

Study of flammable gases generation and radionuclide release during and after drying of damaged VVER SNF*

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Abstract

The paper presents an experimental evaluation of drying the damaged VVER SNF after the wet storage. The aim of the experiments was to justify the fire safety of air-tight canisters with the dried SNF during transportation, storage, and reprocessing. Keeping the SNF in boric acid during the experiments determined the concentration of uranium, plutonium, and specific activity of fission products in the solution inside the model canisters with the SNF. The canisters with the SNF underwent the thermal vacuum drying to determine the process parameters (temperature, residual pressure, drying rate), a hydrogen release, ⁸⁵Kr activity during the drying, and an airborne radionuclide release onto the filters of the SNF thermal vacuum drying system. The results of weighing the baskets of the canisters before soaking in the boric acid and after drying at 160 °C to the residual pressure below 6 mbar showed that the difference in weight is almost the same as the calculated difference in weight of H₃BO₃ loaded into the canister and the weight after the complete decomposition into B₂O₃. Thus, we have discovered that the boric acid undergoes complete decomposition into boric anhydride, and the SNF corrosion products generate hydrogen that accumulates in the air-tight canister. We also considered the hydrogen that accumulated in the air-tight model canister with the dried SNF as a result of the radiolysis of hydrated corrosion products of the spent oxide nuclear fuel, as well as a release of gaseous fission products (GFP) inside the canister. We calculated the quantity of the hydrated corrosion products of uranium oxide after the wet storage and determined their chemical composition after the thermal-vacuum drying. The equation with an exponential decay function describes the hydrogen accumulation. The calculated maximum volume of hydrogen and uranium in the SNF corrosion products suggests that the SNF corrosion product is schoepite with the number of hydrated water molecules corresponding to the formulas from UO₃·0.95H₂O to UO₃·1.5H₂O. The received data allows for the fire safety justification of drying the wet damaged SNF and handling the dried SNF during transportation and storage.

Keywords

fire and explosion safety, thermal-vacuum drying, reactor VVER, damaged SNF, radiolysis, hydrogen, SNF storage, corrosion products

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Introduction

Fire and explosion safety regulations limit the concentration of combustible substances in gaseous media (Sokolov et al. 2021). For spent nuclear fuel in humid environments, this is hydrogen or its compounds formed either by direct radiolysis of water or by radiation-induced oxidation of SNF (Gaiazov et al. 2018, 2021).

The need is routinely arises in the SNF handling process for placing SNF in air-tight canisters for a time much longer than required for the explosive concentration of combustible gases to accumulate (Gaiazov et al. 2018; Sokolov et al. 2021). Hydrogen post-combustion catalysts are used to lengthen the time for which SNF is kept safely inside canisters (Keller et al. 1989). However, it is shown in Gaiazov et al. 2018, 2021 for the case of leaky SNF that nearly all oxygen is consumed to oxidize fuel, which means that the catalyst is not effective. Drying and calcination allow increasing greatly the time for the safe handling of air-tight canisters with SNF. The drying process permits the water absorbed in the material to be removed, and calcination at a higher temperature allows removing chemically bound water as well (Lykov 1968). Chemically bound water in damaged SNF, following its drying, can be found in hydrated UO_2 corrosion products, as well as in boric acid, which is added to ensure nuclear safety in the process of underwater SNF storage.

To obtain experimental data required to justify safe modes of SNF transportation for reprocessing, a series of experiments was undertaken in shielded cells of JSC “SCC RIAR”’s Reactor Materials Testing Department, consisting of bench experiments and experiments with SNF drying after wet storage in a model canister.

In Level 1 experiments, the most conservative state of damaged SNF was identified regarding the accumulation of radiolytic gases for the entire spectrum of the possible canister loading with damaged VVER SNF, which was chosen for further Level 2 experiments.

In Level 2 experiments, kinetics of the hydrogen and GFP release into the canister’s free volume

depending on the amount of remaining water and the ambient temperature.

Results of facility experiments

The purpose of the facility experiments was to determine the state of the VVER-440 SNF, which will provide conservative results on the release of radiolytic gases in experiments with model canisters.

The facility experiments evaluated the effect the following factors have on radiolysis:

- ratio between the weight of SNF and structural materials;
- fragmentation degree of structural materials;
- local depth of zirconium oxidation;
- fragmentation degree of fuel pellets.

