**Carbonate reprocessing of SNF in CARBEX-process**

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CARBEX-process, the concept of which was formulated in 2008 [1], is assigned to water methods and is an alternative one to the widely used PUREX-process. The developing method of uranium and mixed uranium-plutonium fuel processing is based on going from nitrate media widely used for purification of uranium and plutonium from FP and extraction to carbonate media.

The significant difference of the CARBEX-process is carrying out all water processes in the absence of such a strong oxidizer as nitric acid, changing of solubility of all components involved in the process in carbonate media, as well as changing of the selectivity.

At present, the principle flowsheet of CARBEX-process includes the following steps: 1) high temperature voloxidation of SNF in an oxidizing atmosphere in presence of alkali metals carbonates; 2) oxidative (in presence of H2O2) dissolution of uranium, plutonium and some FP in solutions of alkali metals and/or ammonium carbonates; 3) the separation of a solid insoluble residue from the carbonate solution; 4) extraction of U(VI) from carbonate solution using a carbonate of methyltrioctylammonium (MTOA) as the extractant; 5) solid-phase re-extraction of carbonate compounds of U(VI) from saturated organic extracts; 6) re-dissolution of carbonate precipitation of uranium in Na2CO3 or (NH4)2CO3 solution in presence of H2O2; 7) extraction purification of U(VI) from FP, including Pu(IV) from carbonate solutions by the carbonate of MTOA; 8) solid-phase re-extraction of (NH4)4[UO2(CO3)3] from saturated extracts by concentrated solutions of (NH4)2CO3 and/or NH4HCO3; 9) oxidation of Pu(IV) to Pu(VI) in carbonate U(VI) raffinates with a suitable oxidizing agent; 10) extraction of Pu(VI) from carbonate solutions by carbonate of MTOA followed by extraction carbonate refining of Pu(VI) from FP and PuO2 obtaining.

Systematic works on classic of voloxidation of uranium SNF in Russia were carried out at the Radium Institute named by V.G. Khlopin and VNIINM named by academician A.A. Bochvar and published [2, 3].

On studing of oxidative dissolution of the SNF simulator in Na2CO3+H2O2 solutions, it was found that uranium completely goes into solution. The following fission products: MoO3, Cs2O, CaO, I, Tc, Re are well soluble, ZrO2, BaO, SrO, Al2O3 are practically insoluble, and Y2O3, Ln2O3 (Ln = La, Nd, Sm, Gd, Dy), CeO2, Pd, Sb2O3, MnO2 poorly soluble in carbonate media. It was also found that the solubility of Pu, Am, Np, Cm oxides strongly depends on their oxidation degree.

In the presence of H2O2 U(IV) is oxidized to U(VI) and a peroxide carbonate compound Na4[UO2(O2)(CO3)2] is formed, whose solubility can reach up to 200 gU(VI)/l. At the same time, Pu(IV) and Np(IV) are not oxidized in the presence of H2O2. The solubility of PuO2 and NpO2 in Na2CO3+H2O2 solution does not exceed 10-50 mg/l. In the presence of other oxidants such as Na2S2O8, oxidation of Pu(IV) to Pu(VI) in Na2CO3 solution with formation of compound Na4[PuO2(CO3)3], take place concentration of plutonium reaches gram values. Oxidized Np(IV) (Np(VI)) is soluble in Na2CO3 solutions, forming a compound Na4[NpO2(CO3)3].

The concentration of REE in the core of dissolution of the oxides in Na2CO3+H2O2 solutions does not exceed 0,3 gLn2O3/l due to formation of the carbonate Na(n-3)[Ln(CO3)n], where n=2-5 and peroxide-carbonate compounds Na(m+n-3)[Ln(O2)m(CO3)n].

In the course of developing of the extraction part of CARBEX-process it was found that it is necessary to carry out two stages of extraction. The first stage – the extraction of U(VI) from carbonate solutions of oxidizing dissolution of uranium SNF, as the result of which U(VI) goes in organic phase together with some impurities of FP. The second stage is extraction purification of U(VI) from co–extracted impurities-extraction carbonate refining. In Table 1 presents data on the values of the coefficients of uranium(VI) purification from impurities simulators of some FP.

Table 1

The coefficients of uranium(VI) purification from some FP in CARBEX process

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Stage | КPUR. | | | | | |
| La | Zr | Sr | Nd | Y | Ba |
| Oxidative dissolution | 24,5 | 2·103 | 32,9 | 12,9 | 4,5 | 38,3 |
| 1-st stage of extraction | 20,7 | 5,3·103 | 26,3 | 13 | 40,5 | 35,8 |
| 2-nd stage of extraction | 2,5·103 | 5,3·105 | 3,2·103 | 1,3·103 | 4,1·103 | 4,8·103 |
| Stage | КPUR. | | | | | |
| Ce | Sn | Mo | Sm | Cs | |
| Oxidative dissolution | 2,76 | 1,34 | 12,8 | 1,45 | 1,1 | |
| 1-st stage of extraction | 254 | 1,07 | 128 | 14,5 | 52,7 | |
| 2-nd stage of extraction | 2,4·104 | 6,1·102 | 1,3·105 | 1,5·103 | 4,5·105 | |

Investigation of the chemistry of U(VI) extraction showed that, organic phase from carbonate solutions such compound were extracted: solvated by molecules of the extractant - (R4N)4[(UO2(O2)(CO3)2]·n(R4N)2CO3 and (R4N)4[(UO2(CO3)3]·n(R4N)2CO3, where R4N is a quaternary ammonium cation, n=1-2; nonsolvated: (R4N)4[(UO2(CO3)3] and (R4N)4[(UO2(O2)(CO3)2], polynuclear: (R4N)6[(UO2)2(O2)(CO3)4] and (R4N)6[(UO2)3(O2)2(CO3)4].

It was found that the effective separation of plutonium from U(VI) is possible for Pu(IV), the separation factor of U(VI)/Pu(IV) was 107. At the same time, Pu(VI) and U(VI) are effectively extracted together, which allows the development of variants of joint extraction of U(VI) and Pu(VI) in the CARBEX-process to prevent the production of pure plutonium dioxide.

Thus, within the framework of the CARBEX-process, it is possible both as separate and joint extraction purification of U(VI) and Pu(VI) from FP, followed by obtaining individual or mixed powders UO2 and PuO2, which can be sent to the production cycle of ceramic nuclear fuel based on UO2 or MOX fuel.

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