



Review Article

Separation and purification of elements from alkaline and carbonate nuclear waste solutions

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ABSTRACT

This article provides a survey of wet (aqueous) methods for recovery, separation, and purification of uranium from fission products in carbonate solutions during the reprocessing of spent nuclear fuel and methods for removal of radionuclides from alkaline radioactive waste. The main methods such as selective direct precipitation, ion exchange, and solvent extraction are considered. These methods were compared and evaluated for reprocessing of spent nuclear fuel in carbonate media according to novel alternative non-acidic methods and for treatment processes of alkaline radioactive waste.

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1. Introduction

One of the main tasks of modern radiochemistry is to increase the efficiency of SNF reprocessing and ensure nuclear safety at all stages of the fuel cycle, including radioactive waste management. It is of large importance to study the features and possibilities of alternative options for SNF reprocessing in carbonate and alkaline media [1–5], specifics, and improvement of new approaches for reprocessing of high burnup LWRs fuel and new types of SNF (LWR-MOX, etc.), as well as integrated partitioning and recycling of

components, accumulated and current LRW formed after recovery of U, Pu, and Np from SNF solutions, including alkaline HLLW [6]. It is also relevant to search for solutions for the treatment of solid radioactive materials (metal, ceramic or vitroc ceramic) in carbonate and alkaline media, including waste from the fabrication of nuclear fuel, waste from the production of the medical isotope ⁹⁹Mo [7,8], and others.

Alkaline radioactive waste is aqueous or heterogeneous high-intermediate- or low-level radioactive streams with complex chemical and radionuclide composition. Alkaline HLW was generated at nuclear fuel reprocessing plants (processing nuclear fuels and materials for defense programs, primarily PUREX process waste) as a result of neutralization of initially acidic waste solutions with sodium hydroxide. In the form of alkaline slurries, they are currently interim stored in underground carbon steel tanks at the Hanford Site, SRS, INEEL, ORNL (USA) [9] and Mayak Production Association (Russia) [10]. Long-term stewardship of the tanks and

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associated equipment is needed to store, extract, and stabilize these wastes [11]. After a few decades of storage, the nuclear waste alkaline slurries has stratified into three layers: supernate liquid, salt cake (primarily water-soluble sodium salts), and insoluble sludge (metal oxides and hydroxides, including majority of the actinide elements and other radionuclides) [12]. Supernate liquids, which are alkaline solutions containing nitrate, nitrite, phosphate, carbonate, sulfate, chloride, fluoride, and, in some tanks, organics. The concentration of NaOH in supernate can be 0.75–7 mol L⁻¹ [13,14]. The supernate containing are ¹³⁷Cs, ⁹⁰Sr, ¹⁰⁶Ru, ⁹⁹Tc, and other radionuclides. Alkaline radioactive intermediate level liquid waste are generated after the dissolution of salt cake, as well as washing or leaching of sludge, during pretreatment of stored alkaline HLW [12,15]. They contain ¹³⁷Cs, ⁹⁰Sr, Pu and other actinides [16].

Liquid alkaline radioactive waste includes the evaporator concentrates of NPPs and a number of decontamination solutions, which are characterized by high salinity (up to 300–350 g dm⁻³), highly alkalinity (pH > 13) and contain significant amounts of organic complexing agents and surfactants [17]. Evaporator concentrates are formed as a result of accumulation and subsequent evaporation of LRW in order to reduce waste volume at NPPs [18,19]. Activity of this waste is mainly caused by the presence of ¹³⁷Cs.

Decontamination of reactor primary circuit equipment (main circulating pumps, steam generators, pipelines, etc.) using APOX (Alkaline Permanganate and Oxalic acid), AP-CITROX (Alkaline Permanganate, CITRIC and Oxalic acids) processes generates liquid waste that, in addition to the radionuclides, contain sodium hydroxide and potassium permanganate, or citric and oxalic acids. The decontamination solutions (especially the alkaline oxidative one) may also contain several undesired organic compounds (oils, fats, detergents etc.), solid grains and colloid impurities that can carriers of radioactive nuclides [20].

Radioactive hydroxide solutions are generated when decommissioning FNRs utilizing liquid sodium or sodium-potassium blend as a coolant of a primary circuit [21]. Large quantities of spent metallic sodium are treated using a water based process resulting in 10–30 mol L⁻¹ NaOH solution.

The group of alkaline LRW can also include: liquid carbonate and alkaline radioactive streams after purification (regeneration) of the solvent (TBP) from degradation products (mono- and dibutylphosphoric acids); alkaline LWR of NPP (coolant for the primary circuit of a WWER-1000 reactor) containing boric acid (neutron absorber) and sulfate sodium salt [22]; alkaline and carbonate waste solutions after precipitation of U and MAs [23,24], including mother liquors and washing solutions generated in the industrial AUC process (production of UO₂ powders and pellets); radioactive wastewater with uranium and high content of ammonia [25]; and others.

LRWs containing short-lived β - and γ -emitting decay products are kept in monitored storage. After decay to exclusion limit, if these wastes met the regulatory requirements on chemical and biological hazards they can be safely discharged into the environment [26]. The presence of long-lived FPs (⁹⁹Tc, ⁹³Zr, ¹³⁵Cs, ¹⁰⁷Pd, ⁷⁹Se) and especially the MAs makes HLLW potentially dangerous during many thousands of years. One of the directions to reduce the risk of HLLW storage is their treatment for recovery, concentration, and separation of fractions of long-lived radionuclides, i.e. their partitioning. The complete cycle of HLLW partitioning, including the isolation of ¹³⁷Cs, ⁹⁰Sr, ⁹⁹Tc, noble metals, MAs, REEs, and the recovery of residual amounts of U and Pu, if necessary, is an important task. Therefore, the active search and development of new technologies for partitioning of HLLW is ongoing process.

The largest contribution to the HLW activity is provided by isotopes of cesium (¹³⁷Cs, ¹³⁴Cs), TUEs (²⁴¹Am, ²⁴³Am, ²⁴⁵Cm) and, in lesser but remarkable extent, ⁹⁰Sr [21]. Relatively short half lives FPs ¹³⁷Cs (T_{1/2} ~ 30 years) and ⁹⁰Sr (T_{1/2} ~ 29 years) is the major sources of short-term heat load in HLW repository due to its large heat output (¹³⁷Cs – 0.42 W g⁻¹, ⁹⁰Sr – 0.95 W g⁻¹). Heavy radiation shielding is required for HLW treatment due to the β/γ radiation field. Majority of ¹³⁷Cs and ⁹⁰Sr radioactivity and associated heat decays within a few hundred years. Heat generated from radioactive decay is a concern for vessels in which hydrogen gas is generated, because the temperature within the vessel must not exceed the auto-ignition temperature of the hydrogen [15].

The removal of high-heat-emitting and high-activity ¹³⁷Cs and ⁹⁰Sr is a key and important part of pretreatment options in processes being developed for the permanent disposal of HLLW [27]. This is essential to reducing the hazard (reducing of the radiation fields and heat source in the repository), waste classification of the treated waste reducing the further treatment, vitrification and geologic disposal costs [28,29].

Pretreatment of alkaline HLW includes process steps to remove ¹³⁷Cs, ⁹⁰Sr, ⁹⁹Tc, TUEs, sodium as well as entrained solids, from the waste feed. This allows to minimize treated waste volumes and produce waste fractions compatible with final waste forms and their disposal criteria, as well as remove radionuclides from the aqueous waste fractions to produce streams suitable for disposal as immobilized low-activity radioactive waste [15].

The current strategies for the treatment of LRW with high radioactivity content and/or long lived radionuclides include various approaches: IX/sorption, chemical precipitation, coprecipitation, electroprecipitation, membrane methods (micro- or ultrafiltration through membranes and filters, reverse osmosis), methods of decomposition of organic substances (wet oxidation, alkaline hydrolysis, photooxidation), electrochemical separation methods, ferromagnetic separation method, evaporation, combustion, sublimation, and others [26,30–32].

Significant savings in disposal cost could result by recovering the sodium hydroxide for reuse. For this purpose, an IX process of sodium from supernate liquids was developed [33].

The process of treatment of heterogeneous alkaline HLW involves dissolving the salt cake in water, separating it from the sludge, washing the sludge and adding the washings to the dissolved salt cake. The ultra-filtered supernate, solutions after salt cake dissolution, and sludge wash waters is then treated by ion exchange to remove ¹³⁷Cs, plutonium and other actinides and soluble ⁹⁰Sr [34].

The SRS developed the ITP process, according to which sodium tetraphenylborate, Na[B(C₆H₅)₄], was to be added directly to a large HLW tank to produce a cesium-bearing precipitate, which could then be processed like tank sludge [35]. The process removed cesium from the salt solution, but it also resulted in the generation of benzene from radiolytic reactions and possibly from catalytic reactions with trace metals in the waste, in particular, palladium and copper. For handled safely with highly flammable benzene during processing operations, a change in the design of the equipment was envisaged. This process was also investigated for treating LLLW [36].

There are two sequential processes currently applied at SRS in ISDP process for treat waste streams that are high in Cs, Sr, and/or actinides:

- 1) The well-developed NG-CSSX process has addressed Cs separation at Savannah River successfully, by using calixarene ligands [37,38]. The CSSX process, initially termed CSEX process,

was developed by the ORNL in the 1990s and in 2002 it was renamed into CSSX process [39].

- 2) The sorption-based ARP used for removal of Sr and An using monosodium titanate [40].

Recently, a new approach called SCIX it was proposed for the intank treatment of stored HLW [41]. The basic conceptual design for SCIX involves the dissolution of salt cake in SRS HLW tanks. According to the proposed technology, the treatment of stored alkaline streams is carried out when using small relative to industrial sized columns with IX materials, so that it can completely fit down a waste storage tank riser. Spherical resorcinol-formaldehyde (sRF) and granular crystalline silicotitanate (UOP IE 911) are being considered for Cs removal with use within the SCIX unit [42].