The amount and composition of gases in five sealed ampoules filled with wet SNF in different states were compared as part of the facility experiments. Three sets of SNF-filled ampoules were used to determine the amounts of the gases formed as a function of the time for which the ampoules were in a sealed state. A fuel rod laser puncture system was used to puncture the first set of five ampoules a month after the sealing, the second set was punctured two months after the sealing, and the third one was punctured three months after the sealing. The composition of the gas in the ampoules was analyzed using a MI1201E gas mass spectrometer.

Three VVER-440 FA fuel rods with an average burnup of 27.62 MWd/kgU were selected for the facility experiments. Fuel rod and pellet fragments, as well as a granulated SNF fraction were prepared from fuel rods. The fractions were packed into containers to be further placed in ampoules. Pieces of non-irradiated, unoxidized or fully oxidized cladding were added to some of the containers. The composition of SNF in the ampoules is presented in Table 1.

Table 1. Composition of SNF in ampoules

Set	Ampoule No.	Type of loaded SNF	SNF weight, g	Weight of UO_2 , g	Weight of Zr or ZrO_2 , g	Weight of H_2O , g
1	1	Three fuel rod fragments	166.9	131.5	35.4	1.4
	2	UO_2 fraction with particle size of 0.1 mm < d < 2.5 mm	166	166	0	6.9
	3	UO_2 pellet fragments	165.8	165.8	0	3
	4	UO_2 pellet fragments + Zr fragments	166.8	131.3	35.5	3.1
	5	UO_2 pellet fragments + ZrO_2 fragments	166.6	131.2	35.4	4.6
2	6	Three fuel rod fragments	170.6	134.8	35.8	1.3
	7	UO_2 fraction with particle size of 0.1 mm < d < 2.5 mm	170.4	170.4	0	8.2
	8	UO_2 pellet fragments	170.4	170.4	0	2.4
	9	UO_2 pellet fragments + Zr fragments	170.7	135	35.7	1.3
	10	UO_2 pellet fragments + ZrO_2 fragments	170.3	134.6	35.7	4.3
3	11	Three fuel rod fragments	169.1	133.3	35.8	0.6
	12	UO_2 fraction with particle size of 0.1 mm < d < 2.5 mm	169	169	0	7.3
	13	UO_2 pellet fragments	169.2	169.2	0	1.8
	14	UO_2 pellet fragments + Zr fragments	169.1	133.4	35.8	2
	15	UO_2 pellet fragments + ZrO_2 fragments	169.1	133.3	35.8	3

Each container was placed in a tank with a boric acid solution. The boric acid solution was discharged after 24 hours through the tank drain valve. Thereafter, the tank was additionally blown down (dried) with argon for an hour at a flow rate of ~ 3 l/min and a temperature of 26 °C with the same mode used for all containers. Following the blowdown, the container was withdrawn and weighed, and the weight of the remaining water in the container was computed. The container was further placed in an ampoule, which was drained, filled with argon and then sealed for three times running.

The analysis of the results presented in Table 1 showed that, with the SNF container drying mode being the same, the containers filled with the granulated fraction of UO_2 had more residual amount of moisture than the others. The ratio of the water weight to the SNF weight in these containers was over 4%. The smallest amount of residual water was in the containers filled with fuel rod fragments.

Table 2 presents the results of measuring the amount and composition of gases in the ampoules after the end of the tests.

It follows from Table 2 that the initial set of ampoules that were in a sealed state for a month had the largest amount of hydrogen formed in the ampoule filled with UO_2 pellet fragments and fully oxidized zirconium. The second and the third sets of ampoules, which were in a sealed state for two and three months respectively, had the largest amount of hydrogen formed in the ampoules filled with the UO_2 fraction with a particle size of 0.1 to 2.5 mm. The content of hydrogen in ampoule 1 was comparable to the background value. Xenon was found in all ampoules to indicate that UO_2 was oxidized. Since it was not possible to remove all of the air in the process of the ampoule blowdown with argon, there was nitrogen in the ampoules.

The results of the facility experiments have shown that the model canisters need to be loaded with UO_2 fraction with a particle size of 0.1 to 2.5 mm to obtain conservative results in exploring the behavior of fuel in air-tight canisters.

