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Original research paper

APPLICATION OF MICROWAVE RADIATION FOR THE DECOMPOSITION OF URANYL NITRATE IN THE SILICA GEL MATRIX[*]

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Abstract. *The decomposition of uranyl nitrate in a matrix of large coarse-granular silica gel (KSKG trademark) under the action of microwave radiation (MWR) was studied. Microwave irradiation leads not only to the formation of solid decomposition products* UO_3*,* $UO_2(OH)NO_3$*, and their hydrates in the pores of KSKG granules, but also to the accumulation of gaseous* NO_x *and* H_2O*. The presence of* NO_x *in KSKG pores leads to the* HNO_3 *formation in the course of washing of sorbent granules with water. This prevents hydrolysis of uranyl nitrate and the formation of* $UO_2(OH)_2{\cdot}H_2O$ *in KSKG pores. The washout of uranium with water and* $HClO_4$ *solutions from the KSKG fraction containing the products of the decomposition of 2 and 10 g of the initial* $UO_2(NO_3)_2{\cdot}6H_2O$ *under the action of MWR (hereinafter denoted as KSKG-P-I) was studied. Upon the ~7-day contact of the solid and liquid phases at the total ratio S : L = 1 : 20, from 5 to 14% of U passed into the aqueous phase from KSKG-P-I samples obtained in experiments with 10 and 2 g of* $UO_2(NO_3)_2{\cdot}6H_2O$*, respectively. In the course of repeated treatments of KSKG-P-I with water, pH of the wash water increased from 3 to 6, owing to the removal of* NO_x *from KSKG pores. Then an insoluble phase of uranyl hydroxide* $UO_2(OH)_2{\cdot}H_2O$*, which can also be presented as hydroxylated uranium trioxide* $UO_3{\cdot}2H_2O$*, was being gradually formed from the solution obtained by the treatment of KSKG-P-I with water. On treatment of KSKG-P-I with* $HClO_4$ *solutions (pH 1–2), virtually all uranium species formed by MWR treatment of aqueous uranyl nitrate solutions in the KSKG matrix dissolved (at the contact time of the solid and liquid phases of ~21 days, the amount of U that passed into* $HClO_4$ *solutions is ~90%). The amount of the U form that is not extracted with* $HClO_4$ *solutions and remains in KSKG granules is ~12% of its initial amount. The X-ray phase analysis suggests that the uranium species remaining in KSKG are silicate compounds formed by sorbent saturation with a uranyl nitrate solution and the subsequent MWR treatment.*

Key words: *Uranyl nitrate, silica gel, decomposition, microwave radiation*

1. INTRODUCTION

Spent nuclear fuel (SNF) reprocessing results in accumulation of low- (LLW) and intermediate-level (ILW) liquid wastes containing uranium and other fission products [1]. Along with radionuclides, LLW and ILW contain large amount of salts, including alkali and alkaline-earth metal nitrates. Prior to disposal, liquid LLW and ILW are usually concentrated by evaporation, in particular, in various difficultly soluble matrices. For example, superstoichiometric sorption of Cs, Sr, and actinides on the silica gel from liquid radioactive waste (LRW) allows the preparation of the final product, the silica gel matrix containing 500, 200, and 700–1400 mg/g of these elements, respectively [2–4].

One of the ways to prepare ILW and LLW for disposal is their direct evaporation in special metallic containers used for radioactive waste (RW) storage. Recently it was suggested to use microwave radiation (MWR) [5] for this purpose. The disposal of uranium RW and the U regeneration are urgent problems. Use of MWR for this purpose seems to be very important, taking into account such advantages of this process as considerable acceleration of the dehydration and the formation of products meeting the norms for RW disposal and storage.

