

Experimental Investigation and Thermodynamic Modelling of Supergene Processes in the Tailings of Apatite-Nepheline Ores

S. I. MAZUKHINA¹, A. A. NESTEROVA², D. P. NESTEROV², D. V. MAKAROV² and V. A. MASLOBOEV¹

¹*Institute of North Industrial Ecology, Kola Science Centre of the Russian Academy of Sciences, Ul. Fersmana 14A, Apatity 184209 (Russia)*

²*Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials, Kola Science Centre of the Russian Academy of Sciences, Ul. Fersmana 26A, Apatity 184209 (Russia)*

E-mail: makarovdv@chemy.kolasc.net.ru

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Abstract

Supergene processes in the tailings of apatite-nepheline ores have been studied by techniques of physical chemical analysis and thermodynamic modelling. It has been found that under washing conditions characteristic of Kola Peninsula, the finest and lightest particles and the products of hypergenesis are removed by suffosion. Newly formed phases are represented with micas (lepidomelane and giaseckite), amorphous silica, oxides of titanium, manganese, and goethite.

INTRODUCTION

During 75 years of operation of Apatit JSC many of its tailing dumps have accumulated vast amounts of so-called tailings – the minerals remaining after separation of apatite and, partly, nepheline from apatite-nepheline ores. At the present time the tailing dumps can be considered as technogenic deposits: the tailings contain not only residual apatite, but also are a promising source of aluminous material usable for production of aluminium, potash and soda. The tailings are sands with the sizes of mineral particles 0.01–0.5 mm.

Examination of the literature concerning the problem of transformation of minerals of nepheline-containing products revealed their contradictory nature. Thus, according to the author of [1], who investigated mineral and chemical composition of three local specimens of old tailings having different ages, no evolution was observed in the composition of nepheline and apatite within accuracy of routine chemical analysis on prolonged storage of

the tailings. Variation of some physical properties cannot be excluded, in particular, of the surface of nepheline grains. On the opinion of the author of [1], these changes are not a decisive factor excluding reprocessing of tailings and production of nepheline and apatite concentrates. At the same time, it is known that nepheline-containing sands contain 60 % of minerals non-resistant to supergene conditions – nepheline, natrolite, apatite, *etc.* Nepheline is easily broken with mineral and organic acids as well as alkalis [2]. Milling prior to dressing causes essential activation of minerals, what should influence their physicochemical behaviour on storage.

Modelling of erosion of the tailing minerals under the impact of precipitates and wastewaters was carried out in Ref. [3]. It was demonstrated that polymineral tailings deteriorate under the action of brackish waters, including precipitates and ground waters. The reaction products are amorphous compounds comprising hydrated oxides of silicon and aluminium, as well as scarcely soluble fluoroaluminate, alu-

mo- and silicophosphate salts of alkali and alkaline earth metals. Supergene processes are accompanied by the increase in specific surface of tailings, and the density of developed phases is substantially smaller than that of the starting minerals. It promotes high mobility of newly formed phases in existing geosystems and creates fluxes spreading toxic elements [3].

The author of [4], who examined the stability of natural rock material under laboratory conditions and in natural environment (external wall cladding, concrete fillers), came to the conclusion that already after 10–20 years a polished surface of nepheline exhibits observable changes. The process of nepheline transformation, in particular, spreustein formation, also occurs in nature. Spreusteins are common in apatite-nepheline ores and enclosing rocks of the Khibiny Massif [5, 6], and are secondary products developing as small aggregates at diverse feldspathoids, first of all, at nepheline.

Because of the inconsistency of the available information, the determination of the composition of newly developed solid phases and interstitial waters of tailings is of current interest. The revealed laws of physical chemical process occurring on storage of nepheline-containing products may provide a scientific basis for estimating processing characteristics of recoverable materials after prolonged storage and the environmental impact of these products. The results may also appear useful for development of general theory of supergene processes.

EXPERIMENTAL

An out-of-service tailing dump ANOF-2 was chosen for investigation. The location of the object and sampling scheme are shown in Fig. 1.

More than 50 samples were taken within the tailing dump. Chemical composition of the samples and interstitial waters was examined, and pH measured. Besides, a 2.5 m deep pit-hole was made.

X-ray diffraction (XRD) phase identification of solid phases was carried out on a DRON-2 diffractometer, $\text{CuK}\alpha$ radiation. Thermogravimetric studies were made on a Q-1500D derivatograph. IR spectroscopy measurements were performed on an UR-20 device in wave number range $400\text{--}1600\text{ cm}^{-1}$.

Metal concentrations were determined using Perkin-Elmer 5000 atomic absorption spectrophotometer equipped with graphite atomizer and AAS-30 Carl Zeiss Iena with flame atomisation.

