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Physicochemical Characteristics and Radiation-Chemical Processes in the System PuO_2–Sorbed Water

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Abstract—The experimental data on formation of H_2 and O_2 during storage of PuO_2 samples containing sorbed water were analyzed. It was shown that the rates of formation of these gases, all other factors being the same, are governed by the procedure of water sorption: in sorption from the liquid phase these rates are significantly higher than those in sorption from the gas phase. To elucidate the conditions of safe storage of PuO_2, it is necessary to obtain systematic quantitative data on the kinetics of H_2 and O_2 formation in the system consisting of PuO_2 and water sorbed from moist air. The optimized mathematical model of sorbed water radiolysis adequately describing the experimental data on the formation of H_2 and O_2 at room temperature in the system consisting of PuO_2 and water sorbed from the liquid phase is presented. The rate constant of H_2 and O_2 recombination in the presence of PuO_2 containing 2–3% water was found to be $\leq 1 \times 10^{-5}$ mol^{-1} s^{-1}. With the knowledge of the reaction rate constants, the model allows calculation of the amounts of H_2 and O_2 and the pressure in the storage vessel depending on the amount of sorbed water, radiation dose rate, and storage duration.

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Conversion of weapons-grade plutonium is an urgent problem on the global scale. One of the ways of solving this problem is conversion of weapons-grade plutonium into dioxide by calcination of plutonium oxalate whose production is well developed.

The resulting PuO_2 will be stored forever or for a certain period of time with subsequent use for production of mixed uranium–plutonium oxide (MOX) fuel.

Plutonium dioxide is a hygroscopic substance. It was shown previously [1] that, after calcination at 490 and 760°C and storage in air with a relative humidity of 100% for several days, the water content in the PuO_2 samples is 3.5 and 1.5%, respectively. Under α-radiation of Pu, the sorbed water decomposes to form H_2, O_2, and H_2O_2 [2]. Accumulation of H_2 and O_2 is a source of hazard in storage of both liquid and solid radioactive wastes containing water, due to the possibility of formation of detonating gas and the pressure increase in hermetically sealed vessels.

Special containers will be designed for safe storage and transportation of PuO_2. Design of containers is one of the main practical problems of PuO_2 storage. For designing the containers it is necessary to have data on the kinetic of radiolytic decomposition of sorbed water and formation of H_2 and O_2 under given conditions.

The stored plutonium dioxide can have different specific surface areas (SSA) depending on the calcination temperature. The latter also determines the equilibrium content of sorbed water. Plutonium dioxide can sorb water from air or a liquid phase. Individual batches of PuO_2 can have different radiation dose rates and can contain various impurities.

It is well known that the quantitative characteristics of radiolysis for sorbed substances differ essentially from those for “free” substances. Therefore, the data obtained in study of α-radiolysis of “free” water cannot be used for evaluating the amount of H_2 and O_2 released in the radiolysis of water sorbed on PuO_2. In addition, PuO_2 has certain physicochemical features complicating radiation-chemical processes and their study. Plutonium dioxide is a chemically active substance. As shown previously [3–7], it reacts with water to form H_2 and superstoichiometric plutonium dioxide and catalyzes the reaction of H_2 and O_2.

Formation of H_2 and O_2 in storage of PuO_2 containing sorbed water is studied in the United States and Russia.

Table 1. Content of H_2 in the gas phase upon keeping of PuO_2 samples for 7 days. Weapons-grade Pu [8]

H_2O(total S.)		H_2O(outer S.)	
$[H_2O]$, %	H_2, %	$[H_2O]$, %	H_2, %
1.2	0.0	1.03	0.4
1.8	0.5	1.44	0.3
2.3	0.7	2.5	2.3

Table 2. Rates and radiation-chemical yields of H_2 and O_2 in the system PuO_2–H_2O(outer S.) (Pu from power plants, D = 11.6 Gy s^{-1} g^{-1}; 22±2°C) [9]