As we showed previously [6], the MWR treatment of crystalline $UO_2(NO_3)_2{\cdot}6H_2O$ leads to considerable acceleration of its thermal decomposition. The time of decomposition of 2–10 g of crystalline $UO_2(NO_3)_2{\cdot}6H_2O$, as judged from the cessation of the evolution of water vapor and NO_x, is 3–6 min. With an increase in the initial amount of $UO_2(NO_3)_2{\cdot}6H_2O$ from 2 to 10 g, the maximal temperature of the process performed for 35 min increases from 440 to 595 K. We found that the 35-min MWR treatment ensured virtually complete decomposition of $UO_2(NO_3)_2{\cdot}6H_2O$ with the formation of UO_3, $UO_2(OH)NO_3$, and their hydrates [6, 7]:

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$UO_2(NO_3)_2{\cdot}6H_2O \rightarrow UO_2(OH)NO_3 + 5H_2O + HNO_3,$
$UO_2(OH)NO_3 \rightarrow UO_3 + HNO_3.$

At the same time, we found no data in the literature on the possible mechanism of decomposition of uranyl nitrate occurring in the silica gel matrix under the action of MWR. The MWR treatment of hydrated uranyl nitrate immobilized in a silica gel matrix leads to the evolution of gaseous products (NO_x and H_2O) and creates conditions for the formation of a number of uranium compounds such as UO_3, $UO_2(OH)NO_3$, $UO_2(NO_3)_2$, $UO_2(OH)_2$, and also their hydrates and solvates. In this connection, our goal was to study decomposition of uranyl nitrate in a silica gel matrix under the MWR treatment, the identification of the products formed, and the comparison with the mechanism of decomposition of crystalline $UO_2(NO_3)_2{\cdot}6H_2O$ and of uranyl nitrate immobilized in a silica gel matrix in the form of an aqueous solution.

2. EXPERIMENTAL

Chemically pure grade $UO_2(NO_3)_2{\cdot}6H_2O$ and large coarse-granular silica gel (KSKG trademark) (Mendeleev, Tatarstan, Russia) with the granule size of 1–3 mm were used. For used KSKG specific surface, pore diameter and pore volume are 245 ± 5 m^2/g, 10.0 ± 0.5 nm, 0.61 ± 0.05 cm^3/g, respectively.

The experiments were performed with an M1711 NR microwave oven (Samsung) with the output radiation power of 800 W and the frequency of 2.45 GHz. The installation and experimental procedure are described elsewhere [6].

The thermal gravimetric analysis of products formed by the decomposition of uranyl nitrate in a KSKG matrix under the action of MWR was performed with a Q-1500D derivatograph (MOM, Hungary) in platinum crucibles in air at a heating rate of 10 deg/min.

The X-ray diffraction patterns of the samples were obtained with an ADP-10 diffractometer (Philips) using $CuK_{\alpha 1}$ radiation and with an XDC-700 100-mm Guinier camera using $CuK_{\alpha 1}$ radiation and silicon as internal reference.

The experiments on uranyl nitrate decomposition in a KSKG matrix under the action of MWR were performed as follows. A weighed portion of $UO_2(NO_3)_2{\cdot}6H_2O$ (2 or 10 g) was dissolved in 5 and 14 cm^3 of water, respectively. With this solution we impregnated 5 or 8 g of KSKG, respectively, preliminarily placed in the Alundum crucibles. The crucible contents were thoroughly mixed and allowed to stand for 20–24 h to attain the uniform distribution of the uranyl nitrate solution throughout the bulk of KSKG. In so doing, the U(VI) concentration was 190 and 593 mg/g of KSKG at the initial amounts of $UO_2(NO_3)_2{\cdot}6H_2O$ of 2 and 10 g, respectively. After standing for 20–24 h, the Alundum crucible was placed in a microwave oven, and the MWR treatment was performed for 35 min in the rotation mode. Some characteristics of the experiments on uranyl nitrate decomposition in an KSKG matrix under the action of MWR are given in Table 1.

The process temperature was measured with a Chromel–Alumel thermocouple in accordance with the procedure given in [6]. The maximal temperature was attained in 3 min: 465 K and 565 K in the experiments with 2 and 10 g of $UO_2(NO_3)_2{\cdot}6H_2O$, respectively (Table 1). Further irradiation for 6–35 min led to a decrease in the temperature of the reaction mixture to 425 K and 465 K, respectively. This temperature was lower than the temperature attained in irradiation for the same time of crystalline uranyl nitrate hexahydrate (445 K and 595 K, respectively) [6, 7]. The release of water vapor and NO_x, observed visually during the first 3–6 min of the irradiation, was considerably weaker (owing to the localization of these products in KSKG pores) than in the MWR treatment of the similar amount of crystalline $UO_2(NO_3)_2{\cdot}6H_2O$ [6, 7]. A decrease in the temperature of the reaction mixture, observed during 35-min irradiation, is associated with the deeper decomposition of both $UO_2(NO_3)_2{\cdot}6H_2O$ and intermediate products in the KSKG-P-I fraction. As a result, the number of compounds having dipole moments and acting as sources of thermal energy decreased.

