

# DECONTAMINATION OF Cs<sup>137</sup> CONTAMINATED METALS, FABRICS AND SOILS BY ORGANOPHOSPHORIC ACIDS IN LIQUID CO<sub>2</sub>

?. Shadrin<sup>1</sup>, ?. Murzin<sup>1</sup>, D. Shafikov<sup>1</sup>, V. Bondin<sup>2</sup>, S. Bychkov<sup>2</sup>, I. Efremov<sup>2</sup>, V. Ershov<sup>3</sup>, N. Arsent'eva<sup>3</sup>, N. Emel'yanov<sup>3</sup>, S. Rovny<sup>3</sup>

1 – V.G. Khlopin Radium Institute, St.-Petersburg, Russia,  
[shadrin@atom.nw.ru](mailto:shadrin@atom.nw.ru)

2 – Mining and Chemical Combine, Zheleznogorsk, Russia  
3 – «Mayak» PA, Ozersk, Russia

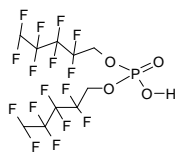
## SUMMARY

It is shown that the solution of potassium salt of dioctafluoroamylphosphoric acid (DOFAPA) in liquid carbon dioxide in the presence of TBP, octanol and water enables the efficient removal of cesium from surfaces of real contaminated dacron, stainless steel, aluminum and brass with decontamination factors 30, 50, 100 and 100, respectively. It is found that this composition allows to remove about 45% Cs from real contaminated soils and thus to reduce the secondary waste volume more than 50 times and the treatment duration more than 20 times as compared to aqueous decontamination techniques.

## INTRODUCTION

It was previously shown that the solutions of di-2-ethylhexylphosphoric acid (D2EHPA), perfluorovaleric acid (PFVA) and dioctafluoroamylphosphoric acid (DOFAPA) may be used for cesium removal from solid surfaces [1]. It was demonstrated that one operation of cotton treatment by DOFAPA solutions in liquid carbon dioxide enables to remove up to 70% Cs. However an attempt to use this composition for decontamination of real samples failed. The objective of the present work was searching for the ways of solving the problem.

## EXPERIMENTAL PROCEDURE



Dioctafluoroamylphosphoric acid (DOFAPA) and its potassium salt (DOFAPK) were synthesized at St Petersburg University (Russia) and used without any additional purification. Tributylphosphate (TBP), octyl alcohol (OctOH), and other reagents were received from "Vekton" Ltd (Russia) and were used without purification as well.

For conducting the investigation at "Mayak" PA, radioactive contaminated samples of cotton, dacron, lead, carbon and stainless steels, teflon and aluminum were taken. Specific  $\gamma$ -activity of the taken samples was  $5-50 \times 10^3$  Bq/m<sup>2</sup>. More than 90 % of the samples activity were caused by Cs<sup>137</sup>. Besides the listed samples, a soil sample was taken from the depth of 0,1-0,2 m at "Mayak" site. The sample was a clay with negligible sandy fraction. The sample was dried at 60 °C for 4 hours

and screened through a 0,5 mm sieve to remove coarse fragments.  $Cs^{137}$  content in the sample was 22000 Bq/g.

The investigation was carried out on a laboratory setup consisting of high-pressure syringe pump (Grant-Instrument, Russia), bubbler and stainless-steel extraction cell (volume 3.5 ml, Keystone Scientific, USA) covered by pyrolytic chrome. Block diagram of the setup is shown on Fig. 1. During experiment complexones were placed into bubbler, and samples to be decontaminate - into extraction cell. Then  $CO_2$  was passed through bubbler up to pressure 70  $\mu$ m., the cell was thermostatically controlled at 25  $^{\circ}$ C and kept for 40 min up to attaining equilibrium - static extraction; next  $CO_2$  was passed through the cell at the same pressure and temperature for 100 min at flowrate 1 ml/min - dynamic extraction. Extract was collected into methanol through capillary restrictor.

