



Original Article

Reprocessing of fluorination ash surrogate in the CARBOFLUOREX process

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ABSTRACT

This work presents the results of laboratory scale tests of the CARBOFLUOREX (CARBONate FLUORide EXtraction) process – a novel technology for the recovery of U and Pu from the solid fluorides residue (fluorination ash) of Fluoride Volatility Method (FVM) reprocessing of spent nuclear fuel (SNF). To study the oxidative leaching of U from the fluorination ash (FA) by Na₂CO₃ or Na₂CO₃–H₂O₂ solutions followed by solvent extraction by methyltriocetylammmonium carbonate in toluene and purification of U from the fission products (FPs) impurities we used a surrogate of FA consisting of UF₄ or UO₂F₂, and FPs fluorides with stable isotopes of Ce, Zr, Sr, Ba, Cs, Fe, Cr, Ni, La, Nd, Pr, Sm. Purification factors of U from impurities at the solvent extraction refining stage reached the values of 10⁴–10⁵, and up to 10⁶ upon the completion of the processing cycle. Obtained results showed a high efficiency of the CARBOFLUOREX process for recovery and separating of U from FPs contained in FA, which allows completing of the FVM cycle with recovery of U and Pu from hardly processed FA.

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1. Introduction

During the reprocessing of spent uranium oxide fuel by Fluoride Volatility Method (FVM), uranium is extracted as UF₆ after high-temperature fluorination, which purifies it from volatile FPs such as: NpF₆, MoF₆, IF₇, TeF₆, SeF₆, SbF₅, NbF₅, RuF₅ and after conversion to UO₂ can be used again as a nuclear fuel [1,2]. Radioactive wastes of FVM are solid fluorides residue (in the form of powders or ashes), which form at the stage of high-temperature fluorination of SNF. This residue – fluorination ash (FA) contains a mixture of non-volatile fluorides of U and Pu in the form of UF₄, UO₂F₂, PuF₄, fluorides of minor actinides (NpF₃, AmF₃, CmF₃) and fluorides of FPs (ZrF₄, CsF, RbF, SrF₂, LnF₃) with high radioactivity. FVM reprocessing of SNF produced by thermal nuclear reactors allows converting 97–99.5% of uranium to the volatile UF₆. Thus, the amount of processed SNF is reduced by more than 10 times.

Residual U and Pu, as well as FPs in the form of non-volatile fluorides, concentrate in FA, which could contain 30–77% of UF₄ [2–4]. Recovery of U and Pu from FA by FVM is not economically feasible.

The most well-known and well-described process of SNF reprocessing includes a combination of the FVM and the PUREX process for the solvent extraction (SE) separation of U, Pu and FPs in nitric acid media is the FLUOREX developed in Japan [2,5]. On the one hand, in FLUOREX process there is a decrease the volume of liquid radioactive waste at the SE stage by the factor of 10 compared to the conventional PUREX process [5], since the main part of U is removed as UF₆ during fluorination. On the other hand, due to incomplete conversion of alkaline-earth and lanthanide metals' fluorides to oxides, F[−] ions are being transferred to the solution during subsequent leaching by HNO₃, resulting in the formation of insoluble PuF₄. Another negative effect of presence of F[−] ions in HNO₃ solutions is formation of HF, which is highly corrosive for the processing equipment and accelerates the degradation of the extractant. To prevent the formation of PuF₄ precipitates and the aggressive HF, it has been proposed to bind F[−] ions into insoluble compounds, for example, with Ln [2]. The purification factors of U from FPs impurities in the FLUOREX process is 10⁷.

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1.1. Concept of the CARBOFLUOREX process

CARBEX process, previously developed for the reprocessing of uranium oxide SNF in aqueous carbonate media [6], can be also used to recovery of U, Pu and, potentially, minor actinides from FA. In combination with FVM this process represents the hybrid method including fluoride volatile and solvent extraction method for SNF reprocessing. At the stage of dissolution of U, Pu and FPs fluorides in carbonate solutions, there is a formation of fluoro-carbonate species, which further undertake solvent extraction purification from carbonate-fluoride media. On this basis, the method was called the CARBOFLUOREX process, or solvent extraction from carbonate-fluoride solutions.

The reprocessing of FA in aqueous carbonate-fluoride media has important advantages compared to nitric acid media: carbonate-fluoride solutions do not possess aggressive chemical impact on materials of the equipment. Another point is that components of an extraction system are less aggressive for the environment and personnel. At the stage of U and Pu leaching from FA by carbonate solution, FPs impurities, which are insoluble in carbonate-fluoride media are selectively separated [6]. CARBOFLUOREX process does not require the conversion of fluorides obtained from FA to oxides before the leaching stage, as it needed in the FLUOREX process.

Thus, the advantages of the CARBOFLUOREX process in comparison with SE from nitric acid solutions are following: 1) decrease in corrosive and oxidative activity of F^- ions in carbonate solutions, which are in contact with the processing equipment and extractant; 2) process does not require pre-treatment of U and other components from fluorine; 3) possibility of obtaining pure carbonate compounds of U and Pu directly after the SE stage; 4) relatively simple route for reprocessing of FA. The main stages of the FA reprocessing in the CARBOFLUOREX process are presented on Fig. 1.