A complex fuel management route called as P&T process includes the separation of TUEs from FPs in SNF, quantitative removal of MAs and their subsequent burning in high flux reactors/accelerators in suitable chemical forms [43–45]. Conversion of all long-lived nuclides into short-lived or even stable species reduces the long-term radiotoxicity of waste for further increase of energy use and reduction of the heat load of the final storage. Partitioning for transmutation can be carried out by both wet (aqueous) and dry (non-aqueous) processes.

Aqueous processes of separation, purification from impurities, and preconcentration of valuable components in carbonate-alkaline media in the technology of SNF reprocessing and handling of HLLW are less known as compared to the process in nitric acid, although research in this field has been carried out for a long time and can be considered successful and more acceptable in both technical and technological respects. This is primarily due to the different selectivity of components separation in such media compared to the acidic ones. It should be noted that there are less alkaline HLLW accumulated than acidic ones, but their partitioning is a complex technological task due to strong ionizing radioactivity (β , γ , and neutron irradiations), high ionic strength, high salinity (high sodium concentration), and high alkalinity [46]. Separation, purification from impurities, and concentration of valuable components in carbonate-alkaline media (like in acid solutions) can be carried out by direct precipitation, IX, or SE techniques. At the moment, laboratory studies of universal extraction mixtures, for example, calixarene-amines, are being carried out to extract all long-lived radionuclides from alkaline media, as well as QACs, which are promising extractants for alkaline and carbonate media. New sorbents are searched for selective extraction of uranium from neutral and alkaline multicomponent solutions. Selective precipitation methods of partitioning of carbonate-alkaline solutions after the oxidative dissolution of SNF are developed with the release of stable low-solubility forms of uranium and FPs.

The most promising methods and processes of partitioning the hazardous components of HLW from alkaline solution, presented in the scientific literature in the period 1948–1976, were summarized by Marsh [6]. Currently, a large number of various options for the treatment of alkaline radioactive waste [30] and radiochemical technologies based on alkaline and carbonate media [10,47] described in the scientific literature. Accumulated considerable amount of information in the area of SNF and HLLW treatment in alkaline media requires more detailed examination and assessment. Therefore, the purpose of this survey was to generalize the known data, systematize, compare, and evaluate aqueous processes, including chemical precipitation, ion exchange, and solvent extraction, to removal of radionuclides, separation and purification of uranium and partitioning options in alkaline and carbonate aqueous media.

2. Separation of elements from alkaline and carbonate nuclear waste solutions

2.1. Chemical precipitation techniques

Chemical precipitation is used in technology for recovery, concentrating and primary purification, as well as refining to obtain pure metal compounds. Almost all components of the SNF solid phase are known to be readily soluble in nitric acid solutions but poorly soluble or insoluble in carbonate-alkaline solutions. It is well known that many precipitation techniques for the separation of valuable components from aqueous solutions are carried out with alkaline (ammonia, sodium hydroxide), carbonate or bicarbonate (sodium carbonate, sodium bicarbonate, ammonium carbonate) reagents.

New approaches to SNF reprocessing in carbonate media [1–4] developed in recent decades make it possible to effectively separate U from the bulk of FPs impurities already at the dissolution stage due to the low solubility of many metals in carbonate-alkaline media. Under conditions of anodic (electrochemical) or oxidative (reagent) dissolution in the presence of H_2O_2 , uranium oxides (UO_2 or U_3O_8) dissolve almost completely and quite quickly in carbonate media ($\text{M}_2\text{CO}_3 - \text{H}_2\text{O}_2$ solutions, where M is Na^+ or NH_4^+), and many FPs, such as REE(III), Ce(IV), Zr(IV), Ru, Rh, Pd, Sr, Ba, Al, and some others remain in insoluble residue. Thus, already at the stage of SNF dissolving in carbonate media, FPs partitioning occurs. At the same time, FPs such as Cs, Mo(VI), Tc(VII), Re(VII), Te(IV), together with uranium, are distributed into the carbonate solution, which requires additional operations for deeper purification in order to obtain purified uranium concentrates for subsequent reprocessing.

The solubility of MAs in alkaline media depends on the oxidation state [48]. Actinides are easily hydrolyzed in aqueous solutions form solid phases and can also form colloids, pseudo-colloids, molecular neutral species, and anions in alkaline media. The reprocessing of SNF and radioactive waste in alkaline hydroxide media can be complicated by the hydrolysis processes. The instability of actinides in alkaline media may be the cause of their unexpected precipitation and accumulation of nuclear materials in separation plants during processing. This leads to a decrease in the operational readiness of the installation and an increase in the potential risk of an accident, which, of course, increases the expected treatment operations costs.

The stability and solubility of actinides in alkaline media can be increased by the addition of complexing ligands due to the formation of soluble and stable anionic (including mixed) species. Such ligands may include carbonate and peroxide anions forming soluble stable carbonate and/or mixed anionic species with actinides. Uranium(VI) forms soluble mixed anionic peroxy-carbonate species, the stability of which in carbonate solutions plays an important role in carbonate methods of SNF reprocessing and great importance for carrying out all necessary technological operations. Carbonate solutions after the SNF oxidative dissolution stage should be stable for a sufficiently long time and the concentration of U(VI) in such solutions should remain stable.

In the conditions of processing of highly active materials, the environment naturally warms up due to the nuclear reactions of fissile isotopes. In addition, the reaction of dissolution of uranium oxide in carbonate solution in the presence of H_2O_2 is exothermic. Consequently, the temperature of the carbonate solution will increase with the dissolution of SNF [49]. This can lead to accelerated decomposition of both H_2O_2 and anionic peroxy-carbonate species of U(VI) in such systems [50]. However, the stability of U(VI) peroxy-carbonate species in carbonate solutions is quite high. The solutions are stable for month. The rate constant of sodium uranylperoxodicarbonate $\text{Na}_4[\text{UO}_2(\text{O}_2)(\text{CO}_3)_2]$ decomposition at its

concentration of 27.8 mmol L⁻¹ in 0.5 mol L⁻¹ Na₂CO₃ solution was only 0.01 day⁻¹ [51]. In the presence of Nd₂O₃, MoO₂, PdO, RuO₂ oxides powders, the decomposition rate of [UO₂(O₂)(CO₃)₂]⁴⁻ increases slightly, which corresponds to the values of the decomposition rate constants 0.016, 0.032, 0.4, and 2.31 day⁻¹, respectively [51]. Despite a slight increase in the rate constants of decomposition of U(VI) peroxy-carbonate species in the presence of the listed metal oxides, the overall stability of these species persists for a sufficiently long time, necessary for the subsequent processing of such solutions by various methods [51,52].

For separation of Cs, Zr, Mo, Tc, and other FPs from carbonate or alkaline solutions, it is proposed to use sequential selective precipitation with NaOH/NH₄OH (to isolate U together with Np, Pu, and partially Zr), sodium tetraphenylborate (NaBPh₄) and tetraphenylphosphonium chloride (PPh₄Cl) (for separation of Cs/Rb and Re(Tc), respectively) [1,53–57]. The process of ¹³⁷Cs separation from alkaline waste by precipitation with tetraphenylborate was developed in the 1980s [58,59].

The separation of Pu(IV) from U(VI) can be achieved by precipitation from carbonate solutions in the presence of excess H₂O₂ with the formation of low-soluble compound Na₈Pu₂(O₂)₂(-CO₃)₆•12H₂O [2,60–64]. Neptunium(V) forming precipitate exhibits similar chemical behavior. Uranium(VI) from carbonate solutions containing peroxy-carbonate species can be separated as UO₄•4H₂O by acidification with HNO₃ to pH = 3–5 [3,65–69]. In this case, soluble impurities of Mo(VI) and Tc(VII) remain in the solution. Additional selectivity of separation processes in alkaline systems [70] can be ensured.

One of the most important tasks of the nuclear fuel cycle is the mutual separation of Am(III) from chemically similar Ln(III)/Cm(III). Good efficiency of single-stage separation could be observed when oxidizing americium in Am^{VO}₂⁺ or Am^{VI}O₂²⁺, however, instability of higher oxidation states of Am complicates any separation process. Koch et al. developed a method of division Am/Ln in which Am(V) remains dissolved in 1M NaOH while Ln(III) stand out in residue [71]. Nash et al. demonstrated an oxidation/precipitation technique for successful separation of Ln(III)/Am(V/VI) based on selective precipitation of Ln(III) in carbonate/bicarbonate or sulfate media in the presence of strong oxidizing agents (e.g. ozone or Na₂S₂O₈ – AgNO₃ mixture) [72,73]. Oxidation of americium hydroxide suspension in 1.0 M NaHCO₃ solution by ozone, allowed one to reach Am/Eu and Eu/Am separation factors (SF) equals 47.0 and 20.4 for aqueous and solid phases, respectively. The separation in the Na₂S₂O₈ – AgNO₃ system allows one to achieve the SP_{An/Eu} values > 10, where An is U, Np, Pu, or Am. In the oxidation/precipitation separation process, Ln(III) precipitates as Ln₂(CO₃)₃ or Ln(OH)CO₃. The oxidized Am(VI) and Am(V) remains in carbonate solution as soluble triscarbonate anion complexes [Am^{VI}O₂(CO₃)₃]⁴⁻ and [Am^VO₂(CO₃)₃]⁵⁻ respectively. In sulfate media, Ln(III) precipitate as sulfates, while AmO₂^{+/2+} remains soluble, probably in the form of sulfate species.

The method of precipitation fractionation in carbonate media was developed by Soderquist et al. [5,74,75] with the isolation of the fractions of Cs, Sr, noble metals, FPs, and U. During carbonate reprocessing of irradiated LWR-UO₂ spent fuel samples (ATM type), it is possible to achieve a fairly good partitioning of radionuclides in the corresponding fractions: 98.3% of Cs in the cesium fraction, 99.1% of U in the uranium fraction, An is distributed between the uranium and FPs fractions, Sr is distributed in the cesium and strontium fractions. The final uranium fraction separated and purified by precipitation operations contained FPs impurities in only small amounts: Sr < 0.35%, Cs < 1.4%, Eu < 5.1%, Pu < 5%, Am, and Cm ~1% of their content in the initial SNF samples.

