

SOLID-PHASE STRIPPING OF RADIONUCLIDES FROM COMPLEXONE SOLUTIONS IN DENSE CARBON DIOXIDE

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ABSTRACT

The present investigation is aimed at developing a method for CO₂ recycle at decontamination of different materials without pressure change in system. The work is concerned with uranium and plutonium sorption on solid acids and their salts from dense CO₂ media. It is shown that 80 - 83 % U may be stripped from its complexes dissolved in CO₂ by dihydrate of oxalic acid and 97 - 100% are stripped by ammonium carbonate. The use of aminoacetic acid enables to strip ~ 30 % U and 40 % Pu from supercritical CO₂ solutions and ~ 32 % U and 60 % Pu from liquid CO₂. It is found that the amount of sorpted uranium decreases with increase of HNO₃ concentration in CO₂ stream.

INTRODUCTION

The existing decontamination techniques are based on the use of aqueous and organic solutions, resulting in generation of secondary liquid radioactive waste. The so-called supercritical fluid decontamination (SFD) may be assigned to promising non aqueous decontamination methods. This method has undeniable advantages over traditional decontamination techniques and permits to reduce liquid waste volumes by a factor of 50 [1]. Despite the available body of experimental data on dissolution of radionuclide compounds and heavy metals in medium of dense CO₂ which suggests the possibility of using SFD in radiochemistry in the future, a number of problems still remain to be solved. As for now, no specific decision has been taken about further handling of extracted radionuclides. Besides, the method providing CO₂ recycle by its evaporation (in this case the compounds dissolved in CO₂ are separated into individual phase) and by subsequent condensation of CO₂ for re-extraction requires some additional energy consumption and does not afford fine purification of solvent.

In our opinion, one of the possible ways to solve the SFD problems is sorption process. Sorption has found wide application in many branches of industry due to its effectiveness, universality and availability of sorption materials. It should be noted that the sorption recovery, separation and concentrating of metals from organic and aqueous solutions is also practiced in radiochemical industry [2]. In [3] the possibility for yttrium stripping from its aqueous solutions of D2EHPA was demonstrated by using the aqueous solutions of oxalic acid.

As to the sorption in the system of dense CO₂ – sorbent, the process regularities similar to those of liquid - sorbent system will be valid, possibly with some corrections for peculiarities of solvent being used.

The objective of the present work is to demonstrate the potential of uranium and plutonium sorption from complexone solutions in dense carbon dioxide.

Insolubility of polar solid acids and their salts in medium of non-polar CO₂ opens up new fields for their use in recovery of radionuclides from complexone solutions in CO₂ through ion-exchange mechanism. The possibility of europium and cesium sorption from complexone solutions in liquid CO₂ on sulphopolystyrene cationite resin KU2*8 (analog of DOWEX-50*8) and on dihydrate of oxalic acid was previously revealed [4]. The present study has confirmed the possibility of uranium and plutonium sorption from complexone solutions in dense carbon dioxide, since these radionuclides are commonly present in large quantities as components of radioactive contaminants. Dihydrate of oxalic acid H₂C₂O₄·2H₂O, aminoacetic acid NH₂CH₂COOH (glycine) and ammonium hydrocarbonate (NH₄)HCO₃ were chosen to conduct the study.

EQUIPMENT

Experiments were carried out with the use of laboratory setup for supercritical fluid extraction, see the diagram in **Figure 1**.

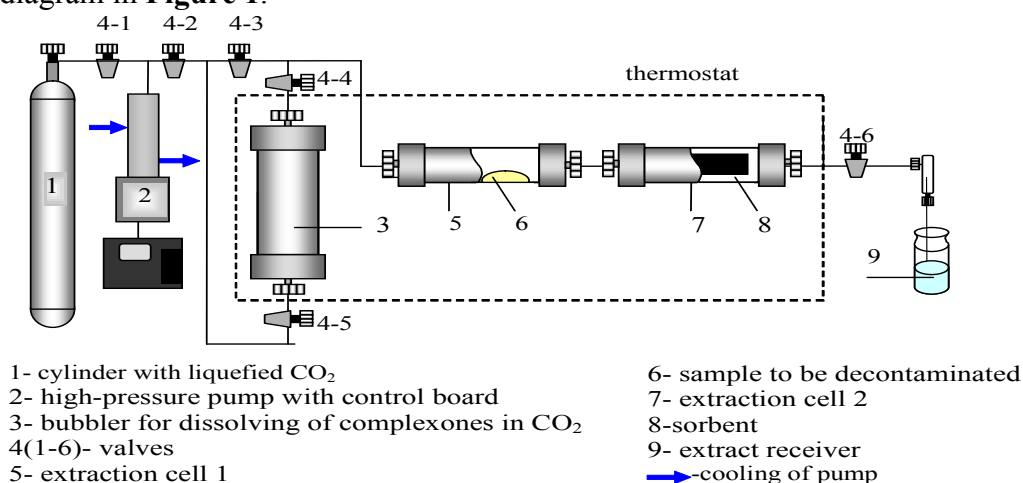


Figure 1: Key diagram of setup for extraction and sorption of radionuclides in dense CO₂.

MATERIALS AND REAGENTS

Tributylphosphate and other reagents were obtained from “Vekton” Ltd (St.-Petersburg, Russia). TBP was successively washed with soda solution, alkaline solution of potassium permanganate, nitric acid and water. The other reagents were used without purification.