Form of PuO_2 sample	Water content, %	Rate, cm^3 g^{-1} day^{-1}		Yield, molecules per 100 eV	
		H_2	O_2	$G(H_2)$	$G(O_2)$
Pellet	0.3	0.01	0.001	1.1	0.09
Pellet	1.0	0.07	0.01	2.2	0.32
Pellet	1.5	0.16	0.025	3.4	0.53
Pellet	2.0	0.29	0.04	4.65	0.65
Pellet	3.0	0.60	0.10	6.4	1.07
Powder	3.0	0.75	0.08	8.0	0.86
Powder*	3.0	0.12	0.015	7.9	1.0

* Weapons-grade Pu, D = 1.9 Gy s^{-1} g^{-1}.

Here we present the experimental data and optimized mathematical model developed for evaluation of the amounts of H_2 and O_2 formed by radiolysis of water sorbed on PuO_2.

EXPERIMENTAL DATA

The quantitative data on formation of H_2 in the system PuO_2–sorbed water are presented in [8–10]. It was shown [8] that the percent content of H_2 in the gas phase released in storage of moist PuO_2 depends on the procedure of water sorption on PuO_2, all other things being the same. In sorption from the liquid phase, the percentage of H_2 is significantly higher than that in sorption of water from gas phase (moist air). These results are very interesting and fundamental.

Apparently, water sorbed on PuO_2 from the gas phase is uniformly distributed in the powder bulk over the whole surface, whereas water sorbed from the liquid phase forms a film at the outer surface of the powder. We denote these two cases as follows: H_2O(total S.) and H_2O(outer S.).

Published data [8] presented in Table 1 show that, at a water content of approximately 1% in the system H_2O(total S.), hydrogen was not found in the gas phase, and at a water content of 2.3–2.5% in this system, the H_2 content is approximately 3 times lower than that in the system H_2O(outer S.).

The systematic data on the kinetics of H_2 and O_2 formation at room temperature in PuO_2 containing water sorbed from the liquid phase, i.e., in the system H_2O(outer S.), were obtained in [9]. The content of sorbed water was within 0.3–3%. The experiments were mainly performed with PuO_2 samples originating from nuclear power plants, and one of the samples was of the weapons-grade; the dose rates were 11.6 and 1.9 Gy s^{-1} per gram PuO_2, respectively. Data on the influence of the dose rate are important, since in conversion of weaponsgrade Pu its initial isotopic composition and, hence, the dose rate of radiation will change due to addition of Pu from power plants.

The amounts of H_2 and O_2 in the gas phase were determined experimentally and the initial rates (exposure time 10–30 days) and radiation-chemical yields of their formation were evaluated. The results obtained are presented in Table 2.

Table 2 shows that, at a given H_2O content, the initial rate of H_2 and O_2 formation is in direct proportion to the dose rate of Pu radiation and does not depend on the physical state of the sample (powder or pellet). It is seen that, with increasing water content by a factor of 10 (from 0.3 to 3%), the rate of formation of the gases increases by a factor of 60–100. This is caused by both an increase in the energy absorbed by water and increase in the radiation-chemical yields of H_2 and O_2. It is seen that $G(H_2)$ and $G(O_2)$ do not noticeably depend on the radiation dose rate; with increasing $[H_2O]$ from 0.3 to 3% $G(H_2)$ increases from 1.1 to 6.4, and $G(O_2)$, from 0.09 to 1.1 molecules per 100 eV. In α-radiolysis of “free” water, $G(H_2)$ and $G(O_2)$ are 1.4 and 0.2 molecule per 100 eV, respectively [2].

It is well known that sorbed substances decompose in radiolysis with significantly higher yields than “free” substances. This is caused by a particular mechanism of energy transfer of ionizing radiation from a solid matrix to a sorbed substance. According to published data [9], the rate of H_2 formation in the system H_2O(outer S.) (3.0% H_2O) with weapons-grade Pu is 0.12 cm^3 g^{-1} day^{-1}. Data for the system H_2O(total S.) with weapons-grade Pu are presented in Table 3.

