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Uranium Migration in the Ground Water of the Region of Sludge Dumps of the Angarsk Electrolysis Chemical Combine

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Abstract

Ground water in the region of slurry dumps of low-activity wastes from the Angarsk Electrolysis Chemical Combine manufacturing enriched uranium was studied. It was established that the E_h values vary from weakly reductive to oxidative, pH varies from neutral to alkaline values. The presence of a hydrodynamic mound in the region of the slurry field provides vigorous diffidence of the technogenic infiltration runoff, which results in possible local increase in the concentrations of NO_3^- , NO_2^- and NH_4^+ in the zone of the hydrodynamic mound above the maximum permissible level. Alkaline sodium nitrate solutions are characterized by higher salt content (up to 9 g/L) but uranium content of all the ground water samples (back-ground, in the region of the stores of solid and liquid radioactive wastes) is below the MPC level. The composition of phases that are able to precipitate from the disposed slurry water after neutralization with $\text{Ca}(\text{OH})_2$ and settling was confirmed with the help of thermodynamic calculations. Possible increase in the concentration of uranium in the interaction of calcium urinate with CO_2 (solution) was demonstrated. Limiting concentrations of uranium in solutions were calculated; the limiting values are determined by the solubility of uranium-containing minerals formed depending on pH, partial pressure of CO_2 , and the presence of cations (Ca, Si, Al).

Key words: store of radioactive wastes, uranium migration, pollution of ground water, forms of uranium migration

INTRODUCTION

Radioactive wastes from conversion works (RAW) occupy a special place in the series of different kinds of technological and domestic wastes and thus they were allocated as a separate class with principally different approaches to their conservation. The main problem connected with RAW is the provision of their radiation and chemical safety during the whole time of storage of these wastes.

The OJSC “Angarsk Electrolysis Chemical Combine” (AECC) is one of four centres manufacturing uranium at the territory of the USSR; it gave the first output in 1960. AECC includes two interconnected works: sublimate (production of fluorine, anhydrous hydrogen

fluoride, and uranium conversion – its transformation into the form of uranium hexafluoride, UHF) and separative (separation of uranium isotopes in gas centrifuges united into multistage cascades, and increase in the concentration of ^{235}U isotope in UHF). At present AECC receives initial uranium raw material of natural origin in the form of uranium oxide U_3O_8 and tetrafluoride UF_4 , in which ^{235}U content is about 0.7 %. During enrichment its concentration increases to 3–5 %.

As a result of neutralization of the acid sewage of sublimate works with the solution of calcium hydroxide (limewater), wastes are formed at the AECC; these wastes are stored as the solid precipitate at special grounds (sludge storage). During the years up to 1993, along

with the raw material of natural origin, also the raw material of secondary origin (regenerated raw material) containing trace amounts of transuranium and fission elements was processed at the AECC. Because of the presence of these elements in precipitates accumulated at the basement of sludge storage, the precipitates were ascribed to the category of radioactive wastes. In view of rather low specific activity of uranium in the precipitates formed from natural raw material processing, these wastes are related to toxic wastes but not to RAW. So, both solid radioactive and toxic wastes are formed during the operation of AECC.

A guarantor of the efficiency of ecological policy of the plant is annually confirmed certificate of conformance of the system of ecological management with the requirements of international standard ISO 14001:2004. Scientists from the Limnological Institute of the SB RAS (Irkutsk) carried out independent ecological audit of the plant in 2007 and concluded that AECC does not bring danger for the environment, and the concentration of uranium within the boundaries of the industrial area is below the MPC level.

At present sludge storages have the status of temporary storages of RAW. It is accepted that liquid and paste-like RAW must be transformed into solid forms excluding leaching and transport of radionuclides out from the storages. However, in view of the enormous amount of wastes accumulated by present, implementation of this approach is held back by the lack of technological, energy-related and financial resources. The Federal Law FZ RF No. 190-FZ [1] introduces the term "special radioactive wastes" for the wastes with low activity. According to this document, in order to substantiate the necessity of extraction, processing and repeated burying of the wastes, it is necessary to establish the ways and intensity of the transport of toxic elements out from the storages at the current moment and to determine the change of these parameters with time. In addition to monitoring of industrial zones, it is necessary to establish the factors that control the intensity of migration processes and, and to determine possible trends of their changes.

The goal of the present study was to reveal the factors affecting redistribution of radioac-

tive elements, first of all uranium, in technogenic-natural systems of ground water in the region of sludge storages of AECC. For the first time, the studies focus on the behaviour of accompanying microelements leached from rocks under the action of ground water which is non-typical for the region (because it is affected by technogenic factors).

OBJECTS AND METHODS OF INVESTIGATION

The object of investigation is the ground water at the territory of the sludge field of AECC, solutions and solid substance from sludge storages, as well as the chemical and mineral composition of host rocks [2].

Sludge pits are situated in the vicinity of the industrial area of AECC. The sludge field includes two regions intended for storage of solid and liquid radioactive wastes (SRW and LRW, respectively). The numbers of holes (AECC network), the line of **A-B** section and holes C-1-C-6 drilled by us are shown in Fig. 1. The structure of sludge storages is composed of six basements and the system of sludge pipelines. The basements are ground-based open rectangular reservoirs 100 × 70 m in size with storage capacity 17 000 (objects I-IV) and 18 000 m³ (objects V, VI). Objects I and II are filled up to the designed level (the thickness of mud layer is about 2.5 m) and reclaimed. Object III is at the stage of conservation: pulp input stopped in 2002, at present the works aimed at its final reclamation are carried out. Objects IV-VI are under operation, the calculated term of ceasing for object IV is 2012. The pulp formed during limewater neutralization of acid wastes from sublimate works is poured into the slime pits. The technology of solid product processing is based on sulphuric treatment of uranium, followed by its subsequent extraction. The solutions are treated preliminarily with sulphuric acid, and then uranium sulphate is precipitated with ammonia water. Settlement of the pulp is accompanied by its separation into mud and highly mineralized solutions. At present, insoluble uranium compounds without transuranium and fission elements enter the settling tanks, so the γ background above settling tanks and at the territory of adjacent