Thermodynamic modelling was carried out with Selektor programme package (PP) [7, 8]. The earlier model [9, 10] has been improved. Independent components: Al–Ar–C–Ca–Cl–F–Fe–K–Mg–Mn–N–Na–Ne–P–S–Si–Ti–Sr–H–O– \bar{e} (\bar{e} is electron); total number of compounds – 268, total number of phases – 131, number of components in water – 101. The list of solid phases of the multisystem was made with

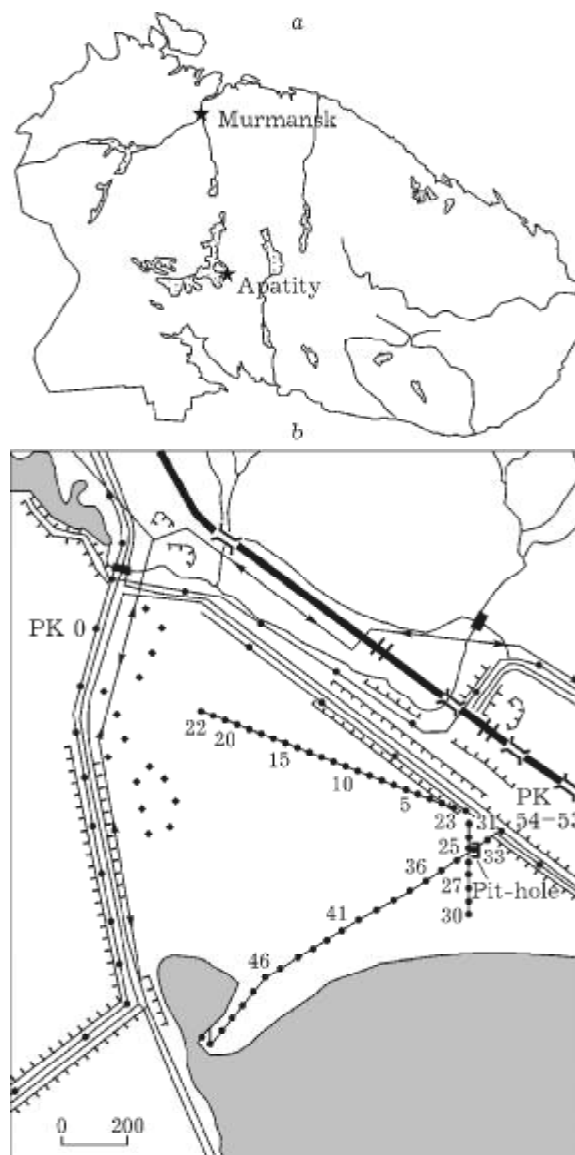


Fig. 1. Location of the object of investigation (a) and the plan of the tailing dump (b). Numbers denote the places of sampling.

account to the mineral composition of the Khibiny Massif and the tailing dump.

With the aid of the developed basic multi-system and Selektor PP the interaction in the system solution–rock–atmosphere was modelled. Solution in this context means the interaction of precipitation waters with the solids of the tailing dump.

Physicochemical modelling was carried out for:

1. Chemical equilibrium of the interaction of the rock and the solution depending on the extent of interaction of the rock and water ξ ($P = 1$ bar, $T = 25$ °C), which made possible elucidation of main features characterizing the solution composition.

2. Interactions of waters with the strata of the tailing dump (reservoirs) for investigation of the spatial and temporal characteristics of solid phase formation by means of reservoir dynamics. In the frame of the model, stored tailings characterized by different degree of compaction, water and gas content, were differentiated as interacting systems (reservoirs), connected by mass transfers.

On description of hydrochemical processes the rates of introduction or removal of the components were taken into account. Therefore, the mass balance of the system “rock + 1 kg of water” included not the entire mass of the rock but its “soluble” fraction [11]. In our case, at the first step the interaction in the solution–rock system was dependent on the extent of interaction ξ . For 1000 kg of the solution there was introduced $98.49 \cdot 10^{-\xi}$ of the rock (*i.e.*, the soluble fraction), $\xi \in (2 < 1.2)$.

Simulation in approximation of 4-reservoir dynamics was carried out admitting that extent of interaction diminishes with infiltration of the solution, and all reservoirs contain 98.49 g of the rock subjected to infiltration (1000 kg). The extent of interaction in each of the reservoirs was taken equal to 2, 1.95, 1.9 and 1.85, respectively. The last reservoir is the accumulator collecting new developed phases. Reproducibility of this event followed with increasing interaction extent $\Delta\xi = 0.01$ at each step enables to examine the process of dissolution (erosion) of the tailing dump in space and time. Here, the solution resulting from the interaction tailing dump–precipitation water is the

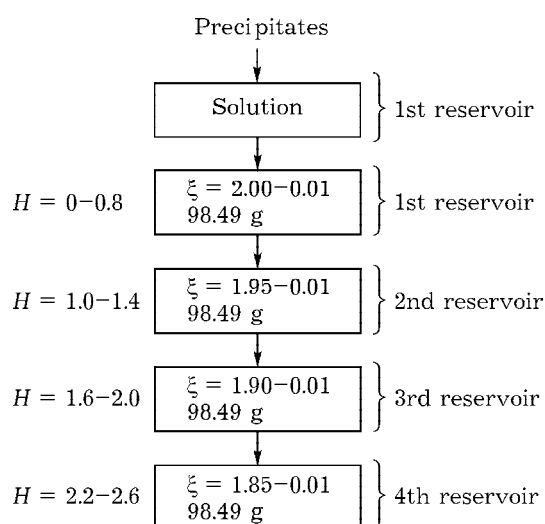


Fig. 2. Block diagram of the reservoir model. Arrows indicate the movement of the solution and newly formed phases.

governing parameter. Block scheme of the model is shown in Fig. 2.

