Study on Flammable Gas Generation and Radionuclide Release During Underwater Handling of AM Reactor Spent Fuel

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INTRODUCTION

Generation of flammable gases in water received little attention for the dispersion fuel of complex composition.

The study aimed to obtain experimental data on the flammable gas generation rate to justify fire and explosion safety in handling the dispersion spent fuel underwater [1].

The paper describes the results of the experiments investigating the accumulation of flammable gases. It also addresses the assessments of radiolytic hydrogen produced during underwater storage of damaged spent nuclear fuel.

Selection and Characterization of Spent Nuclear Fuel for Experiments

The experiment used two types of spent fuel rods from the AM reactor located at the world's first NPP (Table I). (Table I).

TABLE I. Specifications of AM Fuel Rods

Fuel composition	UC+Ca	(U-9%Mo)+Mg
^{235}U enrichment, %	10	6.5
Fuel burn-up, MW·day/kgU	6	20
Maximum specific activity of ^{137}Cs, Bq/kg	$2.7 \cdot 10^8$	$1.08 \cdot 10^9$

The AM reactor fuel rod of the (U-9%Mo)+Mg or UC+Ca type consists of U-9%Mo metallic or UC ceramic particles dispersed in Mg or Ca matrix between two coaxially arranged claddings made of stainless steel [2] (photo in Fig. 1).

Experimental Equipment and Procedure

Paper [3] describes the test rig and measuring equipment. The SNF specimens as fuel rod segments were installed in a basket and a cylindrical canister.

The experiments monitored pressure, hydrogen, and methane concentrations in the free volume of the canister, and ^{137}Cs concentration in water afterward.

Experimental Results and Discussion

Results of Experiment with (U 9% Mo)+Mg Fuel Rod Segments

Seven segments cut from intact (U-9%Mo)+Mg fuel rods with a total mass of 1.565 kg, each 245 mm long, were put underwater (2.9 l) in a leak-tight canister. Before that, the oxide layer was removed from both ends of the fuel segments by cutting off 1 mm. Argon filled up the free volume of the canister (0.51 l) at a pressure of ~1 bar initially and after each gas sampling. A sample of water was taken from the canister in eight days. The total activity of ^{137}Cs in the water made up $(1.6 \pm 0.2) \cdot 10^8$. Upon sampling, the depth of ^{137}Cs leaching at each end of the segment was 12 μm taking into account the maximum linear activity of ^{137}Cs in the fuel rods of $9.74 \cdot 10^9$ Bq/cm. Fig. 1 demonstrates the hydrogen generation kinetics that is approximated best by the exponential dependence.

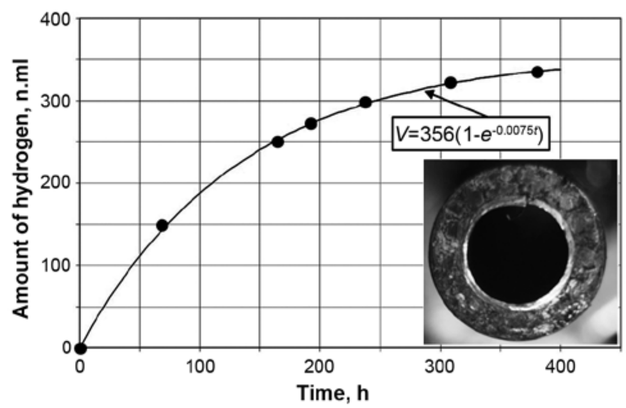

Fig. 1. Kinetics of hydrogen generation in the free volume of the canister during underwater storage of (U9%Mo)+Mg fuel segments and a photo of the cross-section of a segment.

During the experiment, the contribution of the radiolytic hydrogen generated into the free volume of the canister was assessed based on the maximum specific activity of ^{137}Cs in the (U-9%Mo)+Mg fuel.

