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Experimental study of cesium sedimentation from multicomponent water solutions using sodium and ammonium tetraflouroborates at room temperature

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^{137}Cs is one of the most dangerous and, at the same time, valuable isotope of radiochemical manufacture at processing of spent nuclear fuel. Owing to low concentration of cesium in solutions, its separation usually make by an extraction method. However in certain cases, for the concentrated solutions more simple and low cost method of sedimentation can be used. We investigated ces ium sedimentation from nitrate and alkali-carbonate multicomponent (Na, Mg, Al, K, Ca, Sc, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Y, Zr, Nb, Mo, Pd, Ag, Cd, Sn, Cs, La, Ce, Nd, Eu, Gd, Ho, Yb, Hf, W, Hg, Pb, Th, U) water solutions at 20^{o}C by sodium and ammonium tetraflouroborates, based on their higher (on 1-1.5 order) solubilities in water, than solubility of cesium tetraflouroborate. A subject of our research was degree and selectivity of cesium sedimentation as well as the characteristic of received sediments.

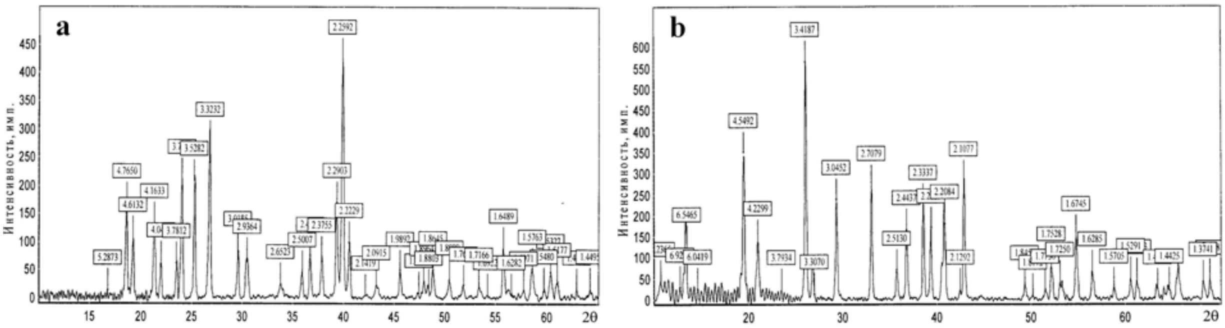

Fig.1. XRPD patterns of CsBF$_4$: (a) and NaCs(BF$_4$)$_2$, (b) Dron-4 diffractometer, CuKα radiation (λ = 1.54018Å)

Besides cationic compound, initial solutions for experiments differed a parity of cesium and sodium concentration, and also on pH (tab.1), controlled by concentration of nitric acid or sodium carbonate in solutions. Sodium and ammonium tetraflouroborates were added to initial solutions in the form of solid substance or the sated water solutions. At addition the tetraflouroborates there was a formation heavy glassy deposits. After deposits filtration and drying white color thin crystal powders were turned out. X-ray powder diffraction (XRPD) patterns of deposits have shown presence in all of them cesium tetraflouroborate CsBF$_4$ (CBF) (fig.1a), crystallizing in orthorhombic system, space group Pnma (XRPD patterns database PCPDFWIN v.2.02, card 95828). Most crystalline single-phase deposits turned out at addition to starting solutions NH$_4$BF$_4$. Addition NaBF$_4$ led to occurrence in deposits of one more crystal phase (fig.1b) which analog in the database it was revealed not. To define chemical compound of this phase deposits have been studied by electron microprobe analysis on a scanning electron microscope (SEM) Tescan Vega II XMU combining with X-ray energy dispersive spectrometer INCAx-sight. The unknown phase has appeared double salt of sodium and cesium having chemical compound close to ideal stoichiometry: NaCs(BF$_4$)$_2$ (NCBF). It is characterized by higher solubility than CsBF$_4$, it is better recrystallized in water and forms joints large tabular crystals (fig.2).

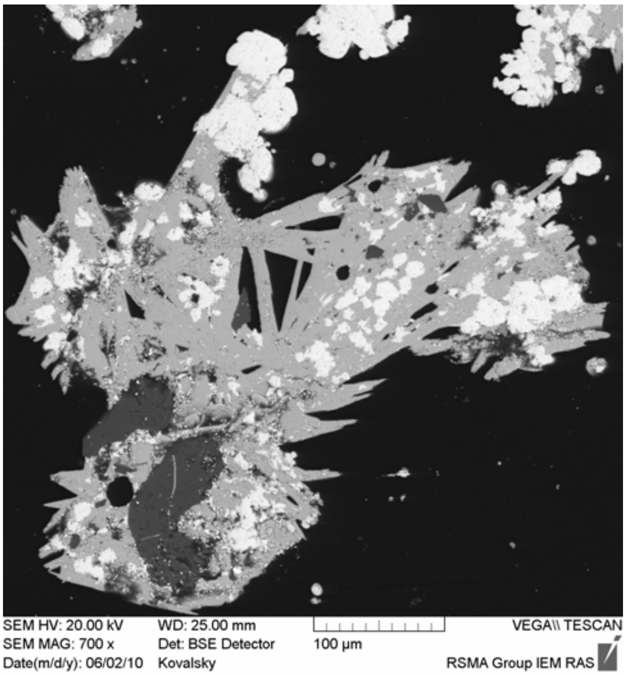

Fig.2 SEM backscattered electron detector image of the polished sample of a two-phase sediment: white - $CsBF_4$, gray - $NaCs(BF_4)_2$.