RESULTS AND DISCUSSION

The tailings have the following chemical composition, mass %: SiO_2 41.53, TiO_2 4.97, Al_2O_3 20.04, Fe_2O_3 5.31, FeO 2.73, MnO 0.2, MgO 1.08, CaO 5.92, Na_2O 8.69, K_2O 4.94, P_2O_5 1.27, H_2O 1.81 ($\Sigma = 98.49$).

According to XRD, the tailings contain nepheline and minor amounts of natrolite (Fig. 3).

Mineralogical and granulometric analysis of the samples taken from the surface of the tailing dump indicated that the finest and lightest material is removed with the products of sili-

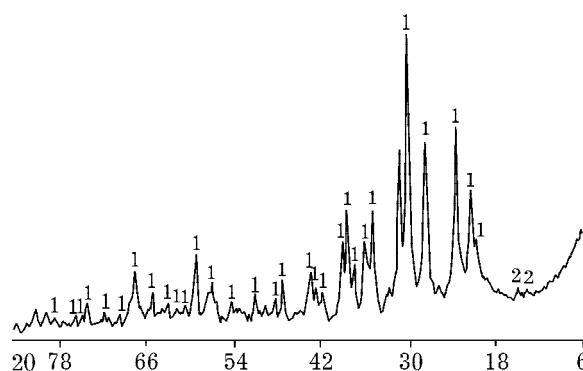


Fig. 3. Powder diffraction pattern of a tailing specimen. Numbers mark the reflections of nepheline (1) and natrolite (2).

cate hydrolysis due to suffosion. As a consequence, the most dense and persistent to supergene transformations minerals are accumulated in the fine class – titanomagnetite, ilmenite, and aegirine. In the coarse class there is observed partial substitution of nepheline with the products of their supergene transformations.

Tailing specimens from the pit-hole are different from the surface samples in increased content of ultra-fine fractions (particle size below 10 μm) and growing specific surface of the particles with increasing depth of sampling. Apparently, these features are related not only to suffosion but also to supergene processes.

XRD examination of fine fractions revealed that generally they are amorphous due to development of silica (opal or chalcedony) originating from weathering of silicates (Fig. 4). Underlain by halo, there are observed poorly defined reflections of nepheline, apatite and

micas (most probably, lepidomelane and gieseckite). As noted by the authors of [5], transformation of nepheline to gieseckite takes place in nature in weathering crusts.

IR spectrum of a sample of the fine fractions is shown in Fig. 5. Apatite is characterized with P–O vibrations of the tetrahedral anion PO_4^{3-} manifested as absorption bands at 585, 605–620 and 1000–1100 cm^{-1} [12]. Nepheline is revealed with absorption bands at 480–490, 507, 698, 1000–1100 cm^{-1} [13]. Micas and hydromicas have a large number of characteristic bands. Complicated composition of the sample causes overlap of bands within range 400–1100 cm^{-1} . The presence of micas is positively proved by a wide absorption band at 3500–3700 cm^{-1} corresponding to stretching vibrations of OH groups present in their structure [14].

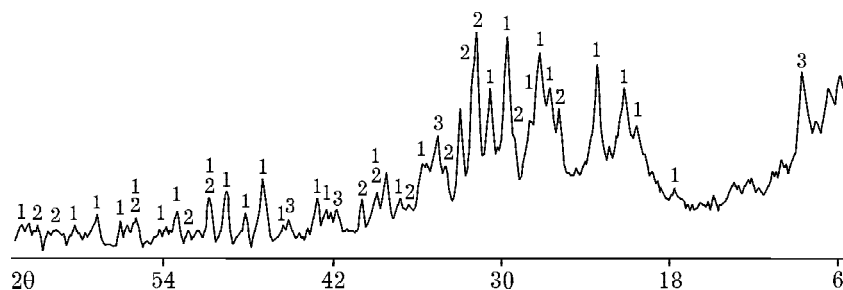


Fig. 4. Typical diffraction pattern of the fine-grain fraction of the tailings. Numbers mark the reflections of nepheline (1) and natrolite (2), micas (lepidomelane, libenerite) (3).