It was shown previously [10] in two experiments that, the higher temperature of PuO_2 calcination, i.e., the smaller its specific surface area, the higher the rate of H_2 formation. Table 3 shows that the rate of H_2 formation increases with increasing amount of sorbed water; in this case, the increase in the reaction rate is significantly more pronounced than the increase in the amount of sorbed water. Unfortunately, only few data were obtained under comparable conditions. Published data presented in [10] and our data differ essentially. A comparison of our data shows that the rate of hydrogen formation in the system H_2(outer S.) at a water content of 3% is higher than that in the system H_2O(total S.) by a factor of 75.

Obtaining reliable quantitative data on the kinetics of H_2 and O_2 formation in the most practically important system H_2O(total S.) is one of the urgent problems related to prolonged storage of PuO_2.

Experiments with the system in which water was sorbed on PuO_2 from the liquid phase gave maximum possible quantitative characteristics of radiolytic formation of H_2 and O_2.

The following conclusions, extremely important from practical and theoretical standpoint, can be made from Tables 2 and 3: The rates of H_2 formation and, hence, the rates of water decomposition, other conditions being the same, are significantly lower for the system in which water was sorbed on PuO_2 from the gas phase, i.e., for the system H_2O(total S.). The rate of H_2 formation for this system essentially depends on the temperature of PuO_2 calcination. A fundamental question arises: why water sorbed on PuO_2 from the liquid phase decomposes at a significantly higher rate than water sorbed from the gas phase?

It was suggested previously [8] that water sorbed from the liquid phase behaves as "free" water, and water sorbed from the gas phase, as sorbed water. I do not agree with this opinion, since an increase in the yields of H_2 and O_2 formation with increasing amount of water sorbed from the liquid phase and high yields of H_2 and O_2 (Table 2) suggest that in this system the water behavior in radiolysis follows the laws of sorbed states.

The mechanisms of H_2 formation in the system PuO_2–H_2O(total S.) were considered in a series of studies carried out in the United States. The general conclusion is that, at a water content of ≤0.5%, H_2 is formed not by the radiolysis but by the reaction of H_2O with PuO_2 ($PuO_2 + H_2O \rightarrow PuO_{2+x} + xH_2$); at larger amounts of water, H_2 is formed by the radiolysis, but the rate of its formation is less than the theoretically possible rate. It was concluded that the discrepancy in the experimental and theoretical rates can be caused by the reaction of H_2 with PuO_2 and radiation-chemical and chemical recombination of H_2 and O_2, catalyzed by the PuO_2 surface. Paffett and Kelly [11] assumed that, at a water content of 0.5% (4 monolayers), H_2 is formed by the radiolysis. However, lower experimental rates in comparison with theoretically possible rates are mainly caused by a decrease in the rate of H_2 formation in passing from the first monolayer to the subsequent one, with an increase in the distance of water from the emitting PuO_2 surface. It should be noted that the mechanisms cited are hypothetical. In the corresponding papers and reports, there are no quantitative data confirming one or other mechanism, and the theoretically possible rates of H_2 formation to which the experimental rates were compared are not given.

Table 3. Initial rates of H_2 formation [$V(H_2)$, $cm^3\ g^{-1}\ day^{-1}$)]

$[H_2O]$, %	$V(H_2)$ at indicated temperature of PuO_2 calcination, °C		
	450 [10]	600*	700 [10]
1.0	–	0.0012	0.00024
1.3	–	–	0.0019
2.0	0.00078	–	0.0089
3.0	0.0038	0.0016	–
3.5	0.0055	–	–

* Unpublished data of Karnozov and Vladimirova.

To elucidate the mechanism of physicochemical and radiation-chemical processes in the system PuO_2–H_2O(total S.), it is necessary to obtain systematic data on the kinetics of H_2 and O_2 formation in the absence and in the presence of air (O_2) in the gas phase depending on the specific surface area of the powder and water content.