EXPERIMENTAL PROCEDURE

A sample was placed into cell 1 (**Figure 1**), cell 2 (**Figure 1**) was filled with sorbent (cross-section area of working cell volume - 62 mm², length 55 mm, volume 3,47 ml). TBP in amount of 0.015 mole/L (V=3,8 ml) was added into bubbler with volume of 7,5 ml (**Figure 1**) for each experiment; as a result, TBP concentration in CO₂ stream was ~ 10% vol.

The system was hermetically sealed, CO₂ was pumped therein up to pressure of 70 atm at 25 °C (liquid CO₂), or to 300 atm at 60°C (SC CO₂). Then CO₂ was pumped through the system at mean volume flowrate of 1 ml/min in amount of 35 ml, i.e. around 10 column volumes. CO₂ with dissolved in it TBP passing from bubbler entered cell 1 where the complexes of metal nitrates with TBP were formed and subsequently dissolved in CO₂ medium; thereafter, metals were sorpted from metal complexes dissolved in CO₂ on sorbent in cell 2. Decompression of CO₂ and collection of extract were conducted into ethyl alcohol through quartz restrictor with diameter of 100 μm.

Analysis for uranium content was performed by vanadometric titration. Analysis for plutonium content was conducted by alpha-radiometry.

In experiments of uranium sorption on H₂C₂O₄ · 2H₂O and (NH₄)HCO₃ the weight quantities of uranyl nitrate hexahydrate at different initial acidity were used as samples. Acidity was adjusted by adding the calculated amounts of HNO₃ (12,3 mole/L) to weighed portion of uranyl nitrate hexahydrate immediately before the experiment. To investigate U and Pu sorption on glycine, the weighed quantities of uranyl nitrate hexahydrate with addition of plutonium nitrate tracers were applied.

RESULTS OF EXIREMENTS

Experiments of uranium and plutonium sorption on NH₂CH₂COOH were carried out; the results obtained are presented in **Table 1**.

Table 1: Sorption of uranium and plutonium on NH₂CH₂COOH from TBP solutions in CO₂.

Phase state CO ₂	Sorpted on NH ₂ CH ₂ COOH , %	
	U	Pu
liquid	33	40
fluid	32	60

As it is evident from the data for glycine obtained in accordance with the above procedure, it is possible to separate ~ 30 % uranium and 40 % plutonium from SC CO₂ and ~ 32 % uranium and 60 % plutonium from liquid CO₂. Sorption of U on H₂C₂O₄ · 2H₂O was tested as well (**Table 2**).

Table 2: Uranium sorption on H₂C₂O₄ · 2H₂O from TBP solutions in CO₂.

Acidity of initial uranyl nitrate, mole/L	Sorpted on H ₂ C ₂ O ₄ · 2H ₂ O, %	
	Liquid CO ₂	SC CO ₂
1	80	87
3	80	83
5	75	74
7	70	74
12	43	65

According to the data given in **Table 3**, uranium can be easily sorpted on H₂C₂O₄ · 2H₂O from both supercritical and liquid CO₂; 80 - 83 % of uranium dissolved in CO₂ transfer into uranyl oxalate being insoluble in CO₂. Interest to oxalic acid at regeneration of CO₂ is primarily caused by possibility for subsequent production of water-insoluble forms of radioactive waste metals (e.g. in the form of metal oxides). However, it is worth noting that in the case of sorption on H₂C₂O₄ · 2H₂O the high indices of uranium sorption ability are retained at acidity of initial uranyl nitrate hexahydrate up to 3-5 Mole/l. This is explained rather by competition between solid acid and HNO₃ for uranyl-ion, resulting in displacement of reaction equilibrium to the left under increasing HNO₃ concentration in CO₂ (i.e. reverse dissolution of metal into CO₂ phase):



High effectiveness was observed in the case of (NH₄)HCO₃ using, the obtained data are given in **Table 3**.

Table 3: Uranium sorption on (NH₄)HCO₃ from TBP solutions in dense CO₂.

Acidity of initial uranyl nitrate, Mole/L	Sorpted on (NH ₄)HCO ₃ , %	
	Liquid CO ₂	SC CO ₂
1	100	99
3	100	98
5	100	100
7	95	97
12	97	99

The data of **Table 3** indicate that with the use of ammonium carbonate one can strip approximately 95 - 100% of uranium from its solutions with TBP in liquid CO₂ and 97 - 100 % of uranium from its solutions with TBP in SC CO₂. NH₃ as a constituent of (NH₄)HCO₃ plays the role of a base for binding HNO₃, and thus no salting-out effect of uranium under the action of nitric acid takes place.

Hence, the results obtained in the framework of this study allow to demonstrate the feasibility of the uranium and plutonium sorption process from dense carbon dioxide media, which makes it possible to re-use not only CO₂, but also complexing agents.

CONCLUSION

The principal possibility of using the sorption process for stripping of uranium and plutonium from their solutions with TBP in CO₂ has been demonstrated, which allows in such a manner to arrange the process of solvent regeneration without pressure release. Solid acids and their salts are tested as sorbents. It is established that the metal sorption degree decreases with increasing HNO₃ concentration in CO₂ medium.

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