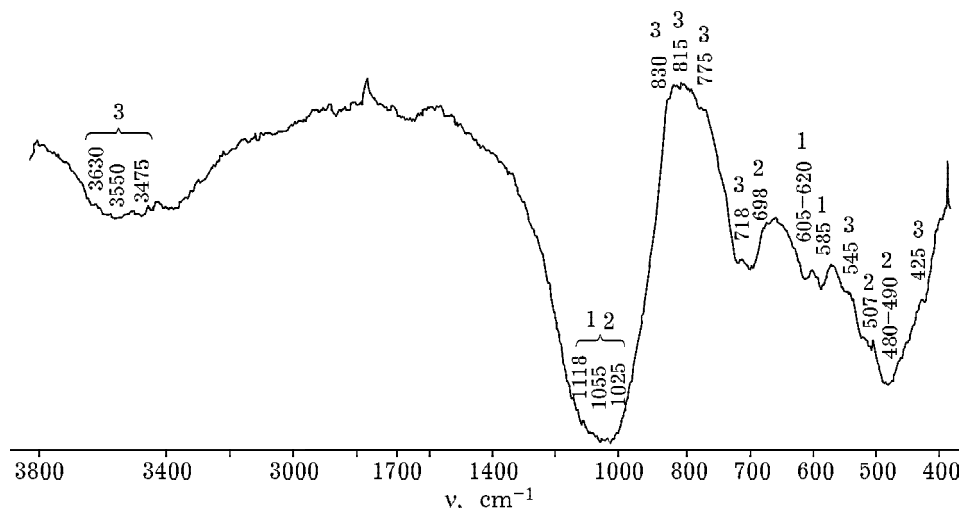


Fig. 5. IR spectrum of the fine-grain fraction of the tailings. Numbers denote bands characteristic of nepheline (1), apatite (2), and micas (3).

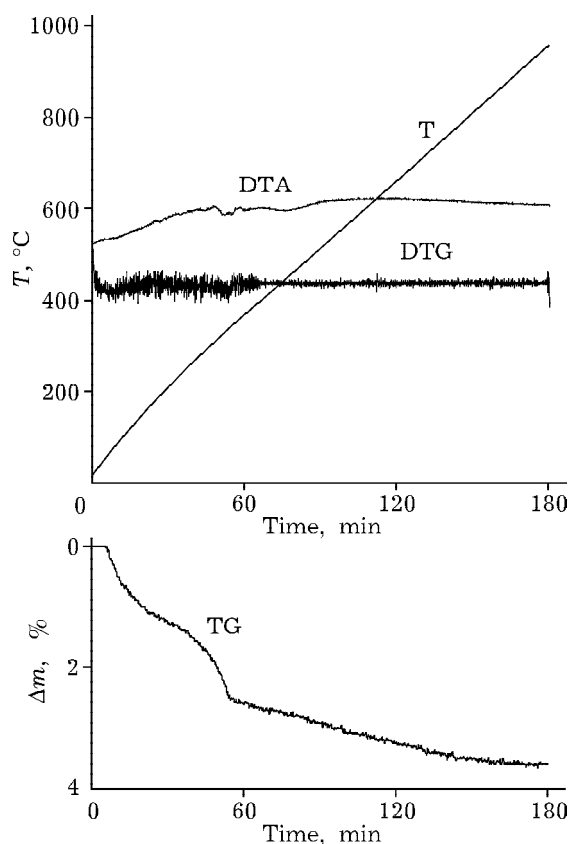


Fig. 6. DTA, TG and DTG curves of the fine-grain fraction of the tailings. Sample mass: 250 mg, heating rate: 25 °C/min.

DTA, TG and DTG curves of a fine fraction sample are shown in Fig. 6. According to thermogravimetry, the content of micas in the sample is *ca.* 42–55 %.

Table 1 reports chemical composition of interstitial waters of the samples of tailings of apatite-nepheline ores taken at different depths. It variation also indicates pronounced zonality. A significant increase in concentrations of Al, Fe, Sr, PO₄ is observed, caused, most likely, by their transportation to deeper horizons by infiltrated solutions, thus suggesting the employment of the reservoir model for simulation of the process [8].

Let us consider the equilibrium in the solution-rock-atmosphere system. Table 2 gives the averaged chemical analysis data of interstitial waters from tailing samples taken from the surface, and the data of the thermodynamic calculations. Good concordance of the results is evident. The computer variant of the ionic composition of the interstitial waters and novel phases is shown in Table 3 in dependence on the extent of interaction ξ . As one can see, developed minerals are represented with micas, manganese oxide and goethite. With increasing extent of interaction, apatite also appears. The ionic

TABLE 1

Parameters of chemical composition of interstitial waters of the tailings of apatite-nepheline ores *vs.* sampling depth (*H*)