MATHEMATICAL SIMULATION OF RADIATION-CHEMICAL PROCESSES IN THE SYSTEM PuO_2–SORBED WATER

For practical purposes, to evaluate the pressure in storage vessels, it is necessary to have data on the kinetics of formation of radiolytic gases for a wide range of time. There is no way to obtain experimentally these data for weapons-grade plutonium, especially for the system H_2O(total S.), since, as seen from Table 3, the rates of H_2 formation are extremely low and observations for many years are required. Data can be obtained using mathematical simulation, which also allows estimation of the process mechanism.

Initial Data for Development of Mathematical Model

It was shown previously [9] that, in storage of the samples for 30 days, the rate of H_2 formation decreases and its amount tends to a constant. At an H_2O content of 3% (1.66×10^{-3} mol), the steady-state amount of H_2 is approximately 45 cm^3, which corresponds to 2×10^{-3} mol, i.e., the steady-state amount of H_2 is approximately equal to the initial water content. Therefore, under the considered conditions, the radiolytic decomposition of sorbed water is complete. It was concluded from these data that the kinetics of formation of H_2 and other radiolysis products of sorbed water are governed by the kinetics of radiolytic decomposition of sorbed water, and the kinetics of their formation are first-order with respect to water concentration.

The reactions giving rise to the radiolysis products can be presented in the form

$$H_2O \rightarrow H_2, \quad (1)$$

$$H_2O \rightarrow O_2, \quad (2)$$

$$H_2O \rightarrow H_2O_2. \quad (3)$$

The expressions for the initial reaction rates are in the form

$$d[H_2]/dt = K_1[H_2O], \quad (I)$$

$$d[O_2]/dt = K_2[H_2O], \quad (II)$$

$$d[H_2O_2]/dt = K_3[H_2O]. \quad (III)$$

Here and hereinafter, the brackets denote the percentage or molar amount of water and the amounts of H_2 and O_2 expressed in moles or in cm^3 per gram of PuO_2.

The matter balance equation (in moles) is in the form

$$[H_2O]_0 = [H_2O]_t + [H_2]_t + [O_2]_t + [H_2O_2]_t. \quad (IV)$$

In expressions (I)–(III), K_1, K_2, and K_3 are the rate constants of formation of radiolysis products. K_1 and K_2 were evaluated using the initial rates of H_2 and O_2 formation presented in Table 2. To evaluate K_3, we postulated that the ratio of K_3 and K_1 is equal to the ratio of $G(H_2O_2)$ to $G(H_2)$ for "free" water in α-radiolysis (0.89 [2]). The evaluated rate constants for the system H_2O(outer S.) are given in [12–14]. It can be suggested that, at a water content of 3%, K_1, K_2, and K_3 for weapons-grade Pu are 4.0×10^{-8}, 5.0×10^{-9}, and 3.5×10^{-8}, and for Pu from power plants, 2.5×10^{-7}, 2.9×10^{-8}, and 2.2×10^{-7} s^{-1}, respectively.

Evaluation of the H_2 Amount

By including reactions (1)–(3) with the corresponding rate constants into the scheme, we evaluated the amounts of H_2 for various experiments with Pu from power plants [12]. It was shown that the evaluated amounts of H_2 are significantly lower than the experimental values. The analysis of the rates of reactions (1) and (3) showed that water is expended for the formation of H_2 and H_2O_2 to approximately the same extent, which results in underestimation of the H_2 amount in the calculations. It was concluded that the decomposition of H_2O_2 to water [12] should be included in the scheme. Among possible reactions we selected the reaction of H_2O_2 with PuO_2, which yields water and superstoichiometric plutonium oxide:

$$PuO_2(s) + H_2O_2(ads) \rightarrow PuO_{2+x}(s) + H_2O(ads). \quad (4)$$

Superstoichiometric plutonium oxide was found experimentally in [4–7] in studying the reaction of PuO_2 with water. To elucidate the role of reaction (4) in the kinetics of H_2 formation and to find its rate constant, we performed the corresponding computer simulations, which showed that satisfactory agreement with the experimental data is reached at $K_4 \geq 2 \times 10^{-3}$ mol^{-1} s^{-1} [12]. Thus, the minimum value of the rate constant of reaction (4) is 2×10^{-3} mol^{-1} s^{-1}.

