POTENTIAL OF SUPERCRITICAL FLUIDS FOR RADIOCHEMICAL TECHNOLOGIES

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ABSTRACT

The potential of supercritical fluids in radiochemical technologies was discussed in this paper. The advantages of supercritical and liquid carbon dioxide and freons were demonstrated as applied to reprocessing of nuclear power plants spent fuel (NPP SNF), to management of radioactive wastes (HLW), to decontamination of equipment and working outfit. The main trends of further studies in the field of supercritical fluid applications in radiochemical are formulated.

INTRODUCTION

At present the main tasks of radiochemical technologies are NPP SNF reprocessing, management of RAW, decontamination of equipment and working clothes and production of isotopes for medical purposes. To solve these tasks, the hydrometallurgical technologies producing the large volumes of secondary radioactive liquid wastes are currently used; in their turn, the latter adversely affect both ecological safety and economical efficiency of radiochemical facilities. It is precisely the low volume of secondary radioactive liquid waste that has aroused considerable interest of radiochemists to supercritical fluids (SCF). Over the past ten years the investigations on supercritical fluid extraction of metals, including radionuclides, demonstrated the potential of SCF for SNF reprocessing, decontamination of solids and the other applications.

Interest of radiochemists to processes of supercritical fluid extraction (SFE) can be explained by the possibility for use of fluid as an easily removable, purified and recycled solvent, i.e. the volume of secondary liquid radioactive waste may be drastically reduced. The applicability of SFE to metal extraction was revealed in the early 90s in works of Ch. Wai's group (Idaho University, USA) [1-4]. By now in the studies of the same group [5-7], as well as in works of scientists at JAERI (Japan) [8,9], Nagoya University (Japan) [10,11], Kying Hee University (Korea) [12,13], Delft University (Netherlands) [14], CEA (France) [15], GEOCHI (Russia) [16,17] and finally in joint team Khlopin Radium Institute and Mining Chemical Combine (Russia) [18-21], it is shown that the solutions of β-diketones ((hexafluoroacetylacetone, HFA), tributylphosphate (TBP) and other neutral and acidic organophosphorus reagents (for example, di-2-ethylhexylphosporic acid, D2EHPA) in supercritical and liquid CO_2 permit to extract micro-- and macroquantities of actinide (U, Th, Pu, Np, Am) and lanthanide cations. Besides, it has been currently disclosed that SFE using, for example, ω-hydroperfluoropropionic acid (PFVA), may be also used for recovery of such hazardous radionuclides as ^{137}Cs, ^{90}Sr, ^{60}Co etc [22-25].

Let us consider the potential of supercritical fluids and liquefied gases as applied to radiochemical technologies by the examples of NPP SNF reprocessing and decontamination of different surfaces. In the present study the literary data and those obtained by us are used. Methods for production of our experimental data are given in [18,19,26,27].

DECONTAMINATION IN CARBON DIOXIDE MEDIUM DECONTAMINATION TECHNOLOGY

Traditional techniques for decontamination of solids and soils involve the use of acidic and alkaline solutions of complexones for radionuclide wash-out. Most of the traditional decontamination techniques result in arising of large volumes of secondary liquid waste. In case of supercritical fluid extraction decontaminating agents dissolve in carbon dioxide, but not in water or organic solvents, which allows sharply to reduce the secondary waste volume. Under changes of pressure or temperature SC CO_2 transforms into gaseous state, which easily permits to remove "solvent" and produce dissolved compounds in compact form. These features of supercritical fluid extraction attract interest to this process as a promising method for decontamination of surfaces.

Investigations in the field of developing the decontamination technologies and the creation of equipment for surface purification in CO_2 medium are being conducted at CEA (France), JAERI and Nagoya University (Japan), Kyung Hee University (Korea), DELFT University (Netherlands), at LANL and INEL(USA), as well as at Radium Institute and Mining Chemical Combine (Russia).