Results of experiments to dry model canisters with dummy SNF

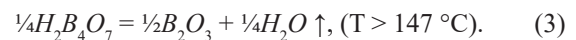
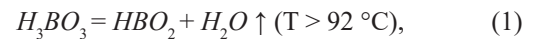
Laboratory bench experiments to dry model canisters with dummy SNF were undertaken at JSC “SSC RIAR” to select the best model canister drying technique. Used for the dummy SNF were loads of electrical foundry porcelain (EFP), non-irradiated fuel cladding (ZrO_2) in an oxidized and fragmented form, non-oxidized fuel cladding fragments (NOC) plugged from below, and oxidized fuel cladding fragments (OC) also plugged from below. Two drying methods were tested: hot gas drying (HGD) and thermal vacuum drying (TVD). Removable parts with dummy SNF loads were weighed prior to and after the drying experiment. The canister was filled with distilled water or a boric acid solution with

a concentration of 24 g/l. The temperature on the walls and inside the canister was monitored in the process of drying.

The key process parameters and the dummy SNF drying experiment results are summarized in Table 3.

It can be seen from Table 3 that the hot gas drying of the SNF loads is slower than the thermal vacuum drying, due to which it was decided to use the thermal vacuum method for further drying, specifically since there is excessive pressure inside the canister in the hot gas drying process, unlike the thermal vacuum drying, in which the pressure in the canister was also negative. A negative pressure in the canister ensures that no fission products are released into the environment in the event of the hypothetical loss of the canister integrity. Also, the gas flow from the canister in the hot gas drying process is much higher than in the thermal vacuum drying process, which, therefore, leads to SNF particles being carried away more intensively.

It was found as the result of weighing the removable parts with dummy SNF loads prior to soaking and after drying that there is a weight difference of 11 to 24 g for experiments in which the boric acid solution was used instead of distilled water. When heated, boric acid in a dry form decomposes into boric anhydride in several stages (Sevim et al. 2006; Balci et al. 2012; Huber et al. 2020):



When transformed into boric anhydride, dry boric acid loses 43.7% of its weight. As it follows from Table 3, the weight difference of the canister removable part with dried product prior to and after the experiment is practically the same (even slightly larger) as the calculated weight difference for H_3BO_3 loaded into the canister and as it fully decomposes into B_2O_3 . This implies that the selected mode of thermal vacuum drying of the canisters leads eventually leads to the complete decomposition of boric acid and, accordingly, to the absence of a source of chemically bound water as H_3BO_3 . A slightly excessive weight difference for the canister removable part with dried product prior to and after the experiment can be explained by a small amount of H_3BO_3 being sublimated in the process of drying, which proceeds in a temperature range of 53 to 90 °C before its decomposition begins (Pankajavalli et al. 2007).

Results of experiments with dried SNF

The experimentation procedure for investigating the behavior of damaged VVER-440 fuel in conditions simulating SNF storage in a air-tight canister is presented in Gaiazov et al. 2018.

Table 2. Amount and composition of gases in ampoules after the tests

Ampoule No.	Type of loaded SNF	Gas pressure, atm	Volume in normal conditions, cm ³					
			H ₂	N ₂	O ₂	Ar	CO ₂	Xe
1	Three fuel rod fragments	1.28	0.013	73.98	18.09	62.91	0.098	2.237
2	UO ₂ fraction with particle size of 0.1 mm < d < 2.5 mm	1.31	0.581	2.844	0.161	149.8	<0.001	0.608
3	UO ₂ pellet fragments	0.88	0.663	1.533	0.088	104.1	<0.001	0.113
4	UO ₂ pellet fragments + Zr fragments	1.32	0.64	1.755	0.051	155.7	<0.001	0.109
5	UO ₂ pellet fragments + ZrO ₂ fragments	1.31	1.29	1.367	0.092	152.8	<0.001	0.572
6	Three fuel rod fragments	1.25	0.158	12.32	0.825	133.213	0.414	1.497
7	UO ₂ fraction with particle size of 0.1 mm < d < 2.5 mm	1.35	6.296	10.209	0.468	134.545	0.511	2.31
8	UO ₂ pellet fragments	1	1.205	1.583	0.034	117.272	0.186	0.265
9	UO ₂ pellet fragments + Zr fragments	1.48	0.158	8.975	0.127	165.663	0.569	0.473
10	UO ₂ pellet fragments + ZrO ₂ fragments	1.37	0.239	6.9	0.037	151.472	0.487	0.144
11	Three fuel rod fragments	1.33	0.05	3.313	0.57	153.415	0.009	1.878
12	UO ₂ fraction with particle size of 0.1 mm < d < 2.5 mm	1.35	1.769	5.262	0.583	149.973	0.041	1.046
13	UO ₂ pellet fragments	1.23	0.359	6.307	0.121	144.783	0.002	0.565
14	UO ₂ pellet fragments + Zr fragments	1.3	0.073	7.331	0.654	148.565	0	0.315
15	UO ₂ pellet fragments + ZrO ₂ fragments	1.26	0.021	29.293	2.762	116.01	0	0.186

