

EXPERIMENTAL STUDY OF Tc-99 SORPTION BY THE BASIC MINERALS AND ROCKS DURING THE DISPOSAL OF NUCLEAR WASTES

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ABSTRACT

Further successful development of nuclear power, not hazardous to the health of the population of the Earth, is strongly dependent on the possibility of safe radwaste storage. Nuclear wastes contain radionuclides of more than 40 fission and transuranium elements, of which long-lived nuclides with a high migration ability in the environment are the most hazardous. Technetium-99 (specific activity $6.3 \cdot 10^8$ Bq/g) is one of these long-lived hazardous radioactive elements.

Technetium compounds exhibit volatility during heating in the air, high solubilities in water, and complex chemical properties. Therefore this element is found in all types of industrial nuclear wastes, each of which is a complex system in both its radiochemical and chemical composition.

As a rule, the main quantity of fission products (FP), including technetium-99, is found in nitric acid high-level wastes. However, part of the FP get into medium- and low-level wastes. The destiny of technetium present in wastes depends on a selected method of the treatment of radioactive wastes. Historically several different methods have been applied to treatment and storage of liquid radioactive waste each of them having its own pluses and minuses.

This paper considers the possible behaviour of technetium in such variant of the treatment of liquid radwastes of various activity levels like their injection into a deep collector layer after appropriate technological treatment of wastes.

This work was performed in two stages. At the first stage, we determined the regions of the stability of a number of technetium-99 valent states as a function the acidity (alkalinity) of the solution and the radiation dose rate. The data available in the literature have forced us to modify the Eh-pH Tc predominance diagram. The additions were made based on the possibility of the formation of complexes. This diagram enabled us to predict the main forms of the existence of technetium-99 in nitrate radioactive wastes of radiochemical enterprises, the ranges of the stability of these forms, and the directions of chemical processes occurring in the collector-layer during the transformation of injected wastes.

At the second stage, we generalized the data obtained under laboratory conditions on the behavior of technetium-99 in wastes of various activity levels during their interaction with host rocks. This allowed us to develop a scheme of the chemical and physicochemical processes occurring in this system.

REVIEW

Technetium is a redox sensitive element. The forms of its existence in solution are significantly affected by the solution redox properties. It was earlier emphasized that the behaviour of radionuclides in the environment is dependent on a number of different parameters especially the concentration of the radionuclide itself (1). As the typical Tc concentration in HLW is rather high it was possible to apply the general predominance diagram of technetium valent states in the Eh-pH coordinates (Fig.1). This diagram is based on the Torstenfeldt (2) diagram, which has already considered seven different ionic and molecular forms for technetium-99 in solution. These forms were pertechnetetic acid HTcO_4 and the pertechnetate anion TcO_4^- for technetium(VII); TcO_2 , $\text{TcO}(\text{OH})_2$, $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, and $\text{Tc}(\text{OH})_4$ for technetium(IV); and Tc^{2+} for technetium(II). Using the data reported later in (3 -13), we made several changes in this diagram.

In concentrated solutions of nitric acid (0.5 - 3 mol/l), no reduction of technetium(VII) to technetium(IV) was observed even when such strong reductants as hydrazine (0.05 to 0.2 mol/l) were used. Instead of the technetium reduction, the process of

the catalytic decomposition of hydrazine took place (and technetium acted as catalyst). This process ended with the transformation of technetium back to Tc(VII) (3-7). At a nitric acid concentration of more than 4 mol and a hydrazine concentration more than 1 mol/l, technetium is stabilized in the Tc(V) oxidation state with the ionic forms TcO^{3+} , TcO^{2+} , the compounds $\text{TcO}(\text{NO}_3)_3$, $\text{TcO}_2(\text{NO}_3)$, $\text{TcO}_2(\text{NO}_3) \cdot n\text{HNO}_3$ being the only ones isolated in the pure form from these solutions and characterized by physicochemical analytical methods (3 - 5).

The possibility of the formation of technetium(III) in the form of Tc or its dimeric complexes and their effect on the rates of redox reactions were discussed in (3-7, 13). This should be considered negligible for the analysis of the ordinary environmental behavior due to low technetium concentration but it could not be completely neglected in case of underground storage of radioactive wastes when acetic acid is added as the existence of technetium(III) - technetium(VII) mixed complexes in the acetate media was reported for the wastes formed in the synthetic studies (13).

