

DECONTAMINATION OF DIFFERENT SURFACES BY COMPLEXONE SOLUTIONS IN CARBON DIOXIDE

V.V. Bondin¹, I.V. Efremov¹, D.V. Kovalev¹, S.V. Podoinitsyn¹,

V.A. Kamachev², R.N. Kiseleva, A.A. Murzin², A.Yu. Shadrin²

1 – Mining and Chemical Combine, Zheleznogorsk, Russia

bondin@mcc.krasnoyarsk.su

2 – V.G.Khlopin Radium Institute, St.Petersburg, Russia

SUMMARY

Decontamination of stainless steel, cotton and Dacron samples contaminated with Pu and Am microquantities was investigated by using hexafluoroacetylacetone (HFA) solution in supercritical carbon dioxide (SC-CO₂) medium in the presence of pyridine (Py) and water. It was found that the HFA solutions in carbon dioxide containing pyridine as a modifier are more efficient than the decontaminating solutions containing tributylphosphate (TBP). It is shown that the decontamination factor 10-100 can be achieved by continuous supply of complexone solution into cell or by two-threefold treatment of the material surfaces.

INTRODUCTION

It is known that the recovery degree of organic compounds and metal complexes depends on the properties of treated matrix [1,2,3,4]. Evidently the properties of material being decontaminated should also affect the efficiency of supercritical fluid decontamination. As subjects of this investigation were chosen Dacron, cotton and stainless steel. Such choice was dictated by the fact that the materials are most commonly used in decontamination practice.

The best conditions of actinide removal were previously determined for artificial samples contaminated with Am and Pu oxides and nitrates. The objective of the work is to select the most efficient extraction system for actinide removal and to test the optimal extraction conditions on real contaminated samples.

WORK DESCRIPTION

Materials and reagents

Hexafluoroacetylacetone was received from “Fluorochem” Co (Great Britain). Other reagents of analytical grade were obtained from “Vekton” Ltd (Russia). All reagents were used without any additional purification.

Experimental procedure

The samples contaminated with plutonium (IV) and americium (III) nitrates were prepared by applying a solution aliquot on sample surfaces and by subsequent drying at 1200C. The samples containing plutonium and americium oxides on stainless steel surface were obtained by calcination of nitrate-contaminated samples at 4000C for two hours; Dacron and cotton samples were prepared by rubbing into them the Fe₂O₃ powder precipitated from Pu or Am-containing solution.

Contaminated samples of stainless steel, cotton or Dacron were placed into extraction cell (Fig.1). Aliquots of complexone, modifier and water were introduced into bubbler (in the case of using the setup without bubbler, the reagents were introduced into cell). The cell and bubbler were sealed; CO₂ was pumped first into the cell and then into the bubbler up to the pressure 300 atm at 600C. (Some experiments were carried out in liquid CO₂ medium at 60-70 atm and 250C.)

Thereafter (in experiments with bubbler – immediately afterwards, and without bubbler – after 20 min keeping, until equilibrium is reached), SC-CO₂ was passed through the system at a flowrate of 0.5-1.5 ml/min in amount of 35 ml. Extract was collected through a capillary restrictor into methanol. Extracted and residual quantities of nuclides were determined by radiometry with the use of β -spectrometer Canberra InSpector 1270.

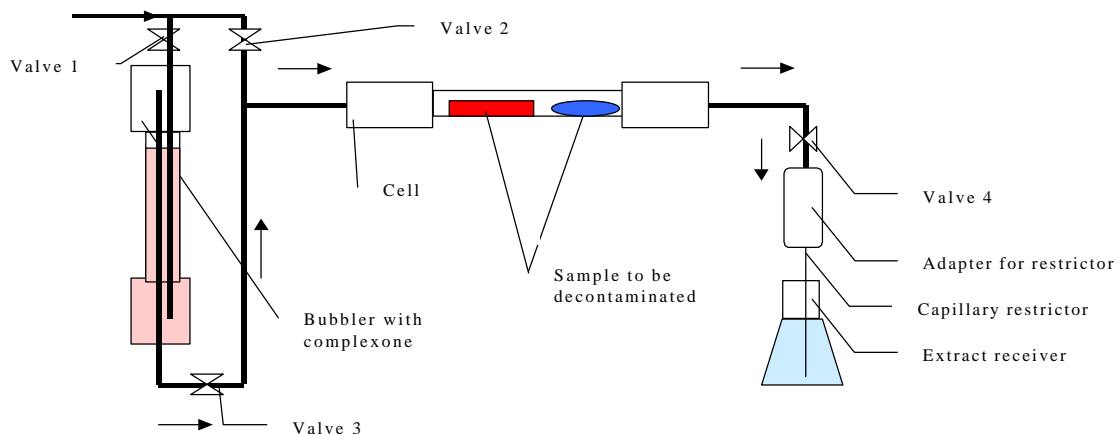


Fig. 1. Block-diagram for research of radionuclide extraction processes in liquid CO₂ medium