2.2. Adsorption and ion exchange techniques

Historically, ion exchange has been used to solve a wide range of problems in the reprocessing of SNF and HLLW (removal and refining of U, Pu, Np, some FPs, transcurium elements, and others) and also in hydrometallurgy for selective extraction of U from solutions and pulps after leaching. Ion exchange resins (IXR) well remove FPs and degradation products of TBP from aqueous solutions and used at NPPs to purify low salinity LWR, to obtain high-purity and softened water. The use of IX techniques for directly extracting of metals, primarily U(VI), from seawater is promising. Ion exchange is one of the most common methods for removing various radionuclides (Cs, Tc, etc.) from aqueous media, including liquid alkaline radioactive materials. The development and integration of IX into industry and production of synthetic ion exchangers for the implementation of this process are associated with the formation and development of the nuclear industry.

2.2.1. Organic sorbents

Polymer ion exchangers have a number of advantages: a wide nomenclature, high selectivity, high content of functional groups and the possibility of directional selection or synthesis of the ion exchangers to solve a specific problem of removal and separation of valuable elements. Both conventional strong-base AXR and weak-base resin are suitable for removal of ⁹⁹Tc (pertechnetate ion, TcO₄⁻) [76]. Ruthenium forms anionic species in alkaline media for the extraction of which, Dowex 1x8 AXR [77] and Chromosorb W based extraction chromatography resin loaded with Aliquat 336 [78] is proposed.

For removal of ¹³⁷Cs, ⁹⁰Sr and ⁹⁹Tc from alkaline HLW can be used macrocyclic polymer resins developed by IBC Advanced Technologies, Inc., such as SuperLig®-644 (SL-644, SLIG-644) and SuperLig®-639 (SL-639) [79,80]. SL-644 can remove Cs from Hanford Site alkaline waste even in the presence of excess quantities of sodium and potassium [81]. Chelating IXR Diphonix-CS™ with phenol groups can be used to simultaneously adsorb An, Cs, and Sr from HLLW [82]. The sorption of Np(VII) with AXRs such as AB-17, Amberlite IRA-400, and Dowex-1 form alkaline solutions was studied by Novikov et al. [83]. Macroporous strong-basic vinylpyridine AXR VP-1AP has been studied to removal of Np(V), Np(VI), Pu(VI) and Tc(VII) from 1–4 mol L⁻¹ NaOH solutions [30].

One technology being pursued at LANL involves the use of the Reillex™ HPQ (poly(4-vinylpyridine) AXR to remove ⁹⁹Tc from Hanford tank waste supernates [84].

Hirsch and Portock [85] showed that strongly basic macroreticular resin with quaternary ammonium functionality (Amberlyst A 29) in significant amounts can extract of Re, Tc, Mo, Cr, Tl, Se from 1.0 mol L⁻¹ NaOH solution. Schulz used the zeolites and granular macroporous (gel type) phenol-formaldehyde polymer IXR with methylene sulfonic acid cation exchange groups Duolite ARC-359 (is a refined version of Duolite C-3 resin) [86] for removal of ¹³⁷Cs from alkaline HLLW. It is noted that satisfactory selectivity of Cs to Na can be achieved when Duolite ARC-359 is used. Ion exchange methods to removal ¹³⁷Cs from HLLW using Duolite ARC-359 have been developed at Hanford B Plant [87] and SRS [88]. These methods include elution of Cs with solutions containing 1.65–2.8 mol L⁻¹ (NH₄)₂CO₃ and 0.75–2 mol L⁻¹ NH₄OH. Replacement of Duolite ARC-359 with weakly acidic phenolic (for example, granular phenol-formaldehyde condensation resin with carboxylate and phenolic functional groups Duolite CS-100) or carboxy-phenolic exchangers allows elution with a formic acid solution which can be recycled or decomposed [89]. Phenolic IXR for selective removal of Cs from highly salted alkaline radioactive

solutions can be synthesized by alkaline polycondensation of phenol, resorcinol, catechol, and a resorcinol-catechol mixture with formaldehyde [90].

In order to efficient removal and concentration of ^{137}Cs from alkaline HLLW in the Savannah River and Hanford, as well as evaporator concentrates, a spherical [91,92] and ground gel [93] RF resin was applied. Powdered and granular RF resin AXIONIT RCs effectively sorbs ^{137}Cs from solutions with $\text{pH} > 10$ in the presence of excess quantities of sodium and potassium [94].

Bibler et al. has been shown to selectively sorb 0.25 mmol L^{-1} Cs from solutions containing up to $6 \text{ mol}(\text{Na}) \text{ L}^{-1}$ [95]. Varadarajan et al. [96] has shown that polycondensation phenolic resin with iminodiacetic acid functional groups can remove both ^{137}Cs and ^{90}Sr from alkaline HLLW. The use of flexible sulfur-containing copolymers [97,98] has been proposed for the separation of ^{106}Ru from HLLW.

2.2.2. Inorganic sorbents

Inorganic sorbents in powder or spherical (granular) form and inorganic membrane materials, can be used for removal of Cs, Sr, Pu, Tc, Ce, Co from alkaline radioactive liquid streams. These materials have higher radiation, thermal and chemical resistance than organic resins. Molecular sieve zeolites [99,100], natural (chabazite, natural occurring zeolite, clinoptilolite) and synthetic zeolites such as pelletized chabazite (IE-96 and Ti-coated version TIE-96), silicotitanates [101] including titanosilicate – $\text{M}_4(\text{TiO})_4(\text{SiO}_4)_3 \cdot x\text{H}_2\text{O}$ (where $\text{M} = \text{Cs, K, H}$), crystalline silicotitanates (preferably $\text{Na}_2\text{Ti}_2\text{O}_3(\text{SiO}_4) \cdot 2\text{H}_2\text{O}$, powdered form - Ionsiv® IE-910, engineered crystalline form - Ionsiv® IE-911) [102] and Nb-doped crystalline $\text{Na}_2(\text{H}_2\text{O})_2\text{Ti}_4\text{O}_5(\text{OH})(\text{SiO}_4)_2\text{Na}(\text{H}_2\text{O})_{1.7}$ (Ionsiv® IE-911) [103] or $\text{Na}_3\text{Si}_2(\text{Nb}_{0.30}\text{Ti}_{0.70})_4\text{O}_{13}(\text{OH}) \cdot 4\text{H}_2\text{O} + 0.93\text{Zr}(\text{OH})_4$ [104]), self-bonded synthetic mordenite (Zeolon-900) [105], as well as antimonic acid, hydrous titanium oxide, manganese dioxide, zirconium phosphate, sodium copper ferrocyanide, titanium phosphate [106,107], ammonium phosphotungstate [108], potassium nickel hexacyanoferrate, potassium cobalt hexacyanoferrate (CsTreat), ferric hydroxide [109], aluminosilicate gel composed of $\text{Na}_2\text{O} \cdot \text{Al}(\text{OH})_3 \cdot 6\text{Si}(\text{OH})_4 \cdot x\text{H}_2\text{O}$ (Decalso®) [110], sodium titanate (SrTreat), monosodium titanate – NaHTi_2O_5 [111–113] belong to inorganic sorbents that have been proposed and applied for the treatment of both low and intermediate level alkaline radioactive waste streams. Hydroxides of La(III), Th(IV), Zr(IV), Ti(IV), and Mg(II) were used as sorbents of Np(VII) from alkaline solutions [114]. For the separation of Np(VII) from Np(VI) and Np(V) in alkaline solution, a column of Al_2O_3 can be used [115].

Relatively recently, composite absorbers have been developed in which inorganic sorbents are incorporated into porous particles [116]. Example of such absorbent is the zeolite-containing titanium dioxide of Ionsiv™ TIE-96 brand which is used for treatment of alkaline HLLW on the West Valley Reprocessing Plant [117]. Other examples of combined absorbents include titanium, nickel and cobalt hexacyanoferrates, as well as hydrous antimony pentoxide in a phenolsulfonic-formaldehyde resin matrix. The combined absorbents can also include ammonium molybdophosphate, potassium nickel hexacyanoferrate, sodium titanate, manganese dioxide, magnesium dioxide, calcium-activated barium sulfate and synthetic mordenite in a polyacrylonitrile matrix [118,119]. Such absorbents can be used in acidic, neutral, and alkaline solutions.

Cationic inorganic materials, such as layered double hydroxides [120], $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl}$ [121], cationic metal-organic frameworks [122] including NDTB-1 with the formula $\text{Th}[\text{B}_5\text{O}_6(\text{OH})_6](\text{H}_2\text{BO}_3) \cdot 2.5\text{H}_2\text{O}$ [123] and cationic polymeric networks with cationic functional quaternary ammonium groups [124] have been investigated and tested for $^{99}\text{TcO}_4^-$ removal from simulated HLWs.

Both inorganic and organic ion exchangers has been tested (IRC-

718, SL-644, RF, sRF) and applied in industrial scale (Decalso®, AW-500, Zeolon-900, Duolite ARC-359, CS-100, IE-96, TIE-96, CST) to remove ^{137}Cs from alkaline HLW at Hanford's B Plant, ORNL, Three Mile Island NPP, West Valley Nuclear Services Company, SRS, and Fukushima Daiichi in Japan [125].

2.2.3. Removal of uranium and plutonium from alkaline and carbonate solutions by adsorption and ion exchange

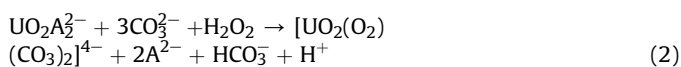
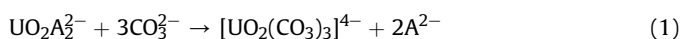
Sakaguchi and Nakajima showed that tannin is strong and highly selective with respect to the uranyl(VI) ion, while the order of sorption from almost neutral solutions is following: $\text{UO}_2^{2+} \gg \text{Cu}^{2+} \gg$ other ions [126–129]. Finely divided tannin can be used to remove ionic and colloidal substances from alkaline HLLW [130]. The Mitsubishi Nuclear Fuel Co. developed a fixed tannin sorbent for removal of An from HLLW [131]. Recently, an ionic liquid-functionalized porous aromatic framework material P-C4 (PPN-6- $\text{CH}_2\text{P}^+(\text{C}_4\text{H}_9)_3\text{Cl}^-$) [132], QAC functionalized silica gel [133], and bi-functionalized magnetic iron oxide composite which was covalently bound by ammonium and phosphonate groups [134] for uranium recovery from alkaline solution was proposed. Li et al. propose a method of IX, based on a cationic metal-organic framework adsorbent, namely Co-SLUG-35, to directly extract U(VI) from alkaline solution and seawater [135].