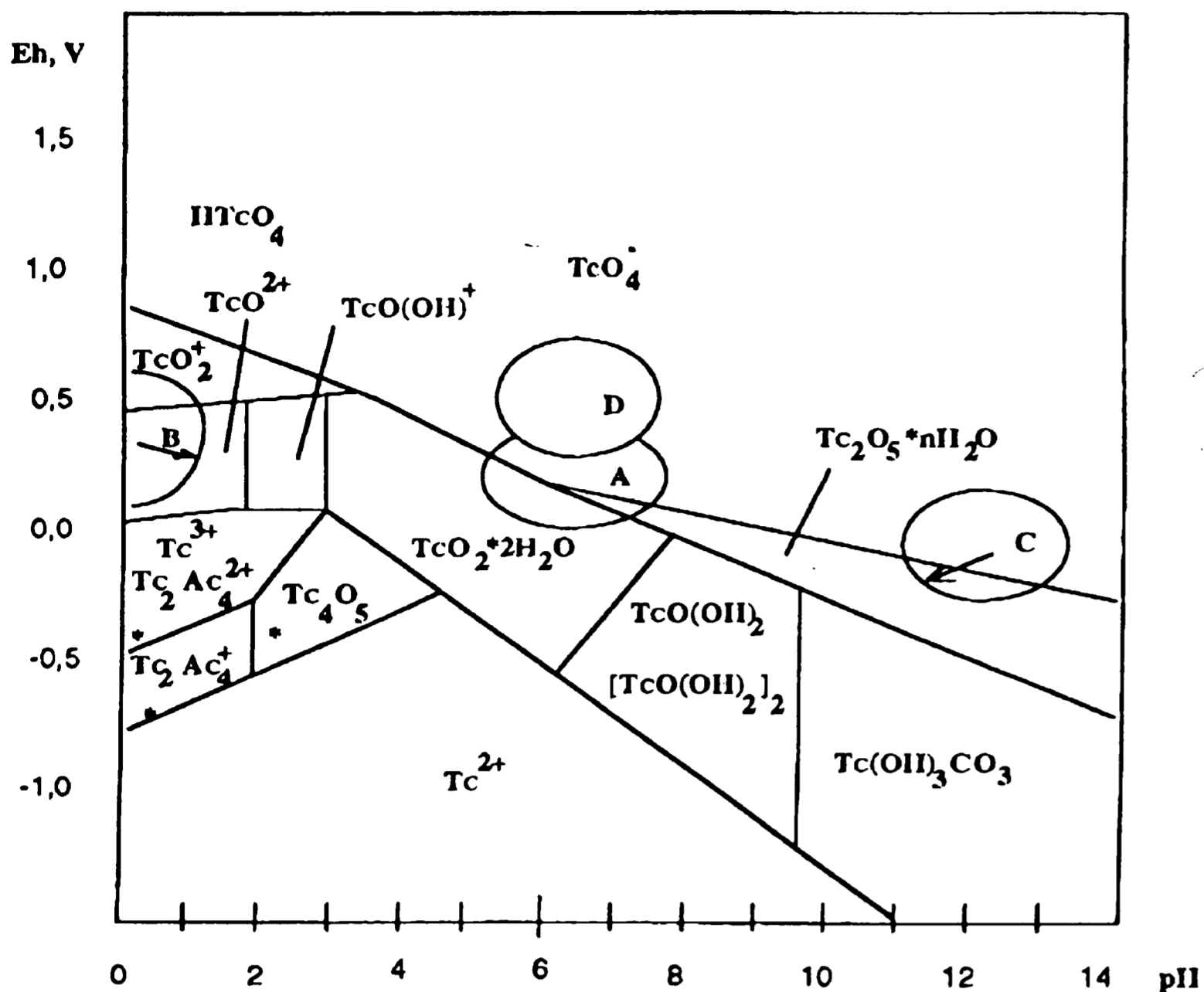


Fig. 1. Eh-pH predominance diagram of Tc. Point frames indicate the regions typical for: A - anaerobic far field seam water; B - HLLW, C - MLLW, D - aerated seam water. The arrows indicate the direction of the condition changes in course of diluting with seam waters, contact with the rocks and gamma-radiolysis.
* - ionic forms characteristic for concentrated solutions,
** - in presence of carbonate.

Similar to general case (1), the stability of the reduced technetium states depends on the technetium concentration in solution (3). The formation of technetium(2.5) dimers and the Tc_4O_5 oxide was observed in solutions with a high technetium concentration. Some of the properties of these compounds were described in (3-5).

In the stability diagram for valent states of technetium-99 (Fig. 1), the area inside the dotted line corresponds to the region with the Eh-pH values characteristic of seam water under anaerobic and aerated conditions for high and medium level alkaline wastes. The arrows indicate the direction of changes in the conditions during dilution with seam water, on contact with host rocks, and during gamma-radiolysis.