RESULTS AND DISCUSSION

It is known that β -diketones, HFA in particular [5], are currently the most promising complexones for actinide extraction. It is also known that the addition of a modifier (Py or TBP)

considerably increases decontamination efficiency [6]. Three extraction systems – HFA, HFA-Py and HFA-TBP – have been selected to compare the decontamination degrees (Fig. 2).

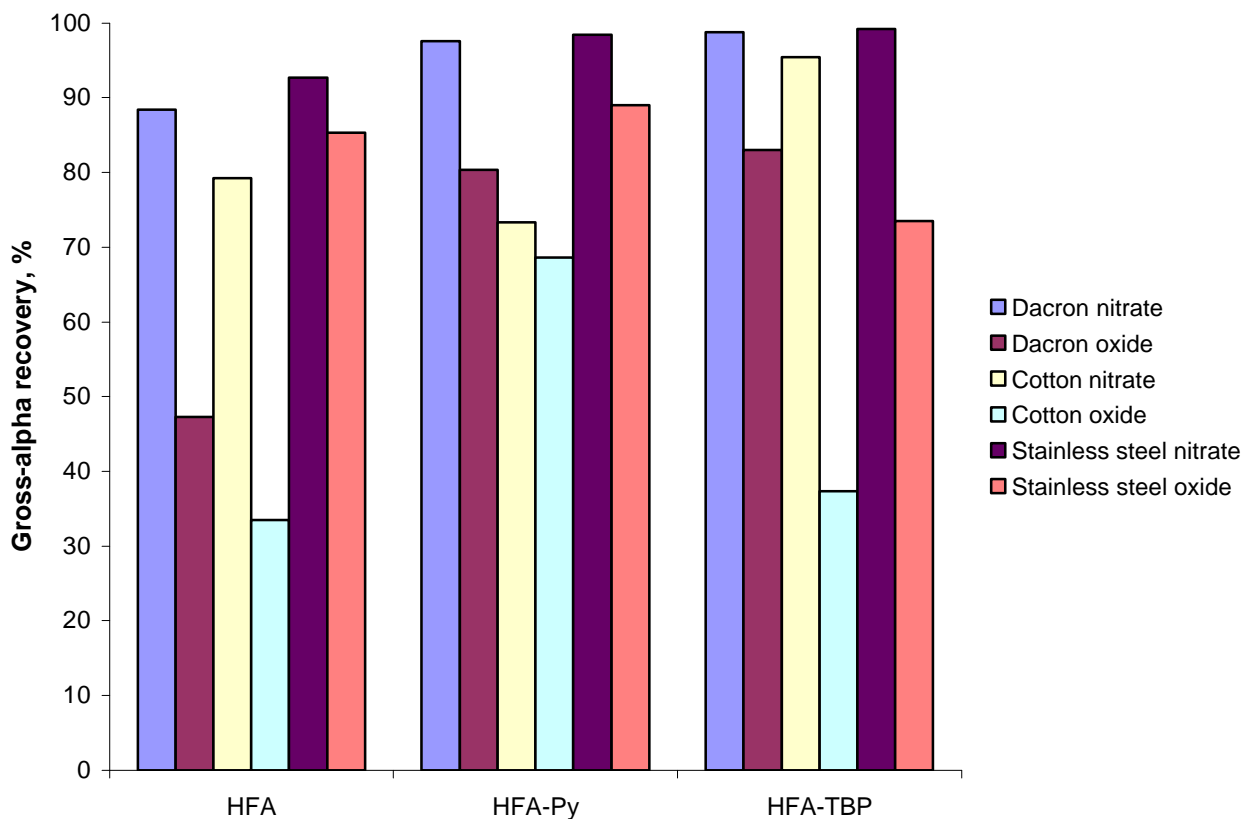


Fig. 2. Effect of modifiers on decontamination of different materials by HFA solutions in SC-CO₂ (10 μl₂, 30 μl HFA, 30 μl of modifier, 300 atm, 60°C)