Process of UO_2F_2 dissolution in carbonate solutions, involves formation of soluble carbonate $[UO_2(CO_3)_3]^{4-}$ and mixed fluoro-carbonate complexes $[UO_2(CO_3)F_2]^{2-}$, $[UO_2(CO_3)F_3]^{3-}$, $[UO_2(CO_3)F_4]^{4-}$, $[UO_2(CO_3)_2F_2]^{4-}$ [7–9]. Concentration of U in carbonate-fluoride solutions can reach up to 20–90 gU L⁻¹, depending on the processing conditions and composition of the initial solution. To dissolve UF_4 in Na_2CO_3 solutions, U(IV) should be oxidized to U(VI). The most suitable oxidizing agent for this process is H_2O_2 , which not only oxidizes U, but also forms mixed peroxy-carbonate complexes corresponding to the general formula $[UO_2(O_2)_x(CO_3)_y]^{(2-2x-2y)}$ (where $x = 1-3$, $y = 3-x$) [10], when added to solutions containing Na_2CO_3 .

Due to low solubility of oxides and fluorides of Ln, Ba, Sr, Zr and other metals in solutions of Na_2CO_3 or $Na_2CO_3-H_2O_2(NaF)$, most of them remain in the insoluble residue, which allows to separate U

from some insoluble FPs at the FA leaching stage. Nonetheless, we should expect a complete transition of Cs and part of Ln in the U-containing solution at the FA leaching stage.

For further separation and purification of U and Pu from soluble FPs in carbonate-fluoride solutions in CARBOFLUOREX process, it is proposed to carry out solvent extraction refining using quaternary ammonium compounds (QACs), in particular, methyl-trioctylammonium carbonate or fluoride (further $(R_4N)_2CO_3$ and R_4NF , where R_4N^+ is a quaternary ammonium cation).

During the solvent extraction separation of U(VI), Ce(IV) and Ln(III) from carbonate-fluoride solutions of $(R_4N)_2CO_3$ in toluene, the separation factor (β) for U(VI) and Ln(III) ranges from 1.5 to 15.5, $\beta(Ce(IV)/Ln(III))$ is 2.3–3.8 [11], $\beta(U(VI)/Pu(IV))$ is 0.5–84.5 and $\beta(U(VI)/Am(III))$ is 1.4–5.4 [12] depending on the conditions of process and the composition of the carbonate-fluoride solution. When Pu(IV) is oxidized to Pu(VI) in Na_2CO_3 solutions, for example, in presence of persulfate ions [13] it leads to formation of $Na_4[PuO_2(CO_3)_3]$ [14], extractability of which by $(R_4N)_2CO_3$ is comparable with $Na_4[UO_2(CO_3)_3]$ [15]. Varying the conditions of the SE stage of CARBOFLUOREX process makes it possible to develop options for both separate and collective SE of U(VI) and Pu(IV)/Pu(VI). Solvent extraction refining is a main stage of U and Pu purification.

Obtaining extracts containing 50–80 gU L⁻¹ allows to remove U in the form of crystalline ammonium uranyl carbonate (AUC) [16] at the stage of re-extraction, using concentrated $(NH_4)_2CO_3$ solutions (solid-phase re-extraction). In the case of collective SE processing of U and Pu, mixed carbonate precipitates are formed. Calcination of obtained carbonates leads to formation of the mixed UO_2 and PuO_2 powders, which can be used for MOX fuel fabrication. After filtration of AUC, unspent $(NH_4)_2CO_3$ could be further regenerated from the carbonate solution by distilling the gaseous NH_3 and CO_2 , for the preparation of $(NH_4)_2CO_3$. The remaining extremely low volume of the solution, containing FPs could be solidified, immobilized and finally sent to nuclear waste disposal.

The goal of this study was to verify and optimize the main stages of the CARBOFLUOREX process on a laboratory scale – leaching of U from FA and its further purification by solvent extraction from FPs in carbonate-fluoride solutions using the FA surrogate.

2. Experimental

Solid salts Na_2CO_3 , NaF and 35% aqueous solution of H_2O_2 of the analytical grade were used. Carbonate of MTOA – $(R_4N)_2CO_3$ was synthesized according to the work [17]. Toluene of the analytical grade was used for dissolving of $(R_4N)_2CO_3$.