The presence of organic impurities in nuclear wastes could play a special role as these impurities may lead to the reduction of technetium to its pentavalent state even in alkaline solutions. Formation of acetate complexes of technetium

In solution of nitric acid, technetium is present in the form of technetic acid $HTcO_4$ and its pertechnetates ($NaTcO_4$ and the like). In alkaline-nitrate solutions, technetium-99 exists in the form of readily migrating metal pertechnetates. However, at decreased solution Eh, technetium can pass, through a number of intermediate valent states (such as TcO_4^{2-} formed as a primary radiolysis products or TcO^{2+} , $TcO(OH)^+$, and other forms stabilized in acid solutions), to sparingly mobile reduced chemical forms (e.g. $TcO_2 \cdot 2H_2O$). The solubilities of technetium(VII) and technetium(IV) compounds depend on both the solution acidity (3, 10-12) and the presence, in solution, of ions capable to form complex compounds with technetium(IV) and technetium(V), e.g., carbonate ions (10), is especially characteristic of alkaline-nitrate solutions. Formation of acetate complexes is also possible if acetic pretreatment of RAW is carried out.

Analogous phenomena may take place during the discharge of technetium into the neutral solutions with a low salt content.

In this case, technetium sorption on some sulfide minerals and in low-level wastes and especially in natural water, its microbiological absorption may take place in addition to technetium reduction by mineral impurities.

In addition to the above-mentioned factors, the forms of the technetium existence are affected by radiation-chemical processes, which a specific feature of liquid nuclear wastes. Radiolytic changes in the waste components depend on the ionizing radiation power, the slat composition, etc. The ionizing radiation dose rate of the disposed solutions is $3 \cdot 10^3$ rem/h. These radiolytic processes should also be taken into account for alkaline solutions, for which the formation of technetium(V) oxide during gamma-radiolysis was observed (3,4). The importance of technetium(V) oxide formation was confirmed by Gibson for gaseous phase (8) and by Henry and Merceron in their simulations (15).

A study of the data on the effect of ionizing radiation on the form of the existence of technetium shows that the primary product of the radiolysis of solutions initially containing hexavalent technetium is the TcO_4^{2-} anion (3,4), which rapidly disproportionates to Tc(V) and Tc(VII) and the attainment of equilibrium between Tc(V) and Tc(VII), as well as the possibility of their subsequent reduction to readily sorbable Tc(IV) depends on the solution potential, the dose rate, the absorbed dose, the irradiation time, the solution concentration, etc. In the absence of atmospheric oxygen and in the presence of even insignificant concentrations of organic compounds in solution, capable to accept OH radicals, one should expect a decrease in the migration ability of technetium as a result of its gradual reduction to sparingly soluble $Tc_2O_5 \cdot nH_2O$ and $TcO_2 \cdot 2H_2O$ (3,4,10,11). As noted by Meyer et al., the solubilities of technetium oxides obtained from alkaline solutions are lower than those precipitated from acid solutions (10).

Note that a study of the behavior of technetium in liquid nuclear wastes is complicated by a multicomponent character of the system and disproportion reactions, which requires additional investigations in this direction.

Radioactive Solutions Simulating Nuclear Wastes

Technetium-99 isotope in the form of potassium pertechnetate supplied by the V/O Izotop was used in the work. The radiochemical purity of this compound complied with the technical specifications in force. Before preparing the solutions to be used in sorption experiments, potassium pertechnetate was additionally recrystallized from bidistilled water. The quantity of technetium-99 added to the solutions was determined by the weighing. If necessary arose, successive dilution of the solutions were carried out. The gamma-radionuclides were not added but their presence was simulated by external gamma-irradiation.

Sorption experiments were carried out in solutions simulating wastes (Table I) and far field seam water (Table II).

Characterization of Main Rock-Forming Minerals and Rocks

Mineralogical tests of the rocks of underground repositories of nuclear wastes show that the main minerals are field spars (orthoclase, $K[AlSi_3O_8]$), quartz, and kaolinite $Al_2[Si_2O_5](OH)_4$. Orthoclase is known to be the primary one, the other two being the products of its leaching occurring according to the equation:



In this work, we studied a wider range of minerals (listed in Tables III and IV), because some of them can be present in rocks as unidentified impurities.

