and BNFL envisage the fixation of this ILW in cement-based matrices also. Due to the high radiation field within the ILW packages, the unbound water in the cement-based fixation matrix is subject to radiolytic disintegration. Depending on the intensity of the radiation field, hydrogen and oxygen are formed as stable gaseous reaction products of water radiolysis.

In addition, hydrogen is formed by the inner corrosion of metallic waste constituents and container materials. Volatile radionuclides such as H-3, C-14 and Kr-85 adhering to or trapped in the surface of waste constituents can be mobilized by corrosive attack by the highly alkaline pore water in the cement matrix.

The formation of gases by radiolysis and/or corrosion may lead to internal overpressure in gastight waste containers. Waste drums that continuously release hydrogen and/or radioactive gases during final disposal may affect the operational as well as the long term safety of the repository.

The released hydrogen when mixed with air might form explosive gas mixtures. This is especially critical for the borehole technique, since hydrogen might accumulate in deep boreholes due to poor ven-tilation.

The formation of gases in six ILW packages with fuel hardware, cladding hulls and dissolver sluge cemented in place from the German pilot reprocessing plant WAK has been investigated ex-perimentally.

ILW PACKAGES UNDER INVESTIGATION

The six ILW packages under investigation resulted from three fuel elements from the Neckar Westheim PWR-station which were repro-cessed in May 1986 at the Karlsruhe reprocessing plant WAK. The fuel elements had a mean burn-up of 37.5 GWd/tU and were dis-charged from the reactor in July 1982. The cooling time at the beginning of the experiments was 4.3 years.

The ILW packages consist of standard 200 l drums with removable inserts. The waste materials from the three GKN fuel elements were cemented in place at the WAK in 120 l insert drums using cement grout. As fixation material ordinary Portland cement, PZ45F, was used. The water-to-cement ratio amounted to 0.45; approx. 1% of concrete thinner was added.

1) Fuel Hardware (FH)

One of the waste packages contains the fuel hardware (i.e. end pieces, grid spacers and control rod guide tubes) of one GKN fuel element. The hardware components are made of stainless steel and Inconel; they are highly

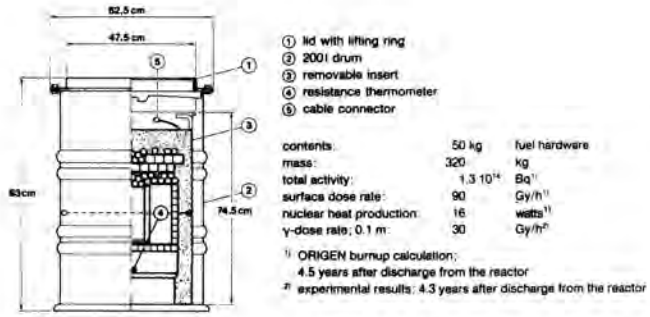

Fig. 1a. 200 1 Standard Drum WithFuel Hardware Cemented in Place.

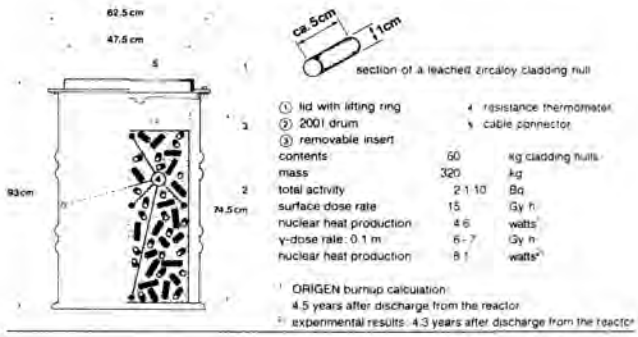

Fig. 1b. 200 1 Standard Drum with Cladding Hulls Cemented in Place.

activated in the neutron flux of the reactor core. The main activation product is Co-60.

The nuclear inventory of the drum was evaluated experimentally and by burn-up calculations. Additional information are given in Fig.1a.

2) Cladding Hulls (CH)

Two of the waste packages each contains 60 kg of leached zirc-alloy-4 cladding hulls. The cladding material is contaminated with fuel solution and with insoluble dissolver residues. A minor part of the activity is due to activation products such as Co-60 and Sb-125. The nuclear decay heat dissipated in one of the drums was determined by the Karlsruhe Research Centre (KfK)using an iso-thermal heat flux calorimeter. Hull samples taken at WAK have been analysed by gamma spectrometry.

More information about the nuclear inventory of the drums with cladding hulls is given in Fig.1b.

3) Dissolver Sludge

At WAK, the fuel solution was clarified of insoluble residues (dissolver sludge) using polypropylene filter bags.