A pyridine-containing sorbent can be used for purification of U(VI) from FPs in carbonate solutions. Data on the resistance of tertiary pyridine resins to radiation were published by Nogami et al. [136]. Organic adsorbents with chelating functional groups (amino, sulfhydryl, carboxyl, amidoxime, imidiacetate), are promising for uranium removal from liquid streams due to their significantly high adsorption capacity for binding uranium. As was demonstrated [137–139], the most efficient material for extraction of U(VI) from seawater, in which it is present in the form of the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ anion, is the sorbents with amidoxime groups. There are few studies dedicated to the application of sorption processes for the treatment of simulated U(VI)/Pu(IV)/Pu(VI)-containing carbonate solutions or carbonate solutions generated during oxidative dissolution simulated SNF. These are mainly the studies of Japanese specialists, who proposed to use a sorbent with amidoxime groups (RC(NH₂)(NOH)) [140,141]. Amidoxime groups formed in the polymer matrix of sorbent can exist in two different structures: diamidoxime and cyclic imide dioxime [142], which form strong complexes with uranium [143,144].

Taking into account formation of $[\text{UO}_2(\text{CO}_3)_3]^{4-}$, $[\text{Pu}(\text{CO}_3)_4]^{4-}$, and $[\text{PuO}_2(\text{CO}_3)_3]^{4-}$ anionic complexes in carbonate solutions, studies were carried out on sorption of U(VI), Pu(IV), and Pu(VI) from 0.5 mol L^{-1} Na_2CO_3 – NaHCO_3 solution at $\text{pH} \sim 9.0$ containing admixtures of the following FPs: Ru(III), Pd(II), Zr(IV), Mo(VI), and Re(VII), as a surrogate of Tc(VII). At the initial U(VI), Pu(IV), and Pu(VI) concentrations in such solutions of $1.34 \cdot 10^{-4} \text{ mol L}^{-1}$, $5.00 \cdot 10^{-5} \text{ mol L}^{-1}$, and $5.00 \cdot 10^{-5} \text{ mol L}^{-1}$, respectively, distribution constants were 131 for U(VI), 229 for Pu(IV), and 10.4 for Pu(VI). The following selectivity was established for sorption on amidoxime resin: $\text{Pu(IV)} > \text{Pu(VI)}$ and $\text{U(VI)} > \text{Pu(VI)}$ on passing carbonate solution of the above composition. Almost all FPs passed through a column containing amidoxime sorbent without sorption into sorbent phase. Uranium and plutonium were desorbed from amidoxime sorbent with 0.5 mol L^{-1} HNO_3 . On the basis of this research, a conclusion was made on the applicability of amidoxime sorbent for the separation of U(VI), Pu(IV), and Pu(VI) from FPs, which are soluble in carbonate solutions. Fibrous “filled” sorbents with amidoxime groups can be used for recovering U(VI), Am(III), and Pu(IV) from alkaline solutions at various (even high) values of pH and salt content [145].

Solutions of Na_2CO_3 can be used for elution of uranium from amidoxime sorbents [146] and membranes based on it [147], in this

process, extraction of U(VI) achieves 67% and 95%, respectively. For elution of U(VI) mixed 1 mol L⁻¹ Na₂CO₃–0.1 mol L⁻¹ H₂O₂ solutions were proposed [142]. High efficiency of elution process (nearly quantitative U(VI) recovery) is explained by the formation of stable U(VI) peroxy-carbonate species. The replacement of acidic elution (aqueous solutions of HCl or HNO₃) by that offered by the authors can allow increase in the increases of service life of the sorbent due to exclusion of the process of acidic degradation. At the same time, there is no need to regenerate sorbent for reuse, which reduces the cost of this technology. Preparation of sorbent for reuse requires only washing with water. The process of U(VI) elution from amidoxime sorbent with carbonate and carbonate-peroxide solutions can be represented by the following chemical equations [142]:



Later it was demonstrated that the use of Na₂CO₃–H₂O₂ solutions for elution provides up to 95% extraction of the absorbed uranium [148]. It is noted that this method is more selective toward U(VI) in comparison with acidic elution.

As was noted above [5], a cation exchange sorbent of the Bio-Rad AG50-X12 in the NH₄⁺ form was used for the sorption-based purification of carbonate U(VI)-containing solutions from Cs. Cesium was eluted from sorbent phase with saturated (NH₄)₂CO₃ solution followed by conditioning of sorbent by washing with 0.1 mol L⁻¹ (NH₄)₂CO₃. As a result of performed sorption-based purification of U(VI)-containing carbonate solution from ¹³⁷Cs, the latter was extracted to Cs fraction by 98.3%, while residual content of ¹³⁷Cs in final uranium product was only 1.3% of its initial content in irradiated UO₂ fuel. These data allow one to choose a rather selective sorbent for the purification of carbonate solutions from ¹³⁷Cs.

A weakly basic anion exchanger Bio-Rex 5 [149] and an inorganic ion exchanger such as Al₂O₃ [150] were studied to purify U(VI) from FPs in Na₂CO₃/NaHCO₃ solutions.

Despite the rich historical experience of SNF reprocessing, a large number of studies and the advantages of IX methods, certain characteristics of IX materials and processes limit their applicability and efficiency. Even if an ion exchanger is highly selective for a certain radionuclide, it needs to meet several other requirements to become a product that can be used in industrial scale separation processes. As notable limitations that affect the application of the treatment method on a industrial scale are incomplete removal, low efficiency, high operating and capital costs, sensitivity to operating conditions, generation of by-products and secondary wastes which require further treatment. Wide use of IX methods throughout the reprocessing plant would lead to increase of the amount of the secondary waste of dilute solutions mainly from the regeneration for the ion exchangers as well as directly discharged secondary solid waste. Complete removal of a specific radionuclide in a column is often difficult owing to leakage or breakthrough. The cause of the leakage is the formation of colloidal, pseudo-colloidal, nonionic and non-exchangeable (hydrolyzed, low soluble and oppositely charged species) forms by radionuclides, as well as mechanical problems (channeling in column systems, shrinkage of the resin beads, uneven settling of the resin bed) [151].

2.3. Solvent extraction techniques

The SE methods is widely used for purification, concentration, and separation of An from various aqueous media. Solvent

extraction, also known as liquid-liquid extraction is a selective separation process consisting of the transfer of a solute from one solvent to another, the two solvents being immiscible or partially miscible with each other.

Such types of solvents as phenolic compounds and derivatives (alkylpyrocatechols, aminomethylphenols, alkylphenol oligomers) [152–154], HDEHP [155], HPMBP, 2-hydroxy-5-tert-butylphenyl disulfide [154,156], calixarenes, neutral solvents (TBP, TOPO), crown ether derivatives, β-diketones [157], aliphatic amines [158–162], QACs [152,163–166], sulfonamide-based ligands [167–169], naphthyridines [170] were used for removal of An from alkaline and carbonate media [10,30].

The phenolic solvents, including alkylpyrocatechols are effective for the removal actinides in different oxidation states from hydroxide and carbonate solutions. Salts of amines and QACs are selective reagents for the extraction of An from acidic, alkaline, and saline solutions. In the technology, tertiary amines were used in the processes of separation and purification of An [171], in particular, triaurylamine was used for the final purification of Pu and Np from nitric acid media. High efficiency of extraction with amines led to their use for analytical purposes for separation of Np(IV) from Pu(III), radioactive and stable FPs (REEs, Zr, Nb, Sr, Cs, and other elements) [172]. Alkylamines can extract An in different oxidation states from carbonate media, while the salts of primary amines are the most effective [160,173]. A significant amount of research on chemical behavior of Am(III), Am(V), La(III), Eu(III), Th(IV), Pu(IV), U(VI), and some other elements upon extraction by Aliquat-336 and other types of solvents from hydroxide, carbonate and bicarbonate solutions it was carried out under the leadership of academician B.F. Myasoedov [30].

The main advantages of amines and QACs as compared to other classes of solvents are as follows: high selectivity in the extraction of Pu and Np; high extraction capacity; good purification from FPs impurities; high boiling point, relatively low viscosity, low solubility in water, high resistance to hydrolysis and radiation resistance in radioactive solutions. Currently, amines and QACs are commercially available extractants (Alamine 336, Aliquate 336, Adogen 464, N₂₆₃, etc.), which can be used on a large scale in various industrial processes. Benzene, toluene, *o*- or *m*-xylene, chloroform, carbon tetrachloride, nitrobenzene, etc. are usually used as diluents for amines and QACs in lab-scale researches [174]. For industrial implementation as safer promising diluents having low volatility and high flash point, low toxicity and solubility in water, high chemical and radiation stability, good phase-disengagement behavior with low emulsion tendency, and good solvation and extraction capability of the desired species may be recommended Isopar® series isoparaffinic hydrocarbons with additives of modifiers (for example: 2-octanone, TBP, and 4-(1-butylpentyl)pyridine), as well as polar fluorinated diluents (DDFHME, DDFHA, Formal-2, F-3, fluorinated sulfones).

Typically, the stripping process of TUEs in alkaline and carbonate media does not cause problems. When organic phase, for example, MTOA carbonate, is contacted with (NH₄)₂CO₃ or NH₄HCO₃ solution, the metal quickly transfers to the aqueous phase and, (NH₄)₄[AnO₂(CO₃)₃] crystallizes from the aqueous phase in the case of excess of these salts. In this case, precipitation stripping [175] occurs, which provides a certain simplification of processing scheme.