<i>H</i> , m	pH	Content, mg/L													
		NH ₄	Ca	Mg	Na	K	HCO ₃	SO ₄	NO ₃	Cl	PO ₄	Si	Al	Fe	Sr
0.2	7.16	<0.05·10 ⁻²	1.46	0.32	10.4	10.0	8.9	22.6	0.9·10 ⁻²	2.57	0.8·10 ⁻²	2.72	74·10 ⁻²	3.7·10 ⁻²	2.4·10 ⁻²
0.4	7.20	0.1·10 ⁻²	0.88	0.27	9.2	8.6	13.9	13.9	1.5·10 ⁻²	1.86	66·10 ⁻²	2.97	12.6·10 ⁻²	6.4·10 ⁻²	1.9·10 ⁻²
0.6	6.94	0.1·10 ⁻²	1.00	0.32	8.3	9.1	11.6	10.4	0.7·10 ⁻²	2.23	34·10 ⁻²	3.34	11.7·10 ⁻²	5.1·10 ⁻²	1.7·10 ⁻²
0.8	7.21	0.1·10 ⁻²	1.04	0.27	7.7	9.1	13.5	11.6	0.8·10 ⁻²	2.29	30·10 ⁻²	3.26	12.0·10 ⁻²	5.8·10 ⁻²	1.9·10 ⁻²
1.0	7.45	0.1·10 ⁻²	1.19	0.27	11.5	10.0	18.9	16.0	0.9·10 ⁻²	2.05	11.3·10 ⁻²	2.98	17.6·10 ⁻²	10.4·10 ⁻²	2.9·10 ⁻²
1.2	7.65	0.2·10 ⁻²	1.54	0.32	12.7	11.8	26.8	13.9	1.1·10 ⁻²	2.23	10.1·10 ⁻²	3.1	17.9·10 ⁻²	9.8·10 ⁻²	3.8·10 ⁻²
1.4	7.32	0	0.77	0.59	7.7	9.1	15.4	7.9	1.4·10 ⁻²	1.61	8.7·10 ⁻²	2.25	6.1·10 ⁻²	2.2·10 ⁻²	1.3·10 ⁻²
1.6	7.52	0.2·10 ⁻²	1.00	0.23	15.0	10.5	22.6	18.2	0.2·10 ⁻²	1.98	3.6·10 ⁻²	2.39	13.3·10 ⁻²	3.5·10 ⁻²	1.6·10 ⁻²
1.8	7.44	0.1·10 ⁻²	0.77	0.23	13.5	10.5	22.1	17.2	0.5·10 ⁻²	2.17	6.5·10 ⁻²	2.24	10.4·10 ⁻²	5.8·10 ⁻²	1.7·10 ⁻²
2.0	7.56	0.8·10 ⁻²	1.12	0.27	14.6	10.0	21.1	19.8	0.6·10 ⁻²	2.54	14.7·10 ⁻²	2.56	4.7·10 ⁻²	3.6·10 ⁻²	3.9·10 ⁻²
2.2	7.70	0.7·10 ⁻²	0.77	0.18	18.5	10.5	27.9	19.8	0.6·10 ⁻²	3.35	10.5·10 ⁻²	3.17	4.0·10 ⁻²	3.0·10 ⁻²	3.6·10 ⁻²
2.4	7.58	1.2·10 ⁻²	1.31	0.23	15.8	10.9	24.9	18.5	0.5·10 ⁻²	2.6	6.8·10 ⁻²	2.98	4.7·10 ⁻²	4.6·10 ⁻²	5.4·10 ⁻²
2.6	7.22	1.3·10 ⁻²	1.73	0.68	16.9	10.0	19.0	20.2	0.3·10 ⁻²	4.32	5.5·10 ⁻²	3.38	6.9·10 ⁻²	42.4·10 ⁻²	6.6·10 ⁻²

TABLE 2

Chemical composition of interstitial waters of the tailings at 25 °C and its computer simulation

Component	Content, mg/L		Component	Content, mg/L	
	Experimental	Calculation		Experimental	Calculation
Ar*		0.51	Na ⁺	10.4	10.40
AlO ₂ ⁻		0.08	NaCl		0.0003
HALO ₂	0.074	0.014	NaHSiO ₃		0.0003
Al(OH) ₂ ⁺		0.0007	NO ₃ ⁻	0.009	0.008
Al(OH) ₃		0.014	CO ₂		1.68
Al(OH) ₄ ⁻		0.096	CO ₃ ²⁻		0.01
CaCO ₃		0.001	N ₂		14.36
Ca(HCO ₃) ⁺		0.009	Ne		0.0002
Ca ²⁺	1.46	1.42	O ₂		8.18
CaSO ₄		0.11	H ₂ PO ₄ ⁻	0.008	0.004
Cl ⁻	2.57	2.57	HPO ₄ ²⁻		0.004
Fe(OH) ₄ ⁻		0.006	HSiO ₃ ⁻		0.013
Fe(OH) ₂ ⁺	0.037	0.0067	SO ₄ ²⁻	22.6	22.49
Fe(OH) ₃		0.058	SiO ₂	2.72	5.81
K ⁺	10	9.98	Sr ²⁺		0.024
KSO ₄ ⁻		0.053	HCO ₃ ⁻	8.9	15.97
MgCO ₃		0.0002	E _h , V		0.794
Mg(HCO ₃) ⁺		0.0028	pH	7.16	7.16
Mg ²⁺		0.32			

composition of the solution does not show essential alteration, little growth of pH is observed.