We used the FA surrogate based on mixture powders of UF_4 , UO_2F_2 , $UO_2F_2 \cdot nH_2O$ where $n = 1.5$ and 2 with the natural content of isotopes ^{235}U and ^{238}U , as well as simulated FPs in the form of

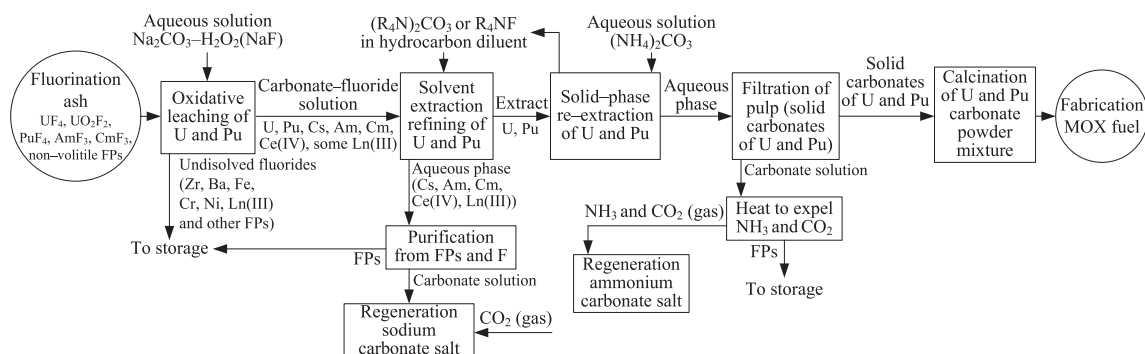


Fig. 1. Flow sheet of the FA reprocessing in the CARBOFLUOREX process.

Table 1

Composition of the FA surrogate based on UF₄ (N[⊖]1) and based on UO₂F₂/UO₂F₂·1.5H₂O/UO₂F₂·2H₂O (N[⊖]2).

Component	UF ₄ (N [⊖] 1); UO ₂ F ₂ /UO ₂ F ₂ ·nH ₂ O (N [⊖] 2)	CsF	SrF ₂	BaF ₂	FeF ₃ ·3H ₂ O			
ω, % (N [⊖] 1)	49.5	0.74	0.74	–	8.91			
ω, % (N [⊖] 2)	45.8	0.76	0.76	2.29	9.16			
Component	CrF ₃ ·3H ₂ O	NiF ₂ ·2H ₂ O	ZrF ₄	LaF ₃	CeF ₃	PrF ₃	NdF ₃	SmF ₃
ω, % (N [⊖] 1)	2.23	8.91	18.94	1.49	2.23	1.34	3.71	1.26
ω, % (N [⊖] 2)	2.29	9.16	19.47	1.53	2.29	1.37	3.82	1.3

fluorides of stable isotopes: CsF, SrF₂, BaF₂, FeF₃·3H₂O, CrF₃·3H₂O, NiF₂·2H₂O, ZrF₄, LaF₃, CeF₃, PrF₃, NdF₃, SmF₃ (Table 1) of the analytical grade. The composition of the FA surrogate was chosen according to the published data [3,4]. Anhydrous UF₄ was obtained by treating a UF₄·2.5H₂O with gaseous HF at a temperature of 500 °C. UF₄·2.5H₂O was precipitated from a solution of U(SO₄)₂ by HF. UO₂F₂ was obtained by precipitation from 70% UO₂(NO₃)₂·6H₂O aqueous solution with concentrated NH₄F aqueous solution [9]. The composition of the synthesized UF₄ and UO₂F₂ powders was confirmed by X-ray diffraction (XRD). Phase composition of obtained powder mixture included anhydrous UF₄ and anhydrous UO₂F₂ mixed with hydrates – UO₂F₂·1.5H₂O, UO₂F₂·2H₂O (Fig. 2).

The concentrations of metals in liquid and solid samples were analyzed with the ICP–MS method by an iCAPTM Q. The concentrations of Na₂CO₃ and (NH₄)₂CO₃ in solutions were analyzed by the potentiometric titration of a samples by 100.00 mM water solution of HCl, with a glass P13/BNC electrode using a digital pH/mV/temperature meter Elite pH Meter 3320. The concentration of H₂O₂ in solutions was analyzed by titration with 20.00 mM KMnO₄ water solution. The concentration of NaF in solutions were analyzed by the titration of a samples by 100.00 mM water solution of LaF₃, with a selective fluoride ion electrode ELIS–131 F and reference electrode ESr–10101 using a digital ionometer Ekoniks EXPERT–001.

The absorption spectra and spectral curve of the second–order derivative were measured using UV–vis HP Diode Array Spectrophotometer 8452 A with a 1–10 mm quartz cuvette. Data was

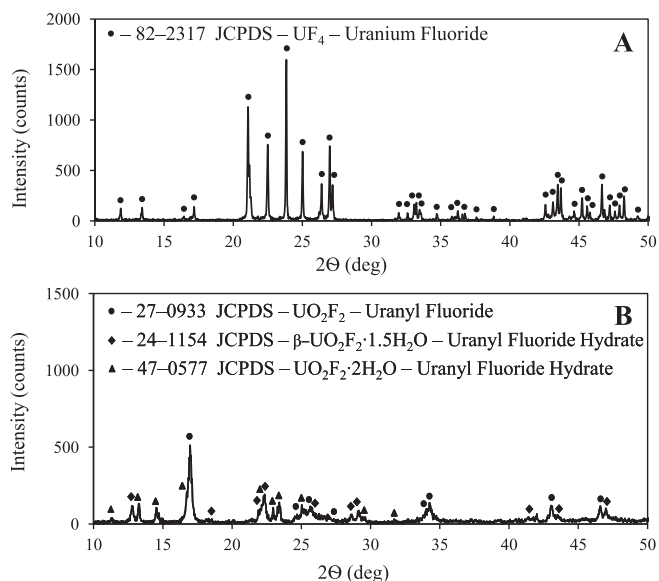


Fig. 2. XRD patterns of UF₄ (A) and UO₂F₂ (B) powders, used for surrogate mixtures preparation.

obtained in a single–beam mode at 2 nm resolution.