In [176], 20–30% solution of CMP in CCl₄ was used for the separation of Am from a synthetic solution containing a mixture of Na₂CO₃, Na₃PO₄, NaCl, Na₂SO₄, and actinides: Pu, Am, U.

The industrial technology of Cs separation from alkaline HLLW using calixarene-crown-ether as a selective extractant was introduced in Savannah River [177,178]. Hydroxycalixarenes, in particular tert-butyl calicalix[4, 6 and 8]arenes [46,179,180], also can be

used for the separation of Cs from alkaline HLLW. An efficient CSSX industrial process based on SE with calixarene [181,182] has been developed for the separation of Cs from HLLW.

Americium(III) and Eu(III) effectively removal from carbonate-alkaline solutions using mixture t-butylthiacalix[4]arene and water-immiscible organochlorine, aromatic, aliphatic or fluoroorganic diluent [183]. A mixture pisononylkalix[6 or 8]arene dissolved in a mixed organic solvent containing limiting hydrocarbon and a polar organic component is proposed for the co-extraction of Cs and Am(III) from alkaline solutions [184]. The developed solvent mixtures can be used in the treatment of alkaline HLLW.

Existing methods for the SE of pertechnetate anion from alkaline media have included the use of cyclohexanone [185], tetraphenylarsonium chloride [186], tetrazolium salts [187], tetraalkylammonium halides [188], polyethylene glycols [189], crown ethers [190,191]. Sulfonamide ligands have been considered for removing Sm(III) from highly alkaline HLW at the SRS [169].

The use of undiluted cyclohexanone has been proposed to remove ^{99}Tc from alkaline HLLW. Recovery of ^{99}Tc can reach 99.2–99.7% over 12 mixer-settler stages. Technetium(VII) can be recovered from cyclohexanone by stripping with water or sorption on a macreticular ion exchanger [185]. Pyridine, quinoline derivatives, and QACs also extract Tc(VII) from alkaline solutions [185]. Alkaline-Side Extraction of Technetium process was proposed to removal of technetium from alkaline HLW using SE with crown ethers and QACs [192].

Mahajan et al. [193] studied the recovery of Pu(IV) from tartrate-containing alkaline solutions with 20% Aliquat 336 in xylene. The extraction of Pu increased with tartrate concentration and reached > 98% when the concentrations of tartrate and alkalinity were equal.

K. Ueno and A. Saito [194] studied extraction of many metals from 0.1–2.0 mol L⁻¹ (NH₄)₂CO₃ solutions with 0.1 mol L⁻¹ MTOA carbonate solution in toluene. It was shown that the differences in distribution ratio (D_M) of studied elements can reach six orders of magnitude depending on the nature of the extracted metal and (NH₄)₂CO₃ concentration, which allows one to determine possibilities for SE purification of U, Pu, and Th from FPs in carbonate media, and to single out groups which are extracted better and worse than the target elements. Z.K. Karalova et al. studied of SE separation of An(III) and Ln(III) with Aliquat 336 in hydroxide form [152–166]. It was the first study to consider the possibility of use of alkaline media to raise the efficiency of An and Ln separation during SNF reprocessing in the presence of complexing agents allowing retention of An and Ln in alkaline solutions; ideas were formulated on the possibility to employ carbonate-alkaline media for SE purification of U, Pu, Am, Np, Th from FPs admixtures during SNF reprocessing with experimental demonstration of their practical implementation. The use of DTPA and DOP in toluene in DOP–NaOH–DTPA system is promising for the separation of TPEs from Ln and An, as well as for separating Am and Cm from Bk and others [159]. At the same time, the degree of element separation can be increased by varying the time of phase mixing, the medium alkalinity, as well as by changing extractant concentration.

S.I. Stepanov and A.M. Chekmarev formulated and published a concept of SE-based reprocessing of SNF in carbonate media, so-called CARBEX process concept [4]. This process uses SE separation of U and Pu from FPs, which allows one to achieve high values of DF equal to 10⁵–10⁶. The development of the CARBEX or CARBOFLUOREX process requires detailed studies of SE of U(VI), Pu(IV), and Pu(VI) from carbonate, carbonate-peroxide and carbonate-fluoride solutions. Many scientific studies were dedicated to this topic, starting with an article by K. Ueno and A. Saito [194]. A peculiarity of application of QACs for SE purification of solutions from

specific components consists in the necessity to use them in the anionic form inherent in the extracted aqueous media. For SE separation of U(VI) from carbonate solutions, QACs is to be in the carbonate anionic form or in the HCO₃⁻ form. This feature imposes additional requirements on the synthesis of QAC-type solvents: the reagent should be in required anionic form or in anionic form that could be easily replaced by hydrophilic anions such as SO₄²⁻, OH⁻, CO₃²⁻, etc. In [194] it was established that the ability of MTOA carbonate to extract U and various elements of FPs is different, which allows one to forecast their efficient separation from carbonate media.

An amine based extractant Aliquat 336 in toluene was proposed as a promising solvent for the uranium recovery without extracting other elements from carbonate streams generated by an alkaline dissolution wastes from the production of the medical isotope ^{99}Mo [7,8,195].

2.3.1. The chemistry of solvent extraction of carbonate species of uranium(VI) from carbonate solutions

The topic of U(VI) carbonate species extraction from carbonate solutions by QACs is the subject of a significant number of studies, their review is presented in [196]. Solvent extraction of U(VI) from carbonate solutions was carried out by organic solutions of MTOA or MTAA (methyltrialkyl(C₇–C₉)ammonium) carbonates under different conditions, varying concentration of alkali metal and/or ammonium carbonates, U(VI), pH of initial solutions, concentration of solvent, etc. Depending on SE conditions, two most stable anionic complexes are extracted to organic phase: [UO₂(CO₃)₂]²⁻ and [UO₂(CO₃)₃]⁴⁻ with formation in organic phase of (R₄N)₂[UO₂(CO₃)₂] and (R₄N)₄[UO₂(CO₃)₃], respectively, where R₄N⁺ is quaternary ammonium salt cation. The primary region of extraction of the doubly charged complex of U(VI) is pH from 7.5 to 8.5, while pH for the four-charged complex is from 9.0 to 12.0. These pH regions correspond to formation and stable state of each of these two complexes in aqueous initial solutions. In adjacent pH regions, simultaneous extraction of the two described complexes is observed.

Special properties are demonstrated by U(VI)-containing carbonate solutions in the pH region of 6.5–7.5. Due to hydrolytic polymerization of U(VI) carbonate species in the presence of carbonic acid proton, in this region there occurs an extraction, by carbonate or bicarbonate of MTOA, of polynuclear carbonate species of U(VI). The most stable and well-studied polynuclear species extracted by MTOA carbonate in this pH region is [(UO₂)₃(CO₃)₄]⁶⁻, which forms (R₄N)₆[(UO₂)₃(CO₃)₄] in organic phase. Described compositions of the extracted compounds were confirmed by different physical and chemical methods, including electronic-, IR-, and NMR-spectroscopy, polarography, method of mathematical modeling of extraction equilibria, methods of distribution, slope analysis, and chemical analysis of aqueous and organic phases. It is necessary to note that the issue of interpretation of electronic spectra of aqueous and organic solutions of U(VI) carbonate species was developed in recent studies [197–199] on the basis of new ideas on the composition of absorbing particles taking into account the processes of hydrolysis, dissociation, association, polymerization and ligand exchange.

2.3.2. The chemistry of solvent extraction of uranium(VI) peroxy-carbonate species from carbonate solutions

The oxidative dissolution of uranium oxide SNF in carbonate solutions in the presence of H₂O₂, U(VI) leads to solution of mixed peroxy-carbonate species mostly [UO₂(O₂)(CO₃)₂]⁴⁻. Anionic species of U(VI) is traditionally extracted with QACs. Earlier in [200], extraction of [UO₂(O₂)(CO₃)₂]⁴⁻ from Na₂CO₃ solutions with MTAA chloride in kerosene was studied. The formation of (R₄N)₄[UO₂(O₂)(CO₃)₂] in organic phase was established by the

methods of saturation and slope analysis. Taking into account changes in the composition of peroxo-carbonate species on increase in U(VI) concentration in initial aqueous solution, the chemistry of U(VI) extraction (present in carbonate solutions in the form of both peroxo-carbonate and carbonate species) with organic solutions of MTOA carbonate was studied [198,201–204]. The methods of distribution (extraction isotherm) [203,204] and derivative electronic spectroscopy of aqueous and organic phases [204,205] showed that, depending on U(VI) concentration in initial aqueous solution, the following species are sequentially extracted to organic phase: four-charged U(VI) carbonate complex $(R_4N)_4[UO_2(CO_3)_3]$, mixed peroxo-carbonate complexes $(R_4N)_4[UO_2(O_2)(CO_3)_2]$ and $(R_4N)_6[(UO_2)_2(O_2)(CO_3)_4]$, and a trinuclear U(VI) peroxo-carbonate complex, presumably $(R_4N)_6[(UO_2)_3(O_2)_2(CO_3)_4]$ or $(R_4N)_6[(UO_2)_3(O_2)(CO_3)(CO_3)_4]$, which forms when U(VI) concentration in organic phase exceeds 70 g L^{-1} [204].