The results of thermodynamic simulation with the 4-reservoir model are listed in Table 4. Newly formed phases (excluding hydroxyapatite Ca₅(PO₄)₃OH) occur in all four layers. The most pronounced content increase on transition from the first reservoir to the fourth one is typically observed for amorphous silica and titanium

oxide, somewhat smaller – for micas and goethite. Apatite is observed in the fourth reservoir.

Table 5 presents temporal evolution of the composition of solid phases and solutions in the reservoirs. Examination of the data reveals pronounced zonality. The amount of newly formed minerals increases in the fourth reservoir, indicating supersaturation of the interstitial waters. The evolution of pH in time in different

TABLE 3

Computer model of ionic composition of interstitial waters and newly formed phases resulting from the interaction rock-solution-atmosphere ($T = 25$ °C, $P = 1$ bar) vs. extent of interaction ξ

ξ	Content, mg/L										pH	Amount, mol			
	Ca ²⁺	Cl ⁻	K ⁺	Mg ²⁺	Na ⁺	SO ₄ ²⁻	SiO ₂	HCO ₃ ⁻	H ₂ PO ₄ ⁻	HPO ₄ ²⁻		Apatite	Goethite	MnO ₂	Mica
2	1.46	2.57	9.94	0.33	10.57	22.5	5.82	16.61	0.0116	0.0138	7.23	0	0.0017	3 · 10 ⁻⁵	0.0022
1.8	1.49	2.57	9.94	0.33	10.67	22.5	5.92	16.94	0.0152	0.0202	7.28	0	0.0023	5 · 10 ⁻⁵	0.003
1.6	1.53	2.57	9.92	0.34	10.83	22.5	6.08	17.47	0.0198	0.0317	7.36	0	0.0032	7 · 10 ⁻⁵	0.0042
1.4	1.56	2.57	9.91	0.34	11.088	22.5	6.34	18.26	0.0135	0.0303	7.51	0.0001	0.0047	0.0001	0.0062
1.2	1.61	2.57	9.88	0.36	11.492	22.5	6.71	19.38	0.0022	0.0105	7.84	0.0004	0.0069	0.0002	0.0093

Note. Mica consists of minerals KAl₂(OH)₂AlSi₃O₁₀, NaAl₂(OH)₂AlSi₃O₁₀, KFe₃(OH)₂AlSi₃O₁₀ for convenience combined in one phase.

TABLE 4

Computer simulation of ionic composition of interstitial waters and newly formed phases for the 4-reservoir model of the tailing dump ($T = 10\text{ }^{\circ}\text{C}$)

Component	Reservoirs				Component	Reservoirs			
	1	2	3	4		1	2	3	4
<i>Content in solution, mg/L</i>									
Ar	0.67	0.67	0.67	0.67	Ne	0.0002	0.0002	0.0002	0.0002
Ca(CO ₃)	0.0008	0.0012	0.0022	0.0054	O ₂	10.93	10.91	10.90	10.87
Ca(HCO ₃) ⁺	0.01	0.0106	0.0114	0.0119	H ₂ PO ₄ ⁻	0.012	0.017	0.018	0.002
Ca ²⁺	1.47	1.51	1.56	1.57	HPO ₄ ²⁻	0.013	0.027	0.048	0.016
CaSO ₄	0.10	0.11	0.11	0.11	HSiO ₃ ⁻	0.0088	0.0123	0.0209	0.0506
Cl ⁻	2.57	2.57	2.57	2.57	NO ₂ ⁻	0.0001	0.0001	0.0002	0.0004
K ⁺	9.94	9.93	9.91	9.90	SO ₄ ²⁻	22.49	22.49	22.49	22.49
KSO ₄ ⁻	0.052	0.051	0.051	0.051	SiO ₂	5.35	5.35	5.35	5.35
MgCO ₃	0.0001	0.0002	0.0003	0.0009	Sr ²⁺	0.024	0.024	0.024	0.024
Mg(HCO ₃) ⁺	0.003	0.003	0.003	0.004	HCO ₃ ⁻	16.63	17.27	17.96	18.56
Mg ²⁺	0.33	0.33	0.34	0.35	E _h	0.81	0.80	0.79	0.77
Na ⁺	10.57	10.77	10.98	11.23	pH	7.27	7.41	7.64	0.77
NaCl	0.0003	0.0003	0.0003	0.0003	<i>Content in newly formed phases, mol/L</i>				
NaHSiO ₃	0.0003	0.0004	0.0007	0.0018	Muscovite	2.22 · 10 ⁻³	3.69 · 10 ⁻³	5.34 · 10 ⁻³	7.19 · 10 ⁻³
NO ₃ ⁻	0.0093	0.0131	0.0221	0.0534	Rutile	3.89 · 10 ⁻⁴	8.26 · 10 ⁻⁴	1.32 · 10 ⁻³	1.86 · 10 ⁻³
CO ₂	1.78	1.31	0.81	0.34	Goethite	1.71 · 10 ⁻³	2.88 · 10 ⁻³	4.20 · 10 ⁻³	5.67 · 10 ⁻³
CO ₃ ²⁻	0.011	0.016	0.028	0.071	Chalcedony	8.00 · 10 ⁻³	1.13 · 10 ⁻²	1.49 · 10 ⁻²	1.88 · 10 ⁻²
N ₂	18.61	18.58	18.56	18.56	Pyrolusite	2.82 · 10 ⁻⁵	5.98 · 10 ⁻⁵	9.53 · 10 ⁻⁵	1.35 · 10 ⁻⁴
					Apatite:				
					Ca ₃ (PO ₄) ₂				
					Ca ₅ (PO ₄) ₃ OH				