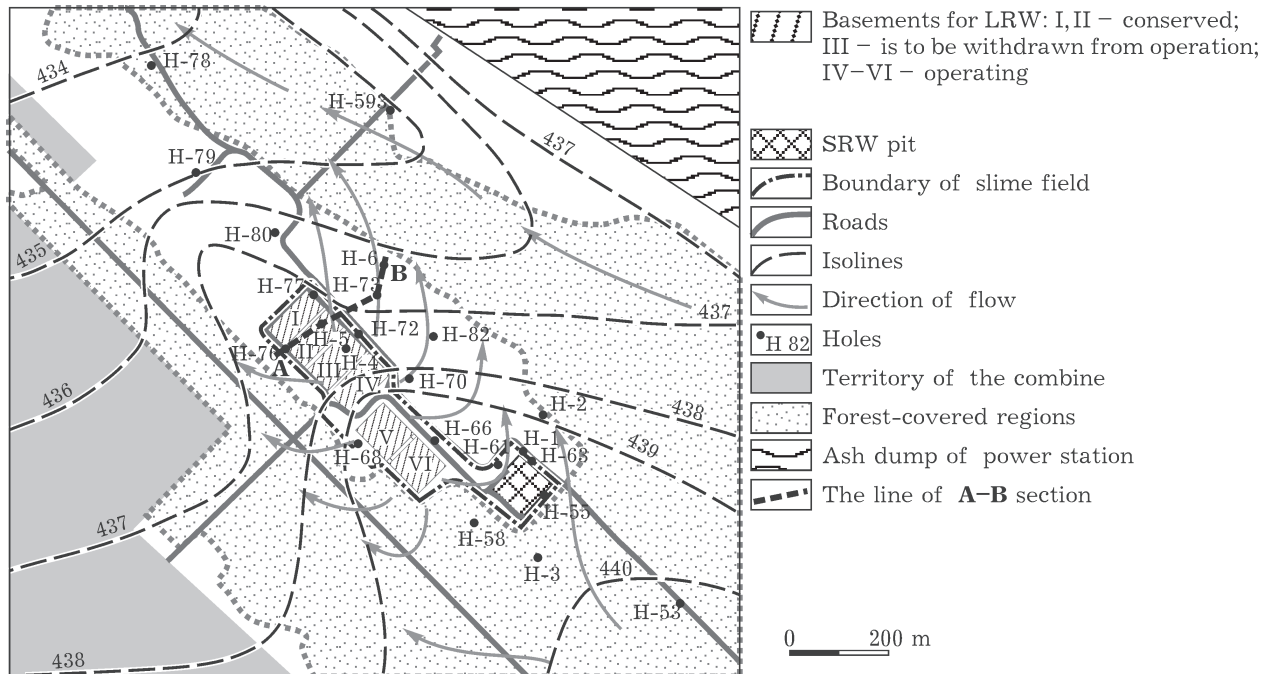


Fig. 1. General scheme of the region of slime field.

landscapes is almost the same and equals 10–15 $\mu\text{R/h}$. The data on the composition of ground water obtained during the present study and in previous investigations [3, 4] are shown in Table 1.

The storages of SRW are a set of structures made of monolith reinforced concrete with total volume about 11 000 m^3 , with wall thickness 160–360 mm, banked from above by the ground embankment (Fig. 2). The composition of wastes varies: SRW from the chemical unit of sublimate works (the slime of hydrometallurgical works, ash from combustion of incinerable RAW, slag from pyrometallurgical deactivation of ferrous metal scrap), substantial amounts of ferric oxide, elastron. Uranium content in the wastes varies from 0.84 to 2 %, dominating form of uranium is oxides.

The geological section of the area is composed by a set of Jurassic formations of Prisayan suite (J_2ps) overlaid by the Middle Quaternary alluvial deposits (Q_2) (see Fig. 2). The Jurassic formations are represented by brown and yellow sandstone, weathered and destroyed to the state of clay loam, loamy sand and dusty sand. The opened alluvial formations conserve the structure of mother rocks (from thin to thick plate-like) and relics in the form of sand-

stone, siltstone, rare lenses and interlayers of black coal. Sand stone is micaceous from fine- to middle-grained, with gravel inclusions accounting for 5 to 20 %, cemented by clay material. The opened thickness of Jurassic deposits is 1.3–4.5 m. Above them, under the soil and plant layer and to the depth of 4.5–10.2 m, alluvial sands and loamy sand of the Middle Quaternary age lie. The sand is brown-yellow to ochre yellow, fine- and medium-grained, with sublayers of plastic loamy sand and clay loam, from rigid to fluid plastic consistency.

The first aquifer (see Fig. 2) is represented by water of the Quaternary deposits, most watered within the limits of over-floodplain terraces. Depending on the relief, the aquifer is revealed at the depth of 0.5–7 m. The salt composition of water from Quaternary deposits is hydrocarbonate: $\text{Ca} > \text{Mg} > \text{Na}$. Mineralization varies within the limits 0.15–0.3 g/L. The depth of ground water occurrence is mainly determined by the natural surface, while at the regions of the vertical arrangement of relief it is determined by the artificial surface. At the tested ground, the upper boundary of technogenically altered ground flux is at a depth of 2.5–6.3 m. The relief of the level surface of ground flux is characterized by the