Along with the SE of U(VI) peroxo-carbonate species, stripping of U(VI)-loaded organic phases by concentrated $(NH_4)_2CO_3$ and/or NH_4HCO_3 solutions was studied [202]. A traditional method for stripping of U(VI) from U(VI)-loaded organic phases is the precipitation stripping by concentrated solutions of $(NH_4)_2CO_3/NH_4HCO_3$ mixture [206]. Stable ammonium uranyl carbonate (AUC), $(NH_4)_4[UO_2(CO_3)_3]$, forms in such systems on transfer from organic to aqueous phase; this compound is low soluble under these conditions [207]. The same complex also forms during stripping of U(VI) from MTOA carbonate organic phases loaded by U(VI) carbonate species [196]. One could expect the absence of U(VI) precipitation into solid phase on stripping of U(VI) peroxo-carbonate species because their solubility in aqueous solutions is significantly higher than that for AUC. Indeed, no solid phase forms on stripping with 6–15% $(NH_4)_2CO_3$ solutions, although the transfer of U(VI) from organic to aqueous phase reaches 98% in one contact. Formation of solid phase was observed only when 20% $(NH_4)_2CO_3$ solution was used for stripping, and, moreover, precipitation of U from aqueous solution did not exceed 15%. Electronic spectroscopy showed formation of $(NH_4)_4[UO_2(O_2)(CO_3)_2]$, $(NH_4)_6[(UO_2)_2(O_2)(CO_3)_4]$, and $(NH_4)_6[(UO_2)_3(O_2)_2(CO_3)_3]$ in strip liquor. According to XRD analysis data, the composition of solid phase resulting from stripping was $(NH_4)_4[UO_2(CO_3)_3]$. Thus, a reaction of ligand exchange between peroxide and carbonate ligands is necessary for precipitation stripping in systems with peroxo-carbonate species. Uranium(VI) carbonate complexes were obtained from peroxo-carbonate species using excess of carbonate anions produced by introduction of CO_2 gas to the system. In fact, more complete recovery of U(VI) into solid phase on U(VI) stripping from organic phases loaded by U(VI) peroxo-carbonate species is observed in the presence of CO_2 .

At the same time, aqueous phase after extraction, according to the data of electronic spectroscopy, contains mainly U(VI) peroxo-carbonate species. This allows one to assume that the ligand exchange reaction proceeds in aqueous phase, with the rate of this reaction being lower than the rate of interphase transfer in SE process.

Thus, precipitation stripping of U(VI) from U(VI) peroxo-

carbonate species loaded organic phases develops under the condition of execution of an efficient ligand displacement of peroxide ligands by carbonate ligands. Such a behavior of U(VI) peroxo-carbonate species allows one to develop a single process of U(VI) precipitation stripping in the form of AUC from organic phases loaded by U(VI) carbonate, peroxo-carbonate, or fluoro-carbonate mixed species.

2.3.3. The chemistry of solvent extraction of uranium(VI) fluoro-carbonate species from carbonate solutions

Extraction of U(VI) from carbonate-fluoride solutions with MTOA or MTAA salts (both carbonate and fluoride) was studied in [205]. Uranium(VI) in aqueous carbonate-fluoride solutions forms mixed carbonate-fluoride species with various structure and can be present in the form of a stable carbonate complex and, on significant excess of fluoride ions, in the form of purely fluoride complex. Such a behavior of U(VI) in the $Na_2CO_3-NaF-UO_2F_2-H_2O$ systems makes the chemistry of SE by QACs significantly more difficult.

To study the chemistry of U(VI) extraction from carbonate-fluoride solutions, an isotherm was experimentally obtained for extraction of U(VI) with 0.25 mol L^{-1} MTOA carbonate in toluene from 0.5 mol L^{-1} solution of Na_2CO_3 in mixture with 0.5 mol L^{-1} NaF at $25 \pm 0.1 \text{ }^\circ\text{C}$. This isotherm is characterized by a sharp rise in U(VI) concentration in organic phase in initial section, and by the absence of the characteristic saturation plateau for high concentrations of U(VI) at equilibrium. The molar ratio $(R_4N)_2CO_3/U(VI) = Q$ changes from 180 to 1.3 in the all-region of U(VI) distribution in the organic phase. These data indicate variety of extracted U(VI) compounds, which can be represented by solvated (by additional solvent molecules) conventional complexes of $(R_4N)_4[UO_2(CO_3)_2F_2]$, $(R_4N)_3[UO_2(CO_3)F_3]$, and $(R_4N)_4[UO_2(CO_3)F_4]$, and polynuclear U(VI) compounds at $Q = 1.3$. Even higher values of saturation of MTOA carbonate by U(VI) fluoro-carbonate species were obtained during U(VI) extraction with high aqueous to organic phase ratios (A/O) (Table 1).

Value of $Q > 1$ certifies deep polymerization with the formation of U(VI) polynuclear species. By analogy with mixed peroxo-carbonate polynuclear species of U(VI) [204], polynuclear fluoride-carbonate species of U(VI) can have both fluoride and carbonate groups as bridge groups.

Studies of the SE chemistry of U(VI) fluoro-carbonate species from carbonate solutions by MTOA carbonate or fluoride by the methods of electron-, ^{13}C , ^{19}F NMR-spectroscopy, physical and chemical analysis of extraction systems, and mathematical modeling of extraction isotherms, the following compositions of the extracted compounds were established: $(R_4N)_2[UO_2(CO_3)_2F_2] \cdot x(R_4N)_2CO_3$, $(R_4N)_4[UO_2(CO_3)_2F_2]$, $(R_4N)_3[UO_2(CO_3)F_3]$, $(R_4N)_2[(UO_2)_2(CO_3)F_4]$, $(R_4N)_4[UO_2(CO_3)F_4] \cdot xR_4NF$, and $(R_4N)_4[(UO_2(CO_3)_3) \cdot xR_4NF]$, where $x = 1-2$. The region of high saturation of organic phase is related to extraction of U(VI) polynuclear species, mostly binuclear, $(R_4N)_2[(UO_2)_2(CO_3)F_4]$. On the basis of obtained experimental data, it can be stated that the extraction of U(VI) fluoro-carbonate species from carbonate solutions by different anionic forms of MTOA or MTAA is accompanied by transfers of some mixed ligand forms of complexes to other ones. These transfers depend on both the ratio of ligands in initial aqueous solution and the change of this ratio during U(VI) distribution to organic phase. At the same time, the ability of fluoride ligand to form bridge bonds determines significant predisposition of U(VI) fluoride species toward formation of polynuclear compounds, which in turn allows preparation of high concentrations of U(VI) in organic phase during extraction for a prolonged period of contact between aqueous and organic phases. High saturation of organic phase by U(VI) provides a more efficient precipitation stripping, which can also be performed by concentrated solutions of $(NH_4)_2CO_3$ or NH_4HCO_3 .

Table 1

Extraction of U(VI) from solution containing $0.5 \text{ mol L}^{-1} Na_2CO_3-0.5 \text{ mol L}^{-1} NaF$ and $93.2 \text{ g U(VI) L}^{-1}$ by 0.25 mol L^{-1} MTOA carbonate in toluene with different A/O. Mixing time = 60 min.

A/O	1	2	4	7	10	12
$[U(VI)]_{ORG}, \text{ g L}^{-1}$	45.5	44.4	64.8	71.4	87	92.4
$[U(VI)]_{AQ}, \text{ g L}^{-1}$	47.7	71	77	83	84.5	85.5
Q	1.3	1.3	0.9	0.8	0.7	0.6

2.3.4. Solvent extraction purification of uranium from fission products in carbonate media

Possibilities of SE-based separation of U, Pu and FPs from carbonate solutions with QAC were demonstrated for the first time in the paper by K. Ueno and A. Saito [194]. Fig. 1 shows the dependences of D_M for U(VI), Pu(IV), Np(V), Am(III), and a number of FPs on concentration of $(\text{NH}_4)_2\text{CO}_3$ during extraction with 10 vol. % solution of MTOA carbonate in toluene at 25 °C.

Almost for all of the elements considered, D_M decreases as $(\text{NH}_4)_2\text{CO}_3$ concentration increases. At the same time, it is possible to single out groups of elements with high, low, and middle levels of the ease of extraction using D_M values. The largest extraction with MTOA carbonate solution in toluene is shown by I and Tc. These elements can be co-extracted with U and other An and require additional purification from them. On the other hand, no additional purification is necessary in extraction cycle if these elements are preliminarily removed from carbonate solutions. Such elements as Cs, Sr, Ba, Ca have low values of D_M , and purification from them is not difficult. To the middle group of elements, one can refer the group of REEs, Mo, Ru, and Nb. Purification from them requires several steps of countercurrent extraction mode. On the whole, efficient purification from all FPs to produce purified U(VI) carbonate compounds can be reached at the stage of precipitation stripping by countercurrent extraction in 5–10 steps with MTOA or MTAA carbonates from carbonate solutions upon saturation of organic phase with U(VI).

Such works were carried out in the course of experimental justification of the CARBEX process [208,209]. After SE purification of U(VI) (which was present in Na_2CO_3 solution in the form of $\text{Na}_4[\text{UO}_2(\text{CO}_3)_3]$) by 0.4 mol L^{-1} MTOA carbonate in toluene with $A/O = 1$ in 5 steps of countercurrent extraction cascade, DF were from 10^3 to 10^5 , which is comparable to those of the PUREX process. Analogous results for U(VI) purification from FPs admixtures were achieved by SE purification from carbonate-fluoride solutions using MTOA carbonate [210]. The considered experimental data confirm the efficient purification of U(VI) from FPs during its extraction from carbonate solutions with MTOA or MTAA carbonates.

Along with purification of U(VI) from FPs in carbonate media, SE separation of U(VI)/Pu(IV) and U(VI)/Pu(VI) using MTAA carbonate

solutions in toluene was studied [211–214]. It was demonstrated that the highest values of SF in carbonate solutions were obtained for the U(VI)/Pu(IV) pair (Table 2). Therefore, it is necessary to stabilize Pu in tetravalent state and U in hexavalent state for efficient purification of U from Pu in carbonate solutions. When U and Pu are present in carbonate solutions in the same valence state, U(VI) and Pu(VI), co-extraction of these two elements without notable separation is observed, this allows their collective SE purification from FPs from such solutions.

2.3.5. Solvent extraction separation of trivalent actinides and lanthanides in alkaline solutions

It is also necessary to note the studies on separation of An(III), mostly Am(III), and Eu(III) from alkaline solutions with Aliquat 336 hydroxide [152,154,163,165,215–224] to solve the problem of An partitioning and their subsequent treatment; this problem causes significant difficulties during reprocessing of SNF in the PUREX process until now.

