

Formation of H₂ and O₂ in Radiolysis of Water Sorbed on PuO₂¹

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Abstract—Samples of PuO₂ containing sorbed water, when stored at room temperature, release hydrogen and oxygen into the gas phase. At a given content of water, the rates of formation of H₂ and O₂ are in direct proportion to the dose rate of plutonium radiation. With increasing concentration of water from 0.3 to 3% the rates of formation of H₂ and O₂ increase by a factor of 60–100, which is caused by increase in both the energy of α -radiation absorbed by water and radiation-chemical yields of formation of H₂ and O₂. The radiation-chemical yields of formation of oxygen and hydrogen at the 0.3% content of sorbed water are lower, and at the water content exceeding 1%, higher than the yields of these products in radiolysis of “free” water. On storage of powder-like and pelletized samples of PuO₂ of power reactor origin with a 3% water content for 150–200 days, the stationary concentration of hydrogen approximately corresponding to the initial concentration of sorbed water is established.

At present, in relation to the reduction of nuclear weapons all over the world, the problem of excess weapons-grade plutonium arises. One of the ways of handling weapons-grade plutonium is conversion to plutonium dioxide and its prolonged storage.

Plutonium dioxide is a hygroscopic substance. When stored in air of ordinary humidity and temperature, plutonium dioxide takes up water to a content of 2–3 wt % [1]. Under the action of α -radiation of plutonium the sorbed water decomposes. As follows from data on radiolysis of “free” water, the resulting stable products are H₂O₂, H₂, and O₂ [2]. Hereinafter we use the term “free” water contrary to sorbed water. Formation and accumulation of hydrogen and oxygen present a hazard in prolonged storage of PuO₂ in hermetically sealed vessels. There are no published data on radiolysis of water sorbed on PuO₂. Available data on radiolysis of water sorbed on oxides of other metals show that the quantitative characteristics of its radiolysis substantially differ from those of “free” water [3–5].

Here we report on the kinetics of H₂ and O₂ release from samples of PuO₂ with various content of sorbed water (from 0.3 to 3 wt %) at various dose rates of α -radiation at room temperature. We used low-burn-up plutonium Pu(l.b.) and high-burn-up plutonium of the power reactor origin Pu(h.b.). Their dose rates were 1.9 and 11.6 Gy s⁻¹ per gram of PuO₂, respectively.

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EXPERIMENTAL

We used powder and pellets of PuO₂. The powder was produced by calcination of plutonium oxalate at 550°C and pellets, by pressing the powder. Samples with a moisture content of 0.3% were produced by calcination at 1000–1200°C, and samples with a moisture content of >1%, by addition of the required amount of water. The samples of PuO₂ were placed into hermetically sealed metallic ampules equipped with ball-cone seal and special valves through which the ampules were evacuated and the gas phase was sampled for chromatographic analysis. The error of measurements of the gas volume was 10–15% and in determination of the gas composition, 5–10%. The ampules with the PuO₂ samples were placed into a hermetically sealed protective box and kept for a prescribed period. The temperature in the box was 20 ± 2°C. The gas phase was sampled at 3–30-day intervals at the beginning of the experiment and then, at 30–100-day intervals; the experiments lasted for 200–600 days. From the concentrations of hydrogen and oxygen, the initial rates of their formation and radiation-chemical yields were determined.

EVALUATION OF THE DOSE RATE OF PLUTONIUM RADIATION

High-burn-up plutonium. In the experiments we used plutonium of the power reactor origin of the following isotopic composition, wt %: ²³⁸Pu 0.5–0.6,

²³⁹Pu 65–67, ²⁴⁰Pu 21.7–22.7, ²⁴¹Pu 7.7–8.1, and ²⁴²Pu 2.5–2.9. ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, and ²⁴²Pu are α -emitters and ²⁴¹Pu is β -emitter. Along with plutonium isotopes, some α - and β -emitting impurities were found in plutonium dioxide. According to the data of physical measurements, the α -activity of plutonium used in the experiments was 0.3 Ci g⁻¹ and β -activity, 19 Ci g⁻¹.