Table 3. Amount and composition of gases in ampoules after the tests

Experiment number	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	1.10	1.11	1.12	1.13
Model canister load type	EFP	EFP	EFP	EFP	OC	OC	EFP	ZrO ₂	EFP	ZrO ₂	NOC	OC	NOC
Boric acid concentration, g/l							24	24	24	24			
Amount of water loaded into the canister, ml	2261	2265	2267	2258	3089	3083	2171	2399	2174	2413	3042	3081	3059
Amount of water discharged from the canister, ml	1620	1658	1604	1581	2298	2231	1392	1693	0	0	2337	0	0
Amount of water in the canister prior to drying, ml	641	607	663	677	791	852	779	706	2174	2413	705	3081	3059
Drying method	HGD	HGD	TVD	TVD	HGD	TVD	TVD	TVD	TVD	TVD	TVD	TVD	TVD
Gas flow through the canister, l/min (in normal conditions)	59.3	102.5			103.4								
Temperature of the gas fed into the canister, °C	147	147			147								
Canister body temperature, °C	147	147	161	161	147	161	161	161	161	161	161	161	161
Amount of condensate in the receiving tank, ml	637	605	626	625	786	788	716	647	2156	2395	657	3077	3051
Drying time, h	6.8	6	5.1	5.1	6.1	6.4	5.8	4.8	8	8.1	5.0	9.8	9.3
Drying rate, ml/h	94	101	123	123	129	123	123	135	270	296	131	314	328
Weight of H ₃ BO ₃ in the solution, g							18.7	16.9	52.2	57.9			
Weight of B ₂ O ₃ corresponding to the weight of H ₃ BO ₃ , g							10.5	9.5	29.4	32.6			
Weight difference between H ₃ BO ₃ and B ₂ O ₃ , g							8.2	7.4	22.8	25.3			
Weight difference prior to and after the experiment, g	<1	<1	<1	<1	<1	<1	13	11	24	21	<1	<1	<1

The interaction of damaged SNF with water in the process of storage leads to corrosion of solid UO₂, this including the sequence of oxidation, dissolution and, under certain conditions, a precipitation reaction (Eriksen et al. 2012; Gaiazov et al. 2018). The uranium oxide contact with water is expected to result in a range of hydrated uranium oxides formed, which accumulate bound water in SNF (Burns et al. 2012, ASTM C1553–21 2021). There are three forms of hydrates based on UO₃: UO₃·2H₂O, UO₃·H₂O and UO₃·0.5H₂O, but the thermal decomposition process is expected to cause the fraction of water in the schoepite to change continuously, e.g., UO₃·2H₂O transforms into (ASTM C1553–21 2021) in a temperature range of 100 to 160 °C, so schoepite is represented by a general formula, UO₃·xH₂O, where 0.5 ≤ x ≤ 2 (Jung et al. 2013).

In the process of thermal vacuum drying, free water is removed from the canister with only chemically bound water remaining in it (excluding H₃BO₃ since it was found earlier that H₃BO₃ decomposes completely in the process of drying), which is the source of hydrogen in the canister owing to the process of its radiolysis. Under the action of

radiolysis, the water decomposition rate, ν , in molecule/s units is described by relationship (Jung et al. 2013):

$$\nu = \frac{dm_{H_2O}}{dt} \cdot \frac{N_a}{M_{H_2O}} = \frac{R_e G m_{H_2O}}{100}, \quad (4)$$

where m_{H_2O} is the water weight in the canister, g; t is the time, s; M_{H_2O} is the molecular weight of water, 18 g/mol; N_a is the Avogadro constant, 6.02×10^{23} molecule/mol; G is the radiation-induced chemical yield of water decomposition with 100 eV of ionizing radiation energy absorbed, molecules/100 eV; and R_e is the absorbed dose rate, eV (g·s).