The phase content of the powders was established from the XRD of the samples. The XRD spectra were obtained with a D2 PHASER Bruker. The spectra were read and the phase content was established using the JCPDS–ICDD database and TOPAS structural refinement software.

The degree of extraction (α) of each element was calculated by the following equation:

$$\alpha(\%) = (W_M / W_{M,i}) \cdot 100 \quad (1)$$

where $W_{M,i}$ is the initial quantity of the metal and W_M is the quantity contained in the filtered solution after leaching.

The purification factor (K_{PUR}) of U from impurities were calculated according to the equation:

$$K_{PUR} = [(W_U) / (W_M)] / [(W_{U,i}) / (W_{M,i})] \quad (2)$$

where $W_{U,i}$ and $W_{M,i}$ are the masses of U and impurities in the initial sample while W_U and W_M are the masses after the treatment. In case of oxidative leaching of the surrogate powder, the calculation of W_U and W_M was carried out using concentration of metal and volume of the carbonate–fluoride solution after filtration.

3. Results and discussion

3.1. Leaching of uranium from the fluorination ash surrogate

CARBOFLUOREX process involves leaching of U from the FA by 0.5–1.0 M Na₂CO₃ aqueous solutions. Leaching of U from a UO₂F₂–based surrogate is based upon dissolution of uranyl fluoride in Na₂CO₃ solutions. Dissolution rate of UO₂F₂ is low: only 41–60% of U was dissolved (concentration of U in solution equal 20–55 gU L^{−1}) in 4 h (Table 2). Higher temperature increases $\alpha(U)$, and an increase in the Na₂CO₃ concentration from 0.5 M to 1.0 M has almost no effect on the leaching of UO₂F₂ from surrogate powder.

For dissolution of UF₄ in carbonate solution, it is necessary to oxidize U(IV) to U(VI). For present study we used 0.5–1.0 M H₂O₂ as an oxidizing agent in carbonate solution. Leaching of UF₄ from a surrogate powder by 1.0 M Na₂CO₃ in the absence of H₂O₂ proceeds rather slowly, after the 240 min of reaction, concentration of U in the carbonate solution was 4 gU L^{−1}, which to $\alpha(U) = 13\%$.

UV–vis spectrum of the solution, obtained after leaching shows absorption in the region of 300–600 nm with peaks at 394 nm, 404 nm, 414 nm. The most prominent characteristic peaks were found at 424 nm, 434 nm, 448 nm and 462 nm (Fig. 3). This data corresponds to the spectrum of the Na₄[UO₂(CO₃)₃] aqueous solution, and is in agreement with the literature [18]. UV–vis spectrum

Table 2

Leaching of U from FA surrogate powders by Na₂CO₃ and Na₂CO₃–H₂O₂ solutions. L:S – mass ratio to liquid and solid phases.

Solution	t, °C	L:S	$\alpha(U)$, %	Concentration, M		
				U(VI)	CO ₃ ^{2−}	F [−]
UF ₄ –based surrogate powder						
1.0 M Na ₂ CO ₃	25	5	13.0	0.02	–	1.20
0.5 M Na ₂ CO ₃ –0.5 M H ₂ O ₂	25	5	84.0	0.10	–	0.10
1.0 M Na ₂ CO ₃ –0.5 M H ₂ O ₂	25	5	92.0	0.12	–	0.19
2.0 M Na ₂ CO ₃ –0.5 M H ₂ O ₂	25	5	96.0	0.12	–	0.21
0.5 M Na ₂ CO ₃ –0.75 M H ₂ O ₂	25	3	28.3	0.19	0.45	2.20
UO ₂ F ₂ –based surrogate powder						
0.5 M Na ₂ CO ₃	50	10	46.4	0.10	–	0.39
1.0 M Na ₂ CO ₃	50	10	41.6	0.08	–	0.49
0.5 M Na ₂ CO ₃	25	5	27.8	0.11	0.37	0.35
0.5 M Na ₂ CO ₃	50	5	60.0	0.23	0.37	1.50