As follows from Fig. 2, in the case of HFA without modifiers, the recovery needed for efficient decontamination is attained in removal of nitrates from surfaces of all the samples under investigation and of oxides from stainless steel surface. The recovery therewith is in the range of 80-90 % with the use of a single-stage extraction operation. Efficiency of oxide removal from cotton and Dacron surfaces makes up 35 and 45 %, respectively. On adding TBP to HFA, the recovery degree increases, on the average, by 10 % for all the nitrate-contaminated samples. As to oxide extraction from Dacron surface, the recovery degree increases from 45 to 80 %, while the removal of oxides from cotton surface remains the same. When using HFA-Py mixture, the recovery degree of actinide nitrates from cotton surface is somewhat lower than in the case of HFA-TBP, but the recovery of oxides from cotton surface increases to a large extent. In regard to the other samples, the recovery values are similar to those in HFA-TBP system. Clearly, HFA-Py system is preferential for actinide removal, because it provides about the same efficient recovery of the contaminants from all surfaces under consideration.

Formerly it was shown that the use of HFA solution (1.5-3.0 % vol.) in SC-CO₂ at 300 atm and 50-70 °C in the presence of pyridine (1.5-2.0 % vol.) and water (0.3-1.0 % vol.) affords the optimal conditions for removal of nitrates and oxides. Under these conditions the experiments with real contaminated Dacron samples were conducted in HFA-Py system (Table 1).

Table 1

Decontamination of real contaminated Dacron samples by HFA solutions in SC-CO₂ (300 atm SC-CO₂, 60 °C, 20 min)

Additives, µl				Recovery, %		
HFA	H ₂ O	Py	TBP	Eu ¹⁵⁴⁻¹⁵⁵	Am ²⁴¹	Σα
10	0	0	0	30 _{±12}	16 _{±6}	28 _{±19}
		10	0	54 _{±16}	53 _{±11}	42 _{±14}
		0	10	27 _{±11}	20 _{±9}	17 _{±11}
	10	10	0	71 _{±5}	67 _{±2}	61 _{±12}
		0	10	19 _{±7}	18 _{±4}	12 _{±9}
30	10	30	0	75 _{±11}	75 _{±8}	68 _{±14}
		0	30	11 _{±4}	12 _{±6}	11 _{±9}

The obtained data indicate that the decontamination conditions determined for simulated samples are optimal for radionuclide removal from surfaces of real contaminated samples as well. By using HFA solutions in the presence of pyridine it has been possible to recover up to 75% of actinides; however such recovery degree is inadequate to attain the efficient decontamination. There are two possible options for solving this problem. The first one is multiple treatment of material surface. As it is seen from the data given in Table 2, one can obtain the decontamination factor above 10 by three successive treatment operations. In accordance with the second variant, the decontaminating agent is uninterruptedly introduced into extraction cell, for example by passing the supplied SC-CO₂, through complexone-containing bubbler. In this event, the decontamination factor ~20 can be obtained in two operations of cotton and stainless steel treatment (Table 3). As a result of three treatment operations, the decontamination factors of cotton and stainless steel surfaces exceed 100 and are equal to 20-30 for Dacron.

On the basis of the conducted studies the decontamination technique in SC-CO₂ and the traditional decontamination methods were compared. Analysis of the data presented in Table 4 shows that for attaining the decontamination factors comparable with those obtained by the traditional methods it is necessary to conduct the decontamination procedure in SC-CO₂ four times and thus the process duration is more by a factor of four. However, in the case of SC-CO₂ the volume of liquid radwaste is less by a factor of 20-200. Therefore, the decontamination in SC-CO₂ seems to be a promising low-waste method which has much lesser impact on the environment than the traditional decontamination.

Table 2

Multiple decontamination of surfaces of different really contaminated materials by SC-CO₂ containing HFA, water and pyridine

(cell 3.47 ml, 300 atm, 60°C, 10 ml H₂O, 30 ml pyridine, 30 ml HFA)

Material	Residue after decontamination, % of initial					
	First decontamination		Second decontamination		Third decontamination	
	Eu ¹⁵⁴⁺¹⁵⁵	Am ²⁴¹	Eu ¹⁵⁴⁺¹⁵⁵	Am ²⁴¹	Eu ¹⁵⁴⁺¹⁵⁵	Am ²⁴¹
Cotton	62	70	30	36	10	15
Dacron	39	28	16	12	6	5
Stainless steel	34	24	8	6	<1	<1

Table 3

Multiple decontamination of surfaces of different real contaminated materials by SC-CO₂ containing HFA, water and pyridine