The solution for equation (4) is the exponential dependence of the water content in the canister, $m_{H_2O}(t)$, on time, t (Jung et al. 2013):

$$m_{H_2O}(t) = m_{H_2O}^0 \cdot \exp\left(-\frac{R_e G M_{H_2O}}{100 N_a} t\right), \quad (5)$$

where $m_{H_2O}^0$ is the initial weight of water in the canister, g.

If we assume that water decomposes into hydrogen and oxygen in the process of radiolysis, then the volume of accumulated hydrogen is proportional to the weight of decomposed water:

$$V_{H_2}(t) = \frac{m_{H_2}^0 - m_{H_2}^o(t)}{M_{H_2}O} \cdot V_M = \frac{m_{H_2}^0 \cdot V_M}{M_{H_2}O} \cdot \left(1 - \exp\left(-\frac{R_e G M_{H_2}O}{100 N_a} t\right)\right), \quad (6)$$

or

$$V_{H_2}(t) = V_{H_2}^{\max} \cdot \left(1 - \exp\left(-\frac{t}{\tau}\right)\right), \quad (7)$$

where V_M is the molar volume of gas, 22.4 l/mol; $V_{H_2}^{\max}$ is the maximum volume of hydrogen in the canister in the process of decomposition of $m_{H_2O}^0$, l; and τ is the time constant, s (or h).

The weight of bound water in the canister can be determined by experimentally determining the maximum volume of hydrogen,

$$m_{H_2O}^0 = \frac{V_{H_2}^{\max} \cdot M_{H_2O}}{V_M} \quad (8)$$

One can estimate the weight of dissolved uranium, m_U , after soaking of UO_2 from the volume of water in the canister and the concentration of uranium in the solution prior to drying. If we assume that all this uranium passes into hydrated uranium oxide after drying, then it is possible to estimate the amount of water n in schoepite ($UO_3 \cdot nH_2O$) from the weight of bound water

$$n = \frac{m_{H_2}^0 \cdot M_U}{M_{H_2O} \cdot m_U} \quad (9)$$

where M_U is the molar weight of uranium, 238 g/mol.

The experiment with SNF drying was undertaken using a bench based in the shielded cell at the reactor materials testing department of JSC “SSC RIAR”, and included the following:

- an air-tight canister for SNF equipped with thermocouples at different axial points on the side surface;
- a heating module;
- a steam-air mixture pumping and condensation line;
- a canister degassing system;
- a pressure measuring line designed to fill the canister with gas and take gas samples for the mass-spectrometric analysis; and
- automated control and data collection systems.

The bench was used for a series of experiments with two model canisters (1 and 2) loaded with VVER-440

SNF fragments with a size of 0.1 to 2.5 mm and an equal SNF weight of 8.75 kg. The average fuel burnup in canister 1 was 27.7 MWd/kgU (the maximum burnup was 31.6 MWd/kgU), and that in canister 2 was 28.8 MWd/kgU (the maximum burnup was 32.2 MWd/kgU). The time from the FA unloading from the reactor to the experiment was 2922 days. The experiments were conducted sequentially for the same canister with SNF and differed in the dried SNF exposure time and temperature (in air at an ambient temperature of 30 °C and in water with a temperature of 80 °C), as well as in that the solution was preliminarily discharged from the canister prior to drying or not.

SNF was preliminarily held for one to four months in a boric acid solution with a concentration of 24 g/l. This time was sufficient for the concentration of uranium in the model canister’s aqueous solution to reach equilibrium (Sokolov et al. 2021), which was about 10^{-5} M (2.4 mg/l) and was close to the theoretical solubility limit of schoepite or another aqueous uranyl hydroxide (Grambow et al. 2000). To determine the specific activity in the process of testing, samples of the solution were taken and analyzed radiochemically. The conditions of the SNF soaking experiments and the key results are presented in Table 4.

Following the soaking, the SNF canisters were dried by thermal vacuum method to the residual canister pressure of 2 to 6 mbar, the canister body temperature being 161 °C. After the canisters were dried, the dose rate was measured right from the filter cartridge elements (FCEs) of the prefiltering system, as well as the dose rate from the frontal filter element at a distance of 1 m, after which gamma spectrometry of FCEs and the condensate from the receiving tank was undertaken and the release of volatile fission products from the canister into the prefiltering system and into the condensate accumulated in the receiving tank was determined. Also, the filter elements of the prefiltering system were weighed prior to and after the experiment, and the weight difference was used to determine the SNF particle release. The conditions of the SNF thermal vacuum drying experiments and the key results are presented in Table 5.