Table 1. Characteristics of the experiments on uranyl nitrate decomposition in an KSKG matrix under the action of MWR

Initial amount of $UO_2(NO_3)_2{\cdot}6H_2O$		Amount of KSKG, g	Amount of U(VI), mg/g KSKG	T_{max}, K	Weight of KSKG-P-I,[a] g
g	mmol				
2.0	3.98	5.0	189.6	465	5.99
10.0	19.92	8.0	592.5	565	13.25

[a] KSKG-P-I is KSKG containing products of $UO_2(NO_3)_2{\cdot}6H_2O$ decomposition under the action of MWR.

After the completion of the MWR treatment, the granulated silica gel mass had orange and red-orange color, respectively, for the experiments with 2 and 10 g of the initial $UO_2(NO_3)_2{\cdot}6H_2O$. It was found previously [6, 7] that the product of $UO_2(NO_3)_2{\cdot}6H_2O$ decomposition under the action of MWR is strongly hygroscopic. On contact with ambient air, it changes its physicochemical properties. To prevent the effect of moisture absorption from the environment on the properties of KSKG-P-I, all manipulations on transfer of the product from the Alundum crucible were performed in a chamber filled with nitrogen. Weighing bottles with KSKGP-I were stored in a desiccator over P_2O_5.

The MWR-treated KSKG-P-I granules were uniformly colored throughout the volume, with no noticeable disintegration observed after the irradiation. On storage of KSKG-P-I granules for ~12 months in Petri dishes in air, some of the granules became yellow and other granules became brown-orange. A change in the color of KSKG-P-I granules is due to a change in the composition of the degradation products in the KSKG matrix as a result of moisture absorption. The observed color of KSKG-P-I suggests possible formation in the KSKG-P-I phase of $UO_2(OH)_2{\cdot}H_2O$ (yellow) or/and $UO_3{\cdot}2H_2O$ (brownish yellow) [8, 9]. These compounds are equivalent in the chemical composition.

KSKG-P-I samples obtained in the experiments with 2 and 10 g of $UO_2(NO_3)_2 \cdot 6H_2O$ were subjected to the thermal gravimetric analysis (Figure 1). We found that the total weight loss by the samples in the course of heating to 1073 K was 6.89 and 4.69 wt %, respectively. The thermal decomposition is multistep but is not accompanied by intense exo and endo effects. The major process is the removal of water and NO_x molecules from KSKG pores.

The KSKG-P-I fractions obtained in the experiments on MWR decomposition of 2 and 10 g of $UO_2(NO_3)_2 \cdot 6H_2O$ appeared to be X-ray amorphous. However, separate lines of crystalline compounds can be seen against the background of the KSKG baseline in the diffraction pattern of the KSKG-P-I sample obtained in the experiment on the decomposition of 10 g of $UO_2(NO_3)_2 \cdot 6H_2O$. At the same time, thermal decomposition on heating to 1073 K of the KSKG-P-I sample obtained in the experiment on the MWR-induced decomposition of 2 g of $UO_2(NO_3)_2 \cdot 6H_2O$ yielded the product whose diffraction pattern was complex, with lines of crystalline compounds clearly seen against the background of the KSKG baseline. Apparently, these lines belong to uranium oxides formed by the heating of KSKG-P-I in air to 1073 K.