Scheme of Radiation-Chemical Reactions

Previously [12–14] I suggested a mathematical model of sorbed water radiolysis involving 5 primary reactions giving the products of water α-radiolysis (H_2, O_2, H_2O_2, e_{aq}, and OH), reactions of PuO_2 with H_2O and H_2O_2, and also 13 secondary reactions involving molecular and radical products of water radiolysis. Here I performed calculations which showed that the rates of 13 secondary reactions are significantly lower than the rates of formation of three molecular radiolysis products: H_2, O_2, and H_2O_2. Based on this fact, here I present a model optimized with respect to the amounts of primary radiolysis products and reactions involving them. This model does not include the reaction of PuO_2 with H_2O, since it was shown previously [4, 6] that the rate of this reaction does not depend on the content of sorbed water. It was found previously [6] that the rate of this reaction is 0.5 nmol h^{-1} g^{-1}.

Reactions (1)–(4) and also reaction (5) describing recombination of H_2 and O_2 with formation of water were included in the optimized scheme (Table 4). Recombination of H_2 and O_2 in the presence of PuO_2 was observed in [3, 4, 7]. In my papers [12–14] reaction (5) was not included in the scheme.

To elucidate the role of reaction (5) and find its rate constant, we evaluated the amounts of H_2 and O_2 for $[H_2O]$ = 2.0 and 3.0% at various K_5 values. The calculations showed that good agreement of the calculated and experimental data for the system H_2O(outer S.) is observed at $K_5 \leq 1.0 \times 10^{-5}$ mol^{-1} s^{-1}.

The quantitative data on recombination of H_2 and O_2 in the presence of PuO_2 at room temperature are presented in [4, 7]. It was found that, at the initial amounts of H_2 and O_2 in the gas phase of 1.9×10^{-4} and 8.37×10^{-5} mol and a time close to 0, 0.125, and 1 day, the rates of water formation are 2.0×10^{-6}, 8.0×10^{-7}, and 2.5×10^{-7} mol g^{-1} day^{-1}, respectively. The decrease in the rate of water formation, i.e., in the rates of H_2 and O_2 recombination, in time is attributed in the papers to decreasing catalytic activity of the PuO_2 surface due to its moistening. At a rate of 2.0×10^{-6} mol g^{-1} day^{-1}, $K_5 = 1.46 \times 10^{-3}$ mol^{-1} s^{-1}. This value of the rate constant is maximum possible for dry PuO_2. It is two orders in magnitude higher than the maximum K_5 found in this study for $[H_2O]$ equal to 2–3%. It can be noted that the rate of reaction (8) depends on the presence of impurities in PuO_2 [5].

Evaluation of the H_2, O_2, and H_2O_2 Amounts

The amounts of H_2 and O_2 were evaluated using the scheme given in Table 4 and the corresponding values of the rate constants. It was shown that the calculated amounts of H_2 and O_2 reasonably agree with the experimental values for plutonium from power plants at the content of sorbed water of 0.3–3%. This fact proves the validity of the mathematical model suggested and adequate accuracy of the rate constants found.

The amounts of water radiolysis products and water itself were evaluated. The results are presented in Table 5; it is seen that the main amounts of H_2 and O_2 (80% of the maximum) are formed within 100 days, and then $[H_2]$ slowly increases and $[O_2]$ decreases. Thus, under these conditions, i.e., for a given amount of sorbed water and a given radiation dose rate, the calculations allow determination of the time interval in which a gas pressure close to the maximum will be reached and which should be under a particular control.