Following its thermal vacuum drying, the canister was blown down with argon for three times (with the canister filled with argon to a pressure of 1.5 bar, held for two minutes, and evacuated to a pressure of 2 to 4 mbar).

Table 4. Conditions and key results of SNF soaking experiments

Experiment	2	3	5	6
Canister number	2	1	2	1
Soaking time, months	3	4	1	2
Volume of solution after soaking, l	2.422	2.444	2.394	2.283
Pu concentration after soaking, µg/l	1.0	1.1	1.3	1.3
U concentration after soaking, mg/l	2.7	2.8	3.5	3.4
Dissolved U during soaking, mg	6.5	6.8	8.8	7.8
Volumetric gamma activity of solution prior to drying, Bq/ml	3.3107	4.8107	2.0107	4.3107
Volumetric activity of ^{137}Cs , Bq/ml	3.0107	4.2107	1.8107	3.9107
Volumetric activity of ^{134}Cs , Bq/ml	3.0106	4.4106	1.5106	3.6106
Volumetric activity of ^{60}Co , Bq/ml	6.4104	8.2104	8.5104	9.5104
Volumetric alpha activity of solution prior to drying, Bq/ml	102	220	83	130

Table 5. Conditions and key results of SNF thermal vacuum drying experiments

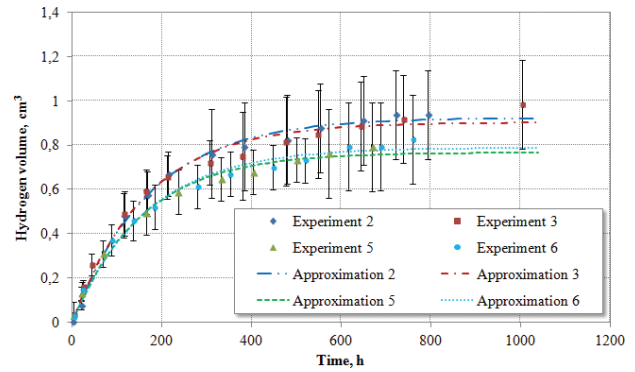
Experiment	2	3	5	6
Canister number	2	1	2	1
Discharge prior to drying	Yes	No	Yes	No
Volume of solution after discharge, ml	487	2444	493	2283
Canister body temperature, °C	161			
Pressure after the end of drying, mbar	6	2	6	3
Volume of condensate in receiving tank, ml	486	2380	457	2240
Drying time, h	3.0	6.7	3.0	6.9
Drying rate, ml/h	162	355	152	325
Hydrogen release during drying, ml	–	4.1 ± 0.2	3.0 ± 0.2	3.9 ± 0.2
Release of ⁸⁵ Kr activity during drying, GBq	–	0.35 ± 0.08	0.32 ± 0.08	0.34 ± 0.08
Release of SNF onto FCEs during drying, g	0.0051	0.0032	–	0.016
Activity in the receiving tank after MC drying, Bq	¹³⁷ Cs 738			
	⁶⁰ Co 1.6104	5.5	22.4	22.4
Frontal FCE activity, Bq	–	¹³⁷ Cs 1.4107	1.7108	1.7·108
	–	¹³⁴ Cs 1.3106	1.5107	1.5·107
	–	⁶⁰ Co 1.5104	4.3105	4.3·105
Activity of FCE 2, Bq	–	¹³⁷ Cs 6.5103	4.2 104	4.2·104
	–	¹³⁴ Cs 1.2103	3.7103	3.7·103
	–	⁶⁰ Co 6.1102	7.2102	7.2·102
Dose rate from frontal FCE at a distance of, mSv/h	0 m 14	0.552	5.2	5.2
	1 m –	4.810-3	4.5 10-2	4.5·10-2

The canister was further filled with argon to an absolute pressure of 1.5 bar and sealed. The volume fraction of water vapor in argon did not exceed 0.0003%, that is, the weight of water in the post-drying canister gas phase did not exceed 0.01 mg. To measure the concentrations of H₂, O₂, and GFP formed in the canister's free volume, gas phase samples were taken from the canister for one month. Hydrogen was found in the samples and no oxygen detected, which led to a conclusion that the oxygen formed by radiolysis was spent to oxidize UO₂. Krypton and xenon were accumulated in very small quantities in the process of storage: not more than 0.07 ml (in normal conditions) per canister or 0.008 ml per kg of SNF.