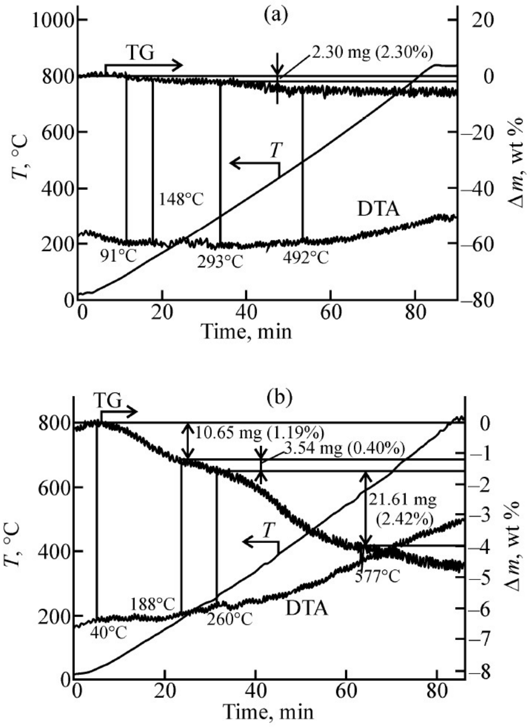

Figure 1. Thermal gravimetric analysis data for KSKG-P-I prepared in experiments on MWR-induced decomposition of $UO_2(NO_3)_2 \cdot 6H_2O$ immobilized in a KSKG matrix. $UO_2(NO_3)_2 \cdot 6H_2O$ sample weight, g: (a) 2 (weighed portion 100.1 mg) and (b) 10 (weighed portion 893.7 mg).

To identify the water-soluble uranium species in KSKG-P-I, its weighed portion was repeatedly treated over a period of ~7 days with 5–7 ml portions of distilled water, with measuring pH of each portion of the solution formed. In the course of repeated treatments of KSKG-P-I with water, pH of the wash solutions increased from 3 to 6. After the treatment completion, all the solution portions were combined in one fraction (hereinafter denoted as P-S). Its final pH was 6, and the total S : L ratio was 1 : 20. In the course of the treatment of KSKG-P-I with water, the granule color changed from orange to yellow and from red-orange to orange-yellow in experiments with 2 and 10 g of the initial $UO_2(NO_3)_2 \cdot 6H_2O$, respectively.

In the P-S fraction, we determined the amounts of UO_2^{2+} and NO_3^- and calculated the $[NO_3^-] : [UO_2^{2+}]$ molar ratio. The amount of NO_3^- in the solution obtained after uranium separation by the precipitation of $Na_2U_2O_7$ at pH > 11 and the amount of UO_2^{2+} in the solution obtained after dissolving $Na_2U_2O_7$ in $HClO_4$ were determined by spectrophotometry using the Beer's equation. The absorption spectra of UO_2^{2+} in 0.1 mol/dm^3 $HClO_4$ solution were recorded with a UV-3100 spectrophotometer (Shimadzu) in quartz cells with the working layer thickness of 1–5 cm. The quantity $[UO_2^{2+}]$ was calculated from the absorption at λ = 413.5 nm (ε = 7.8 dm^3·mol/cm). The absorption spectra of NO_3^- in 0.1 mol/dm^3 $HClO_4$ were recorded with a Specord M40 spectrophotometer (Carl Zeiss) in quartz cells with the working layer thickness of 1–5 cm. The NO_3^- concentration was calculated from the absorption at λ = 301–304 nm (ε = 7.0 dm^3·mol/cm). The water-treated granules of KSKG-P-I fractions (hereinafter denoted as KSKG-P-Iw) were dried in air, ground, and examined by the X-ray phase analysis.

3. RESULTS AND DISCUSSION

The treatment of KSKG-P-I with water at 293 K yields two fractions: the aqueous fraction P-S and the solid fraction KSKG-P-Iw in the form of granules containing water insoluble decomposition products. The data on U(VI) washout from KSKG-P-I with water at 293 K are given in Table 2.