The studies conducted at Radium Institute and Mining and Chemical Combine concerning the development of decontamination technology in supercritical and liquid CO_2 have shown that :

- the developed decontamination technologies in CO_2 medium allow to remove the radionuclides of different valences - IV (U), V (Np), IV (Pu), III (Am), II (Sr) and I (Cs) from solid surfaces (**Figure 1**);
- metals, fabrics (**Figure 2, Table 1**) and soils (**Figure 3**) may be effectively decontaminated;
- the use of supercritical and liquid CO_2 enables to reduce secondary radioactive waste volume by a factor of more than 50 (**Figure 3**);
- complexone solutions in supercritical and liquid CO_2 may be used (**Figure 4**);
- treatment in CO_2 medium is efficient to decontaminate both strongly (**Table 1**) and weakly radioactively contaminated materials (**Table 2**).

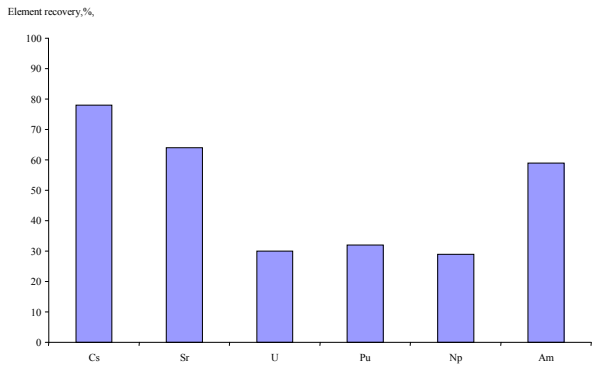

Figure 1: Recovery of elements by water-containing SC CO_2, into polyether - OP-7 and ω-hydroperfluoropropionic acid (40 mg OP-7; 0.2 mmole H_2O; 30 μmole acid; 300 atm.; 80 ^oC; 20 min)

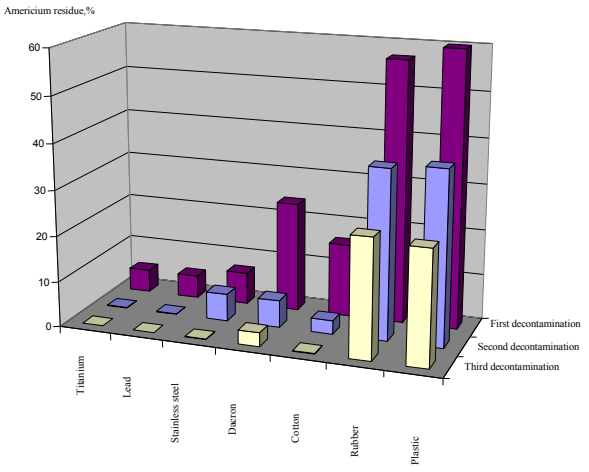

Figure 2: Multiple decontamination of in SC CO_2, containing HFA, water and Py

Analogous investigations are being conducted at several laboratories in the world. The used approaches and results of these investigations are rather similar. However, it should be noted that there are the investigation on potential SC CO_2 solutions of HNO_3-H_2O microemulsions (Kuyung Hee University (Korea) [12,13] and the investigation on the use of TBP – HNO_3 adduct solutions in CO_2 in JAERI (Japan) [28,29]. Specialists of JAERI and Nagoya University (Japan) proposed to apply short-acting pressure change (pulsation) to increase the recovery degree of radionuclides from porous materials [9]. This method is of great interest to decontamination practice in SC CO_2. In addition to that, the possibility for removal of the different uranium and plutonium forms from labeled soils was demonstrated at INL [30].

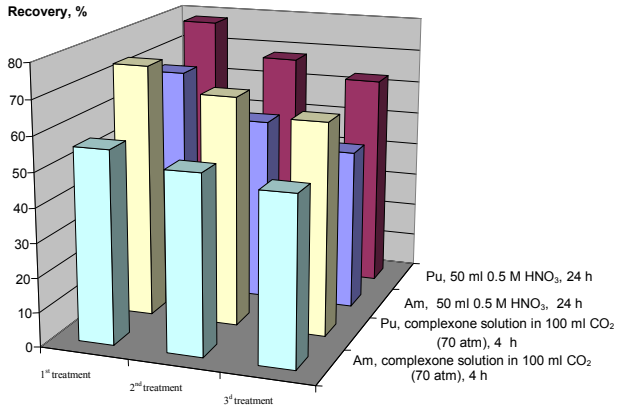

Figure 1: Leaching of nuclides from soil by aqueous HNO_3 solution and by solutions of TBP, D2EHPA, octanol and water in liquid CO_2