The dose rate was evaluated by the formula

$$\dot{D} = 3.7 \times 10^{10} \times 1.6 \times 10^{-16} (E_{\alpha} A_{\alpha} + E_{\beta} A_{\beta}), \text{ Gy s}^{-1}, \quad (1)$$

where E_{α} and E_{β} are the energies of α - and β -particles, eV; A_{α} and A_{β} are the α - and β -activities of plutonium, Ci g⁻¹; 3.7×10^{10} is the conversion factor from curie to becquerel (decay s⁻¹); and 1.6×10^{-16} is the conversion factor from eV to Gy. Taking into account that the average energy of α -particles is 5.3 MeV and that of β -particles, 0.02 MeV, we obtain

$$\dot{D} = 5.9 \times 10^{-6} (5.3 \times 10^6 \times 0.3 + 2 \times 10^4 \times 19) = 11.6 \text{ Gy s}^{-1}.$$

The fraction of the energy of α -particles is 81%.

Low-burn-up plutonium. The α -activity of this plutonium was 0.0625 Ci g⁻¹ and the energy of α -particles was 5.1 MeV.

The dose rate of α -radiation was evaluated by the formula

$$\dot{D} = 5.9 \times 10^{-6} E_{\alpha} A_{\alpha} = 1.9 \text{ Gy s}^{-1}. \quad (2)$$

It is seen that the dose rates of α -radiation for the two types of plutonium differ by a factor of 6.

To explain the results obtained, it is necessary to know the energy absorbed with sorbed water. Since the main mechanism of interaction of charged α -particles with substance is the electromagnetic interaction with the substance electrons (ionization and excitation), the distribution of the absorbed dose between PuO₂ and H₂O was evaluated from the following expression considering the ratio of the electron densities of these compounds:

$$D_{\text{H}_2\text{O}} = D_{\text{PuO}_2} \times 10 M_{\text{H}_2\text{O}} / (110 M_{\text{PuO}_2}), \quad (3)$$

where $D_{\text{H}_2\text{O}}$ and D_{PuO_2} are the doses absorbed by water and plutonium dioxide, 10 and 110 are the numbers of electrons in the molecules of these compounds, and $M_{\text{H}_2\text{O}}$ and M_{PuO_2} are the numbers of moles of H₂O and PuO₂.

The doses absorbed by water, evaluated by expres-

Table 1. Dose rates, Gy s⁻¹, absorbed with sorbed water

H ₂ O content, %	Pu(l.b.)	Pu(h.b.)
0.3	0.0077	0.047
1.0	0.025	0.154
1.5	0.038	0.235
2.0	0.05	0.31
3.0	0.076	0.465

sion (3), are presented in Table 1. It is seen that they are in direct proportion to the water concentration.

RESULTS AND DISCUSSION

We studied the kinetics of release of hydrogen and oxygen from various samples of PuO₂. For high-burn-up plutonium Pu(h.b.) we used the pellets with the content of sorbed water of 0.3, 1.0, 1.5, 2.0, and 3.0% and a powder with the water content of 3%. Each sample contained from 5 to 7 g of PuO₂. For low-burn-up plutonium Pu(l.b.) the powder with 3% water content was used. The sample contained 15 g of PuO₂.

Samples of PuO₂ with the water content of 0.3 and 3% were monitored for 5–600 days, and the other samples, for 5–30 days.

The main quantitative characteristics of radiolysis of sorbed water were the concentrations of H₂ and O₂ in the gas phase and the rates of their formation. Data on the kinetics of H₂ release from PuO₂(h.b.) with various water content, obtained during 5–30-day monitoring, are presented in Fig. 1. It is seen that the amount of hydrogen increases with increasing water concentration at a given storage time of PuO₂ samples. In the time range presented in Fig. 1 the hydrogen concentration increases linearly. Similar pattern

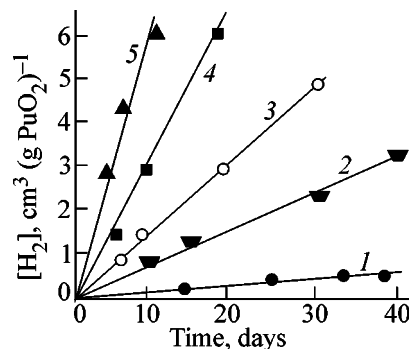


Fig. 1. Kinetics of hydrogen release from PuO₂ pellets (high-burn-up plutonium) as a function of the content of sorbed water. Water content, %: (1) 0.3, (2) 1.0, (3) 1.5, (4) 2.0, and (5) 3.0.