TABLE 1

Chemical composition of water in the region of slime field of AECC

No.	Sample code	pH	E_h , mV	M , g/L	Content, mg/L	NO_3^-	NO_2^-	NH_4^+	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Na^+	Mg^{2+}	Ca^{2+}	Al^{3+}	Mn	Fe	Ni	Cu	Zn	Sr	Zr	Mo	V	U
1	S-1	7.28	19	0.13	0.79	19.2	0.007	n.d.	275	60	12.4	25.8	101	0.045	0.09	0.062	<0.001	0.001	<0.001	0.35	0.003	0.002	<0.001	n.d.	
2	S-2	6.31	334	0.01	0.008	2.0	0.1	n.d.	153	20	84	7.5	26.9	0.026	0.24	<0.005	0.010	<0.001	<0.001	0.11	0.002	0.004	<0.001	n.d.	
3	S-3	6.53	196	0.09	0.041	6.0	0.016	n.d.	214	22	61	12.8	55.8	0.010	0.36	0.010	0.010	0.002	<0.001	0.15	<0.001	0.003	<0.001	0.0013	
4	S-5	9.23	312	0.45	3.90	14.8	4.7	210	H.o.	406	1214	17.0	178	0.064	0.02	0.102	0.005	0.031	<0.001	0.51	0.005	0.044	0.002	0.0030	
5	S-55	7.40	342	0.09	0.092	15.4	n.d.	n.d.	275	20	68	21.3	82.5	0.016	0.09	<0.005	<0.001	<0.001	<0.001	0.26	<0.001	<0.001	<0.001	0.0011	
6	S-58	7.25	387	0.09	0.230	5.4	n.d.	n.d.	92	30	53	13.0	43.7	0.020	0.08	0.027	<0.001	0.025	<0.001	0.17	<0.001	<0.001	<0.001	0.0005	
7	S-53	7.57	160	H.o.	<0.005	4.9	0.001	n.d.	153	49	46	8.7	29.4	0.003	0.30	<0.005	<0.001	<0.001	<0.001	0.11	<0.001	0.002	<0.001	0.0002	
8	S-61	7.35	377	0.09	0.21	4.1	0.001	n.d.	320	20	68	19.4	75.0	0.009	0.09	<0.005	0.003	0.002	<0.001	0.26	<0.001	<0.001	<0.001	0.0009	
9	S-63	7.61	391	0.11	0.05	5.6	n.d.	n.d.	336	19	51	21.6	54.9	0.037	0.23	0.035	<0.001	<0.001	<0.001	0.29	<0.001	0.001	<0.001	0.0012	
10	S-66	7.35	352	1.10	1.8	7.3	4.6	n.d.	275	335	146	46.7	242	<0.001	0.07	<0.005	<0.001	0.001	0.005	0.56	<0.001	0.005	0.001	0.0018	
11	S-68	9.12	358	4.22	3.8	15.3	9.2	360	H.o.	340	642	34	35.3	0.039	0.04	<0.005	<0.001	0.008	<0.001	0.73	0.001	0.059	0.001	0.0002	
12	S-73	7.62	148	5.76	5.46	5.9	12	n.d.	92	523	1173	118	687	<0.001	0.31	<0.005	0.010	0.001	<0.001	1.89	0.002	0.109	<0.00003	0.0004	
13	S-76	7.14	361	1.38	4.5	5.6	7.5	n.d.	244	425	172	56.6	260	0.055	0.19	0.015	<0.001	0.002	0.004	0.58	0.001	0.007	0.001	0.0017	
14	S-77	9.28	329	3.96	2.53	24.5	5.2	240	92	313	1026	4.5	61.9	0.043	<0.01	<0.005	0.005	0.005	0.003	0.37	0.007	0.081	0.001	0.0008	
15	S-82	7.46	256	1.87	6.2	3.5	4	n.d.	214	424	217	89.0	428	<0.001	0.03	0.018	0.001	<0.001	0.004	0.95	<0.001	0.012	<0.001	0.0013	
16	S-51	7.10	478	0.59	2.8	10	0.08	60	357	29	70	38.8	181	<0.05	0.12	n.d.	<0.02	<0.005	<0.01	0.54	<0.001	<0.001	<0.001	0.0034	
17	S-53	6.70	402	0.08	0.540	9.3	0.14	54	171	50	28	14.8	80.0	<0.05	0.35	n.d.	<0.02	<0.005	<0.01	0.18	<0.001	<0.001	<0.001	0.0003	
18	S-55	7.20	474	0.42	1.3	20	1.8	54	256	19	4.1	26.3	115	<0.05	0.06	n.d.	<0.02	<0.005	<0.01	0.29	<0.001	<0.001	<0.001	0.0009	
19	S-58	7.10	460	3.34	2.7	25	8.1	72	240	28	3.4	24.0	94.7	<0.05	0.15	n.d.	<0.02	<0.005	<0.01	0.26	<0.001	<0.001	<0.001	0.0006	
20	S-61	7.20	454	0.44	2.9	24	0.13	96	326	23	40	26.4	110	<0.05	0.08	n.d.	<0.02	<0.005	<0.01	0.31	<0.001	<0.001	<0.001	0.0007	
21	S-63	7.40	472	0.40	1.7	22	0.11	54	207	23	3.9	26.5	110	<0.05	0.20	n.d.	<0.02	<0.005	<0.01	0.30	<0.001	<0.001	<0.001	0.0009	
22	S-66	7.40	443	1.29	1.63	21	6.1	120	156	258	131	46.6	265	<0.05	0.04	n.d.	<0.02	<0.005	<0.01	0.54	<0.001	0.001	0.002	0.0014	
23	S-68	9.10	333	5.64	2.73	10	14.0	96	67	267	711	1.9	40.2	<0.05	0.03	n.d.	<0.02	<0.005	<0.01	0.75	<0.001	0.071	0.002	0.0001	
24	S-70	9.90	246	9.05	13.300	3.4	18.9	360	n.d.	436	2356	0.7	61.1	0.115	<0.01	n.d.	<0.02	0.020	<0.01	1.34	<0.001	0.276	0.010	0.0006	
25	S-72	8.80	294	5.21	8.100	10	12.0	n.d.	106	276	1162	15.8	533	<0.05	0.05	n.d.	<0.02	<0.005	<0.01	1.06	<0.001	0.057	0.003	0.0003	
26	S-73	7.90	333	5.91	18.800	2.4	2.1	n.d.	79	358	1208	12.7	580	<0.05	0.33	n.d.	<0.02	<0.005	<0.01	1.80	<0.001	0.079	<0.001	<0.0001	
27	S-76	7.20	371	1.64	1.300	1.3	1.2	96	186	316	145	49.5	239	<0.05	0.11	n.d.	<0.02	<0.005	<0.01	0.44	<0.001	0.003	0.001	0.0011	
28	S-77	9.30	290	3.86	7.500	2.1	9.8	162	128	336	1277	5.7	82.6	0.112	<0.01	n.d.	<0.02	<0.005	0.01	0.40	0.002	0.091	0.051	0.0006	
29	S-78	7.30	384	0.73	2.25	10	3.6	54	232	151	134	40.3	193	<0.05	0.18	n.d.	<0.02	<0.005	0.01	0.47	<0.001	0.001	<0.001	0.0013	
30	S-79	7.60	406	0.48	3.7	7.8	0.23	48	207	55	12.5	25.0	126	<0.05	<0.01	n.d.	<0.02	<0.005	<0.01	0.34	<0.001	0.006	<0.001	0.0006	
31	S-80	7.40	405	2.23	2.700	8.1	1.4	54	171	390	115	95.6	418	<0.05	0.19	n.d.	<0.02	<0.005	<0.01	1.02	<0.001	0.001	<0.001	0.0012	
32	S-82	7.30	398	2.66	4.600	9	8.7	72	170	303	219	103	490	<0.05	0.01	n.d.	<0.02	<0.005	0.01	0.98	<0.001	0.009	<0.001	0.0008	
33	311/VI	9.60	257	6.48	1.370	2.4	2.38	702	n.d.	508	1615	10.0	156	0.10	0.12	n.d.	1.70	1.72	0.03	0.21	0.004	0.055	0.003	0.0005	
34	1	7.10	364	0.50	3.0	1.2	3.1	66	137	140	45.3	36.6	75.7	<0.05	0.95	n.d.	<0.02	<0.005	<0.01	0.17	<0.001	<0.001	<0.001	0.0001	

Notes. 1. Samples Nos. 1–15 were collected during winter, Nos. 16–32 in spring, Nos. 33, 34 – from slime pit. 2. n. d. – not determined.

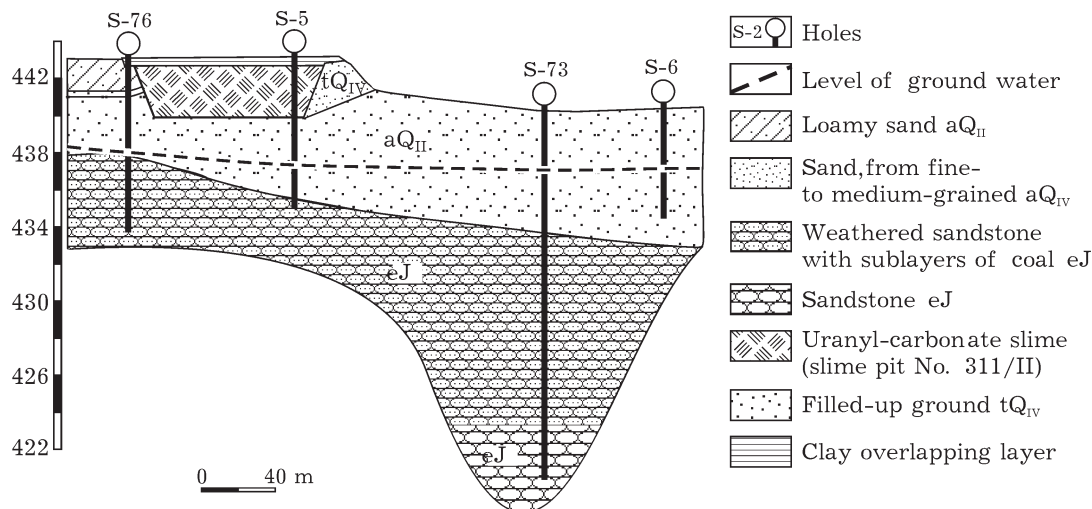


Fig. 2. Geological section along **A-B** line.

presence of hydrodynamic groundwater ridge formed as a result of leakage of solutions from sludge storage basements (see Fig. 1). The average slope reaches 0.01–0.02 m, which provides vigorous diffuence of technogenic infiltrated sewage. The structure of the cupola is asymmetric in the hydrogeodynamic respect. Closeness of equipotentials is observed from south-southeast, which is connected with the hindrance of cupola spread upward along the flux of ground water. Quite contrary, downward the stream to the north-west hydroisohypses are located at a substantial distance from each other. The direction of ground water movement is north-northeast, from the ground of SRW structure towards the Angara River, which flows at a distance of almost 5.5 km to northeast.