TABLE I
Composition of Simulated Acidic and Alkaline RAW Solution
Pretreated for the Underground Storage

Alkaline RAW 1		Acidic RAW 2	
Component	Concentration, g/l	Component	Concentration, g/l
NaNO ₃	200	NaNO ₃	200
Tc(VII)	0.01	Tc(VII)	0.01
Al(NO ₃) ₃	15.5	Nitric acid	15.5
NaOH	20	Fe ³⁺	3.1
TBP	0.04	Cr ³⁺	3.2
BuOH	0.01	Mn	4.9
HDBP	0.02	TBP	0.04
Acetat Na	14.5	BuOH	0.01
		HDBP	0.02
		Acetic acid	14.5

TABLE II
Composition of Simulated Far Field Seam Water

Cations	Concentration, mg-eq/l	Anions	Concentration, mg-eq/l
Na ⁺	2,52	HCO ₃ ⁻	4,00
Mg ²⁺	0,74	Cl ⁻	0,5
Ca ²⁺	2,10	SO ₄ ⁻	0,93
NH ⁴⁺	0,01	NO ₃ ⁻	0,01
Fe ³⁺	0,04	TcO ₄ ⁻	10 ⁻⁶

These minerals were taken from a standardized mineralogical collection. They were ground and divided into fractions through soil sieves. Before investigations, the selected fractions were washed with distilled water several times, until dustlike suspensions were fully absent in the washing solutions.

In addition to individual minerals, we also studied kern (core) ground samples obtained in the region of an underground repository. In this case, we studied four fractions with the following particle sizes (mm): (1) d 0.05, (2) 0.1 d, 0.2, (3) 0.315 d 0.4, (4) 0.75 d 0.63.

Sorption Changes

A sorption study was carried out under static conditions, using a WU-4 reciprocal shaker ("Premed", Poland) at the S : L = 1 : 10 ratio. The degree of the attainment of equilibrium was determined by periodic radiometric measurements of the isotope concentration in solution. For natural minerals, the time of exposure was from 1 week to 2 months.

The sorption properties of minerals we characterized using the distribution ratio calculated according to the well-known equation

$$K_d = \frac{V}{W} * \frac{C_1 - C_2}{C_2} \quad (1)$$

where

- V is the solution volume, ml
- W is the sample weight, g
- C₁ is the initial activity in one ml of the solution,
- C₂ is the activity in one ml of the solution after contact between the solution and the mineral for the time t.

The radioactivity measurements were carried out as follows: from each solution volume in equilibrium with the sorbents, aliquots of the solution were taken for radiometric measurements and dried on a metal or paper disk. For aliquots of alkaline solutions, extractive methylethylketone concentration with a simultaneous removal of the salt background were carried out.

The radioactivity of the samples was determined by the relative method with an NRQ-605 counter (Tesla) with an alpha-particle stilbene scintillation detector, using reference technetium-99 sources (produced at the Laboratory of Radiochemical Investigations of the Institute of Physical Chemistry, Russian Academy of Sciences).

Irradiation Procedure

To study technetium sorption under g-radiation, the samples were subjected to g-irradiation of a Co-60 source for 1 - 25 h at 35°C. The absorbed dose was determined using a bichromate dosimeter. The dose rate was normally 3.94 * 10 rem/h. A simultaneous preparative separation of the technetium compound formed in alkaline wastes from a solution analogous to model solution, but with a higher sodium pertechnetate concentration (25 g/l) was carried out.; the irradiation time was equal to 6 h.

RESULTS AND DISCUSSION

Tables III - VIII show the experimental data on the technetium distribution ratios on natural minerals and on the core material of an underground nuclear waste repository.

During technetium(VII) sorption on the fine-grain fraction of minerals from seam water, all minerals, except for the last three ones, exhibited low technetium distribution ratios (from 0.05 to 2.7 ml/g). For minerals No.1 - 8 and 10 - 13 (Table III), the quantity of technetium desorbed during the subsequent 10 times repeated washing (S : L = 1 : 10) with a solution simulating seam water was never below 95%.

During technetium(VII) sorption on medium-dispersity minerals and rocks of from seam water (Table IV), the distribution ratios were lower, which made it necessary to more accurately analyze the effect of the dispersity of the samples.

Equation 1 used for the calculation of the distribution ratios, the sample dispersity is not explicitly taken into account. In a more accurate form, technetium(VII) sorption on sedimentation rocks composed of a number of individual polydispersed miner-

TABLE III
Sorption of Tc(VII) from Simulated Seam Water by Several Natural Minerals
(fine fraction 0,05 mm < d < 0,1 mm)