Table 2. Rates and radiation-chemical yields of formation of H₂ and O₂ for various samples of PuO₂ (time 5–30 days)

Type of PuO ₂ sample	H ₂ O content, %	Rate, cm ³ (g PuO ₂) ⁻¹ day ⁻¹		Yield, molecules per 100 eV	
		V _{H₂}	V _{O₂}	G _{H₂}	G _{O₂}
High-burn-up plutonium					
Pellet	0.3	0.01	0.001	1.1	0.10
"	1.0	0.07	0.01	2.4	0.35
"	1.5	0.16	0.025	3.65	0.57
"	2.0	0.29	0.04	5.0	0.7
"	3.0	0.6	0.1	6.9	1.1
Powder	3.0	0.75	0.08	8.6	0.92
Low-burn-up plutonium					
Powder	3.0	0.12	0.015	8.5	1.1

was observed for the kinetics of oxygen release. The initial rates of formation of H₂ and O₂, listed in Table 2, were found from the slopes of the curves. It is seen from Table 2 that with increasing water concentration by a factor of 10, from 0.3 to 3%, the rate of formation of H₂ in pellets increases by a factor of 60, and that of O₂, by a factor of 100. It is seen that at a given water content the rates of formation of H₂ and O₂ for Pu(l.b.) are by a factor of 6–8 lower than for Pu(h.b.). This ratio approximately corresponds to the ratio of the dose rates produced by these two types of plutonium (Table 1). To explain the results obtained, we evaluated the radiation-chemical yields of H₂ and O₂. The calculations were carried out by the expressions

$$G_{\text{H}_2} = 5.37V_{\text{H}_2}/\dot{D}, \quad (4)$$

$$G_{\text{O}_2} = 5.37V_{\text{O}_2}/\dot{D}. \quad (5)$$

In these expressions, G_{H_2} and G_{O_2} are the yields in molecules per 100 eV; V are the rates of formation of H₂ and O₂, cm³ per gram of PuO₂ in a day; \dot{D} is the dose (Gy) absorbed by a given amount of water in 1 s (Table 1); 5.37 is the total conversion factor from cm³ g⁻¹ day to mol l⁻¹ s⁻¹ and from mol l⁻¹ s⁻¹ to molecules per 100 eV.

The evaluated yields are given in Table 2. Since, as shown above, for Pu(h.b.) the fraction of the α -radiation energy is 81% of the total radiation energy, the yields of H₂ and O₂ for this sample can be compared with the yields obtained for Pu(l.b.). It is seen from Table 2 that the yields of H₂ and O₂ do not noticeably depend on the plutonium origin, i.e. on the radiation dose rate, but essentially depend on the concentration

of adsorbed water. With increasing concentration of adsorbed water from 0.3 to 3% the yield of H₂ increases by a factor of approximately 6, and the yield of O₂, by a factor of approximately 10. Along with increase in the radiation dose rate by a factor of 10 (Table 1), this results in increase in the rates of formation of H₂ and O₂ by factors of 60 and 100, respectively.

We compared the obtained yields of H₂ and O₂ with the yields obtained in α -radiolysis of "free" water. According to [2], in α -radiolysis $G_{\text{H}_2} = 1.4$ and $G_{\text{O}_2} = 0.2$ molecule per 100 eV. It is seen from Table 2 that at [H₂O] \leq 1% the G_{H_2} and G_{O_2} values are significantly higher than the yields for "free" water.

Formation of hydrogen from water sorbed on various solids was studied in a number of works. For example, it was shown [3] that quantitative characteristics of formation of H₂ (γ -radiolysis) depend on the concentration of sorbed water and chemical composition of the sorbent. At an H₂O concentration less than 0.1% the yield of hydrogen is 0.45 molecule per 100 eV, i.e., it is the same as in γ -radiolysis of "free" water [6]. At the H₂O content equal to 3–5% the yield of H₂ from water adsorbed on silica gel is 11.3, and from water adsorbed on Al₂O₃, La₂O₃, and Er₂O₃, within 10–15 molecules per 100 eV. The release of hydrogen in γ -radiolysis of water vapor in the presence of various solids was studied in [4]. It was shown that in the presence of ZnO, TiO₂, MgO, and SiO₂ the yield of H₂ is 1.7–2.2, and in the presence of PbO, 30 molecules per 100 eV. Formation of H₂ and O₂ in γ -radiolysis of water sorbed on Al₂O₃, ZrO₂, and TiO₂ was studied in [5]. It was found that the amount of gases is 4–8 times greater than that in

radiolysis of “free” water, all other conditions being the same.