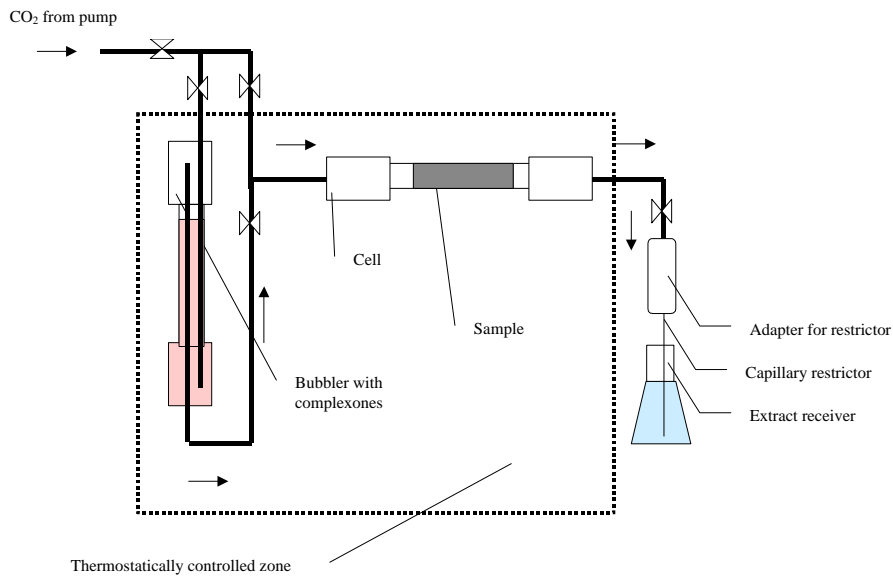


Fig. 1. Block diagram for investigation of dissolving actinide oxides

Furthermore, to conduct the experiments, a setup with  $CO_2$  self-circulation was used. Its block diagram is given in Fig. 2.  $CO_2$  volume in the setup was 600 ml. Treatment duration of samples – 4 hours. The experimental procedure is described in detail in [2].

To compare cesium leachability, use could be made of a solution containing 0,01 M/l aluminum chloride 0,01 M/l iron(III) chloride, which is frequently applied for assessment of radionuclide migration [3] and a solution containing 0,5 M/l  $HNO_3$ , which is often applied for leach-out of cesium and plutonium [4,5]. A weighed portion of 3 g soil was poured with 23 ml of the above solution and kept on periodical stirring for 24 h. Then soil was separated from solution on filter and poured with the fresh solution.

Extracted and residual quantities of nuclides were determined by radiometry with the use of  $\gamma$ -spectrometer Canberra InSpector 1270.

## RESULTS AND DISCUSSION

It is evident that that in formation of extractable complexes by cation-exchange mechanism the initial form of dissociating complexone is of importance [5]. Solutions of lithium salts of dialkyldithiocarbonates in supercritical carbon dioxide are known to remove radionuclides to a

higher degree than those of acidic forms of dialkyldithiocarbonates in  $\text{CO}_2$  [6]. It may be assumed that the use of potassium salt of dioctafluoroamylphosphoric acid should allow increasing the cesium removal efficiency. The performed experiments have confirmed the truth of the assumption (Table 1). For all the materials under investigation the replacement of acid with its potassium salt has made it possible to double cesium recovery. Further investigations were conducted with the use of potassium salt of dioctafluoroamylphosphoric acid.

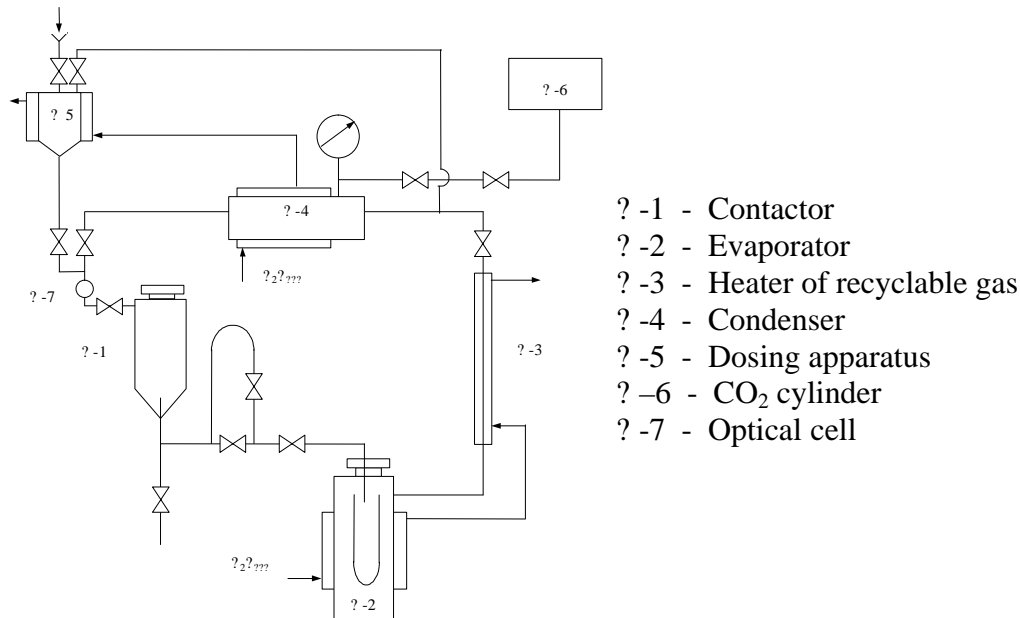


Fig. 2 Hydraulic block diagram of  $\text{CO}_2$  self-circulation setup

Table 1  $\text{Cs}^{137}$  removal from surface of different contaminated materials by complexone solutions in liquid  $\text{CO}_2$  (material area 4  $\text{m}^2$ , 0,2 ml  $\text{CO}_2$ , 0,2 ml BP, 0,2 ml octanole, 70 atm, 25 °C, treatment duration – 140 min, laboratory set up equipped with bubbler )