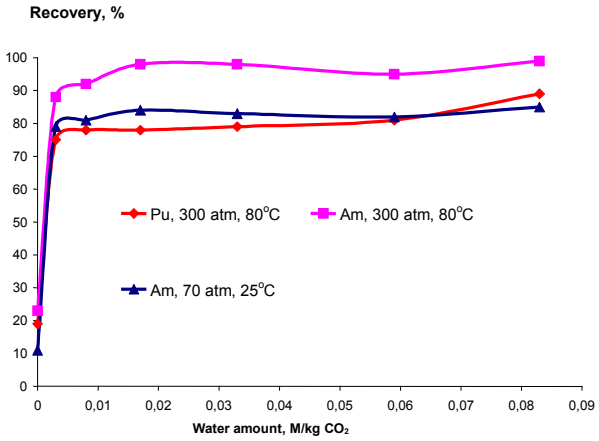

Figure 2: Removal of Pu and Am nitrates by solution of HFA an Py in CO_2

Table 1: Decontamination of different materials in CO_2 medium at CO_2 natural circulated pilot facilities

Value	Decontamination factor		
	1 ml HFA; 1 ml Py, 1 ml H_2O	0.5 ml TBP; 0.5 ml D2EHPA, 0.5 ml PFVA; 1.0 ml octanol	Total
Stainless steel (weakly fixed contaminants)			
β-activity	57	5	285
α-activity	110	15	1650
Σ γ-activity	10000	15	150000
Aluminum (weakly fixed contaminants)			
β-activity	210	4	840
α-activity	57	14	798
Σ γ-activity	64	13	832
Brass (weakly fixed contaminants)			
β-activity	18	6	108
α-activity	72	12	864
Σ γ-activity	54	14	756

Table 2: Decontamination of really contaminated dacron overalls (65 atm., 25°C ,four successive treatment operations by 20 ml TBP, HFA and H_2O in CO_2, alternating with 3gr PFVA and by 10 ml TBP, octanol and H_2O in CO_2)

Value to be measured	Contamination		Decontamination factor
	Initial	Final	
β-activity	from 2.4 to 8.1 Bq/cm^2	from 0.32 to 0.81 Bq/cm^2	from 3 to 13
Σ γ-activity	1.7 μSv/h	0.15 μSv/h	11

EQUIPMENT FOR DECONTAMINATION IN CO_2 MEDIUM

In the USA in 1996 the first facility for laundering in SC CO_2 (**Figure 5**) was demonstrated at Los-Alamos National Laboratory, and in 1998 the first dry-cleaner's with the use of liquid CO_2 was opened [31]. Two years ago CEA created pilot facility for purification of soils from organic contaminants and lead in SC CO_2 (**Figure 6**) and in 2003 - a facility for decontamination [32,33]. Pilot facilities for removal of heavy metals and organic compounds are also being developed in Spain [34] and Netherlands [14,35]. Furthermore, many producers elaborated and tested equipment prototypes for decontamination of different surfaces and laundering of fabrics in supercritical and liquid CO_2. The available equipment may be adapted to resolving the radiochemical problems.

Figure 5: Facility for laundering work clothes (LANL, USA)

Figure 3: Pilot facility for soil decontamination (CEA, France)

At MCC and Radium Institute the investigations on decontamination in SC CO_2 are conducted at laboratory setup with chamber capacity ~ 50 mL, and in liquid CO_2 at CO_2 natural circulated setups with chamber volume from 250 mL (**Figure 7**) to 5 L (**Figure 8**).
By now the technology and equipment for decontamination and in CO_2 medium (thus far in non-radiochemical modification) have been developed. As compared to traditional techniques, this technology is more time-consuming - by factor of 2-3, but it enables to reduce the secondary radioactive waste volume by the factor of more than 20.