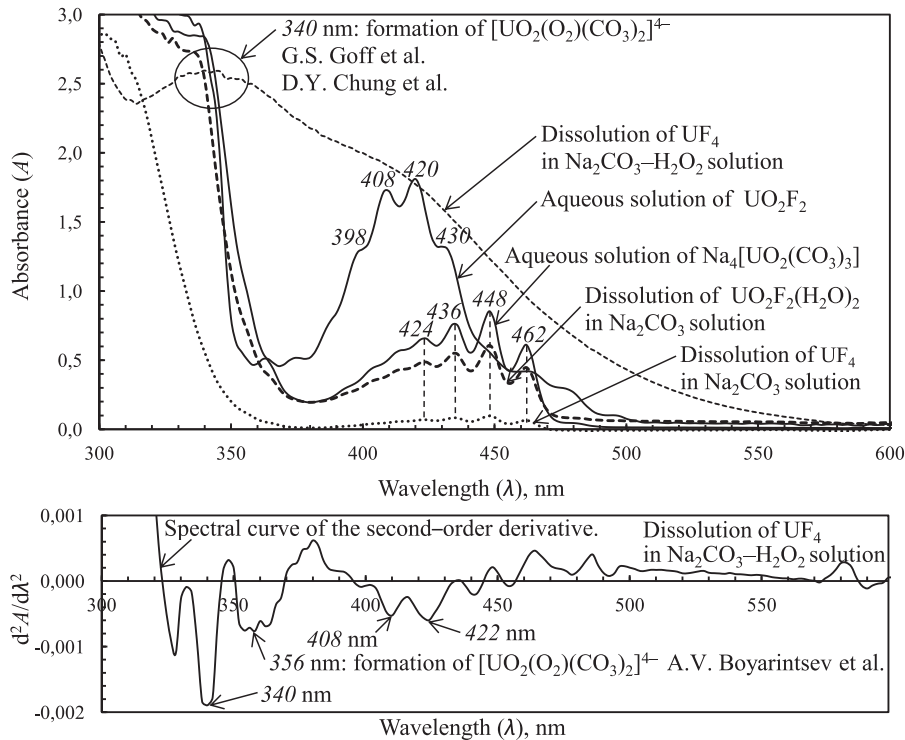


Fig. 3. UV-vis spectra of the $\text{Na}_4[\text{UO}_2(\text{CO}_3)_3]$, UO_2F_2 aqueous solutions, and the typical UV-vis spectra of solutions obtained after dissolving UF_4 or UO_2F_2 in Na_2CO_3 and $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}_2$ solutions.

of the same range of 300–600 nm for UO_2F_2 solution in 1.0 M Na_2CO_3 was also obtained. Spectrum of the UO_2F_2 aqueous solution had characteristic peaks at 364 nm, 374 nm, 388 nm, 398 nm, 430 nm, 448 nm in the region of 300–600 nm, shoulders at 456–464 nm, 472–476 nm, 490–496 nm, and a prominent peaks at 408 nm and 420 nm. Structure of this spectrum significantly differed from the spectrum of $\text{Na}_4[\text{UO}_2(\text{CO}_3)_3]$ in the considered absorption region.

In the presence of 0.5 M of H_2O_2 , the degree of extraction of U from UF_4 -based surrogate increased up to 96%, while the leaching time is reduced by factor of 4. It should be noted that during the leaching of U by carbonate solutions, the O_2^{2-} ions plays the role of both the oxidizing agent and the ligand as it forms the mixed peroxo-carbonate species of U(VI) in the carbonate solutions. The U(VI)-containing solutions obtained after leaching of UF_4 in the presence of H_2O_2 have a characteristic red-brown color. The UV-vis spectra of these solution has a nearly featureless peak (from 300 to 600 nm), containing a peak at approximately 340 nm and shoulder at 400–420 nm, which corresponds to the formation of mixed peroxo-carbonate species of U(VI) – $[\text{UO}_2(\text{O}_2)(\text{CO}_3)_2]^{4-}$ [19–21]. On the spectral curve of the second-order derivative there is a minimum at 340 nm and two minima at 408 nm and 422 nm correspond to the shoulder at 400–420 nm on the absorbance spectrum. The most characteristic feature of a second-order derivative is a negative band with minimum at the same wavelength as the maximum on the zero-order band (absorbance spectrum) [22]. The second-order derivative of the absorption spectrum allowed us to determine hidden peaks, thus, the minimum observed at 356 nm has previously been attributed to absorption of $[\text{UO}_2(\text{O}_2)(\text{CO}_3)_2]^{4-}$ [21].

Cs, Sr and Ln jointly with U dissolve in the carbonate solution. The value of $\alpha(\text{Cs})$ during leaching of the UO_2F_2 -based surrogate by 0.5–1.0 M Na_2CO_3 solutions was 49–50%. With an increase in the

concentration of Na_2CO_3 from 0.5 to 1.0 M, the value of $\alpha(\text{Sr})$ decreases from 1.5% to 0.2%, $\alpha(\text{Ce})$ from 5.2% to 0.8%, $\alpha(\text{Pr})$ from 0.6% to 0.4%.