Three of the ILW packages each contain two of these filter bags. Through each of the filter bags the fuel solution of one dissolver batch corresponding to about 180 kg of UO_2 has been passed. Due to its extremely fine grain size only a small part of the total amount of dissolver sludge is being separated by the rather coarse-meshed filter bags.

For short cooling times of up to about 10 years the activity of the dissolver sludge is dominated by Ru-Rh-106. The nuclear decay heat of the three drums with dissolver sludge was determined at KfK by calorimetry. More information is given in Fig.1c.

HOT CELL EXPERIMENT

After curing, the six ILW packages were transported to KFA Jülich. They were transferred into one of the Hot Cells at KFA where the gas release experiments were performed.

On delivery, i.e. 3-4 months after cementation at WAK, gas samples were taken from the void volume in the drums; the samples were analysed with respect to their concentration of hydrogen and gaseous activity. Furthermore the gamma dose rate and the internal drum pressures were determined.

The inserts with the cemented ILW were then transferred into gas-tight overpacks made of stainless steel. The leak-tightness of the overpacks was tested to be better than 10E-5 mbar l/sec, their void volume amounted to 45-50 l each.

In order to be able to study the formation of gases at elevated (i.e. repository-relevant temperatures) of up to 80 °C the overpacks were equipped with jacket heaters. The temperatures and the pressures in the overpacks were continuously monitored.

Each of the six overpacks was connected to a valve control panel located outside the Hot Cell.

Various analytical devices could be connected to the valve control panel for gas sampling and for in-line gas

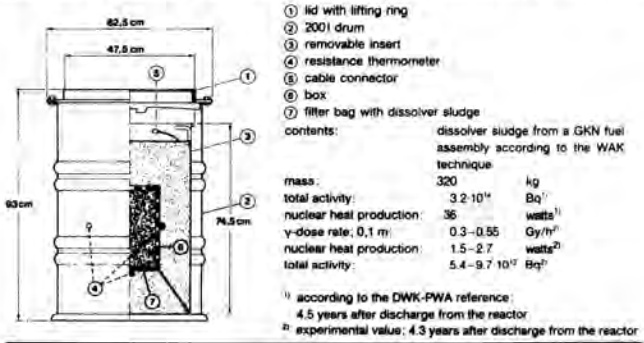

Fig. 1c. 200 1 Standard Drum With Filter Bags Containing Dissolver Sludge Cemented in Place.

analysis. The gas analytical methods applied are the following:

- gas sampling; gas chromatography
- gas sampling; radio gas chromatography
- sampling of liquid condensate; scintillation counting for H-3
- radiochemical analysis of C-14
- gamma-spectrometric in-line analysis of Kr-85

Figure 2 shows a picture of the experimental set-up in the Hot Cell.

EXPERIMENTAL RESULTS

Three of the six ILW packages (one with fuel hardware, one with cladding hulls and one with dissolver sludge) were hermitically sealed in their overpacks for about three years. The void volume in the overpacks was initially filled with air at normal pressure. The pressure in the overpacks was continuously monitored. For the three different types of waste packages, the resulting gas pressure as a function of time is shown in Fig.3.

The oxygen from the air initially enclosed in the overpacks is readily consumed within the first few months. This leads to a decrease of pressure of up to 200 mbar. After this initial phase, pressure steadily increases due to the radiolytic formation of hydrogen. In the overpack with cladding hulls, hydrogen is formed at a very low rate; as a result, pressure increases very slowly and is still below normal pressure after 2.5 years. In the overpacks with fuel hardware and dissolver sludge considerable overpressures can be observed due to their high formation rates of hydrogen.

After about 400 days, the temperature in the overpacks was in-creased from 23 to 50 °C. As a result, the internal system pres-sure increases abruptly due to the thermal expansion of the gas atmosphere and due to the build up of additional water vapor.

Gas samples were taken from the overpacks. They were analysed with respect to their concentration of hydrogen. As an example, Fig.4 represents the corresponding formation rates of hydrogen in the overpack with fuel hardware.

Fig. 2. Experimental Set-up in the Hot Cell.

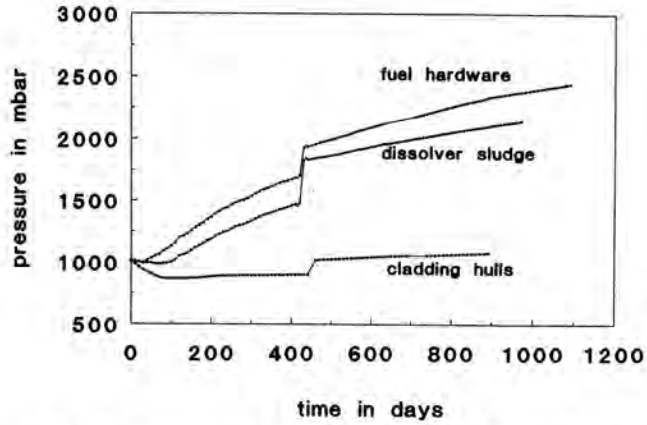

Fig. 3. Gas Pressure in Three Overpacks as a Function of Time.