Hydrogen accumulation was monitored for one month. The experiment conditions and key results are presented in Table 6, and Fig. 1 shows the kinetics of hydrogen accumulation in the canisters.

As shown in Table 4, the steady-state concentration of U after soaking varied in a range of 2.4 to 3.5 mg/l. The weight of dissolved uranium in the canister water in the process of prior SNF soaking varied between 6.8 and 8.8 mg.

As it follows from Fig. 1, the hydrogen accumulation kinetics was well approximated by equation (7); the approximation parameters are presented in Table 6. The estimated maximum volume of hydrogen for canisters with

**Figure 1.** Hydrogen accumulation in the canister after SNF drying.

a storage temperature of 80 °C is 15% less than for SNF with a storage temperature of about 30 °C, while the hydrogen accumulation measurement data for all four experiments have overlapping errors. The weight of bound water in SNF after drying, estimated on an approximation basis, was 0.62 to 0.74 mg (or 0.073 to 0.085 mg of water per 1 kg of UO₂). According to this data, the estimated amount of water in schoepite as per formula (9) was in line with their chemical composition, or in a range of UO₃·0.95H₂O to UO₃·1.5H₂O, which does not contradict essentially the above literature data on the possible structures of schoepite as the key product for the oxide SNF corrosion under water.

Table 6. Conditions and key results of dried SNF experiments

Experiment	2	3	5	6
Canister number	2	1	2	1
Dried SNF storage temperature, °C	30	30	80	80
Dried SNF storage time, h	793.76	1003.73	668.20	759.27
Accumulated volume of krypton during storage, ml (normal conditions)	0.031	0.066	0.06	0.001
Accumulated volume of xenon during storage, ml (normal conditions)	0.06	0.066	0.029	0.002
Approximated maximum volume of hydrogen $V_{H_2}^{max}$, ml (normal conditions)	0.924	0.903	0.766	0.789
Approximated time constant t, h	172.3	163.4	155.6	164.1
Estimated weight of bound water, mg	0.74	0.73	0.62	0.63
Estimated weight of bound water per kg of SNF, mg/kgUO ₂	0.085	0.083	0.073	0.074
Estimated amount of water, n, in schoepite (UO ₃ ·nH ₂ O), mol	1.50	1.40	0.97	1.08

Conclusions

When SNF is held for up to four months in a boric acid solution with a concentration of 24 g/l, the concentration of uranium reaches equilibrium, which corresponds to the theoretical solubility limit of aqueous uranyl hydroxide (schoepite), the accumulator of chemically bound water in SNF.

It has been shown that it is possible to use thermal vacuum drying for wet VVER SNF with high efficiency of removing unbound water in the canister and with residual chemically bound water in SNF corrosion products in the amount of less than 0.1 mg of water per kg of SNF. The parameters of the wet SNF drying technology, the amount of GFPs and hydrogen formed in the process of drying, and the airborne radionuclide release onto the SNF thermal vacuum drying system filters have been determined.

Following the thermal vacuum drying at 160 °C to a residual pressure of not more than 6 mbar, it was found that boric acid decomposes completely into boric anhydride

and the hydrogen accumulation source in an air-tight canister is SNF corrosion products. The accumulation of hydrogen is described by an equation with the accumulation rate decreasing exponentially. The estimated maximum amount of hydrogen and the estimated amount of uranium in SNF corrosion products suggest that the SNF corrosion product is schoepite, the amount of hydrated water in which is as found by formulas ranging from $\text{UO}_3 \cdot 0.95\text{H}_2\text{O}$ to $\text{UO}_3 \cdot 1.5\text{H}_2\text{O}$.

There is no oxygen in all air-tight canisters following the thermal vacuum drying, with oxygen likely to be spent for fuel oxidation, so it is ineffective to place catalysts in the canisters.

Krypton and xenon accumulated in very small quantities in the process of storage – not more than 0.008 ml per kg of SNF.

The data obtained can be used to justify fire and explosion safety of the technology for drying wet damaged SNF and handling dried SNF in the process of transportation and storage.

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