The climate of Angarsk is sharply continental, annual air temperature is negative and equals -0.9°C . The distribution of precipitation over the year is non-uniform, the maximum is in June–August; the average annual amount of precipitation is 466 mm according to the data of perennial observations. The snow cover is insignificant; its thickness reaches 36 cm as an average in a protected place.

Water samples were collected in 2011 in two steps – at the end of January (winter low water period) and at the end of March (spring snowmelt flood). At the sampling site, we determined pH value and the anion composition of water by means of potentiometric, colorimetric, nephelometric and volumetric methods.

Specific electric conductance was measured using the conductometric method. The concentrations of Cl^- , HCO_3^- and CO_3^{2-} were determined under laboratory conditions through titration, SO_4^{2-} by means of turbidimetric analysis with a PE-5300 VI photocolimeter. The error of anion determination was 10–15 %; for the determination of gram-scale concentrations of nitrate ion the error increases by a factor of 2–3. The salt content in ground water was determined from the dry residue. Determination of cations was carried out at the IGM of the SB RAS (Novosibirsk) by means of high-resolution mass spectrometry with inductively coupled plasma (ICP-MS) (Element Finnigan Mat, Germany) and atomic emission spectroscopy (ICP-AE) (IRIS Advantage). Detection limits vary from 0.001 mg/L for V, Mo and Zr to 0.005 mg/L for Cu and 0.0n mg/L for Al, Ni, and Zn.

The solid samples were analyzed by means of X-ray fluorescence analysis using the synchrotron radiation with Si(Li) detector at the station of elemental analysis of VEPP-3 at the Institute of Nuclear Physics, SB RAS (Novosibirsk). The concentrations of natural radionuclides were determined by means of scintillation γ spectrometry (SGS) at the IGM, SB RAS. The mineral composition of samples was determined by means of powder X-ray diffraction using DRON-3 instrument (CuK_α radiation). To differentiate fine-grained layered aluminosilicates, some samples were impregnated with ethylene glycol before determination.

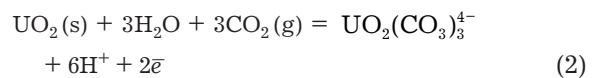
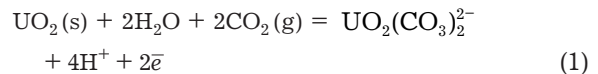
Thermodynamic calculations in the heterophase 26-component system H–O–C–Cl–N–S–Al–Si–Na–Ca–Mg–Mn–Fe–U–Pu–Am–Cs–Co–Ni–Mo–Zr–Cu–Zn–Cd–Ba–Sr were carried out at 25 and 5 °C at the total pressure of 1 atm according to GIBBS algorithm using the built-in thermodynamic database UNITERM of HCh software package [5]. The initial database was supplemented by the consistent values of free energy of formation for the minerals of uranium and its complexes in solution [6–8]. Calculations of equilibria were carried out under the conditions of the water–rock–gas systems, open to different extents with respect to CO₂ and O₂ (mobile components).

RESULTS AND DISCUSSION

The mobility of uranium is directly dependent on the oxidation-reduction (redox) potentials in the water–rock system, so the physico-chemical characteristics of ground water are to be considered. According to the data of tests, E_h values vary from weakly reductive to oxidative (0.019–0.478 V), pH from neutral to alkaline (pH 6.31–9.90). According to the results of testing in spring (in March) water is distinguished by the increased concentration of oxygen and therefore by high E_h values (Fig. 3) because of dilution with melted surface runoff, which promotes nitrate carry-over from basements. (An increase in sulphate concentration is almost absent.) Minimal E_h values, that

is, maximally reductive conditions, were identified for samples from C-1 hole situated lower along the slope from SRW storage (see Fig. 1). At the same time, ground water around sludge storages where the slurry after neutralization is stored are highly alkaline and highly mineralized (up to 5–9 g/L) in comparison with background samples from holes C-3 and C-53 (mineralization 0.08–0.13 g/L). At the deepest well C-73, situated lower than the conserved structures I, II, with neutral pH values (7.6–7.9) high mineralization (about 6 g/L) was detected during winter and spring.

The lines of the equilibrium of UO₂ (s) phase of low crystallinity degree with the leading carbonate complexes of hexavalent uranium UO₂(CO₃)₂²⁻ and UO₂(CO₃)₃⁴⁻ are shown in Fig. 3, too. Calculation was carried out for the maximal uranium concentration in the test region, equal to 3 µg/L (C-5 and C-51), and CO₂ partial pressure close to the measured ones, equal to 10^{-2.5} atm:



It follows from the data shown in Fig. 3 that uranium should migrate in the ground water of the region mainly in the form of U(VI) complexes.

The scheme of wastes storage at the plant implies possible spread of nitrate solutions, so it is important to estimate their contribution into

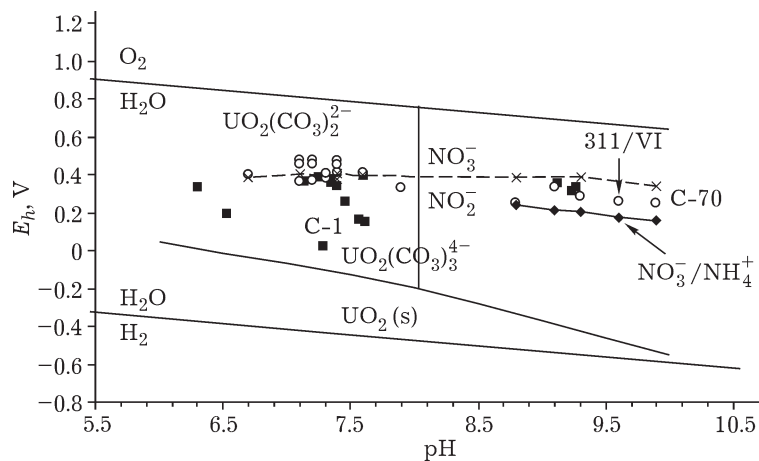
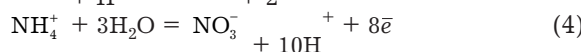
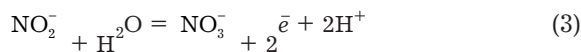


Fig. 3. Oxidation-reduction (E_h) and acid-base (pH) potentials of ground water (except 311 VI point) in the region of AECC slime pit. Black squares mean sampling in winter 2011; hollow circles mean sampling in Spring 2011.

the control of redox settings. To calculate E_h value with the help of Nernst equation, we used the results of sampling analysis of ground water samples collected during spring flood. The concentration of nitrate ion in ground water increases substantially during this season, so solutions will be either neutral or alkaline:



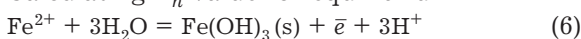
Nernst's electrochemical equation (5) binds the redox potential of the system with the activity of heterovalent pairs, for example NO_3^- and NO_2^- , and the standard potential of this pair (E^0):

$$E_h = E^0 + RT/nF \ln \frac{a_{\text{NO}_3^-}}{a_{\text{NO}_2^-}} \quad (5)$$

where R is the universal gas constant; T is absolute temperature; F is Faraday constant; n is the number of moles of electrons participating in reactions (3), (4).