Table 2. Data on U(VI) washout from KSKG-P-I with water at 293 K

Characteristics	Value for initial amount of $UO_2(NO_3)_2 \cdot 6H_2O$, g	
	2.0	10.0
Total weight of KSKG-P-I, g	5.99	13.25
Weighed portion of KSKG-P-I, g	1.5	2.0
Amount of U(VI) in KSKG-P-Iw,		
mg	237.2	715.2
%	85.97	94.63
Amount of U(VI) in P-S,		
mg	33.25	38.44
%	14.03	5.38

It was found that with an increase in the initial amount of $UO_2(NO_3)_2 \cdot 6H_2O$ from 2 to 10 g the percentage of uranium washed out with water from KSKG-P-I into the P-S fraction decreases by a factor of almost 3. This is due to the fact that, in the course of the MWR treatment, the maximal temperature in the experiments with 2 g of $UO_2(NO_3)_2 \cdot 6H_2O$ does not exceed 465 K. Therefore, a significant number of gaseous products of $UO_2(NO_3)_2 \cdot 6H_2O$ decomposition remains in the silica gel pores. The treatment of KSKG-P-I with water results in the formation of HNO_3 in the P-S fraction, which favors the uranium washout from the granules in the form of uranyl nitrate due to the dissolution of water insoluble uranium compounds in HNO_3.

In the experiment with 10 g of $UO_2(NO_3)_2 \cdot 6H_2O$, with an increase in the maximal temperature to 565 K, the removal of gaseous products of uranyl nitrate decomposition, in particular, NO_x from KSKG pores becomes more complete. Furthermore, uranyl nitrate decomposes more deeply, practically to the insoluble UO_3. As a result, only ~5.4% of U is washed out with water.

The fractions P-S, KSKG-P-I, and KSKG-P-Iw were analyzed for the content of NO_3^- and U.

3.1. The P-S fraction

The results of analyses of the P-S fractions obtained by the treatment with water at 293 K of KSKG-P-I samples from the experiments with 2 and 10 g of $UO_2(NO_3)_2 \cdot 6H_2O$ are given in Table 3. As can be seen, the $[NO_3^-]$: $[UO_2^{2+}]$ molar ratio in these fractions is ~9 and ~3, respectively. As we showed previously [6], in the decomposition of crystalline $UO_2(NO3)_2 \cdot 6H_2O$ under the action of MWR, the $[NO_3^-]$: $[UO_2^{2+}]$ molar ratio in the aqueous phase in all the experiments with 2- and 10-g portions of $UO_2(NO_3)_2 \cdot 6H_2O$ was close to 1, in agreement with the formula $UO_2(OH)NO_3$. The $[NO_3^-]$: $[UO_2^{2+}]$ molar ratios obtained in this study suggest that the NO_x formed by the decomposition of uranyl nitrate under the action of MWR is partially localized in KSKG pores. This assumption is confirmed by the evolution of fine gas bubbles in the course of the treatment of KSKG-P-I with water. In so doing, the reaction of water with NO_x leads to the formation of HNO_3 in the solution and to an increase in the $[NO_3^-]$: $[UO_2^{2+}]$ molar ratio to values exceeding 1.

Table 3. Results of analyses of P-S fractions prepared by treatment with water at 293 K of KSKG-P-I samples from experiments with 2 and 10 g of $UO_2(NO_3)_2 \cdot 6H_2O$

Characteristics	Value for initial amount of $UO_2(NO_3)_2 \cdot 6H_2O$, g	
	2.0	10.0
Weighed portion of KSKG-P-I, g	1.5	1.53
NO_3^-, mmol	1.25	0.492
UO_2^{2+}, mmol	0.140	0.164
$[NO_3^-]$: $[UO_2^{2+}]$ molar ratio	8.92	3.13
Compounds present in aqueous solution	$UO_2(NO_3)_2$, HNO_3	

The $[NO_3^-]$: $[UO_2^{2+}]$ molar ratios equal to ~9 and ~3 may correspond to the simultaneous transfer of $UO_2(OH)NO_3$, $UO_2(NO3)_2$, and HNO_3 into the solution. However, in the presence of HNO_3, the existence of the hydroxy compound $UO_2(OH)NO_3$ in the solution is improbable, because this compound should react with HNO_3 to form water molecules and additional free NO_3^- ions. Therefore, more probably, the P-S fraction mainly contains $UO_2(NO_3)_2$ and HNO_3 in the dissociated forms.