No	Mineral	Contact time, month	Distribution coefficient, ml/g
1	Sandstone	0,5	2,5±0,2
		1	2,7±0,2
		2	2,7±0,3
2	Feldspar	0,5	1,9±0,2
		1	2,0±0,2
		2	2,1±0,2
3	Kaolinite	0,5	0,1±0,03
		1	0,1±0,03
		2	0,1±0,03
4	Quartz	0,5	0,1±0,03
		1	0,1±0,03
		2	0,1±0,03
5	Gneis shale	1	2,3±0,08
		2	2,7±0,09
6	Steatite	1	2,1±0,1
		2	1,9±0,1
7	Limonite shale	2	2,5±0,3
8	Talc shale	2	2,7±0,2
9	Black shale	0,5	6,4±0,05
		1	6,0±0,05
		2	6,5±0,05
10	Bauxite	2	1,5±0,02
11	Basalt	0,5	1,2±0,2
		1	0,9±0,2
		2	1,0±0,2
12	Mergel	0,5	0,1±0,03
		1	0,1±0,03
		2	0,1±0,03
13	Pyrite	0,5	0,3±0,03
		1	0,2±0,03
		2	0,3±0,03

TABLE IV

Sorption of Tc(VII) from Simulated Far Field Seam Water by Several Natural Minerals (grain fraction $0,75 \text{ mm} < d < 1,0 \text{ mm}$)

No	Mineral	Conact time month	Distribution coefficient, ml/g
1	Sandstone	0,5	$0,1 \pm 0,02$
		1	$0,1 \pm 0,02$
		2	$0,12 \pm 0,02$
2	Fieldspar	0,5	$0,11 \pm 0,02$
		1	$0,11 \pm 0,02$
		2	$0,13 \pm 0,02$
3	Kaolinite	0,5	$0,05 \pm 0,01$
		1	$0,05 \pm 0,01$
		2	$0,05 \pm 0,01$
4	Quartz	0,5	$0,18 \pm 0,03$
		1	$0,18 \pm 0,03$
		2	$0,20 \pm 0,03$
5	Gneis shale	2	$0,27 \pm 0,03$
6	Steatite	2	$0,19 \pm 0,03$
7	Limonite shale	2	$0,25 \pm 0,03$
8	Talc shale	2	$0,27 \pm 0,03$
9	Black shale	2	$0,65 \pm 0,03$
10	Bauxite	2	$0,15 \pm 0,02$
11	Basalt	0,5	$0,2 \pm 0,2$
		1	$0,2 \pm 0,2$
		2	$0,15 \pm 0,2$
12	Mergel	0,5	$0,1 \pm 0,03$
		1	$0,1 \pm 0,03$
		2	$0,1 \pm 0,03$
13	Pyrite + 3% Pyrrothine	0,5	$2,5 \pm 0,2$
		1	$4,6 \pm 0,3$
		2	$7,8 \pm 0,3$
14	Lignite	0,5	$9,3 \pm 0,3$
		1	$10,2 \pm 0,3$
		2	$9,8 \pm 0,3$
15	Ilmenite	2	$0,65 \pm 0,03$
16	Magnetite	2	$0,1 \pm 0,03$
17	Gaetite	2	$0,3 \pm 0,03$

TABLE V
Sorption of Tc(VII) from Simulated Acidic Radioactive Wastes RAW 2 by Basic Minerals
 (grain fraction 0,05 mm < d < 0,10 mm)

No	Mineral	Conact time, month	Distribution coefficient, ml/g
1	Sandstone	0,5	1,1±0,02
		1	1,1±0,02
		2	1,2±0,02
2	Fieldspar	0,5	0,9±0,02
		1	1,1±0,02
		2	1,0±0,02
3	Kaolinite	0,5	0,05±0,01
		1	0,05±0,01
		2	0,05±0,01
4	Quartz	0,5	0,06±0,03
		1	0,05±0,03
		2	0,05±0,03

TABLE VI
Sorption of Tc(VII) from Simulated Alcaline Medium Level Radioactive Wastes RAW 1 by Basic Minerals
 (grain fraction 0,05 mm < d < 0,10 mm)

No	Mineral	Conact time, month	Distribution coefficient, ml/g
1	Sandstone	0,5	1,1±0,2
		1	1,0±0,2
		2	1,2±0,2
2	Fieldspar	0,5	0,9±0,2
		1	0,8±0,2
		2	0,8±0,2
3	Kaolinite	0,5	0,05±0,02
		1	0,08±0,03
		2	0,05±0,02
4	Quartz	0,5	0,05±0,03
		1	0,05±0,03
		2	0,07±0,03

TABLE VII

Sorption of Tc(VII) on the Real Core Samples of Different Dispersity from Seam Water and Radioactive Wastes
(t - equilibr.time, D- irradiation dose)

No	Core fraction, mm	Liquid phase	Kd, ml/g t= 3 d	Kd, ml/g t = 90 d	Kd, ml/g t = 120 d	Kd, ml/g D = 20 Mrem
1	< 0,05	Seam water	0,31	1,10	1,15	130±9
2	0,1-0,2	Seam water	0,27	0,97	0,96	11±1
3	0,32-0,4	Seam water	0,09	0,33	0,32	4,1± 0,3
4	0,63-0,75	Seam water	0,05	0,09	0,1	3,9± 0,3
5	0,05-0,1	RAW 1	0,12	1,0	1,0	1,6± 0,03
6	0,2-0,32	RAW 1	0,08	0,9	0,85	1,3± 0,03
7	0,4-0,63	RAW 1	0,05	0,7	0,7	1,2± 0,03