Comparative analysis of measured and calculated E_h values allows assuming that the potential-ascribing pair is $\text{NO}_3^-/\text{NO}_2^-$ (the line of $\text{NO}_3^-/\text{NH}_4^+$ equilibrium lies below the line of $\text{NO}_3^-/\text{NO}_2^-$ equilibrium even for the samples with high ammonium content). Therefore, this pair promotes an increase in E_h and total oxidative potential. Thus, the presence of nitrates affects an increase in uranium mobility; this is connected not with the formation of weak nitrate complexes [9, 10] but with the fact that nitrates hinder uranium (VI) reduction to U(IV). It is necessary to stress that sulphates do not produce such effect [10].

As far as the situation around the SRW is concerned, it was established that the redox potentials of buffers $\text{Fe(s)}/\text{Fe(OH)}_3(\text{s})$, $\text{FeO(s)}/\text{Fe(OH)}_3(\text{s})$, $\text{Fe}^{2+}/\text{FeOH}_3^0$ for solutions with $\text{pH} \geq 7$ are within the region of negative E_h values stimulating uranium immobilization yet inside the containers. As we have already mentioned earlier, water samples from hole C-1 situated near the SRW storage are characterized by the minimal E_h value. In addition, they contain the maximal amount of iron (0.062 mg/L). Calculating E_h value for equilibrium



for pH 7–8, we obtain that the $\text{Fe}^{2+}/\text{FeOH}_3^0$ pair can be potential-presetting.

Thermodynamic calculations confirm that iron is present in solution in water from hole C-1 in the form of aquated Fe^{2+} cation (70 %) and FeHCO_3^0 ; the presence of other forms is insignificant. It should be noted that iron also plays a key part determining the behaviour of uranium in ground water. Iron (II) reduces uranium to U(IV) which is stable in the solid phase, while Fe(III) precipitating in weakly alkaline ground water in the form of diverse oxides and hydroxides sorbs U(VI). This picture is observed at some natural ore deposits where the front of uranium mineralization coincides with the oxidative front of iron [11]. In addition, the presence of iron hydroxides in the system of water circulating in ground enhances the sorption properties of all the present minerals [12].

According to previous [3] and our data, solutions directly in sludge storages (objects I–VI) are in their chemical composition alkaline and multicomponent with pH 9.55–10.25, mineralization more than 5 mg/L, sometimes reaching 30 mg/L. It was established that Ni concentrations in them exceed MPC (1.72 against 0.1 mg/L). Along with nitrates and sulphates, these solutions also contain NH_4^+ (from several hundred mg/L to several g/L). This unambiguously points to the non-equilibrium character of the system, and this imbalance is characteristic of technogenic systems. Substantial excess of ammonium in ground water samples collected during spring in comparison with background values (98–189 mg/L at pH 8.8–9.9 against 0.14 mg/L, while MPC is equal to 0.5 mg/L) points to the technogenic pollution of water with this compound (see Table 1). The concentration of nitrates in ground water usually varies within the range 10–20 mg/L and is approximately the same for water around sludge storages and SRW storages. Therefore, drainage from sludge storages has a substantial effect on the composition of ground water. This is confirmed also by the results of comparative analysis of the composition of solutions in sludge storage (sample 311/VI) and water from hole C-5: their cation composition is approximately the same (as an average this is several g/L Na, several tenths g/L Ca and

several hundredths g/L Mg, pH > 9). However, the concentrations of nitrates and sulphates in sludge solutions are much higher (up to several g/L). Further descending filtration of drainage in the region of holes C-76, C-5, C-73 (see Figs. 1, 2) in the northwestern and northeastern directions was previously noted by the authors of [3, 4] and is confirmed by the data of our work. In particular, mineralization of solutions from C-5 hole is 4.73 mg/L, while lower along the relief (hole C-73) it is already 6.07 mg/L (see Table 1), which points to the spread of hydrogeodynamic cupola. Alkaline solutions near sludge storages are characterized by increased permanganate oxidability: for the solutions of sludge storage 311/VI it is 11.2 mg O₂/L, for the solutions from C-68 and C-77 holes it is up to 14.5 mg O₂/L, while the MPC is 5 mg O₂/L for drinking water and 10–15 mg O₂/L for technical-grade water.

It is necessary to stress that the changes of salt load for the same testing points have seasonal character (see Table 1), which is connected with the dissolution of sludge neutralization wastes by floodwater. First of all, a sharp increase in nitrate content occurs in spring, especially around sludge storages (for example, for holes C-76, C-73 and C-77 nitrate concentrations in winter/spring is 45/1300, 253/7500 and 546/18 800 mg/L, respectively. Attention should be paid to the fact that nitrate concentrations in water samples taken around sludge storages often exceed those in samples taken from sludge storages. Metamorphization of host rocks by polluted drainage water is also accompanied by carryover of larger amounts of cations; a change of the qualitative composition is noticeable: water in the region is characterized by Ca > Mg > Na as average, while water in holes has Na > Ca > Mg. Migration of solutions in porous media (mainly sandstone and loam), according to the data for the holes of the **A–B** section, is accompanied by small variations of sodium content (conservative element), while the fraction of calcium and magnesium increases due to ion exchange reactions and dissolution of the solid phases of rocks. Water from holes around the SRW storage is hydrocarbonate-calcium-magnesium, neutral, mineralization is much lower than 1 g/L. Total

uranium content in all solutions including sludge solutions is lower than MPC (0.05 mg/L).

Attempts to reveal a correlation between the concentrations of separate ions, pH and mineralization provide evidence (Fig. 4, *a*) that the concentrations of major ions vary depending on pH not proportionally. The dependences are L-like, that is, the concentrations increase until pH reaches ~7.5, and then set at a high level (till higher pH values). One can see that sodium concentrations in water from holes around SRW storages are low, while they are high around LRW (sludge storages), even with neutral pH values.

Modern methods of instrumental analysis of the chemical composition of water allowed us to reveal some microelements that mark the propagation of nitrate drainage. Figure 4, *b* shows the dependence of Mo and Zr content on NO₃⁻ (larger symbols stand for the solutions from sludge storage). A direct correlation of Mo and NO₃⁻ concentrations points to their joint migration from sludge storages where they are incorporated in the liquid phase of sludge (the material balance of these elements is controlled at the plant). For example Mo concentration in water from hole C-70 is somewhat higher than MPC and equals 276 µg/L (1.1 MPC), while in C-73 it is 109 µg/L. Since anionogenic Mo and W are prone to migration in alkaline solutions, the solid phase of underlying ground does not get enriched with these elements. For example, the solid phase of sludge may contain 2 to 12 g/t molybdenum, though its content in underlying sandstone is less than 1 g/t. An inverse situation is observed with zirconium: its content in host rocks at AECC objects is comparable with that for clay and sandstone – 200 g/t (in few samples up to 400 and 600 g/t), while in the solid phase of sludge it is only 5–20 g/t. It is generally accepted that zirconium only weakly participates in water-based and biogenic migration under natural conditions, that is, its compounds are poorly soluble. However, with the background values of 0.001 mg/L and less (C-3 and C-53), its concentration in water from holes around sludge storages may reach 0.007 (C-77) and even 0.0032 mg/L (C-1, around SRW storages). Zirconium can be incorporated into the structure of UO₂ (s) lattice or a complex