Thus, the leaching of UF_4 and UO_2F_2 from the FA surrogates by Na_2CO_3 solutions proceeds with the formation of $\text{Na}_4[\text{UO}_2(\text{CO}_3)_3]$, in the presence of NaF, the formation of U(VI) fluoro-carbonate species occurs [7–9]. Leaching of UF_4 by $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}_2$ solutions occurs more intensively with the formation of $\text{Na}_4[\text{UO}_2(\text{O}_2)(\text{CO}_3)_2]$. FPs' fluoride surrogates (Ba, Sr, Zr and Ln) partially dissolve in carbonate solution. CsF has the highest solubility in studied systems. At the leaching stage of the FA surrogates by Na_2CO_3 solution, U is being purified from Ln, Ba, Sr, Zr. Purification from Cs does not occur at this stage. Obtained carbonate solutions of U(VI) and impurities of soluble FPs surrogates after filtration from the insoluble fluorides residue were further purified by SE using $(\text{R}_4\text{N})_2\text{CO}_3$ in toluene.

3.2. Solvent extraction refining of uranium from carbonate-fluoride solutions

Purification of U from impurities by SE was performed using 0.4–0.5 M solution of $(\text{R}_4\text{N})_2\text{CO}_3$ in toluene. The SE refining stage consisted of 3–5 steps of counter-current mode, one step of washing and 1–2 steps of re-extraction. Organic phases (extracts of U) was washed by 0.5 M Na_2CO_3 , and the re-extraction was performed by 2.0 M $(\text{NH}_4)_2\text{CO}_3$.

Solution obtained after leaching of the UO_2F_2 -based surrogate by Na_2CO_3 contained 24.3 gU L⁻¹ along with FPs impurities. This solution was later processing by SE in accordance with the operating scheme (Fig. 4) in two different variants.

According to first variant, three steps of SE were carried out at volume ratio of aqueous to organic phases (A:O) equals two. The extraction yield of U from the carbonate-fluoride solution was

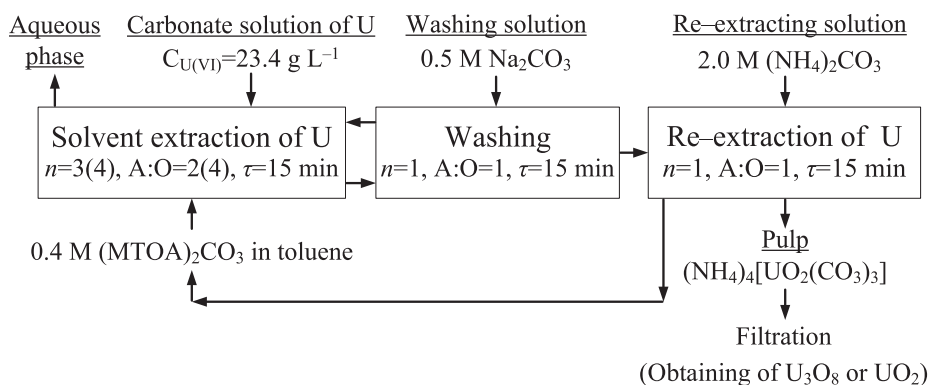


Fig. 4. Operating scheme of the SE processing of U(VI) carbonate–fluoride solution after leaching UO_2F_2 -based surrogate. A:O – volume ratio of aqueous to organic phases; τ – agitation time; n – number of steps.

Table 3

The K_{PUR} values of U purification from impurities after leaching of U from UO_2F_2 -based surrogate and SE stages.

Stage	$K_{PUR} \cdot 10^3$											
	Ce	Nd	Pr	Sm	La	Zr	Ba	Sr	Cs	Fe	Cr	Ni
Leaching	0.008	–	0.077	–	–	–	–	0.027	0.001	–	–	–
3 steps of SE	310	–	18	–	–	–	–	160	720	–	–	–
4 steps of SE	44	26	73	77	65	9.8	110	160	330	30	130	27

99.8%. Concentration of U in organic phase was 46.2 gU L^{-1} . The residual concentration of U in the aqueous phase at equilibrium was 0.042 gU L^{-1} . The re-extraction yield of U after the two steps was 96.8%. The final yield of U in the form of carbonate precipitate was 91.8%.

According to second variant, four steps of SE were carried out at A:O = 4. The extraction yield of U from the carbonate–fluoride solution was 77.3%. Concentration of U in organic phase was 54.2 gU L^{-1} . The residual concentration of U in the aqueous phase at equilibrium was 5.3 gU L^{-1} . The re-extraction yield of U after the one stage was 88%. Final yield of U in the form of carbonate precipitate was 74.8%.

The AUC precipitates obtained at the re-extraction stage, were washed on a filter with 5% $(\text{NH}_4)_2\text{CO}_3$ solution, dried in air, and calcined at 800°C for 2 h to form U_3O_8 . The K_{PUR} values of purification of U from impurities calculated for the obtained U_3O_8 samples are presented in Table 3.

The K_{PUR} values for all FPs impurities at the SE stage reached values of 10^4 – 10^5 . Calculated total K_{PUR} values for leaching and SE purification stages of U from Cs, Sr, Ce and Pr were $7.6 \cdot 10^5$, $4.3 \cdot 10^6$, $2.6 \cdot 10^6$ and $1.4 \cdot 10^6$, respectively. This allows us to consider the CARBOFLUOREX process as an effective method of U purifying from FPs, comparable with conventional SE of U from nitric acid solutions by tri-n-butyl phosphate in the PUREX process.