The radiolytic hydrogen production rate was calculated by the equation:

$$v = \frac{V_M \cdot G_\gamma \cdot D_{Cs} \cdot m_W}{100 \cdot N_a \cdot 1,6 \cdot 10^{-19} \cdot 3600}, \qquad (1)$$

where v is the rate of radiolytic hydrogen accumulation under normal conditions, l/s; V_M is the gas molar volume under normal conditions (22.4 l/mol); $G\gamma$ is the radiolytic G-value for molecular hydrogen per 100 eV energy absorbed from γ-radiation (0.45 molecules/100 eV [4]); D_{Cs} is the absorbed dose rate of γ-radiation in water due to ^{137}Cs, Gy/h; m_W is the mass of water in the canister, g; N_a is Avogadro's number ($6.02 \cdot 10^{23}$ molecules/mol).

The estimates did not take into account the radiolysis of water due to α- and β-emissions, since these particles spread only from the thin layer at the fuel ends as thick as the particle path in uranium metal (17.5 mg/cm^2 [5] or 9 µm for 5 MeV α-particles with a density of 348 mg/cm^2 [6] or 183 µm for 500 keV β-particles). The fuel rod segments had a length of 245 mm; so, a negligible mass fraction of the fuel at the ends of the segments took part in α- and β-radiolysis of water in the canister. In addition, the total activity of α–emitting radionuclides in the AM reactor fuel was one to two orders of magnitude less than that of ^{137}Cs, whereas the total activity of β–emitting radionuclides was assumed to be equal to that of ^{137}Cs.

The γ–radiation dose rate was calculated with the MAVRIC sequence [7] of SCALE 6.1.2 code package [8]. The absorbed dose rate in the water inside the canister was estimated conservatively for different arrangements of the fuel rod segments in the canister. One fuel segment sat on the central axis of the canister, and the others formed a peripheral row being placed symmetrically at the same distance from the central axis. Fig. 2 demonstrates a computational model of the canister containing seven segments of the AM reactor fuel rods. The calculated dose rate in the water of the canister in Fig. 3 is a function of the radius of the peripheral segments.

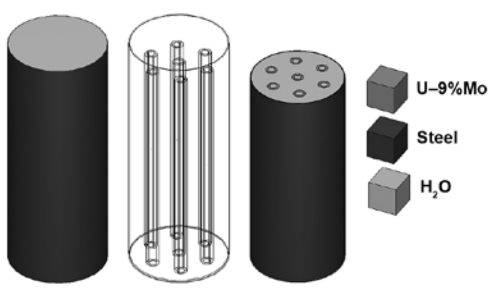

Fig. 2. The geometry of Scale 6.1.2 computed model.

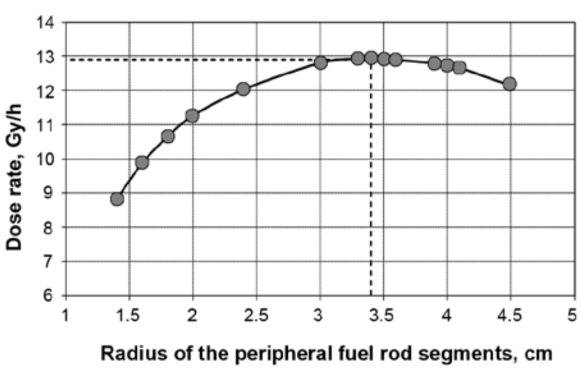

Fig. 3. The calculated dose rate in the water of the canister as a function of the radius of the peripheral fuel rod segments.

It identified geometry with the maximum dose rate of 12.9 Gy/h in the water in the canister. The calculated accumulation rate for radiolytic hydrogen under normal conditions is $1.1 \cdot 10^{-8}$ n.l/s (l/s under normal conditions). It corresponds to 15 n.cm^3 of hydrogen accumulated during the experiment, i.e. 4.2 % of the measured value. Thus, the electrochemical corrosion of the fuel materials govern the hydrogen generation kinetics during the storage of the AM (U-9%Mo)+Mg spent fuel with insoluble hydroxides formed through the following reactions with hydrogen depolarization [9] in the absence of oxygen:

$$Mg + 2H_2O = Mg(OH)_2 \downarrow + H_2\,, \tag{2}$$

$$U + 4H_2O = UO_3 \cdot H_2O \downarrow + 3H_2\,, \tag{3}$$

$$U + 5H_2O = UO_2(OH)_2 \cdot H_2O \downarrow + 3H_2\,, \tag{4}$$

$$U + 4H_2O = UO_2(OH)_2 \downarrow + 3H_2\,. \tag{5}$$

The decrease in hydrogen production rate observed during the experiment could be due to the formation of insoluble corrosion products, which impede access to the metal surface for the water, thus gradually decreasing the rate of reactions (2) - (5) until they cease.