TABLE VIII

Technetium Sorption in Form of Oxides of Tc(V) and Tc(IV) on the Core Samples Under Gamma-Radiolysis in Presence of
[HDBP] = 0.05 mol/l, [BuOH] = 0.02 mol/l

RAW Type	Technetium Oxide Determined in Precipitate	Radiation Dose, rem	Initial Tc concentration, mol/l	Kd, ml/g	Colloidal fraction, %
Acidic HLW with small content of TBP destruction products and acetic acid	TcO ₂ *nH ₂ O	1.21 * 10 ⁷	1.2*10 ⁻⁷	0.8*10 ²	0.5
		1.23.* 10 ⁷	1.2*10 ⁻⁶	0.93*10 ³	0.5
		1.20 .* 10 ⁷	1.3*10 ⁻⁵	1.1*10 ⁴	0.5
		1.26 .* 10 ⁷	1.3*10 ⁻⁴	1.5*10 ⁵	0.8

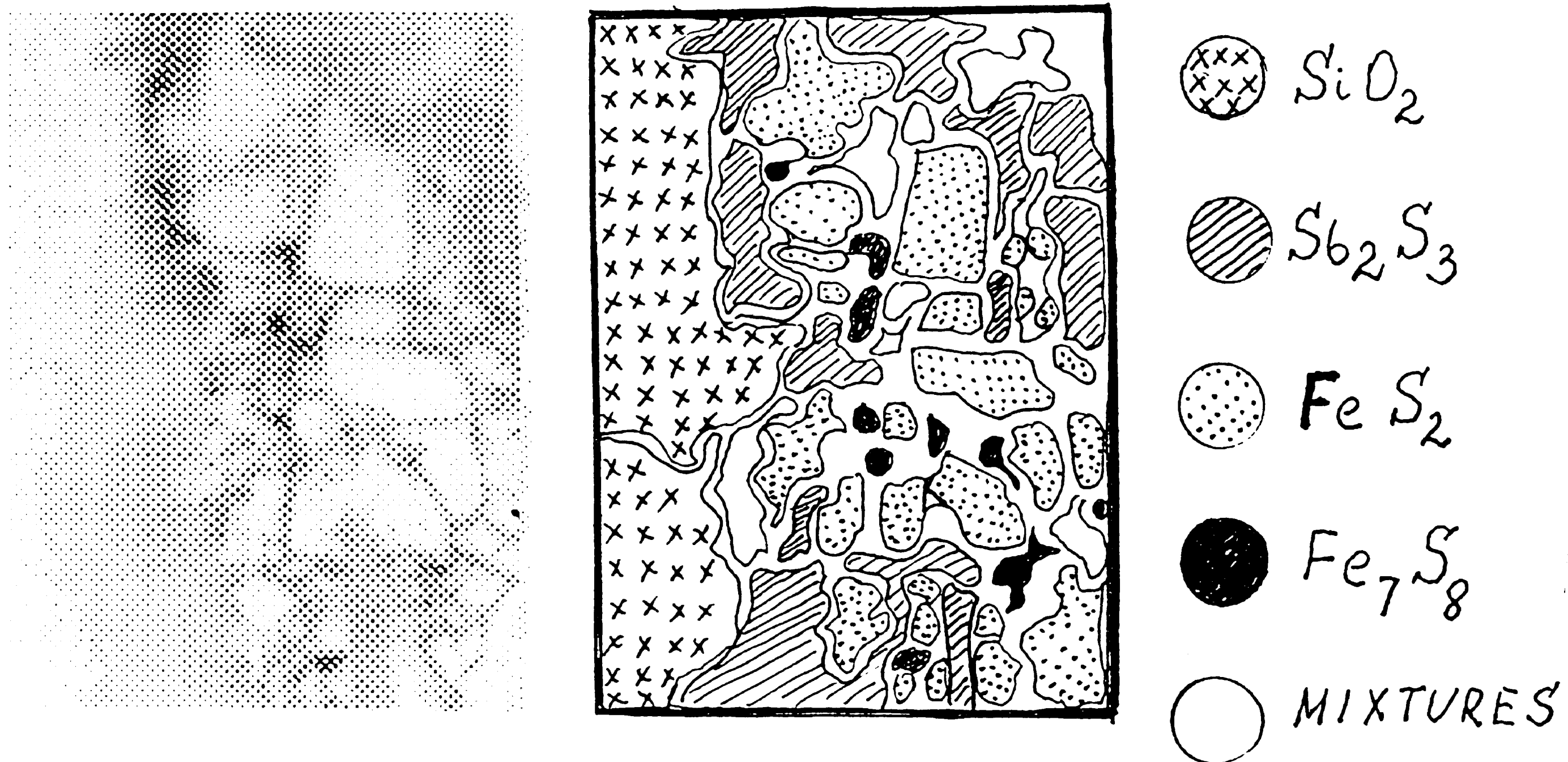


Fig. 2. Typical autoradiography of rock sample containing quartz, pyrrhotine, pyrite and antimonite contacted with pertechnetate solution (initial concentration of Tc = 10^{-4} mol/l, exposition time 7 d).

als (subject to the condition that it is determined by a physical adsorption of pertechnetate ions on the outer surface of the sediment) is described in accordance with Lieser by the formula

$$K_d(\text{observed}) = \sum_{q,p} (k_{q,p} * F_p (m_p / m)) \quad (2)$$

where $k_{q,p}$ is the sorption coefficient for the TcO_4^- ion on the surface of the mineral phase p (in ml/cm²), F_p is the specific surface area of the mineral phase p (cm²/g), m_p is the mass of the mineral phase (g), m is the total mass of the precipitate (g).

In the case of only one mineral phase or mineral phases with close distribution ratios, Eq. 2 used to be simplified to

$$K_d(\text{observed}) = k * F \quad (3)$$

where k is the averaged sorption coefficient (ml/m²), F is the specific surface area.

The results reported in Table VI and indicate, within experimental error, that technetium(VII) sorption by individual minerals is directly proportional to dispersity (1/d) of the samples of sorbents, and for the cases of a reversible technetium(VII) sorption, the k values fall within the range from 5 to 25 ml/m².

The minimal K_d values (0.05 - 0.18 ml/g) are observed for the medium-dispersity samples: kaolinite, field spar (orthoclase), sandstone, basalt, and quartz (specific surface area 90 - 120 cm²/g).

The sorption retainment of Tc(VII) on ferrous rocks is characterized by about the same K_d values as those on aluminosilicates (Tables III - IV). The fact that magnetite exhibits the minimal sorption in the series of ferrous rocks can be explained by its closer packed crystal lattice and a smaller real specific surface.