Solvent extraction processing of the carbonate solution obtained after leaching of UF_4 -based surrogate in the presence of H_2O_2 , containing 42.5 gU L^{-1} , and impurities was also carried out in accordance with the operating scheme shown in Fig. 4. The extraction yield of U from the carbonate solution after five steps of counter-current SE was 99.8%. Concentration of U in organic phase was 73.4 gU L^{-1} . The residual concentration of U in the aqueous

phase at equilibrium was 0.092 gU L^{-1} . The re-extraction yield of U by 2.0 M $(\text{NH}_4)_2\text{CO}_3$ at A:O = 1 after two steps was 88.1%. The final yield of U in the form of carbonate precipitate was 81.4%.

The calculated K_{PUR} values (Table 4) for all impurities except Cs are equal to 10^4 – 10^5 , that indicates the possibility of carrying out effective purification of U in peroxide–carbonate solutions along with carbonate–fluoride solutions for the studied systems.

Present study has shown feasibility of solid phase re-extraction of U from organic phases, saturated by fluoro–carbonate and peroxy–carbonate U(VI) species, to produce crystalline carbonate precipitates, mainly AUC. The fluorine content in such precipitates was 0.036–0.054%. Thus, SE processing of solutions after leaching of FA containing fluoro–carbonate and peroxy–carbonate U(VI) species allows to separate not only FPs impurities, but also fluorine, which is perspective for obtaining pure UO_2 suitable for fabrication of nuclear fuel of ceramic quality.

4. Conclusions

The present study of oxidative leaching of fluorination ash surrogates by carbonate solutions has shown that after oxidation by H_2O_2 , more than 95% of UF_4 dissolves in carbonate solution and could be purified from admixtures by solvent extraction, using $(\text{R}_4\text{N})_2\text{CO}_3$ in toluene. At the leaching stage of the fluorination ash surrogate, FPs' fluoride impurities and F^- ions partially dissolve in carbonate solutions. However, they practically don't have a corrosive effect on the materials of the reactor (pH = 10–11). The dissolution of fluorination ash in Na_2CO_3 solutions was carried out in a glass reactor for several hours at high temperatures, without any sign of corrosion of glass.

Studies on the solvent extraction of U from carbonate–fluoride

Table 4

The K_{PUR} values of U purification from impurities after SE processing of carbonate solution produced by leaching of the UF_4 -based surrogate.

$K_{PUR} \cdot 10^5$											
Ce	Nd	Pr	Sm	La	Zr	Sr	Cs	Fe	Cr	Ni	
2.2	3.7	1.4	1.3	1.5	0.1	2.5	0.01	0.32	0.41	2.3	

and peroxide–carbonate solutions for the processing of fluorination ash surrogates have shown the high efficiency of the CARBO-FLUOREX process for extracting U and purifying it from impurities, including fluorine. Ammonium uranyl carbonate precipitates after solid–phase re–extraction could be easily converted to U_3O_8 or UO_2 after calcination in a reducing atmosphere. Achieved purification factors of U from FPs impurities at the solvent extraction refining stage reached values of 10^5 , and up to 10^6 throughout the processing scheme. This data is comparable to the purification factors of UF_6 from FPs (10^6 – 10^9) during the processing of uranium oxide SNF by FVM.

Developed fluorination ash reprocessing scheme in carbonate systems makes it possible to carry out a full cycle of FVM for the reprocessing of SNF and the management of waste generated by this process.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.net.2019.06.025>.