By evaporation of the P-S fraction in air at room temperature, we obtained yellow crystalline precipitates (hereinafter denoted as P-S-C). The results of the chemical analyses of P-S-C fractions obtained from the P-S fractions from the experiments with 2 and 10 g of $UO_2(NO_3)_2 \cdot 6H_2O$ are given in Table 4. As can be seen, the $[NO_3^-]$: $[UO_2^{2+}]$ molar ratios in P-S-C virtually coincide with the values given in Table 3. Thus, the precipitates contain virtually all the components present in the P-S fraction, except the water removed in the course of drying. The products of the P-S-C fractions were examined by the X-ray phase analysis. The powder diffraction patterns of the P-S-C samples are shown in Figure 2. The comparison of these X-ray patterns shows that they are essentially different, i.e., the P-S-C fractions obtained by evaporation of the P-S fractions differ in the composition. The analysis of the diffraction patterns obtained in combination with the data from [7] and with the patterns theoretically calculated from the crystallographic data available in JCPDS-ICDD for $UO_2(NO_3)_2 \cdot 6H_2O$ and $UO_2(OH)NO_3 \cdot nH_2O$ [10–12] shows that the experiment with 10 g of $UO_2(NO_3)_2 \cdot 6H_2O$ yields a polymer of the composition $(UO_2)_2(OH)_2(NO_3)_2 \cdot 4H_2O$ [13]. At the same time, because of the lower uranium concentration in the aqueous solution, the experiment with 2 g of $UO_2(NO_3)_2 \cdot 6H_2O$ yields a mixture of compounds whose diffraction patterns have no lines characteristic of $(UO_2)_2(OH)_2(NO_3)_2 \cdot 4H_2O$ and $UO_2(NO_3)_2 \cdot 6H_2O$. Taking into account the $[NO_3^-]$: $[UO_2^{2+}]$ molar ratio (Table 4), we have good grounds to believe that the crystallization of P-S-C in this system results in the formation of solvates of various uranyl nitrate salts.

Table 4. Results of analyses of P-S-C product prepared by drying in air of aqueous solution from washing of KSKG-P-I fraction

Characteristics	Value for initial amount of $UO_2(NO_3)_2 \cdot 6H_2O$, g	
	2.0	10.0
Weighed portion of KSKG-P-I, g	2.02	2.02
NO_3^-, mmol	0.565	0.446
UO_2^{2+}, mmol	0.0656	0.1388
$[NO_3^-]$: $[UO_2^{2+}]$ molar ratio	8.61	3.21

The presence of strong lines at 2θ ~15°–16° in the diffraction pattern of the P-S-C product from the experiment with 2 g of $UO_2(NO_3)_2 \cdot 6H_2O$ (Figure 2a) suggests the formation of uranyl hydroxynitrate hydrates $UO_2(OH)NO_3 \cdot nH_2O$ [11, 12]. They can be formed in the course of evaporation of the P-S fraction owing to uranium hydrolysis. The diffraction lines at 2θ ~29.3°–29.4° can be assigned to the lines belonging to uranium silicate hydrates of various compositions [14–16].

The solutions of the P-S fraction became turbid with time, and yellow-green precipitates becoming yellow on drying formed on the test tube walls. The precipitates (hereinafter denoted as P-S-P) were separated from the solutions, washed at room temperature, and analyzed. The $[NO_3^-] : [UO_2^{2+}]$ molar ratio in P-S-P appeared to be equal to 0.5. This ratio can correspond to a mixture of difficultly soluble uranium compounds $UO_2(OH)NO_3$ and $UO_2(OH)_2$, which can be formed by the hydrolysis of uranyl nitrate with an increase in pH of the P-S fraction to 6–6.5. It is known that the solubility product of $UO_2(OH)_2$ is 10–22 [9] and that the solubility of $UO_2(OH)NO_3$, according to [6], is $6.83\cdot10^{-2}$ mol/dm^3 (16.3 mg/cm^3) at pH ~3. The amount of the P-S-P precipitate formed in the experiment with 2 g of $UO_2(NO_3)_2\cdot6H_2O$ was considerably lower than in the experiment with 10 g of $UO_2(NO_3)_2\cdot6H_2O$, which is due to differences in the uranyl concentrations in solutions and in the extent of decomposition of the initial $UO_2(NO_3)_2\cdot6H_2O$ to UO_3.