(cell 3.47 ml, 300 atm, 60°C, 0,2 ml H₂O, 1,7 ml pyridine, 1,7 ml HFA in bubbler)

Material	Residue after decontamination, % of initial					
	First decontamination		Second decontamination		Third decontamination	
	Eu ¹⁵⁴⁺¹⁵⁵	Am ²⁴¹	Eu ¹⁵⁴⁺¹⁵⁵	Am ²⁴¹	Eu ¹⁵⁴⁺¹⁵⁵	Am ²⁴¹
Cotton	21	16	4	3	<1	<1
Dacron	38	24	14	6	5	3
Stainless steel	11	7	8	6	<1	<1

Table 4

Comparison of decontamination parameters for different materials in aqueous solutions and in SC-CO₂ solutions

Material, 10 cm ²	Decontamination in SC-CO ₂			Decontamination in aqueous solution		
	Residue after decontamination, % of initial		Volume of LRW, ml	Residue after decontamination, % of initial		Volume of LRW, ml
	Eu ¹⁵⁴⁺¹⁵⁵	Am ²⁴¹		Eu ¹⁵⁴⁺¹⁵⁵	Am ²⁴¹	
Cotton	2	3	0.4*	1	<1	10**
Dacron	1	1		5	5	
Stainless steel	<1	<1		5	5	

* - four-fold treatment (300 atm, 60°C, each treatment operation – 1 h);

** - 2% solution SF-2U and double washing with water (60°C, washing 30 min; two washing operations, 15 min each); volume of LRW is given without account for washing operations; total volume of LRW may be about 15 ml;

*** - 1.5% solution of oxalic acid and 0.2% HNO₃ (60°C, 1 h; water washing; volume of LRW is given without account for washing operation; total volume of LRW may be about 20 ml).

One of the main drawbacks of SC-CO₂ decontamination is high pressure (~300 atm). Working pressure can be considerably reduced by using the solutions in liquid carbon dioxide at pressure 60-70 atm. It is evident that the time taken for the process in liquid CO₂ may exceed the duration of treatment operation in SC-CO₂. The conducted experiments have revealed that the keeping time 40 min is sufficient to attain equilibrium in the liquid CO₂ systems (Table 5). Further experiments with keeping time 40 min have demonstrated that the americium oxides can be efficiently removed in medium of liquid carbon dioxide as well (Table 6).

Table 5

Influence of keeping time on removal efficiency of americium nitrate from cotton surface by HFA-Py solution in liquid carbon dioxide (10 μ l HFA, 10 μ l H₂O, 10 μ l Py, 25⁰C)

Pressure, atm	Recovery of Am ²⁴¹ depending on keeping time. %		
	20 ???	40 ???	60 ???
70	58 \pm 13	77 \pm 1	79 \pm 11
60	28 \pm 11	59 \pm 5	56 \pm 13

Table 6

Removal of americium oxide from different materials surfaces by HFA-TBP or HFA-Py solutions in liquid carbon dioxide (10 μ l HFA, 10 μ l H₂O, 70 atm, 250C, 40 min)

Material	Complexone	Recovery of Am ²⁴¹ , %
Cotton	Pyridine, 10 μ l	17 \pm 2
	TBP, 10 μ l	20 \pm 4
Dacron	Pyridine, 10 μ l	13 \pm 2
	TBP, 10 μ l	12 \pm 2
Stainless steel	Pyridine, 10 μ l	71 \pm 5

CONCLUSION

It is established that the decontaminating pyridine-containing compositions are more efficient for actinide removal than those containing TBP. It is shown that the decontamination conditions determined for simulated samples are also optimal for decontamination of real samples: CO₂ at 300 atm, 50-70⁰C, 0.3-1.0 % vol. H₂O, 1.5-3.0 % vol. HFA and 1.5-2.0 % vol. Py. It is revealed that the SC-CO₂ containing HFA, H₂O and Py can be used for decontamination of real contaminated Dacron, cotton and metal by means of continuous supply of complexone into cell or by two-threelfold treatment of material surfaces; the decontamination factor therewith is equal to 10-100. It should be noted that at the same decontamination efficiency of real contaminated samples in SC-CO₂ and by routine water techniques (laundering for overalls and washing with aqueous acidic solutions for stainless steel) the volume of liquid radioactive waste is lower by a factor of 20-200 in the case of SC-CO₂.

The work was carried out under the financial support of RF MinAtom and ISTC (Projects 1160 and 2055).

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