REPROCESSING OF NPP SNF IN CO_2 MEDIUM

Investigations on applicability of CO_2 to SNF reprocessing were conducted in two main directions: (i) application of SC CO_2 as solvent for TBP at extraction of U and TRU from HNO_3 solutions and (ii) direct dissolution of SNF in SC CO_2, containing a complexone. In the first case SC CO_2 permits to abandon inflammable, toxic solvents and to simplify regeneration of both solvent and extractant [36-39]. This process is jointly developed by BNFL (Great Britain), JAERI (Japan) and by Universities in Leads (UK) and Idaho (USA). The process

described above does not solve the problem concerning the volume reduction of secondary wastes arising from traditional PUREX-process. From this standpoint the variants of direct SNF dissolving in CO_2, containing TBP•2HNO_3 complex seem more promising. Such approach is presently investigated at Idaho University (USA) and RAS GEOCHI (Russia) [16,40,41] and by a group of Japan specialists (JAEA and Nagoya University) under the aegis Mitsubishi Co (Japan) [10,42]. On the basis of conducted research Mitsubishi Co proposed a variant of low-temperature anhydrous reprocessing - Super-DIREX (**Super**critical fluid **DIR**ect **EX**traction) (**Figure 9**) [42]. As compared to hydrometallurgical and non-aqueous methods of SNF reprocessing, the direct dissolution of fuel in carbon dioxide may have the following advantages: (i) drastic reduction of secondary radioactive liquid waste volume; (ii) abandonment of organic solvents; (iii) moderate (60-80^{o}C) process temperature. As a chief drawback one can consider (i) high working pressure (up to 300 atm.); (ii) complexity of continuous multi-stage process and (iii) moderate purification coefficients (~ 10^2-10^3).

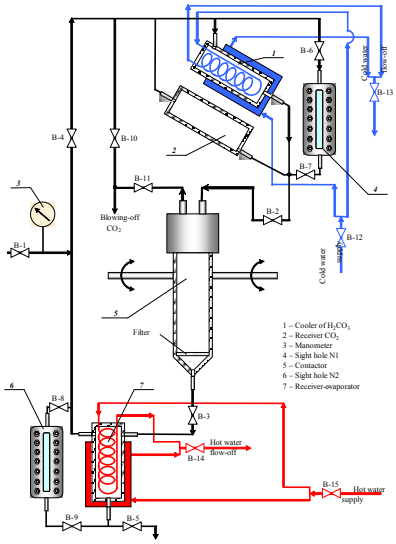

Figure 7*:* Diagram of setup with natural circulation of CO_2

Figure 8*:* General view of enlarged pilot facility

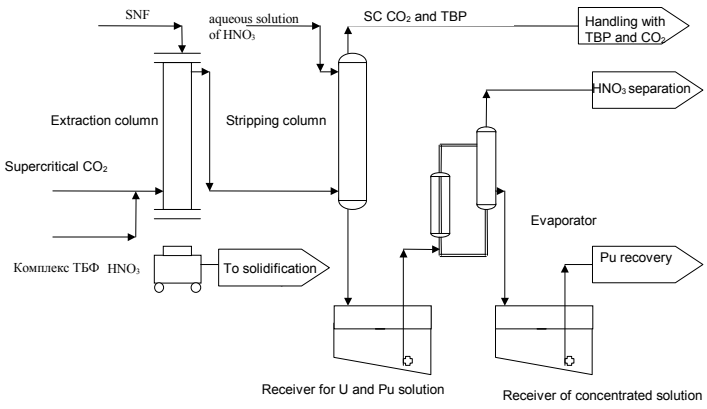

Figure 9: Super DIREX process (key flowsheet)

In addition to the above-described processes, RI and MCC are developing the SNF reprocessing technologies in liquid CO_2 medium (25^{o}C, 60-70 atm.). This row of process received the name RELICT (**RELICT** - **RE**processing by **LI**quid **C**arbon dioxide **T**reatment) [20,43,44]. The investigations are conducted with the use of solutions in CO_2, TBP•2HNO_3 complex and β-diketones [45,46].

Investigations on SNF dissolving are carried out at many laboratories of the world. The studies performed at RI and MCC have revealed that the macroquantities of uranium oxides similarly dissolve in complexone solutions in both supercritical and liquid CO_2 (**Figure 10**), and it is necessary to introduce an extract washing operation for attaining the technically acceptable uranium purification coefficients from fission products (**Figure 11**).