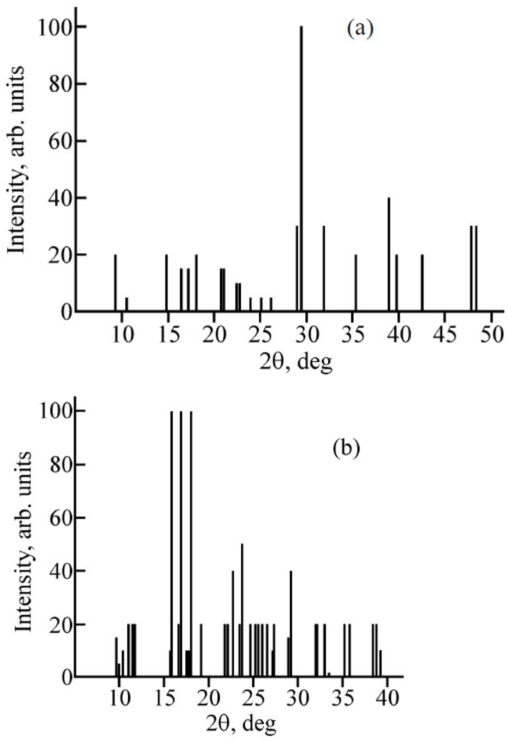

Figure 2. Powder diffraction patterns of P-S-C fractions obtained by evaporation of P-S fractions in air [initial amount of $UO_2(NO_3)_2\cdot6H_2O$ in KSKG, g: (a) 2 and (b) 10].

The P-S-P fractions were subjected to the X-ray phase analysis. Figure 3 shows the powder pattern (recorded with a Guinier camera) of a P-S-P sample obtained in the experiment with 2 g of $UO_2(NO_3)_2\cdot6H_2O$. The X-ray diffraction pattern of the sample obtained from 10 g of $UO_2(NO_3)_2\cdot6H_2O$ is virtually identical. The diffraction lines essentially coincide and are in good agreement with the patterns theoretically calculated from the crystallographic data available in JCPDS-ICDD for $UO_3\cdot2H_2O$ [17, 18]. Apparently, drying of the insoluble phase of $UO_2(OH)_2\cdot H_2O$ formed from the P-S fraction results in restructuring of the precipitate with the formation of hydrated uranium trioxide $UO_3\cdot2H_2O$.

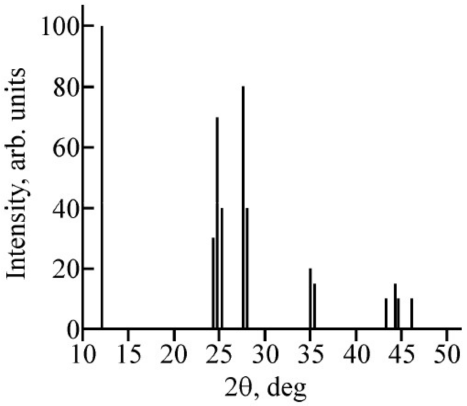

Figure 3. Powder diffraction pattern of the dried sample of P-S-P, crystallized from P-S fractions [initial amount of $UO_2(NO_3)_2\cdot6H_2O$ in KSKG 2 g].

3.2. The KSKG-P-Iw fraction

As seen from Table 2, after the 7-day treatment of KSKG-P-I with water at 293 K, 85 or 95% of uranium remained in the KSKG-P-Iw matrix [experiments with 2 and 10 g of $UO_2(NO_3)_2\cdot6H_2O$, respectively]. Taking into account deeper decomposition observed in the experiment with 10 g of $UO_2(NO_3)_2\cdot6H_2O$, it was interesting to examine the KSKG-P-Iw fraction specifically from this experiment. The solid KSKG-P-Iw fraction obtained by the treatment of KSKG-P-I from this experiment with water contained after drying in air nontransparent orange and brown granules. To identify the uranium species in the solid KSKG-P-Iw fraction, its weighed portion was treated with $HClO_4$ solutions of various concentrations for 21 days. On the treatment of KSKG-P-Iw with the 0.25 mol/dm^3 $HClO_4$ solution, pH of the solution increased from 1 to 3 within the first 10 min. The change in the solution pH is apparently due to the fact that the major fraction of the acid reacted with UO_3 and the other products of the MWR-induced decomposition of $UO_2(NO_3)_2\cdot6H_2O$, remaining in KSKG-P-I granules after their 7-day treatment with water. Despite the reactions occurring in the KSKG-P-Iw matrix, a part of granules remained orange or brown. Therefore, KSKG-P-Iw was left in contact with 0.25 mol/dm^3 $HClO_4$ for 24 h. Within this time, all KSKG-P-Iw granules became transparent and light yellow. The granules were separated from the yellow-green mother liquor (this color is characteristic of uranyl nitrate solutions), washed with distilled water, and dried in air. The mother liquor was combined with the wash waters, and the uranium content of the combined solution was determined. We found that 588.4 mg of U passed into the solution in 24 h.