References

- [1] V.V. Shatalov, M.B. Seregin, V.F. Kharin, L.A. Ponomarev, Gas–fluoride technology for processing spent oxide fuel, *Atom. Energy* 90 (3) (2001) 224–234.
- [2] Y. Kani, A. Sasahira, K. Hoshino, F. Kawamura, New reprocessing system for spent nuclear reactor fuel using fluoride volatility method, *J. Fluorine Chem.* 130 (2009) 74–82.
- [3] V.N. Prusakov, N.M. Trotsenko, V.A. Khokhlov, E.P. Marinenko, B.P. Bolozarov, Yu.G. Degaltsev, Yu.M. Utkin, V.V. Davydov, "Dry" methods of regeneration of the irradiated nuclear fuel, in: *Nuclear fuel cycle, power, technology, ecology, safety*, vol 2, 2006, pp. 45–54.
- [4] M.B. Seregin, A.Yu. Kuznetsov, A.A. Mikhailichenko, Gas–fluoride technology of processing of irradiated nuclear fuel, level of development and prospect of its application, in: *VNIHT – 60 Years. The Anniversary Collection of Works, LLC Leonardo–Dizayn, Moscow, Russia*, 2011.
- [5] O. Amano, F. Kawamura, T. Fukasawa, M. Takahashi, A. Sasahira, Y. Shibata, J. Yamashita, New reprocessing technology, FLUOREX, for LWR fuel cycle hybrid process of fluoride volatility and solvent extraction, in: *NUCEF 2001 Conference, Tokaimura, Japan, October 31–November 2, 2001*.
- [6] S.I. Stepanov, A.M. Chekmarev, Concept of spent nuclear fuel reprocessing, *Dokl. Chem.* 423 (1) (2008) 276–278.
- [7] S.I. Stepanov, A.V. Boyarintsev, A.V. Tyuremnov, San Tun, E.G. Il'in, A.M. Chekmarev, A.Yu. Tsivadze, NMR study of U(VI) extraction from carbonate–fluoride solutions with methyltriethylammonium fluoride, *Dokl. Chem.* 460 (1) (2015) 17–20.
- [8] Z. Szabó, W. Aas, I. Grenthe, Structure, isomerism, and ligand dynamics in dioxouranium(VI) complexes, *J. Inorg. Chem.* 36 (23) (1997) 5369–5375.
- [9] I.I. Chernyaev, *Complex Compounds of Uranium*, Daniel Davey & Co., Ink., New York, 1966.
- [10] W. Runde, L.F. Brodnax, S.M. Peper, B.I. Scott, G. Jarvinen, Structure and stability of peroxo complexes of uranium and plutonium in carbonate solutions, in: *Eight Actinide Conference, Actinide 2005*, Manchester, United Kingdom, July 4–8, 2005.
- [11] A.V. Boyarintsev, L.M. Abashev, S.I. Stepanov, V.I. Zhilov, A.M. Chekmarev, A.Yu. Tsivadze, Carbonate extraction–based refining of uranium. Separation of U(VI), Ce(IV), and Ln(III) from aqueous carbonate solutions with methyltriethylammonium carbonate, *Dokl. Chem.* 473 (2) (2017) 70–73.
- [12] A.S. Wolf, L.M. Abashev, G.V. Kostikova, A.V. Boyarintsev, S.I. Stepanov, Extraction separation of U(VI), Pu(IV) and Am(III) from carbonate–fluoride solutions by carbonate MTOA, *Achiev. Chem. Chem. Technol.* 31 (10) (2017) 67–69.
- [13] A.B. Yusov, A.Yu. Garnov, V.P. Shilov, N.N. Krot, Kinetics of Pu(IV) oxidation with persulfate in alkali solutions, *Radiochemistry* 39 (6) (1997) 521–524.
- [14] R. Guillaumont, T. Fanghaenel, J. Fuger, I. Grenthe, V. Neck, D.A. Palmer, M.H. Rand, *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, Elsevier, Amsterdam, The Netherlands, 2003.
- [15] S.I. Stepanov, A.V. Boyarintsev, M.V. Vazhenkov, B.F. Myasoedov, E.O. Nazarov, A.M. Safulina, I.G. Tananaev, H.V. So, A.M. Chekmarev, A.Yu. Tsivadze, CARBEX Process, A new technology of reprocessing of spent nuclear fuel, *Russ. J. Gen. Chem.* 81 (9) (2011) 1949–1959.
- [16] B.V. Shevchenko, B.N. Sudarikov, *Technology of Uranium*, Gosatomizdat, Moscow, Russia, 1961.
- [17] Certificate of authorship USSR N \circ 664355 S.I. Stepanov, Y.A. Leikin, V.D. Gorchakov, V.V. Sergievsky, G.A. Yagodin, V.N. Andrievsky, *The Method of Obtaining Salts or Hydroxides of Quaternary Ammonium Bases*, 1979.
- [18] C. Götze, G. Geipel, G. Bernhard, Thermodynamical data of uranyl carbonate complexes from absorption spectroscopy, *Uranium Min. Hydrogeol.* (2008) 907–914.
- [19] G.S. Goff, L.F. Brodnax, M.R. Cisneros, S.M. Peper, S.E. Field, B.L. Scott, W.H. Runde, First identification and thermodynamic characterization of the ternary U(VI) species, $UO_2(O_2)(CO_3)_2^{2-}$, in UO_2 – H_2O_2 – K_2CO_3 solutions, *J. Inorg. Chem.* 47 (6) (2008) 1984–1990.
- [20] D.Y. Chung, M.S. Park, K.Y. Lee, E.H. Lee, K.W. Kim, J.K. Moon, Decomposition of uranylperoxo–carbonato complex ion in the presence of metal oxides in carbonate media, *J. Radioanal. Nucl. Chem.* 306 (2015) 761–768.
- [21] A.V. Boyarintsev, S.I. Stepanov, A.A. Chekhlov, A.M. Chekmarev, A.Yu. Tsivadze, Chemistry of the CARBEX process: identification of absorption bands of the ligands in the electronic spectra of aqueous solutions of $Na_4[UO_2(O_2)(CO_3)_2]$, *Dokl. Chem.* 469 (2) (2016) 227–232.
- [22] A.J. Owen, *Uses of Derivative Spectroscopy*. Application Note. UV–Visible Spectroscopy, Agilent Technologies, 1995. Publication number 5963–3940E.