Note. Muscovite – KAl₂(OH)₂AlSi₃O₁₀ · 4.5(H₂O); rutile – TiO₂; goethite – FeO(OH); chalcedony – SiO₂; pyrolusite – MnO₂.

strata is illustrated in Fig. 7. As one can see, the decrease in pH with time is characteristic of all the strata, but it is most expressed on transition from the first reservoir to the fourth one.

According to the modelling, micas dominate in the fourth reservoir (67 % of all newly developed mineral phases). The content of amorphous silica is 26 %, goethite – 5 %.

CONCLUSIONS

The tailings of apatite-nepheline ores has been shown to undergo changes on storage: the finest and lightest particles and supergene products are transferred downwards by suffosion processes. Wind weathering is of importance in upper horizons. The analysis of interstitial waters has revealed that they are enriched with

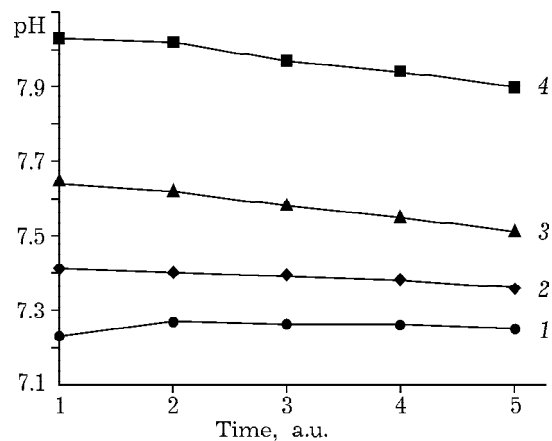


Fig. 7. Evolution of pH of interstitial waters with time: 1-4 – reservoirs 1-4, respectively.

TABLE 5
Computer simulation of temporal evolution of newly formed phases and ionic composition of solutions in the 4-reservoir model of the tailing dump

Time, a. u.	Amount, mol										Content, mg/L					pH
	Muscovite	Apatite	TiO ₂	FeOOH	SiO ₂	MnO ₂	Mica	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	HCO ₃ ⁻				
1	2.22 · 10 ⁻³	0	3.00 · 10 ⁻⁴	0.0017	7.9 · 10 ⁻³	2.8 · 10 ⁻⁵	0	1.47	9.93	0.32	10.57	16.63	7.23			
2	2.22 · 10 ⁻³	0	2.96 · 10 ⁻⁴	0.0015	8.17 · 10 ⁻³	0	0	1.46	9.93	0.32	10.57	16.62	7.27			
3	0	0	1.95 · 10 ⁻⁴	0.0010	8.24 · 10 ⁻³	0	2.18 · 10 ⁻³	1.46	9.93	0.32	10.57	16.58	7.2			
4	0	0	8.8 · 10 ⁻⁵	0.0007	8.44 · 10 ⁻³	0	2.13 · 10 ⁻³	1.46	9.92	0.32	10.57	16.55	7.26			
5	0	0	0	0.0006	8.63 · 10 ⁻³	0	2.08 · 10 ⁻³	1.45	9.91	0.32	10.57	16.52	7.25			
<i>1st reservoir</i>																
1	3.70 · 10 ⁻³	0	8.26 · 10 ⁻⁴	0.0029	0.011	6 · 10 ⁻⁵	0	1.51	9.93	0.33	10.77	17.27	7.41			
2	3.6 · 10 ⁻³	0	6.14 · 10 ⁻⁴	0.0022	0.012	0	0	1.51	9.92	0.33	10.76	17.24	7.40			
3	3.5 · 10 ⁻³	0	3.86 · 10 ⁻⁴	0.0015	0.012	0	0	1.50	9.90	0.32	10.76	17.16	7.39			
4	3.40 · 10 ⁻³	0	1.41 · 10 ⁻⁴	0.0008	0.013	0	0	1.49	9.89	0.32	10.76	17.09	7.38			
5	3.28 · 10 ⁻³	0	0	0.0007	0.013	0	0	1.48	9.87	0.32	10.75	17.03	7.36			
<i>2nd reservoir</i>																
<i>3rd reservoir</i>																
1	5.34 · 10 ⁻³	0	1.32 · 10 ⁻³	4.20 · 10 ⁻³	0.015	9.5 · 10 ⁻⁵	0	1.57	9.91	0.34	10.98	17.96	7.64			
2	5.19 · 10 ⁻³	0	9.53 · 10 ⁻⁴	3.10 · 10 ⁻³	0.016	0	0	1.56	9.89	0.33	10.98	17.90	7.62			
3	5.01 · 10 ⁻³	0	5.63 · 10 ⁻⁴	1.92 · 10 ⁻³	0.016	0	0	1.54	9.87	0.32	10.97	17.77	7.58			
4	4.82 · 10 ⁻³	0	1.45 · 10 ⁻⁴	8.38 · 10 ⁻⁴	0.017	0	0	1.53	9.85	0.32	10.97	17.66	7.55			
5	4.61 · 10 ⁻³	0	0	6.63 · 10 ⁻⁴	0.018	0	0	1.51	9.82	0.32	10.96	17.56	7.51			
<i>4th reservoir</i>																
1	7.20 · 10 ⁻³	2.51 · 10 ⁻⁴	1.87 · 10 ⁻³	5.67 · 10 ⁻³	0.019	1.35 · 10 ⁻⁴	0	1.57	9.90	0.35	11.23	18.55	8.03			
2	0.014	2.17 · 10 ⁻⁴	3.18 · 10 ⁻³	9.67 · 10 ⁻³	0.038	1.35 · 10 ⁻⁴	0	1.59	9.88	0.34	11.23	18.55	8.02			
3	0.021	1.55 · 10 ⁻⁴	3.89 · 10 ⁻³	0.012	0.059	1.35 · 10 ⁻⁴	0	1.59	9.87	0.34	11.22	18.50	7.97			
4	0.027	6.4 · 10 ⁻³	4.04 · 10 ⁻³	0.013	0.081	1.35 · 10 ⁻⁴	0	1.59	9.85	0.33	11.22	18.44	7.94			
5	0.033	0	4.04 · 10 ⁻³	0.013	0.104	1.35 · 10 ⁻⁴	0	1.59	9.83	0.33	11.21	18.38	7.90			