The results of SE removal and separation of REEs and TPES from alkaline solutions with QACs were published for the first time by E.S. Palshin et al. [215]. Later, Z.K. Karalova et al. carried out systemic studies on the extraction of trivalent REEs and TPES with QACs (mostly Aliquat-336-OH) from alkaline media in the presence of complexing agents retaining metals in alkaline solutions: α -hydroxycarboxylic acids (AHAs) [163], complexons (CSs) [163,165], hydroxycomplexons (HCSs) [216], and alkylphosphonic complexons (ACSSs) [217]. In all studied systems, cyclohexane or μ -xylene were used as diluents. The chemistry of REEs extraction from alkaline solutions in the presence of complexons of various types is related by researchers to extraction of both hydroxocomplexes of metals and anionic species with complexing ligands [218]. It was demonstrated by iontophoresis and mole-ratio method that species extracted to organic phase in most cases are represented by singly charged anionic species of REEs [152,219]. For AHAs, which form less stable species in aqueous phase, a distribution of $[\text{Ln}^{\text{III}}(\text{OH})_4]^-$ with formation of $\text{R}_4\text{N}[\text{Ln}^{\text{III}}(\text{OH})_4]$ is observed [220]. In the event of transition to CSs, HCSs, and ACSSs, which form stronger complexes with REEs, $\text{R}_4\text{N}[\text{Ln}^{\text{III}}\text{L}_4]$ compounds are extracted to organic phase, where L is singly charged complexon anion [152,219,220]. The complexation of

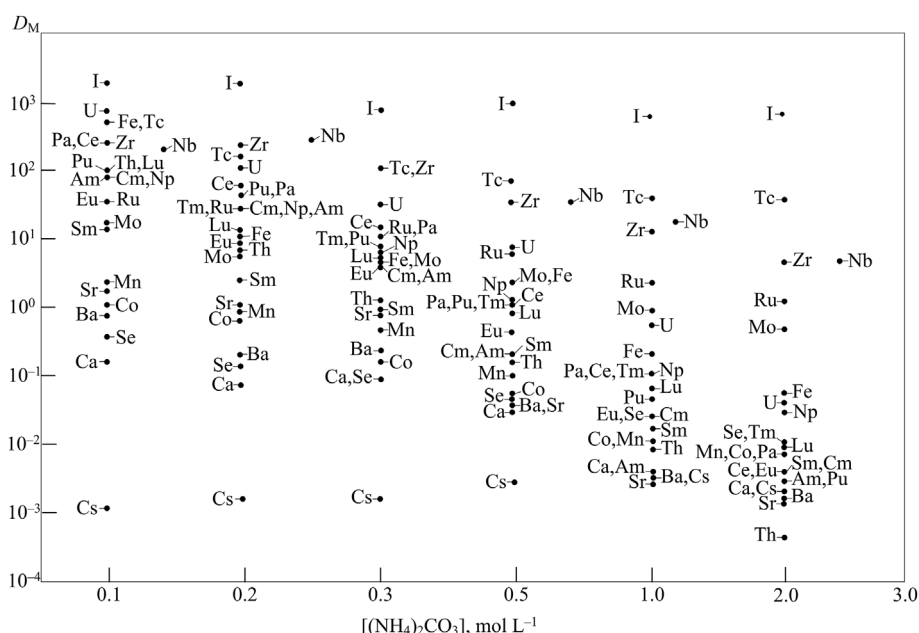


Fig. 1. Dependence of D_M on $(\text{NH}_4)_2\text{CO}_3$ concentration during SE with 10 vol. % MTOA carbonate solution in toluene at 25 °C [194].

Table 2

Modeling of a three-step extraction cascade for separation of U(VI) and Pu(IV) from aqueous carbonate solution containing 94.8 gU(VI) L⁻¹, 82.2 μgPu(IV) L⁻¹ and 1.0 mol L⁻¹ Na₂CO₃ using 0.8 mol L⁻¹ MTAA carbonate. A/O = 1, 20 ± 1 °C. Mixing time = 5 min.

Step no.	[U(VI)] _{AQ} , g L ⁻¹	[U(VI)] _{ORG} , g L ⁻¹	D _{U(VI)}	[Pu(IV)] _{AQ} , μg L ⁻¹	[Pu(IV)] _{ORG} , μg L ⁻¹	D _{Pu(IV)}	SF
1	29.1	71.3	2.5	81.1	1.1	0.014	178
2	26.6	68.8	2.6	80.1	0.5	0.006	433
3	26.3	68.5	2.6	79.6	0.5	0.006	433

REEs with AHAs in alkaline solutions includes the participation of hydroxyl groups and depends on their number and mutual arrangement, which significantly affects $D_{\text{REE(III)}}$ values. Depending on the nature of hydroxycarboxylic acid, $D_{\text{Eu(III)}}$ decreases in the following order: gluconic > trihydroxyglutaric > tartaric > glyceric. Along with the growth of concentration, the acids also show a decrease of $D_{\text{Eu(III)}}$, which is caused by competitive extraction of acid anion. As alkali concentration increases, $D_{\text{Eu(III)}}$ pass their maximum at 0.25–0.3 mol L⁻¹ NaOH [221].

Complexes $\text{R}_4\text{N}[\text{La}^{\text{III}}(\text{OH})_4]$ and $\text{R}_4\text{N}[\text{Eu}^{\text{III}}(\text{OH})_4]$ are extracted in La(III)(Eu(III))–NaOH–TOG(EDTMP)–Aliquat-336-OH systems [222] (PMR- and IR-spectroscopy, distribution method). Trace amounts of Eu(III) are extracted in the presence of tartaric acid by Aliquat-336-OH mostly in the form of $\text{R}_4\text{N}[\text{Eu}^{\text{III}}(\text{C}_4\text{H}_2\text{O}_6)]$ complex [154]. Europium(III) polymer compounds, where tartaric acid anions serve as bridge ligands [223], or hydrolyzed forms ($\text{R}_4\text{N})_2[\text{Eu}^{\text{III}}(\text{OH})(\text{C}_4\text{H}_2\text{O}_6)]$ are extracted from 0.2–1.0 mol L⁻¹ NaOH at Eu(III) concentration from 10⁻⁴ to 10⁻³ mol L⁻¹, colloidal forms are extracted at Eu(III) concentration over 10⁻³ mol L⁻¹ [224].

Extraction of Eu(III) from alkaline solutions in the presence of polyaminepolyacetic acids is related by researchers to the distribution of the following complexes: $\text{Eu}^{\text{III}}\text{L}^-$, $\text{Eu}^{\text{III}}\text{L}(\text{OH})^{2-}$, and $\text{Eu}^{\text{III}}\text{L}_2^{3-}$ for EDTA, $\text{Eu}^{\text{III}}\text{HL}^-$ and $\text{Eu}^{\text{III}}\text{L}^{2-}$ for DTPA and OPDTA [165]. Ligand denticity increases on transition to hydroxyl-containing derivatives of polymethylenediaminetetraacetic acid, which ensures extraction of singly charged Eu(III) species from more alkaline solutions. Extraction of Eu(III) increases in the order: OEDTTA < OEDTA < OEIDA < OPDTA < resorcinol complexon < DOBTA < OFIDA [216]. It was also established that HCSs from aromatic series ensure extraction of Eu(III) in a wider range of NaOH concentrations than HCSs from aliphatic series.

On transition to ACSs, such as EDTPA and DTPPA, there is a shift of extraction curves to more alkaline region ($C_{\text{NaOH}} = 0.05\text{--}0.6$ mol L⁻¹), which is caused by the formation of strong complexes with these acids [217]. In other respects, the features of extraction remain the same as for AHAs, CSs, and HCSs.

Along with the possibility of extraction of REEs and TPEs from alkaline solutions, a possibility of their separation from each other was discussed. It was demonstrated that the following order is observed for extraction of metals with different oxidation degrees: M(III) > M(IV) > M(V) > M(VI) on extraction from alkaline solutions and in the presence of tartaric acid or CSs. Separation factor values of 100 and more were achieved for pairs of polyvalent metals. At the same time, SF values for trivalent REEs and TPEs did not exceed two in one-step mode of extraction process [219]. The value of SF_{Am(III)/Eu(III)}} reaches five for Am(III) and Eu(III) separation in columns with Aliquat-336-OH on fluoroplastic-4 support in 0.3 mol L⁻¹ NaOH – 0.02 mol L⁻¹ EDTA system [224]. Thus, alkaline solutions of REEs and TPEs, when complexons of various types are used for retaining metals in solutions, can be employed for efficient partitioning of FPs obtained by SNF reprocessing in carbonate media.

3. Comparison and evaluation of chemical precipitation, ion exchange and solvent extraction for SNF reprocessing and radioactive waste treatment

To evaluate the use of treatment methods for removal of radionuclides from alkaline waste solutions and liquid streams during SNF reprocessing, the capabilities and limitations of the processes must be recognized and understood. To reduce disposal costs, in any process for the removal of radionuclides from a liquid waste it is important to minimize the volume of the secondary waste to be conditioned and disposed of in a final repository as well as to minimize the number of separation processes utilized. The chemical precipitation, IX and SE are suitable methods for separation and purification of fissile materials in the hydro-chemical technology of nuclear fuel production, SNF and radioactive wastes reprocessing.

In the technology of hydro-chemical reprocessing of SNF on an industrial scale, schemes involving SE processes are widely used to separate the uranium and plutonium from radioactive FPs. Other separation methods, such as IX typically used to treat secondary waste streams, for dilute solutions, to collect and concentrate species, when the use of organic solvents is not desired, and when the column media may be part of a final waste form. Chemical precipitation processes are generally employed for removing radioactive matters from LLLW and ILLW in research laboratories, nuclear reprocessing facilities, and NPPs [225]. Chemical precipitation is versatile process having low initial and operational costs and generally suitable for the treatment of large volumes of different liquid waste containing relatively low concentrations of radioactive elements, large amounts of particulates or high concentrations of salts [226]. As a rule, these processes use readily available chemical reagents and are economical compared to some alternative processes such as evaporation.

Chemical precipitation method generally involves the addition of reagents and adjustment of pH to form precipitate [227]. The waste volume reduction and decontamination factors achieved with precipitation strongly depend on the method of solid liquid separation used (include sedimentation and decantation, filtration, or centrifugation). Despite the fact that chemical precipitation is often less expensive compared with SE and IX but is not always effective in removing radionuclides from solution.