Within the first 1.5 years of the experiment, 51 l of hydrogen were liberated from the cementitious waste matrix with fuel hardware. The formation rate seems to decrease with time. The increase of temperature to 50 °C seems to have no influence on the formation rate of hydrogen.

Gas samples taken from the six overpacks were analysed by gamma spectrometry with respect to their ac-

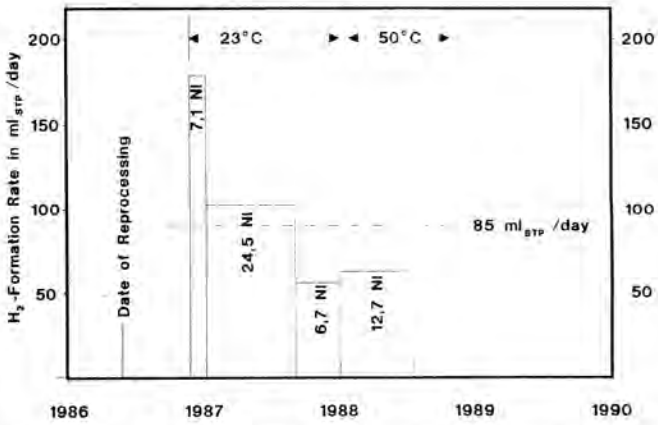

Fig. 4. Formation Rate of Hydrogen in the Drum with Fuel Hardware.

tivity concentration of Kr-85. The formation rates of Kr-85 were calculated from the increase of activity concentration. As an expample, Fig.5 represents the release rates of Kr-85 for one of the two drums with cladding hulls. Since April 1987, when the temperature in the overpack was increased to 50 °C, the activity concentration was continuously monitored by in-line analysis.

The figure illustrates, that an increase of temperature results in a short peak-release of Kr-85. Under long-term aspects, elevated temperatures seem to have no major influence on the liberation of Kr-85.

The mean formation rates of hydrogen and of Kr-85 obtained in the experimental program over more than 2.5 years are summarized in Table I.

The total amounts of hydrogen and of Kr-85 that are expected to be formed inside the drums during interim storage can be estimated using the formation rates given in Table I. Extrapolations, taking the formation rates as constant with time, give conservative estimates.

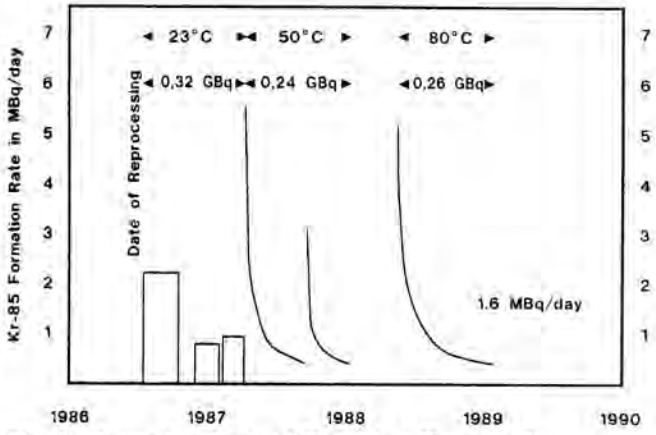

Fig. 5. Formation Rate of Dr-85 in a Drum with Cladding Hulls.

TABLE I

Mean Formation Rates of Hydrogen and of Kr-85

ILW waste package from WAK	mean H_2 formation rate cm^3_{STP} /day	mean Kr-85 formation rate MBq/day
fuel hardware FH-190	85	---
cladding hulls CH-187	6.4	0.77
cladding hulls CH-190	2.2	1.6
dissolver sludge DS-1	28	0.11
dissolver sludge DS-2	77	0.36
dissolver sludge DS-3	65	0.13

The moisture contained in the gas atmosphere of the overpacks was collected and analysed with respect to its H-3 activity. Additionally, samples of the liquid condensate taken from the container sump were analysed for H-3. The H-3 concentration of the unbound water in the cement matrix turned out to be of the order of up to 100 Bq/ml.

The gaseous activity concentration of C-14 in one overpack with cladding hulls and one with dissolver sludge was analysed by radiochemical methods. The C-14 activity released over a period of about 150 days amounts to 16 kBq for cladding hulls and 1.8 kBq for dissolver sludge, respectively. Carbon-14 escapes from the waste matrix as ^{14}CO or $^{14}CH_4$. Radioactive $^{14}CO_2$ was not found.