The increase in the yield of hydrogen in radiolysis of sorbed water is explained by the catalytic effect of the solid phase [5] or by the special mechanism of transfer of the ionizing radiation energy from the solid to the adsorbed substance [7].

It is seen from Table 2 that at the water content of 0.3% G_{H_2} and G_{O_2} are 1.1 and 0.1 molecule per 100 eV, respectively. These values are lower than the yields for “free” water. This is presumably due to the presence of an additional channel (along with water) of absorption of the α -radiation energy. This channel may be associated with impurities in plutonium dioxide, making significant contribution to energy dissipation at low water content.

Thus, our data on the yields of hydrogen and oxygen from water adsorbed on PuO₂ are in good agreement with published data showing the difference in the quantitative characteristics of substances in the sorbed and free states. However, it should be noted that the yields obtained in this work and by other researchers are not absolute quantities, since, as seen from expressions (4) and (5), they depend on the absorbed energy. The latter depends on the procedure of evaluating the energy distribution between the adsorbate and adsorbent. This problem has no an exact solution.

Let us consider the kinetics of formation of H₂ and O₂ in prolonged storage of PuO₂ samples (Figs. 2–5). It is seen from Fig. 2 that at a water content of 3% for two samples of high-burn-up plutonium after 500-day monitoring the hydrogen accumulation noticeably deviates from linearity, and in approximately 150 and 200 days the amount of hydrogen reaches stationary values of 48 and 55 cm³. These volumes of H₂ correspond to 2.1×10^{-3} and 2.5×10^{-3} mol. The concentration of sorbed water in these experiments was 1.7×10^{-3} M, i.e., the amount of hydrogen formed was approximately equal to the amount of sorbed water. Thus, establishment of a stationary concentration of hydrogen is caused by complete decomposition of sorbed water as a result of its radiolysis. The excess H₂ may originate from the moisture sorbed on plutonium dioxide from air that penetrated into ampules during their prolonged storage (chromatographic analysis revealed the presence of nitrogen in the gas mixture). The greater amount of hydrogen released from the PuO₂ powder is due to the more developed surface and hence to greater sorption of moisture from air.

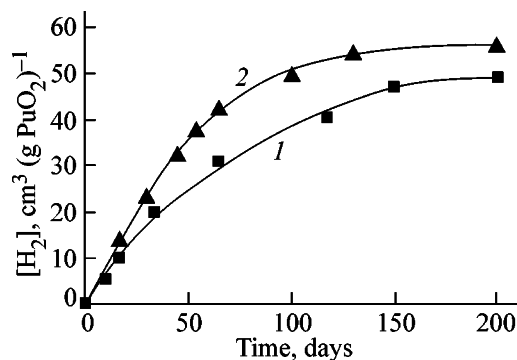


Fig. 2. Kinetics of hydrogen release from PuO₂ samples (high-burn-up plutonium) with a water content of 3%. (1) Pellet and (2) powder.

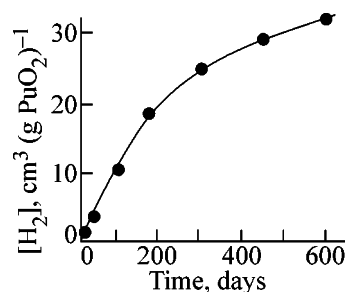


Fig. 3. Kinetics of hydrogen release from PuO₂ powder (low-burn-up plutonium) with a water content of 3%.

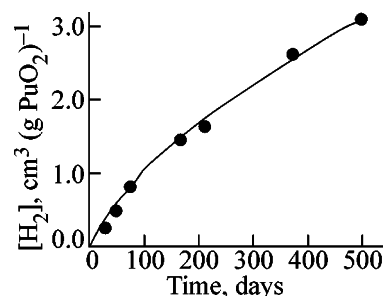


Fig. 4. Kinetics of hydrogen release from PuO₂ pellet (high-burn-up plutonium) with a water content of 0.3%.