Table 4. Scheme of reactions included in the mathematical model

Reaction	Rate constant
$H_2O \rightarrow H_2$ (1)	See [12–14]
$H_2O \rightarrow O_2$ (2)	″
$H_2O \rightarrow H_2O_2$ (3)	″
$PuO_2 + H_2O_2 \rightarrow PuO_{2+x} + H_2O$ (4)	$\geq 2.0 \times 10^{-3}$ mol^{-1} s^{-1} [12]
$H_2 + 1/2\,O_2 \rightarrow H_2O$ (5)	$\leq 1.0 \times 10^{-5}$ mol^{-1} s^{-1} (this work)

Table 5. Evaluated amounts of H_2O, H_2, O_2, and H_2O_2 (moles) at various storage times of PuO_2 from power plants with an H_2O content of 3% (1.66×10^{-3} mol). System H_2O(outer S.)

Time, days	$[H_2O]$	$[H_2]$	$[O_2]$	$[H_2O_2]$
1	1.6×10^{-3}	3.5×10^{-5}	4.3×10^{-6}	2.2×10^{-5}
3	1.5×10^{-3}	1.0×10^{-4}	1.2×10^{-5}	4.0×10^{-5}
5	1.4×10^{-3}	1.6×10^{-4}	2.0×10^{-5}	4.3×10^{-5}
10	1.27×10^{-3}	3.1×10^{-4}	3.8×10^{-5}	4.1×10^{-5}
50	5.0×10^{-4}	1.0×10^{-3}	1.1×10^{-4}	2.0×10^{-5}
100	1.6×10^{-4}	1.3×10^{-3}	1.5×10^{-4}	7.0×10^{-6}
150	5.0×10^{-5}	1.43×10^{-3}	1.47×10^{-4}	1.1×10^{-6}
200	2.3×10^{-5}	1.46×10^{-3}	1.45×10^{-4}	4.1×10^{-7}
300	8.7×10^{-6}	1.47×10^{-3}	1.3×10^{-4}	7.3×10^{-7}
400	6.7×10^{-6}	1.47×10^{-3}	1.2×10^{-4}	3.0×10^{-7}
≥500	5.8×10^{-6}	1.47×10^{-3}	1.1×10^{-4}	2.7×10^{-7}

Table 5 shows that, after the lapse of 100 days, the amount of O_2 starts to decrease. Analysis of the calculated data showed that this is due to reaction (5). The calculations without consideration of reaction (5) showed that the content of both O_2 and H_2 continuously increases in time [14].

It is seen from Table 5 that, when the steady-state amount of H_2 is reached, the sum $[H_2] + [O_2]$ is practically equal to the initial water content. In this connection, the equation of matter balance transforms from expression (IV) to relationship (V):

$$[H_2O]_0 = [H_2]_{st} + [O_2]_{st}, \qquad \text{(V)}$$

where the amounts of substances are expressed in moles.

Based on expression (V), we obtained the following relationship between the initial amount of sorbed water and steady-state amounts of H_2 and O_2:

$$[H_2]_{st} + [O_2]_{st} = [H_2O]_0/(8 \times 10^{-2}). \qquad \text{(VI)}$$

Table 6. Rates of reactions (1), (2), and (5) (V_i, pmol s^{-1}) at $[H_2O] = 2.5\%$, $[O_2] = 2.3 \times 10^{-3}$ mol, and $D = 2$ Gy s^{-1} g^{-1}. System PuO_2–H_2O(outer S.)

Time, days	V_1	V_2	V_5
7	46	5.4	0.07
50	40	4.7	0.47
100	34	4.0	0.9
200	25	2.9	1.7
500	10.7	1.2	2.7
800	5.5	0.64	2.5
1000	3.9	0.45	2.25

In this relationship, $[H_2]_{st}$ and $[O_2]_{st}$ are expressed in cm^3 per gram PuO_2 and $[H_2O]_0$, in %; 8×10^{-2} is the scaling factor from cm^3 to moles and from moles to per cents of H_2O.

Using expression (VI), it is possible to find the maximum amount of H_2 and O_2 in 1 cm^3 under given conditions and, by so doing, the maximum pressure of gases. It should be emphasized that the maximum amounts of H_2 and O_2 do not depend on the Pu form, i.e., on the radiation dose rate. The latter will affect only the period of establishment of steady states, i.e., the period in which expressions (V) and (VI) are valid.