The sorption capacities of the organic soil components are somewhat higher than those of the mineral components, but only in the case of sorption on lignite this difference may significantly change the residual Tc concentration in seam water. This comparatively high K_d value of 10 ml/g for lignite agrees with the well known affinity of Tc to activated carbon reported for example by Kubota. The difference of one order of magnitude is obviously due to the difference in the specific surface. An analogous presence of carbon in black shale obviously leads to the highest Tc(VII) sorption on this mineral among the minerals of the shale group.

The obtained experimental data show that a reversible physical adsorption takes place for minerals of fine size fraction No 1 - 8 and 10 - 13 (Table III) and almost all the minerals of medium size fraction with the exception for No 9,13,14 (Table IV) under aerobic conditions.

The experimental data presented in Tables III and IV show that some of the sulfide minerals have the highest sorption capacity with respect to Tc(VII). In the case of pyrrhotine and antimonite (Tables III and IV), the quantity of technetium desorbed during washing with 10 portions of the solution simulating seam water (S : L = 1 : 10) does not exceed 5%; i.e., the technetium sorption is irreversible. Thus, a series of sulfide rocks possessing a noticeable selectivity for technetium-99 sorption were found. A high distribution ratio for senarmonite is obviously related to the reduction properties of this mineral.

Because of the ambiguity of the K_d values obtained for pyrite, we carried an autoradiographic study of sorption by rocks simultaneously containing a number of minerals, including quartz, pyrite, pyrrhotine, and antimonite.

Figure 2 shows characteristic autoradiography. From the regions with different obscurity indicating different technetium sorption, we took samples of minerals for an X-ray diffraction study of their nature.

This study showed that in the simultaneous presence of pyrite and pyrrhotine in minerals, pyrrhotine was the most effective technetium sorbent, even if it was present in form of an impurity, while pyrite had almost no affinity to technetium.

Table V shows the results of a study of technetium(VII) sorption on basic rock-forming minerals (field spar, quartz, kaolinite, and sandstone) from model solution simulating acid high-level wastes. Table VI presents the data on technetium sorption on the same minerals and mergel from model solution simulating alkaline medium-level wastes. Attempts to obtain reliable data on technetium sorption from acid solutions on mergel were unsuccessful, because this mineral contains a large quantity of calcium carbonate decomposed in the presence of acid. From the data obtained, it follows that technetium(VII) sorption from acid and alkaline radioactive wastes is lower than that from seam water.