Complexone	Recovery $\text{Cs}^{137}$ , %				
	Stainless steel	Dacron	Lead	Aluminum	Brass
Dioctafluoroamylphosphoric acid (DOFAPA), 0,3 g	57 ± 8	29 ± 2	71 ± 4	40 ± 15	36 ± 7
Potassium salt of dioctafluorophosphoric acid (DOFAPK), 0,32 g	93 ± 7	61 ± 8	92 ± 7	86 ± 11	74 ± 9

Experiments on decontamination of the above samples at self-circulation setup have shown that rather high decontamination coefficients may be obtained for the most materials (Table 2). Hence, the proposed composition can be used to remove cesium from solid surfaces. Cesium can be also removed from soil by solutions of DOFAPK, BP, octanol and water in liquid carbon dioxide, but the decontamination degree is much lower in this case (Table 3).

Table 2 Cs<sup>137</sup> removal from surface of different contaminated materials by complexone solutions in liquid CO<sub>2</sub> (material area 100 cm<sup>2</sup>, 1 g DOFAPK, 1 ml CO<sub>2</sub>, 1 ml TBP, 1 ml octanol, 70 atm, 25 °C, treatment duration – 4 hours, pilot facility with CO<sub>2</sub> self-circulation)

Complexone	Stainless steel	Dacron	Lead	Aluminum	Brass
Recovery Cs, %	98	97	74	99	99
Decontamination factor	50	33	3,9	100	100

Table 3 Cs<sup>137</sup> removal from real contaminated soil sample by complexone solutions in liquid CO<sub>2</sub> (3 g soil, 0,32 g DOFAPK, 0,2 ml CO<sub>2</sub>, 0,2 ml TBP, 0,2 ml octanol, 70 atm, 25 °C, treatment duration - 4 hours, Laboratory setup equipped with bubbler)

Treatment cycle	Cs <sup>137</sup> recovery, %
1	45
2	<0,1
Total	45

In order to compare the cesium removal degrees from soil by means of complexone solutions in liquid carbon dioxide and traditional decontamination techniques, the soil being investigated was treated with aqueous solutions of salts and acids. Experimental results are presented in Table 4.

Table 4 Cs<sup>137</sup> removal from real contaminated soil sample by aqueous solutions of salts and acids (3 g soil, 25 °C, duration time - 24 h)

Treatment cycle	Cs <sup>137</sup> recovery, %	
	50 ml of solution 0,01 M NH <sub>4</sub> Cl + 0,01 M FeCl <sub>3</sub>	50 ml of solution 0,5 M HNO <sub>3</sub>
1	4,1	3,7
2	3,8	3,8
3	2,9	4,5
4	2,3	6,1
5	1,1	7,0
6	0,4	7,7
Total	14,6	32,8

Thus, with the use of real contaminated soil sample it has been established and demonstrated that the decontamination by complexone solutions in liquid carbon dioxide is more efficient than the soil treatment by aqueous solutions of salts or acids. The use of complexone solutions in liquid carbon dioxide enables to reduce the secondary waste volume more than 50 times and to decrease the duration of treatment operation - more than 20 times with the simultaneous increase of cesium recovery degree.

## CONCLUSION

The experiments conducted on real contaminated soils have shown that the use of solutions of potassium salt of dioctafluoroamylphosphoric acid (DOFAPK) in liquid carbon dioxide in the presence of TBP, octanol and water makes it possible to increase the cesium removal degree from

dacron, stainless steel, aluminum and brass surfaces as compared to analogous solutions of dioctafluoroamylphosphoric acid. It is found that one treatment operation of the materials under consideration by solutions of DOFAPK,  $\gamma$ BP, octanol and water in liquid  $\text{CO}_2$  permits to achieve the decontamination factors as follows: 30 for dacron, 50 for stainless steel and 100 for aluminum and brass.

The solutions of DOFAPK,  $\gamma$ BP, octanol and water in liquid carbon dioxide allow removing about 45 % Cs from real contaminated soils, reducing the secondary radwaste volume more than 50 times and decreasing the duration of treatment operation more than 20 times as compared to routine decontamination methods.

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