Assuming that corrosion on the exposed fuel surface (~12.6 cm^2) induced the hydrogen production, we concluded that the specific yield of hydrogen per unit area of the exposed surface would not exceed 30 n.ml/cm^2 for any period of the underwater storage of the segmented AM spent fuel with the magnesium matrix. On the assumption that all the hydrogen was generated by reaction (2), the estimated depth of the fuel layer at both ends of the specimen that had reacted with the magnesium matrix made up 370 µm. It is much bigger than the one calculated by the depth of ^{137}Cs leaching from the spent fuel.

Thus, the experiment with the segmented (U-9%Mo)+Mg fuel rods from the AM reactor in the absence of oxygen in the free volume of the canister demonstrated an evident effect of chemical passivation on the fuel surface during reactions (2)–(5) with hydrogen depolarization due to the insoluble corrosion products generated.

Results of Experiment with a UC+Ca Fuel Rod Segment

The experiment used a cladded UC+Ca fuel rod segment 10 mm long with a mass of 7.12 g. The canister contained 0.98 l of water and a free volume of 2.6 l. The total soaking time was 150 hours. The gas samples contained hydrogen and methane.

Fig. 4 presents the kinetics of gas generation. An incubation period of about 20 hours precedes vigorous gas generation. The gas production rate decreases exponentially over time and nearly stops in about 100 hours due to the total corrosion of the fuel composition.

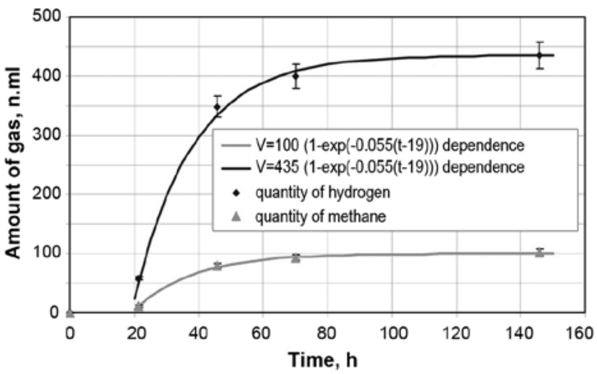

Fig. 4. Amounts of hydrogen and methane in the free volume of the canister containing the UC+Ca fuel specimen soaked in water.

The contribution of the radiolytic hydrogen generated inside the canister was estimated based on the maximum specific activity of ^{137}Cs in the UC+Ca fuel rods. Assuming that the specimen had totally dissolved in the water and the radionuclides were evenly distributed in the solution, the hydrogen production rate was calculated by the equation:

$$v = \frac{V_M \cdot G_\gamma \cdot D_{Cs} \cdot m_W}{100 \cdot N_a \cdot 1{,}6 \cdot 10^{-19} \cdot 3600} + \frac{V_M \cdot (G_\alpha \cdot A_\alpha \cdot E_\alpha + G_\beta \cdot A_\beta \cdot E_\beta)}{100 \cdot N_a}, \quad (6)$$

where G_α and G_β are the radiolytic G-values for molecular hydrogen per 100 eV energy absorbed from α- and β-emitting (1.8 [10, 11] and 0.45 molecules/100 eV, respectively [4]); A_α and A_β are the activities of the α- and β-emitting radionuclides in the water of the canister, Bq; E_α and E_β are the maximum energies of the α- and β-emitting radionuclides, eV (5.5 and 0.5 MeV, respectively). The α-activity of the specimen was conservatively taken to be half the activity of ^{137}Cs.

The calculated production rate of the radiolytic hydrogen was $3.8 \cdot 10^{-9}$ n.l/s. It accumulated only 2 n.cm^3 of hydrogen during the entire experiment, which was 0.5 % of the measured value.