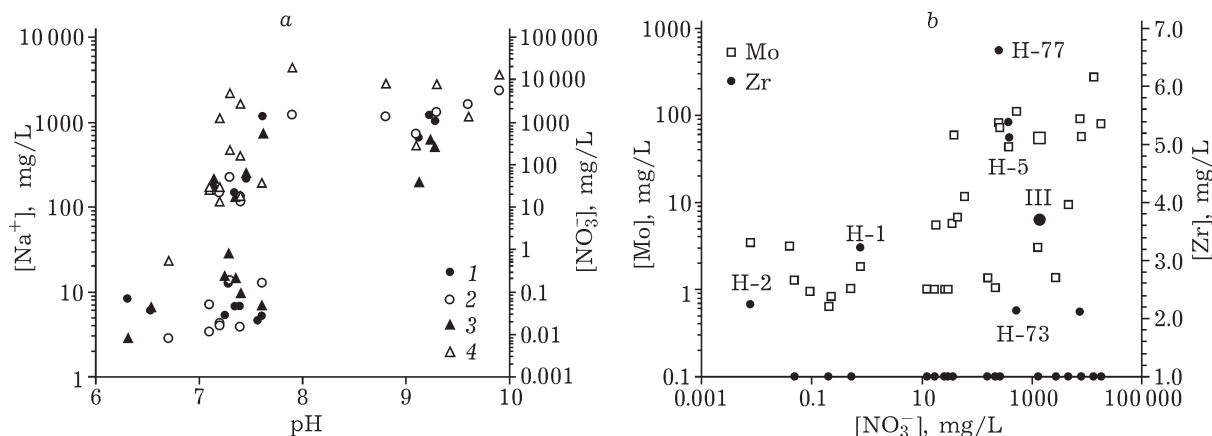


Fig. 4. Changes of the concentrations of Na^+ (1, 2) and NO_3^- (3, 4) depending on pH during winter (1, 3) and spring (2, 4) testing (a), and the dependence of Mo and Zr content in water from the holes around AECC slime pits on NO_3^- content (b).

oxide with perovskite structure ($\text{Ba,Sr,Cs}(\text{U,Pu,Zr,Mo})\text{O}_3$ (s) [13]; it occurs in nature as brazilite mineral ZrO_2 (s) and zircon ZrSiO_4 (usually radioactive). Only the established fact of its presence in the indicated samples of ground water may be considered reliable yet. In view of the interest expressed by researchers [14], additional investigations of zirconium behaviour are necessary. Among elements prone to migration in alkaline water, vanadium is also to be noted. For example, its concentration in ground water samples from C-70 hole (pH 9.9) almost reaches the MPC level and is equal to 0.094 mg/L. The very fact that vanadium gets concentrated in alkaline ground water, while its content in host rocks is at a level of 100 g/t, is interesting. It is noteworthy that manganese content in the samples of background water at neutral pH is higher (about 300 mg/L while MPC is 100 mg/L) in comparison with that in water under technogenic load (alkaline). The character of Mn concentration changes differs from that for Fe.

The behaviour of elements and ions (Fig. 5) must be considered together with the scheme of hole location around sludge storages (see Fig. 1). In particular, points 70, 72 and 77 are situated along one line at the northeastern boundary of sludge storages, similarly to points 73, 82; sampling point 53 is background. It is evident that the versions of solution mineralization are determined by the changes of the concentrations of technogenic NO_3^- and Na^+ and Ca_{total} because the concentration of SO_4^{2-}

in drainage remains almost constant, except for C-53 hole. The curve of molybdenum concentrations corresponds in its shape to the curves for NO_3^- and Na^+ . Magnesium exhibits its own character of migration over holes, due to its leaching from host rocks. Uranium concentrations in tested solutions are too negligible (see Table 1) to establish significant regularities. However, judging from the dependence $U/\Sigma(\text{HCO}_3^- + \text{CO}_3^{2-})$, the behaviour of uranium is directly dependent on CO_2 (solution) and opposite to the behaviour of calcium.

To simulate the changes of phase composition of the system during settling discharged sludge, we chose one of the solutions of operating basement (settled solution without the solid phase) with mineralization 31 g/L, $E_h \sim 200$ mV, pH 9.55. Calculation of the equilibrium at 25 °C showed that alkaline solutions (ionic force $I > 0.5$) disposed into the basement are supersaturated with respect to a series of (hydr)oxides and carbonates. If the phases are ranged in the descending order, the series will look like follows: fluoride $\text{CaF}_2 > \text{SiO}_2 > \text{calcite-dolomite} > \text{FeOOH} > \text{CuO} > \text{Ni}(\text{OH})$ (s) $> \text{illite-smectite} > \text{SrCO}_3 > \text{MnCO}_3$. Such representative set of carbonates implies the formation of the solid solutions of various metals on the basis of calcite $\text{Ca}_x(\text{Mg,Sr,Mn})_{1-x}\text{CO}_3$. For example, up to 40 g of calcite and 14 g of dolomite, about 1 g FeOOH and nickel hydroxide $\text{Ni}(\text{OH})$ (s) can precipitate from 100 L of solution. This means that the concentrations of many elements can decrease substantially as a

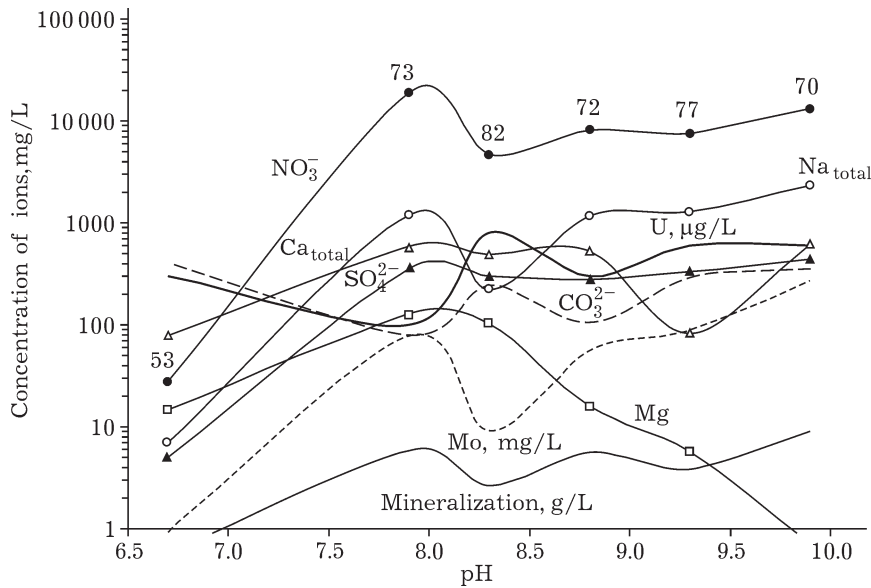


Fig. 5. Change of mineralization, anion concentration (black symbols), cations (hollow symbols) and microelements in the region of **A-B** cross section.

result of solution settling. For example, magnesium content is only 0.056 mg/L, which corresponds to the data obtained during tests in 2005, pointing to the disappearance of magnesium from the composition of drainage. The same is true for nickel; it precipitates in the form of hydroxide and its content in ground water does not exceed MPC. Sulphate sulphur, Na, Cl were not detected in the composition of model solid phases, similarly to Zn, in spite of its high concentration in solution (6 g/L). Therefore, a decrease in their concentrations, like NO_3^- , should be promoted by dilution during mixing with ground water. Uranium remains in solution in the form of $\text{UO}_2(\text{CO}_3)_3^{4-}$, other complexes do not play any part (nitrate, chloride, sulphate); the solid phase of the sludge contains, as an average, uranium up to 20 g/t (in some samples up to 200 g/t). This is evidence of the efficiency of the sued technology of neutralization of worked out sludge involving the formation of insoluble calcium uranates. At the same time, with a decrease in calculation temperature to 5 °C the species appearing in the composition of solid phases include sodium sulphate mirabilite $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, secondary calcium hydrosilicates CaH_2SiO_4 and cadmium carbonate otavite CdCO_3 (s). The model composition of solid phases differs from the

composition determined by means of X-ray phase analysis by the absence of brucite $\text{Mg}(\text{OH})_2$ (s), ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ and $\text{CaAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$ in the former, in spite of their presence in the thermodynamic database. They appear in calculations only at $\text{pH} > 10$, which may be connected either with the accuracy of thermodynamic data or with actual non-equilibrium state of the real system.