INTERPRETATION OF THE RESULTS

The radiolytic formation of hydrogen in cement-based matrices has been thoroughly investigated in the past. Specific formation rates caused by beta/gamma and alpha radiolysis have been evaluated in laboratory experiments using external irradiation and actinide doping /3,4/. The results of these experiments are usually ex-pressed by a so-called G_{H2} value defined as:

$$G_{H2} = V_{H2} / E_{abs}$$

V_{H2}: volume of hydrogen produced by radiolysis in cm^3 (STP)

E_{abs}: absorbed radiation energy in kJ

For beta/gamma radiolysis of pure Portland cement G_{H2} values of 0.3-0.5 cm^3/kJ were reported, whereas alpha radiolysis resulted in a G_{H2} value of 0.7 cm^3/kJ /3,4/.

The nuclear decay heat dissipated in the ILW packages under investigation is well known from the calorimetric measurements and from burn-up calculations. For the three different types of ILW packages investigated, experimental G_{H2} values were calculated taking into account the well known decay heat and the hydrogen formation rates observed in the first few months of our experi-ments. The G_{H2} values obtained in this way are given in Table II. They have to be compared with the above-mentioned G_{H2} values de-rived from laboratory experiments.

The mean dose rates were calculated taking into account the self-absorption of the metallic waste materials and a correction for some losses of gamma radiation leaving the drums.

FH For the drum with fuel hardware the derived G_{H2}-value is a factor of two less than reported in the literature. The discrepancy might partially be caused by inaccurate correction for self-absorption.

CH For the two ILW packages with cladding hulls the measured G_{H2} value is very low and in evident contradiction to the theoretical estimate. There are two possible explanations for this disagreement:

TABLE II

GH2 Values Derived from the Measured H2 Formation Rates

	fuel hardware FH	cladding hulls CH	dissolver sludge DS
absorbed heat rate watt	20	5	2.5
H_2 formation rate cm^3_{STP} /day	183	8	50
mean dose rate Gy	180	50	3
mean G_{H_2} value cm^3_{STP} /kJ	0.2	0.03	3.8

1) Part of the hydrogen formed by radiolysis is absorbed by the zircalloy material, especially through the fresh cutting edges of the hull sections. The hydrogen is fixed in the Zr lattice as zirconiumhydride.

2) The cladding material was found to be strongly contaminated with dissolver sludge. According to the results of our laboratory work, dissolver sludge exhibits catalytic properties thus recombining oxygen and hydrogen. The latter interpretation seems to be more plausible.

DS For short cooling times, more than 80% of the total radiation energy is due to beta-radiation. As the dissolver sludge is in close contact with the material of the filter bag, a considerable part of the total radiation energy is transferred to the polypropylene bag. G_{H2} values of organic materials are known to be higher than that of water. As a consequence, the major fraction of the observed hydrogen is believed to be caused by the radiolytic disintegration of polypropylene rather than by water radiolysis. This argument is supported by the fact that a few % of methane were found in the atmosphere of the drums with dissolver sludge. Methane is a radiolytic degradation product of polypropylene. It is interesting to note that, in spite of the catalytic activity of dissolver sludge, high specific formation rates of hydrogen were observed. As oxygen is not produced by the radiolytic disintegration of polypropylene, the lack of free oxygen disables the catalytic recombination of hydrogen to water.

From theoretical considerations, the radiolytic production rate of hydrogen should be proportional to the nuclear heat power dis-sipated in the cementitious waste matrix. As mentioned above, the absorbed nuclear power for drums with fuel hardware decreases with the half-life of Co-60 (5.272 a). For short cooling times (up to about 10 years) the absorbed dose rate in drums with dissolver sludge is dominated by Ru-Rh-106 with a half-life of 368 d.

On the basis of the this argument, the rate of formation of hydrogen is expected to decrease with the effective half-life of the different waste types. According to the results of our experiments, there is some indication that the observed formation rates decrease with time. The accuracy of the experimental data over a comparatively short period of observation time is too poor, however, to prove the strict proportionality between the absorbed dose rate and the formation rate of hydrogen.

At first sight, it seems to be surprising that considerable amounts of Kr-85 are liberated from waste packages with cladding hulls and dissolver sludge. On the other hand, it is well known that cladding material and dissolver sludge are contaminated with some Kr-85.

Due to their high kinetic fission energy, some Kr-85 ions escape from the outer boundary zone of the fuel pellet. They are then recoil implanted within the first few microns of the inner cor-rosion layer of the cladding material. A similar process seems to be responsible for the contamination of dissolver sludge with Kr-85.

The most plausible explanation for the release of recoil-implanted Kr-85 is that some Kr atoms are mobilised from the surface of the waste materials by corrosion. The mobilised Kr-85 partly escapes to the gas phase by diffusing through the pore system of the matrix material. Part of the mobilised Kr-85 is retained in the pore water. It is liberated, when temperature is increased.

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