The dried KSKG-P-Iw granules were greenish yellow, which suggests the presence of residual uranium. Therefore, they were left in contact with 0.1 mol/dm^3 $HClO_4$ with intermittent stirring. After 14 days, the slightly greenish solution was separated from the granules by decantation, the granules were washed with distilled water, and the wash waters were combined with the mother liquor. The U(VI) content of the combined solution was found to be 3.1 mg.

Despite the 15-day treatment of KSKG-P-Iw granules with $HClO_4$ solutions, they preserved light lettuce green color. To assure the uranium washout, the wet granules were treated with 2 mol/dm^3 $HClO_4$ for 6 days. However, even after such a treatment the granules the color remained. The solid phase was separated from the mother liquor, washed several times with distilled water, and dried at room temperature. Then the granules were finely divided, and the resulting virtually white powder was subjected to the X-ray phase analysis. It was found that the sample was X-ray amorphous, with its powder pattern virtually coinciding with that of pure KSKG. All the wash waters were combined with the mother liquor, and the U content of the combined solution was determined. It appeared to be close to zero.

Thus, the total amount of U recovered from KSKGP-I containing the products of decomposition of 10 g of $UO_2(NO_3)_2{\cdot}6H_2O$ under the action of MWR was 630.0 mg. Knowing the amount of U in the initial weighed portion of KSKG-P-I, we calculated its amount in the KSKG-P-Iw fraction remaining after the treatment of the granules with water and $HClO_4$ solutions for 28 days. It was 86.1 mg, or ~12% of the initial U amount.

It can be assumed that a certain fraction of U immobilized in the silica gel in the course of its saturation with aqueous uranyl nitrate solution forms under the action of the MWR difficultly soluble silicate species with the KSKG matrix. Uranyl polysilicate and monosilicate complexes [19, 20] and uranyl orthosilicate of the composition $UO_2SiO_4{\cdot}2H_2O$ [21] have been reported. The solubility of uranyl silicate compounds in water does not exceed $2{\cdot}10^{-2}$ mol/dm^3. The solubility of, e.g., $UO_2SiO_4{\cdot}2H_2O$ depends on the solution acidity and is minimal at pH 6–7 [21].

4. CONCLUSION

It should be noted in conclusion that the MWR treatment of uranyl nitrate immobilized in a granulated silica gel matrix from the aqueous solutions results in its decomposition with the formation of gaseous products NO_x and H_2O and the solid fraction containing a mixture of uranium compounds UO_3, $UO_2(OH)NO_3$, $UO_2(NO_3)_2$, $UO_2(OH)_2$, as well as their hydrates and solvates. The process mechanism differs from that of the decomposition of crystalline $UO_2(NO_3)_2{\cdot}6H_2O$, which under the MWR treatment forms, along with UO_3, only $UO_2(OH)NO_3$ [6]. The silica gel matrix plays a significant role in the uranyl nitrate decomposition under the action of MWR. Namely, the gaseous products of the uranyl nitrate decomposition (NO_x and H_2O) formed in the course of the MWR irradiation are localized in KSKG pores, which creates conditions for HNO_3 formation in the course of the subsequent contact of the KSKG-P-I fraction with water.

The use of MWR for immobilization of uranium salts in the silica gel matrices allows considerable acceleration of the process, with significant power and time saving.

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