To define cell parameters of $NaCs(BF_4)_2$ XRPD pattern of the single-phase sample together with the internal standard (spectral pure Si, a = 5.4305 Å) has been removed at 25°C on Bruker D8 ADVANCE X-ray diffractometer, using $CuK\alpha_1$ radiation (λ = 1.5406 Å) with step of 0.010°2Θ. CRYSFIRE 2004 (THEOR90 procedure) and CHEKCELL computer programs have been used for definition of reflection indexes and calculation of unit cell parameters. There were 37 experimental reflections in a range 13-71°2Θ which angular positions were corrected by internal standard. The decision for unit cell parameters has been found in terms of the rhombohedral system: a = 5.4575(1) Å, c = 20.1508(5) Å, V = 519.77 Å^3, Z = 3, several space groups without systematic absences are possible. It is established that $NaCs(BF_4)_2$ has higher symmetry in comparison with unicomponent salts ($NaBF_4$: orthorhombic, Cmcm; $CsBF_4$: orthorhombic, Pnma). At the same time, the size of relation $V/n{\cdot}Z$ = 86.63 Å^3 lies in an interval between its values for end-members (72.69 Å^3 and 108.73 Å^3, respectively).

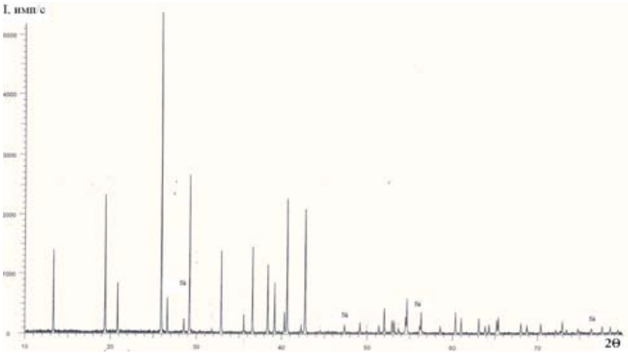

Fig. 3. XRPD pattern of $NaCs(BF_4)_2$. $CuK\alpha_1$ radiation (λ = 1.5406 Å). Si - spectral pure silicon, a = 5.4305 Å

Chemical compounds of solutions as initial, and after cesium sedimentation were analyzed on a mass spectrometer with inductively coupled plasma Agilent 7500ce (tab.1). From all set of cations being in starting solutions after cesium sedimentation by tetraflouroborates the maintenance of potassium, rare earth elements (TR) and thorium (the last only for sour solutions) in solutions stably decreased. On fig.4 degrees of sedimentation of these elements from solutions are presented:

$$S_i=(C_{i\ ini}-C_{i\ fin})/C_{i\ ini}\cdot 100\%,$$

where $C_{i\ ini}$ and $C_{i\ fin}$ are initial and final concentration of i-th component in a solution taking into account diluting. It is visible that in many cases sedimentation of cesium - rare earth elements - thorium fraction is close to 100 %. At the same time cesium can be taken rather selectively by ammonium tetraflouroborate from alkaline solutions. Potassium, most likely, is sedimented in a kind of tetraflouroborate, having low solubility in water; rare earth elements are sedimented presumably in the form of fluorides; the form of thorium sedimentation isn't clear. In contrast to them alkali earth elements, transition metals and uranium remain in a solution.

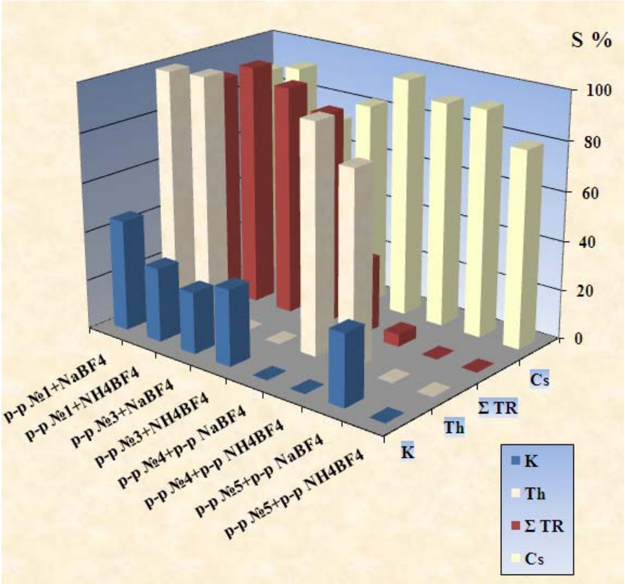

Fig.4. Degrees of K, Th, Σ TR and Cs sedimentation by $NaBF_4$ and NH_4BF_4 from solutions of various chemical compounds .