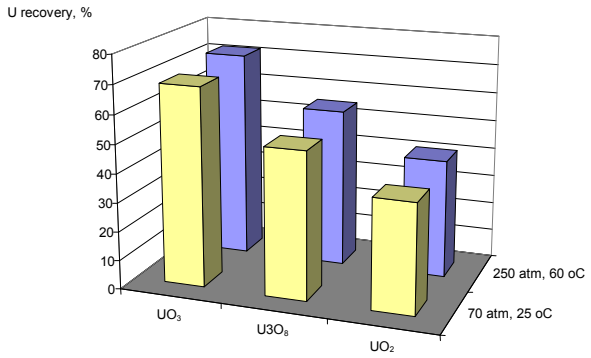

Figure 10: Recovery of U from its oxides (3g) by 10 % solution of TBP-HNO_3 complex in CO_2

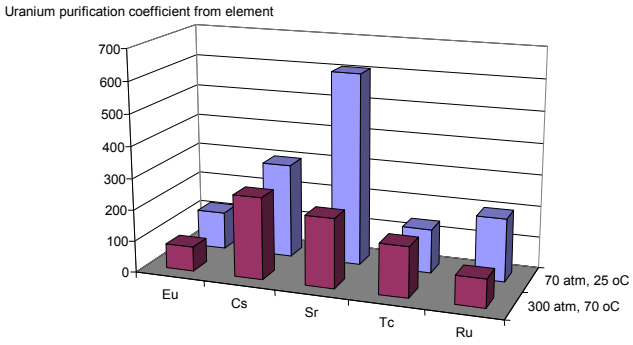

Figure 11: Purification coefficients of U on dissolving in 10% solution of TBP-HNO_3 in CO_2, after extract washing with 5 mole/L HNO_3 solution

In addition to that, at Radium Institute the feasibility of SNF reprocessing in CO_2 medium has been confirmed by experiments with real RBMK SNF. The principal possibility of SNF reprocessing in CO_2 is also substantiated by experiments on real WWER-1000 SNF. It has been possible to recover more than 95% U and Pu by TBP-HNO_3 adduct solutions in SC CO_2 due to three operations of dissolution and extraction. The total molar ratio between [U]:[ТБФ] is equal to 1:6 for three operations.

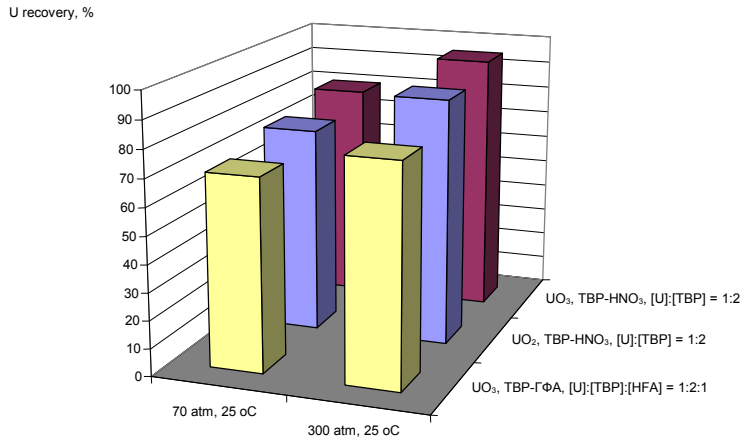

Figure 4: Dissolution of real SNF in solutions of TBP-HFA or TBP-HNO_3 in CO_2 (0,5-1 g SNF, [U]:[TBP] = 1:2, three operations*)*

With the use of liquid CO_2 as solvent the above operation should be repeated five times to attain the uranium recovery by 95%. The total molar ratio between [U]:[TBP] is 1:10 in five operations. However, the pressure release to 60-70 atm. reduces equipment cost several times.

Hence, the principal feasibility of NPP SNF reprocessing in liquid and supercritical CO_2 media has been now scientifically substantiated and experimentally confirmed.

CONCLUSION

The data on radionuclide extraction obtained by now allow to state that the savings due to reduction of secondary radioactive liquid waste volume may exceed the expenses on safety

provision in the course of high-pressure processes. So, in radiochemical technologies one can use SC CO_2, as a medium for decontamination and reprocessing of NPP SNF, as well as for production of medical radionuclides like ^{90}Sr [47] and for elimination of organics-containing radioactive waste, for example oxidation in supercritical water [48].

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