Like with the Mg-matrix fuel, the calculations demonstrated that the hydrogen generation due to the water radiolysis was negligible.

The incubation period could be due to the slow dissolution of the corrosion products (oxides) generated on the cut surfaces of the fuel segment in the air.

Based on the fuel assembly specifications and the specimen geometry, uranium carbide and calcium masses were calculated to be 4.63 g and 0.88 g, respectively. When in contact with water, 1 g of calcium generates 560 cm^3 calcium hydroxide, and hydrolysis of uranium carbide yields hydrated uranium dioxide, the methane-hydrogen mixture, and a small amount of higher hydrocarbons [12–16]. Table II presents published data on the volume of the gas yield per 1 g of uranium carbide and the fractions of methane and hydrogen in the gas during the hydrolysis of irradiated and non-radiated uranium carbide. The Table also presents estimates of the maximum possible amount of hydrogen and methane for the fully corroded specimen of the AM reactor spent fuel. The maximum hydrogen yield due to the interaction of calcium with water was 493 n.ml for the specimen under normal conditions.

TABLE II. Published data on the gas volume yielded per 1 g of non-irradiated UC, fractions of CH_4 and H_2 in the gas during the UC hydrolysis at 80 °C, the maximum possible amount of CH_4 and H_2 for the experimental specimen

Source	[13]	[14]	[15]	[16]	[16]	[16]	[13]	[16]	[16]	[13]	[16]
Temperature, °C	80	80	80	25–99	25–99	80	80	25–99	60–80	80	99
Fuel burn-up, MW·day/kgU	0	0	0	0	0	0	600	3375	4333	6000	16667
Gas volume under normal conditions, n.ml/gUC	90.4	92	67.3	90.6	91.5	98.9	96,2	98.7	–	–	–
Fraction of CH_4, %	88	86	86	82.2	87.7	76.7	67	69	37–62	–	19.1
Fraction of H_2, %	8.9	11	11	11	8.8	20.9	28	25.8	33–59	–	77.1
Estimated volume of CH_4 for AM spent fuel under normal conditions, n.ml	369	367	268	345	372	351	299	315	–	–	–
Estimated volume of H_2 for AM spent fuel under normal conditions, n.ml	37	47	34	46	37	96	125	118	–	–	–

Although the experiment with the AM spent fuel demonstrated that hydrogen was due to the UC hydrolysis and the calcium-water interaction, the estimates assumed that only 25–40 % of uranium carbide and 80–85 % of calcium reacted with water in soaking the UC+Ca fuel specimen.

According to [13, 16], the higher is the burn-up, the smaller is the fraction of CH_4 resulting from the UC hydrolysis, and the larger is the fraction of hydrogen. However, with the burn-up higher than 4300 MW·day/tU, the specimens become inert to water. Paper [13] states that uranium carbide irradiated up to a burn-up of

6000 MW·day/tU did not hydrolyze (no evidence of gas yield) at all, with the specimens soaked for 24 hours at least. Paper [16] describes that the gas generation rate was so low and the hydrolysis was so slow for the burn-up of 4333 MW·day/tU and higher that the experiments were stopped before the reaction completed, although all the specimens had turned into powder in a short time.

The tested AM fuel specimen had a high burn-up (about 6270 MW·day/tU), but it yielded a significant amount of methane yield after the incubation period of about 20 hours. It contrasts with the conclusions of papers [13, 16] that uranium carbide irradiated up to a high burn-up reacts with water poorly.

CONCLUSIONS

The experiments studied the accumulation of flammable gases during underwater handling simulations for the damaged spent nuclear fuel from the AM reactor. The kinetics of hydrogen production for the (U-9% Mo)+Mg and UC+Ca fuel and the kinetics of methane generation for the carbide spent fuel were obtained.

The estimates demonstrated that the contribution of radiolytic hydrogen to the gas yield was negligible, and the determining source of gases was the chemical interaction between the spent fuel and the water.

The findings may be helpful to justify fire and explosion safety of underwater handling techniques for the damaged spent nuclear fuel with the considered fuel compositions.

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