Thus, in process of sedimentation from solutions of dangerous technogenic elements by means of tetraflouroborates degrees of sedimentation Cs, Th, TR can be close to 100 %. This fact can be a basis for creation of a new technological method of allocation of the specified group of elements or selectively cesium from a high level waste at processing of spent nuclear fuel, and also their separation at processing of ores.

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Table 1. The concentration of elements and pH modeling solutions before and after cesium sedimentation by sodium and ammonium tetraflouroborates and phase composition of deposits: CBF – $CsBF_4$, NCBF – $NaCs(BF_4)_2$

№ exp	sol №1	4	7	sol №3	6	8	sol №4	23	24	sol №5	26	27
Reagents		sol №1 + $NaBF_4$	sol №1 + NH_4BF_4		sol №3 + $NaBF_4$	sol №3 + NH_4BF_4		sol №4 + sol $NaBF_4$	sol №4 + sol NH_4BF_4		sol №5 + sol $NaBF_4$	sol №5 + sol NH_4BF_4
Concentration in solution, g/l												
Na	0.31	54	0.95	220	270	170	1.7	35	0.5	99	83	47
Mg	0.22	0.23	0.25	0.11	0.0038	0.0041	0.13	0.086	0.086	0.0018	0.0079	0,0025
K	0.2	0.11	0.14	0.16	0.12	0.11	0.088	0.002	?	0.038	0.018	0,026
Cr	0.69	0.73	0.78	0.0084	0.0076	0.014	0.21	0.13	0.13	$8.5 \cdot 10^{-4}$	0.0016	0,0021
Fe	0.5	0.52	0.56	0.01	0.02	0.04	0.067	0.061	0.058	0.004	0.011	0,015
Ni	0.56	0.56	0.63	0.022	0.037	0.044	0.064	0.04	0.043	$4.5 \cdot 10^{-4}$	0.0015	$9{,}2 \cdot 10^{-4}$
Cu	0.56	0.56	0.65	0.031	0.12	0.16	0.18	0.13	0.11	0.024	0.019	0,018
Sr	0	0	0	0	0	0	4.7	2.9	2.9	0.039	0.077	$3{,}3 \cdot 10^{-4}$
Zr	0.061	0.11	0.12	0.01	0.024	0.07	0.13	0.11	0.12	0.0057	0.034	0,0086
Nb	$1.4 \cdot 10^{-4}$	$4.8 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$	$1.7 \cdot 10^{-5}$	$2.3 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$6.5 \cdot 10^{-4}$	0.0017	0.0019	$8.2 \cdot 10^{-4}$	0.0016	0,0035
Ag	$5.4 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	$7.2 \cdot 10^{-4}$	$3.4 \cdot 10^{-5}$	$8.6 \cdot 10^{-5}$	$3.6 \cdot 10^{-4}$	$4.5 \cdot 10^{-4}$	$4.8 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$	0.0021	0.0073	0,006
Cd	1	0.98	1.2	0.0094	0.0077	0.022	0.12	0.07	0.07	$1.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	0
Cs	130	16	11	98	26	17	22	0.37	1.3	29	1.6	3,8
Σ TR	0.34	0.035	0.0056	$4.5 \cdot 10^{-4}$	$3.3 \cdot 10^{-5}$	$6.3 \cdot 10^{-5}$	0.14	0.067	0.091	$1.4 \cdot 10^{-4}$	$7.2 \cdot 10^{-4}$	$2{,}2 \cdot 10^{-4}$
Hf	0.64	1	1.1	0.093	0.22	0.67	0.12	0.12	0.13	0.007	0.3	0,064
Pb	0.45	1	0.45	0.049	0.16	0.19	0.0037	0.11	0.11	$7.6 \cdot 10^{-4}$	0.0038	0,0042
Th	0.57	0.0035	$6.5 \cdot 10^{-4}$	0.046	0.068	0.19	0.02	$8.8 \cdot 10^{-4}$	0.0028	$3.8 \cdot 10^{-4}$	0.0076	0,0029
U	0.61	0.57	0.66	0.18	0.35	0.39	0.1	0.24	0.12	0.074	0.047	0,046
pH	1.94	2	2.81	10.8	8.78	8.5	1.29	2.33	2.24	11.99	7.51	7,9
Solid products		CBF + NCBF	CBF		CBF	CBF		CBF + NCBF	CBF		NCBF	CBF