The calculations showed that, at the H_2O content equal to 3%, the steady-state maximal amount of superstoichiometric Pu oxide is 1.3×10^{-3} mol or 0.35 g per gram of PuO_2, which is 35% of the initial amount of PuO_2. This amount is sufficiently large to be determined experimentally, provided that H_2O_2 actually decomposes to form water by reaction (4).

Calculation of the Rates of Individual Reactions

We calculated the rates of reactions (1) and (2) of H_2 and O_2 formation and reaction (5) of their recombination in an air-containing ampule (initial content of O_2 2.3×10^{-3} mol). The results are presented in Table 6, from which it is seen that at a time of ≥200 days the rate of reaction (5) is significantly lower than the rate of H_2 formation, and at a time longer than 500 days V_5 approaches V_1. This is explained by a decrease in the rate of reaction (1) due to decreasing amount of sorbed water. Thus, our calculations showed that, in air-containing ampules, the contribution of recombination of H_2 and O_2 to the apparent rate of H_2 formation at a dose rate of 2 Gy s^{-1} increases in time. Presumably, for the system H_2O(total S.) in which the rate of H_2 formation is significantly lower than that in the system H_2O(outer S.), the role of reaction (5) will be significant at a short storage time of PuO_2 samples also.

For a certain period of time depending on the radiation dose rate and O_2 content in the ampule, the expression for the rate of H_2 formation has the form

$$d[H_2]/dt = K_1[H_2O] - K_5[H_2][O_2]. \qquad \text{(VII)}$$

Thus, we developed a model allowing calculation of the H_2 and O_2 amounts and the pressure in the vessel for storage of PuO_2 depending on the amount of sorbed water, radiation dose rate, and storage time.

REFERENCES

1. Caldwell, C. and Menis, O., *USAES Report, NUMEC P-90*, 1962, p. 13.
2. Vladimirova, M.V., *Radiatsionnaya khimiya aktinoidov* (Radiation Chemistry of Actinides), Moscow: Energoatomizdat, 1983.
3. Haschke, J., Allen, T., and Stakebake, J., *J. Alloys Comp.*, 1996, vol. 243, p. 23.
4. Haschke, J. and Allen, T., *Report of Los Alamos National Laboratory, LA-13537-MS*, 1999.
5. Morales, L., Allen, T., and Haschke, J., *Proc. Int. Conf. Plutonium Futures—The Science*, Pilay, K.K.S. and Kim, K.C., Eds., Am. Inst. of Physics, 2000, p. 114.
6. Haschke, J., Allen, T., and Morales, L., *Science*, 2000, vol. 287, p. 285.
7. Haschke, J., Allen, T., and Morales, L., *J. Alloys Comp.*, 2001, vol. 314, p. 78.
8. *Report of Los Alamos National Laboratory, LA-13781-MS*, 2000, p. 32.
9. Vladimirova, M.V. and Kulikov, I.A., *Radiokhimiya*, 2002, vol. 44, no. 1, p. 83.
10. Duffey, J. and Livingstone, R., Abstracts of Papers, *5th Topical Meet. on Spent Nuclear Fuel and Fissile Materials Management*, Charlestone (the United States), 2002.
11. Paffett, M and Kelly, D., Abstracts of Papers, *5th Topical Meet. on Spent Nuclear Fuel and Fissile Materials Management*, Charlestone (the United States), 2002.
12. Vladimirova, M.V., *Radiokhimiya*, 2002, vo. 44, no. 5, p. 455.
13. Vladimirova, M.V., *J. Nucl. Sci. Technol.*, Suppl. 3, 2002, November, p. 379.
14. Vladimirova, M.V., Abstracts of Papers, *5th Topical Meet. on Spent Nuclear Fuel and Fissile Materials Management*, Charlestone (the United States), 2002.