Model calculations of the component composition of the solution from hole C-5 passing through the sludge storage (see Table 1) showed that at 5 °C, $\text{pH} 9.2$, $E_h = 312$ mV and $p_{\text{CO}_2} = 10^{-3}$ atm (corresponding to the analyses of the amount of CO_3^{2-}) the solution is supersaturated with respect to the phases indicated above but to a smaller extent. Keeping in mind the goal to evaluate possible behaviour of other actinides and fission elements (products of decay) under the considered conditions we added Pu, Am, Cs into the composition of the model solution in the amount of 50 µg/L each. It turned out that americium, similarly to uranium, will be present only in solution in the form of $\text{Am}(\text{CO}_3)_3^{3-}$, cesium in the form of aquated cation Cs^+ , while plutonium may precipitate as PuO_2 (s). Plutonium differs from uranium by the ability of plutonium forms in high oxidation degrees (+5 and +6) to appear only at high

E_h (>600 mV at pH 7), while plutonium (IV), similarly to uranium, forms weak carbonate complexes. A specific feature of solutions in the holes around SRW storages (see Fig. 1) is subsaturation with respect to carbonate minerals and minimal supersaturation with respect to goethite FeOOH and kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Recalculation of the concentrations of bicarbonate ion for the partial pressure of CO_2 (g) at pH 6.3–7.6 showed increased p_{CO_2} values ($\sim 10^{-2}$ atm). Possible concentration of uranium in the solutions of these holes possessing the high potential of carbonate complex formation was estimated theoretically. It turned out that till uranophane $\text{Ca}[\text{UO}_2(\text{SiO}_3\text{OH})]_2 \cdot 5\text{H}_2\text{O}$ precipitation, that is, up to 9 mg/L, uranium can migrate in ground water in the form of carbonate complexes. An exclusion is water from hole C-1 ($E_h = 0.019$ V) where uranium is also present in the form of carbonate complexes of uranium (VI) but at the concentration of 4.38 mg/L (5°C) the solid phase uraninite UO_2 (s) might precipitate. In addition, in the water-rock system of C-1 supersaturation with respect to dolomite, metal copper and barium sulphate was stressed.

Assuming underflooding of sludge storages in the case of catastrophic rise of the level of ground water, we composed a model (Table 2) of dynamic mixing of the alkaline solution from sludge storage and neutral background water of the region (hole C-53). This model was called the model of propagation of the front of polluted water. The initial amount of uranium was accepted to be equal to MPC ($50 \mu\text{g/L}$). Calculations were carried out for 5°C in the system which was open for O_2 (g) and CO_2 (g). It should be noted that the samples of ground water from hole C-53 (see Table 1) have balanced cation-anion composition; the equilibrium is achieved after the first iteration almost in complete agree-

ment with the measured E_h and pH values. The equilibrium of water-rock system is also confirmed by the absence of supersaturation of solutions (only nano-amounts of goethite and kaolinite were marked in the solid phase). However, after mixing at the first step (see Table 2) the solutions become metastable with respect to a series of minerals (Table 3). Then at each step of dilution the number of phases decreases: for example, at the fourth step $\text{Ni}(\text{OH})_2$ (s) and $\text{Cd}(\text{CO}_3)$ disappear, at the sixth step – sulphate mirabilite, at the seventh – strontianite SrCO_3 (s), and quartz disappears at the eighth step. Excluding the last step (pure ground water), the composition of solutions is determined by the solubility of calcite and dolomite. Changes in the composition of solid phase are depicted in the component composition of solutions (Fig. 6). For example, inflection on Na_{total} and SO_4^{2-} curves clearly corresponds to the removal of mirabilite from the composition of solid phases. It follows from the data shown in Fig. 5 that the solutions of the system “discharge + ground water” become neutral as they are diluted; the cation composition Na–Ca–Mg changes for Ca–Na–Mg and Ca–Mg–Na. At the same time, sodium dominates in solutions till the ninth step, that is, pollution can migrate over large distances. For the considered elements including uranium as example, we may assume that the dilution of solutions, even by a factor of 10, will lead to the establishment of the front of usually observed concentrations. Another aspect of the problem under consideration is that an increase in water/rock ratio during underflooding of sludge storages causes additional leaching of host ground and wash-out of cations and anions sorbed on it previously (desorption). Because of this, 10-fold dilution is only approximate estimation. In order to reveal the role of sorption-desorption pro-

TABLE 2

Scheme of calculations of the dynamic mixing of solutions from slime pit of AECC and ground water of the region

Solutions	Step No.										
	0	1	2	3	4	5	6	7	8	9	10
	Fraction in solution										
From slime pit	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
Ground water (background)	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1

TABLE 3

Amount of solid phases precipitating from 1 L of model solution at the first step, mol/L

Minerals	Amount	Minerals	Amount
Fluorite CaF_2	$3.08 \cdot 10^{-3}$	SrCO_3 (s)	$3.28 \cdot 10^{-6}$
Goethite FeOOH	$1.21 \cdot 10^{-5}$	MnCO_3 (s)	$1.15 \cdot 10^{-6}$
Calcite	$4.66 \cdot 10^{-3}$	CdCO_3 (s)	$3.56 \cdot 10^{-9}$
Dolomite	$7.48 \cdot 10^{-4}$	$\text{Ni}(\text{OH})_2$ (s)	$2.68 \cdot 10^{-4}$
Quartz	$5.51 \cdot 10^{-4}$	PuO_2 (s)	$2.04 \cdot 10^{-7}$
Cuprite CuO	$2.79 \cdot 10^{-6}$	Mirabilite $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	$7.72 \cdot 10^{-2}$
		Clay minerals	$7.79 \cdot 10^{-7}$

cesses in the transformation of the composition of drainage, we carried out experimental modelling of the interaction of real ground and solutions (the results are being prepared for publication).

Let us image another situation, that is, discharge and spread of solutions containing high uranium concentrations (U stops to be conservative element and is able to form solid phases). The dependence of uranium content in solutions on E_h value is shown in Fig. 7. For convenience of discussion, the data on MPC for uranium in drinking water (0.05 mg/L) is presented there, too. The ionic force of solutions was assigned in calculations with the help of NaNO_3 ; quartz, kaolinite were present for reference in the solutions of Si and Al; alkalinity

was increased by adding $\text{Ca}(\text{OH})_2$ and /or NaOH . The addition of OH^- anions imitates the hydrolysis of aluminosilicates from host rocks under the action of the alkaline filtrates of sludge storages, proceeding with cations carry-off or re-precipitation of secondary phases. In reality, the alkalinity of the majority of ground natural water is determined by bicarbonates, so water seldom has $\text{pH} > 8.5$. The ground water at the territory under study have pH up to 9.9 (host rocks are sandstone), which points to their mixing with water arriving from sludge storages.