Alone or in combining with chemical precipitation, or filtration, electro dialysis or evaporation, IX methods is extensively used to remove soluble radionuclide's from LRWs produced in nuclear fuel cycle operations. Ion exchange processes are more productive and simpler (simplicity and reliability of technological equipment) compared to chemical precipitation methods. Despite the high cost of selective ion exchangers and the low rate of the process, IX methods are interchangeable when it is necessary to cost-effective remove and concentrate valuable elements from dilute solutions, including LRWs. In the case when the radioactive wastes contain high concentration of salts, organic contaminants, suspended solids, or the radionuclides ions, the liquid wastes must be

Table 3
The main features and limitation of chemical precipitation, ion exchange and solvent extraction.

Technology	Features	Limitations
Chemical precipitation	Easy non-expensive operations Suitable for large volumes and high salt content waste Low capital cost Most of metal can be removed	Low decontamination factor Large amounts of sludge produced Efficiency depends on solid-liquid separation step Disposal problems
Ion exchange	Good chemical, thermal and radiation stability High performance Large choice of products ensuring high selectivity Applicability for low pollutant concentrations Simplicity and reliability of technological equipment Possible regeneration of materials Resin in Pulp - pulp processing without pre-filtration (for processing raw and technogenic materials)	Low efficiency Incomplete removal Generation of by-products and secondary wastes High cost of ion exchangers High operating and capital costs Regeneration and recycling often difficult employed (not quantitative regeneration, regeneration is time-consuming) Sensitivity to operating conditions (physicochemical pretreatment needed, problems of processing solutions with high salinity, narrow range of the working pH) Swelling Low process rate
Solvent extraction	Separation from solutions with high concentrations of metals and salts High decontamination factor High selectivity (selectivity enables removal, recovery or recycle of actinides) Energy saving High solvent capacity High productivity	Third-phase formation Generation aqueous and organic secondary waste Solvent losses Difficulty in the regeneration Large volume of solvent required Toxic and flammable solvents and diluents Solvent recovery is expensive energy intensive Costly and high purity solvents are required

pretreated before the IX process [151,228–330]. The combining of leaching and IX processes (resin in pulp) during the processing of mineral pulps in the uranium technology avoids duration and expensive filtration processes.

The earlier serious limitations of relatively low thermal and radiation stabilities are being overcome by the new synthetic inorganic materials. The resins can be regenerated by remote methods, if necessary, and reused a large number of times with a small loss in the process. In many instances, the high selectivity of the inorganic exchangers, both natural and synthetic, is adapted to the effective reprocessing of specific wastes. However, most of the known adsorbents have a number of limitations of application, such as a narrow range of the working pH of the solution [331], low capacity, swelling, high cost of some ion exchangers, low kinetic parameters of radionuclide adsorption (compared to SE), and the use under conditions of low mineralization [332] due to the strong influence of competing ions.

Solvent extraction has advantages compared with precipitation or IX in relation to purification and separation of radioactive elements. The advantages of SE processes ensured their rapid integration and use in large-scale operations. Solvents have a large capacity and good selectivity. Chemical precipitation and crystallization is a relatively long and complex process, while SE equilibrium is usually established within a few minutes. As a result of the SE separation processes the solid phase, as a rule, is not formed. This is their great advantage over chemical precipitation techniques since the capture of impurities during the formation of sediments is excluded. Due to the presence of only liquid reagents, the design of apparatus is simplified and full automatization of processes is facilitated. In the case of SE, the concentrating of valuable components is achieved simultaneously with their purification. Solvent extraction has become indispensable in radiochemical technology, in the processing of SNF. The use of multi-stage countercurrent processes makes it possible to achieve complete removal of valuable components even with low extractability and almost completely separate elements of similar properties from the mixtures.

The disadvantages of SE techniques include the loss of the solvents as a result of some solubility in the aqueous phase, as well as due to entrainment in the form of microemulsion, the inability to

process of slurries, the flammability and toxicity of a number of solvents and diluents. The solubility of solvents in water determines not only the cost of solvents losses, but also the toxicity of waste solutions. Regeneration of solvents is usually difficult. Spent solvents and ion exchangers are considered to be problematic waste that in many cases requires special approaches and precautions during its utilization.

A comparison of IX, SE and chemical precipitation for radionuclide's removal from liquid waste both with their features and limitations are presented in Table 3 [333].

It should be noted that solvents are becoming increasingly selective, allowing specific chemical species to be separated from the aqueous phase while the others are retained, also are being developed new ion exchangers that can recover the difficulties faced during industrial application of this treatment option as well as to improve its performance.

4. Conclusions

This review deals with the state of the art in the separation processes of uranium, plutonium and fission products in alkaline and carbonate media, with particular emphasis on precipitation, ion exchange, and solvent extraction techniques to assist the development of new alternative non-acidic aqueous technologies for reprocessing of spent nuclear fuel.

To date, numerous approaches have been proposed for recovery of various radionuclides from alkaline radioactive waste using a large number of reagents. Particular attention is paid to the development of new aqueous methods for the reprocessing of spent nuclear fuel and its fabrication wastes in carbonate media, involving methods of selective precipitation, ion exchange, and solvent extraction. All these methods are developed for the purpose of partitioning of spent nuclear fuel and radioactive waste for the separation and purification of uranium compounds, with the possibility of its reuse in the production of nuclear fuel. The priority of these methods changes periodically over time as a result of the creation of certain more advanced, effective and promising types of reagents (sorbents, solvents or other materials). The development of all these types of separation and purification processes meets the expected needs for future fuel cycles.

The results of many studies conducted in scientific laboratories around the world in recent decades, and the accumulated experience and understanding of the physical and chemical foundation of separation processes provide significant progress in the development of efficient, selective and workable methods for the recovery of uranium and other valuable components from spent nuclear fuel using safe carbonate media as well as methods for treatment of alkaline high-level radioactive waste.

CRedit authorship contribution statement

Alexander V. Boyarintsev: Methodology, Writing – original draft. **Sergei I. Stepanov:** Conceptualization. **Galina V. Kostikova:** Writing – review & editing. **Valeriy I. Zhilov:** Writing – review & editing. **Alfiya M. Safulina:** Writing – review & editing. **Aslan Yu Tsvadze:** Funding acquisition, Resources, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

SNF	spent nuclear fuel
LWR	light-water reactor
MOX	mixed-oxide fuel
HLLW	high level liquid waste
ILLW	intermediate level liquid waste
LLW	low level liquid waste
HLW	high level waste
LRW	liquid radioactive wastes
PUREX	Plutonium–Uranium Recovery by EXtraction
CSEX	Cesium Solvent EXtraction
CSSX	Caustic–Side Solvent EXtraction
NG-CSSX	Next–Generation Caustic Side Solvent EXtraction
CARBEX	CARBonate EXtraction
CARBOFLUOREX	CARBonate FLUORide EXtraction
SRS	Savannah River Site
INEEL	Idaho National Engineering and Environmental Laboratory
ORNL	Oak Ridge National Laboratory
NPP	nuclear power plant
FNR	fast neutron reactor
WWER	water-water energetic reactor
ITP	in-tank precipitation
ISDP	Integrated Salt Disposition Process
ARP	Actinide Removal Process
SCIX	Small Column Ion Exchange
P&T	Partitioning & Transmutation
RF	resorcinol-formaldehyde
sRF	spherical resorcinol-formaldehyde
IXR	ion exchange resins
AXR	anion exchange resin
NDTB-1	Notre Dame Thorium Borate-1
MA	minor actinide
REE	rare earth element
TUE	transuranium element

TPE	transplutonium element
An	actinide
Ln	lanthanide
FP	fission product
IX	ion exchange
SE	solvent extraction
SF	separation factor
DF	decontamination factor
QAC	quaternary ammonium compound
Alamine 336	tri-n-octylamine
Aliquate 336	methyltrioctylammonium chloride
Adogen 464	methyltrialkyl(C ₈ –C ₁₀)ammonium chloride
N ₂₆₃	methyltrioctylammonium chloride
MTOA	methyltrioctylammonium
MTAA	methyltrialkyl(C ₇ –C ₉)ammonium
DDFHME	2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl methyl ether
DDFHA	2,2,3,3,4,4,5,5,6,6, 7,7-dodecafluoroheptyl acetate
Formal-2	1,1,2,2,3,3,4,4,10,10,11,11,12,12,13,13-hexadecafluoro-6,8-dioxatridecane
F-3	meta-nitrobenzotrifluoride
TBP	tri-n-butyl phosphate
TOPO	tri-n-octylphosphine oxide
HDEHP	bis(2-ethylhexyl)phosphoric acid
HPMBP	1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one
CMP	carbamoyl methyl phosphonate
DTPA	diethylene-triamine-pentaacetic acid
DOP	4(α,α -dioctylethyl)pyrocatechol
AHA	α -hydroxycarboxylic acid
CS	complexon
HCS	hydroxycomplexon
ACS	alkylphosphonic complexon
TOG	trihydroxyglutaric acid
EDTMP	ethylenediamine-N,N,N',N'-tetra(methylphosphonic) acid
OPDTA	2-oxypropylene-1,3-diamino-N,N,N',N'-tetraacetic acid
OEDTTA	oxyethylene-diamine-tetraacetic acid
OEDTA	oxyethylene-diamine-triacetic acid
OEIDA	oxyethylene-imino-diacetic acid
DOBTA	dioxidiamine-butan-tetraacetic acid
OFIDA	oxyphenyl-imino-diacetic acid
EDTPA	ethylenediamine-tetramethyl-phosphonic acid
DTPPA	diethylene-triaminepentamethyl-phosphonic acid
EDTA	ethylenediaminetetraacetic acid
AUC	ammonium uranyl carbonate
XRD	X-ray diffraction
IR	infrared radiation
NMR	nuclear magnetic resonance
PMR	proton magnetic resonance
D _M	distribution ratio of metal
Q	molar ratio of solvent and uranium(VI)

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