It is seen from Figs. 3 and 4 that at a water content of 0.3% for Pu(h.b.) and of 3% for Pu(l.b.) the hydrogen concentration increases linearly for approximately 200 days, after which a small deviation from the linearity is observed. The distinction in the kinetics of hydrogen release for the two types of plutonium (Figs. 2 and 3) is due to the fact that at a given time of the sample storage the integral dose of α -radiation for Pu(h.b.) is greater than that for Pu(l.b.) by a factor of 6. This results in the greater degree of radiolytic decomposition of sorbed water and, as a result, in greater variation of the rate of hydrogen formation in time for Pu(h.b.). The distinction in the kinetics of

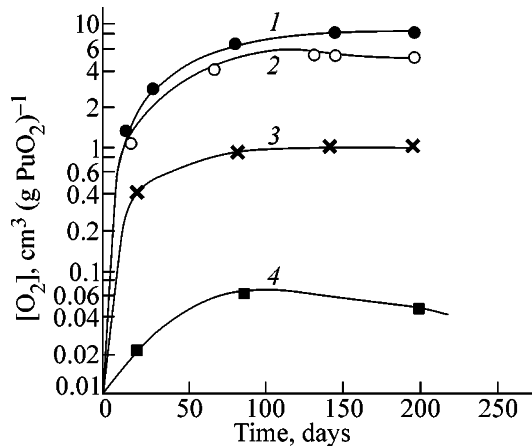


Fig. 5. Kinetics of oxygen release from various PuO_2 samples. Water content: (1–3) 3% and (4) 0.3%. Pu sample: (1, 2, 4) Pu(h.b.) and (3) Pu(l.b.); (1, 4) pellets and (2, 3) powder.

hydrogen release for Pu(h.b.) with a water content of 0.3 and 3% (Figs. 2 and 4) is due to the differences in the radiation dose rate (Table 1) and in the radiation-chemical yields of H_2 formation (Table 2). At $[\text{H}_2\text{O}] = 0.3\%$ these values are significantly lower, which causes the linear increase in the H_2 concentration for a long time.

The kinetics of release of radiolytic oxygen are presented in Fig. 5. It is seen that in all runs the stationary concentration of oxygen is established. After that in some cases the oxygen concentration decreases, which is apparently caused by radiation-

chemical reactions in the gas phase and in the bulk of plutonium dioxide between oxygen and nitrogen to form nitrogen oxides (N_2O , NO , and NO_2) [8].

REFERENCES

1. Stakebake, J., *J. Nucl. Mater.*, 1971, vol. 38, pp. 241–260.
2. Vladimirova, M.V., *Radiatsionnaya khimiya aktinoidov* (Radiation Chemistry of Actinides), Moscow: Energoatomizdat, 1983.
3. Garibov, A.A., Melikadze, M.M., Bakirov, M.Ya., and Ramazanova, M.Kh., *Khim. Vys. Energ.*, 1982, vol. 16, no. 2, pp. 130–134.
4. Bukhareva, V.I., Mitel'man, M.G., Murav'eva, A.K., et al., *Khim. Vys. Energ.*, 1977, vol. 11, no. 3, pp. 276–277.
5. Cecal, A., Paraschivescu, A., Colisnic, D., and Popa, K., *Extended Abstracts, 5th Int. Conf. on Nuclear and Radiochemistry*, Pontresina (Switzerland), September 3–8, 2000, vol. 2, p. 633.
6. Pikaev, A.K., *Sovremennaya radiatsionnaya khimiya. Radioliz gazov i zhidkosti* (Modern Radiation Chemistry. Radiolysis of Gases and Liquids), Moscow: Nauka, 1986.
7. Pikaev, A.K., *Sovremennaya radiatsionnaya khimiya. Tverdoe telo i polimery* (Modern Radiation Chemistry. Solids and Polymers), Moscow: Nauka, 1987.
8. Pshezhetskii, S.Ya. and Dmitriev, M.T., *Radiatsionnye fiziko-khimicheskie protsessy v vozdushnoi srede* (Radiation Physicochemical Processes in Air), Moscow: Atomizdat, 1978.