Calculated data (see Fig. 7) confirm that only under reducing conditions (at negative E_h) the minerals of U(IV) are able to provide its concentrations below MPC. The E_h value is to a

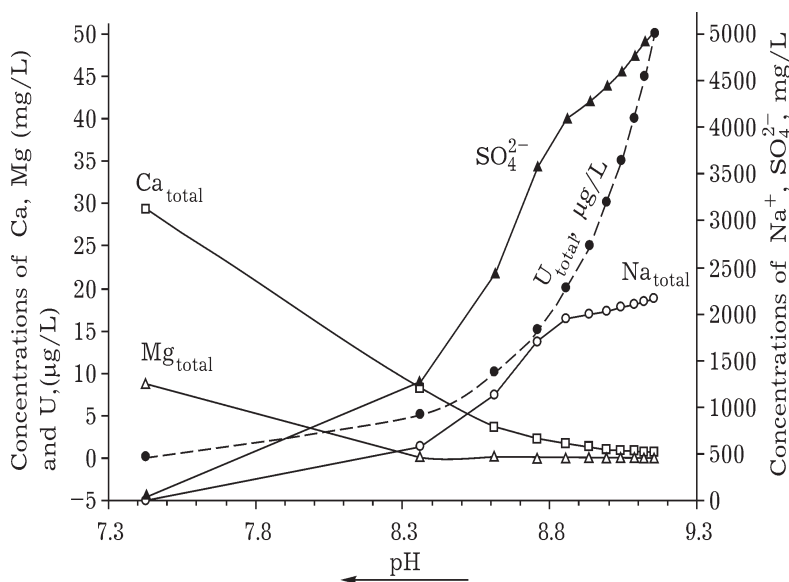


Fig. 6. Model of mixing the discharge to the basement (alkaline solutions with $\text{pH} \sim 9.5$) and neutral ($\text{pH} \sim 7.5$) ground water in the region. The direction of the arrow corresponds to the propagation of pollution front; points on the curve correspond to steps from 0 to 10.

high extent dependent on pH and p_{CO_2} . A group of black points below MPC in the left part of Fig. 7 corresponds to alkaline solutions with pH > 8. The major form of uranium migration is carbonate complex $\text{UO}_2(\text{CO}_3)_3^{4-}$. Hollow symbols mean neutral solutions (pH 6–8); calcite is absent from the associate, the major form of uranium migration is $\text{UO}_2(\text{CO}_3)_2^{2-}$ under reducing conditions, while it is $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3$ under oxidative conditions. The appearance of the latter depicts the fact that hexavalent uranium UO_2^{2+} is extremely prone to polymerization if its concentration is higher than 10^{-5} mol/L.

Oxidation causes a sharp increase in uranium concentration in solution. The bold line marks its limiting concentrations in equilibrium with calcium uranates like CaUO_4 (s) directly after neutralization, that is, before inevitable and gradual interaction between CO_2 and the solutions equilibrated with atmosphere ($p_{\text{CO}_2} = 10^{-3.5}$ atm). Then, provided that Si and Al are present (quartz, kaolinite), such phases like uranophane $\text{Ca}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2 \cdot 5\text{H}_2\text{O}$ and /or soddyite $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$, amy control the equilibrium but in this case uranium content is substantially higher than MPC. For $E_h > 0.1$ V, the concentration of uranium is only weakly dependent on the partial pressure of CO_2 and the composition of solid phases controlling it, but it depends on pH (see Fig. 7).

Thermodynamic calculations of the solubility of U(VI) minerals within a broad range of

pH and p_{CO_2} values allowed us to outline the limits of its concentration in contact with aqueous solutions. In oxidative alkaline solutions reach in carbon dioxide this is several tens g/L, while in neutral solutions at atmospheric p_{CO_2} it is several ten mg/L. Not only reducing but also weakly acidic solutions promoting decomposition of carbonate complexes and stability of uranium (hydr)oxides will provide minimal mobilization of uranium from stored sludge. In this case the results of modelling are just estimates and do not take into account the development of other processes leading to a decrease in the concentration of uranium, in particular dilution, precipitation on geochemical barriers etc. For example, sludgy fraction present in sands is able to precipitate up to 6 g/t of uranium (while the background concentration of this element in sand is about 0.5 g/t) (see Fig. 1, hole 6). After termination of the discharge of highly mineralized solutions into sludge storages, water geochemistry at the territory under consideration will change substantially, in particular, the absence of high concentrations of nitrate ions will shift redox potential into the reducing region.

SUMMARY

1. The chemical composition of ground water in the region of storage of low-activity wastes from AECC – one of the centres of

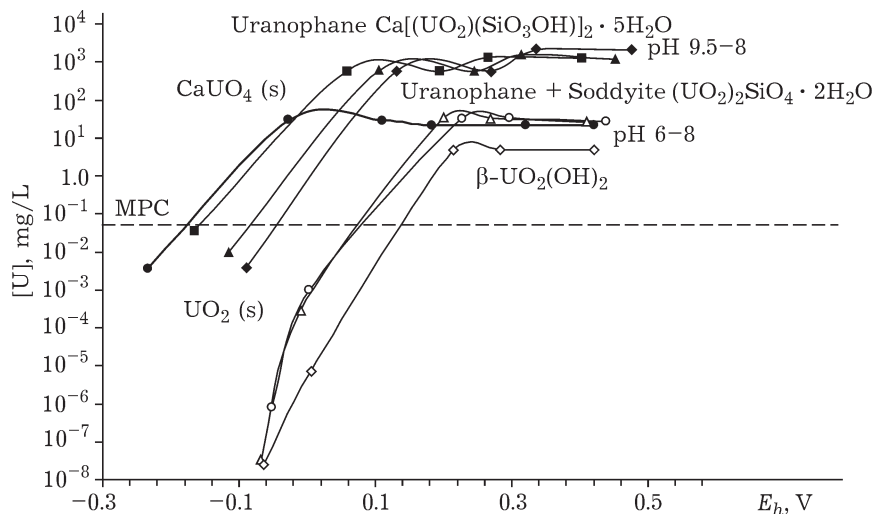


Fig. 7. Dependence of total uranium concentration in solutions on oxidation-reduction conditions at 5 °C and variable pH and p_{CO_2} . Uranium concentration in each point corresponds to the equilibrium with the indicated solid phase.

the production of enriched uranium – was studied. It was shown that U content in them is much lower than the MPC level for drinking water. Under the formed geochemical conditions, uranium transport with ground water out from the sludge field is at a level of background concentrations characteristic of the given climatic zone.

2. Nevertheless, it was established that the spread of the hydrogeochemical cupola and penetration of alkaline nitrate solutions into the underground horizons occur around sludge storages. According to calculations, redox conditions in them are controlled by the oxidation-reduction pair $\text{NO}_3^-/\text{NO}_2^-$, especially during spring floodwater when nitrate content increases sharply. These oxidative conditions promote migration of U(V) in the form of carbonate complexes.

3. Ground water around the reinforced concrete storages of solid wastes are distinguished by low mineralization and neutral pH.

4. Determination of the composition of ground water by means of ICP-MS allowed us to reveal microelements that correlate with nitrates which are responsible for mineralization in solution. It is assumed that Mo, V, Zr, prone to migration under natural conditions, are able to serve as the markers of expansion of the technogenic pollution of definite type.

5. Modelling of the composition of solid phases able to precipitate from supersaturated solutions confirms the data of mineralogical analysis: these are CaF_2 , SiO_2 , various carbonates, oxides and hydroxides. No solid phases of uranium were detected, except in one possible case. This circumstance proves the possibility to dissolve calcium uranates formed in the precipitate through the interaction with CO_2 (solution)

from the atmosphere and ground water. The necessity to withdraw these deposits from the zone of active water exchange after termination of sludge storage functioning was substantiated.

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