strontium and aluminium highly dangerous for aquatic ecosystems.

Experimental data and results of thermodynamic modelling give evidence that newly formed phases are represented with micas (lepidomelane and gieseckite), amorphous silica, titania, manganese oxide, and goethite. These processes also take place on formation of residuals in nature [5, 6], but they are much more intensive in tailings because of activation of the surface of minerals during milling and dressing.

Further detailed mineralogical investigation of samples is necessary, preceded by classification by grain size, with individual examination of each class. It will improve the model of the tailing dump.

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REFERENCES

- 1 K. I. Polyakov, *Geologiya i mineralogiya mestorozhdeniy apatita Kolskogo poluostrova*, Apatity, 1987.
- 2 V. T. Kalinnikov, A. I. Nikolaev, V. I. Zakharov, *Gidrometallurgicheskaya kompleksnaya pererabotka netraditsionnogo titano-redkometalnogo i alyumosilikatnogo syr'ya*, Apatity, 1999.
- 3 T. I. Priymak, A. P. Zosin, Yu. V. Fedorenko *et al.*, *Ekologicheskiye aspekty protsessov geokhimicheskoy transformatsii khvostov obogashcheniya apatito-nefelinovykh rud Khibinskogo mestorozhdeniya*, Apatity, 1998.
- 4 V. V. Lashchuk, *Dolgovechnost' oblitsovochnogo kamnya Kolskogo poluostrova*, Apatity, 1996.
- 5 T. N. Ivanova, O. B. Dudkin, L. V. Kozyreva, K. I. Polyakov, *Iyolit-urtity Khibinskogo massiva*, Nauka, Leningrad, 1970.
- 6 O. B. Dudkin, L. V. Kozyreva, N. G. Pomerantseva, *Mineralogiya apatitovykh mestorozhdeniy Khibinskikh tundr*, Nauka, Leningrad, 1964.
- 7 I. K. Karpov, *Fiziko-khimicheskoye modelirovaniye na EVM v geokhimii*, Nauka, Novosibirsk, 1981.
- 8 K. V. Chudnenko, I. K. Karpov, S. I. Mazukhina, *Geol. Geofiz.*, 40 (1999) 45.
- 9 O. B. Dudkin, S. I. Mazukhina, *Obogashch. Rud*, 4 (2001) 36.
- 10 S. I. Mazukhina, S. S. Sandimirov, *Primeneniye fiziko-khimicheskogo modelirovaniya dlya resheniya ekologicheskikh zadach Kolskogo Severa*, Apatity, 2005.
- 11 B. N. Ryzhenko, S. G. Kraynov, Yu. V. Shvarov, *Geokhim.*, 41 (2003) 630.
- 12 I. I. Plyusnina, *Infrakrasnye spektry mineralov*, Izd-vo MGU, Moscow, 1976.
- 13 V. C. Farmer, *The Infra-Red Spectra of Minerals*, Mineralogical Society, London, 1974, 540 p.
- 14 *Mineraly*, vol. 4, issue 1, Nauka, Moscow.