Technetium desorption from these minerals with a seam solution not containing technetium was equal to 92 - 97%, which indicates that this process is reversible.

During gamma-radiolysis, some change in the sorption behaviour of technetium (Tables VII - VIII) was observed. The extent of this change depends on the presence or absence of dissolved organic compounds in the system.

As noted above, in the absence of organic additives, technetium is not reduced during gamma - radiolysis, because the resulting technetium(VI) is oxidized back to technetium(VII) by water radiolysis products. This allows us to understand the low distribution ratios if technetium(VII) obtained for technetium(VII) sorption on core samples of various dispersities from seam water and model solution RAW 1 (Table VII). The increased K_d values for low-dispersity phases (No. 1, 2, Table VII) are obviously not equilibrium, and are due to decrease of the rate of the reaction of back technetium oxidation, due to the removal of technetium from solution by adsorption of the reduced forms on the developed surface of the fine-grain fraction of minerals.

In the presence of organic admixtures, the standard electrochemical potential may shift to the region, where $E_h < 0.3$ for acid solutions and $E_h < 0.0$ for alkaline solutions. In this case, technetium is reduced to Tc(IV) and Tc(V), respectively. Tc(IV) and Tc(V) are sorbed in the form of oxides, and this process could be described in accordance with Lieser (11) by the distribution ratio represented as the ratio of the quantity of the appropriate oxide forming the precipitate on the mineral surface to the residual technetium concentration in solution; i.e., this ratio is not independent of the initial Tc concentration in solution.

We also found that radiolysis of alkaline nuclear wastes in the presence of organic admixtures (TBP radiolysis products) and at the initial technetium concentrations in solution from 10^{-2} to 10^{-5} mol/l leads to the formation, in addition for the individual phase of technetium(V) of the composition $Tc_2O_5 \cdot nH_2O$, of colloidal brown solutions, which remained unchanged during their storage for several weeks in air and dilution up to pH 8.

These observations add to the data reported by Lieser, who did not observe the formation of technetium colloids under either oxidizing or reducing conditions in the absence of radiolytic fields (11).

CONCLUSIONS

The effect of ionizing radiation on the forms of existence of technetium in nuclear wastes was determined. In the absence of reducing components from solutions designed for disposal, gamma-radiolysis, in view of a high rate of disproportionation of technetium(VI) to technetium(V) and technetium(VII), may be the reason for a partial change in the ratio of the basic chemical forms of technetium-99 in high-level nuclear wastes. For solutions having high oxidation potentials due to the presence of nitric acid, the dominant form is Tc(VII). In alkaline solutions of medium-level wastes containing organic compounds (NaAc, DBPA, and SF-3-1), coprecipitation of Tc-99 in the form of technetium(V) on host rocks is possible.

When technetium-99 penetrates into neutral solutions with a low salt content, its sorption absorption on some sulfide minerals may take place, and in low-level nonconcentrated solutions (e.g., during a significant dilution with seam water) its microbiological absorption may take place, even under anaerobic conditions (16).

Using the reported data on technetium sorption, the chemical and radiochemical compositions of solutions, and the mineralogical compositions of the rocks, we can predict that technetium will be sparingly sorbed on the basic host rocks from underground water, until this water contains dissolved oxygen

or any oxidants. The critical parameters indicating the possibility of a sharp increase in the technetium sorbability will a decrease in the standard electrochemical potential below 0.3 V for acid solutions and below 0.0 V for alkaline solutions and the presence of intense gamma fields. Note that a study of the technetium behaviour in liquid nuclear wastes is complicated by the presence of numerous components involved in disproportionation and redox reactions.

The obtained experimental results together with the literature data (3 - 14) allow us to determine the main chemical and physicochemical processes, which should be taken into account in the model of the technetium migration with radioactive wastes and underground water.

The data obtained on the main physicochemical processes determining the forms of existence of technetium as a function of acid-basic and redox parameters of the medium, sorption interaction with rocks and minerals allow us to pass over to the theoretical prediction of the technetium migration in underground repositories of nuclear wastes. Nevertheless it is necessary to obtain additional experimental data on the temperature dependence of pertechnetate-ion diffusion coefficient as the first layer of the hydrate shell of the pertechnetate ion TcO_4^- undergoes rearrangement in the temperature range from 5°C to 45°C, as indicated by the negative temperature coefficient of the tetrahydrate of sodium pertechnetate and the presence of a first-order polymorphic transition at 40°C in this compound (15). The quantitative mathematical modeling still requires further experiments on obtaining reliable parameters of some more processes.

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