

DECONTAMINATION OF SOILS IN LIQUID CO₂ AND IN OZONE FRIENDLY FREON HFC-134a.

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ABSTRACT

Removal of radionuclides from solid surfaces is one of the main problems at taking out of exploitation of the nuclear energy object and rehabilitation of contaminated territories. At present, along with known decontamination technologies of polluted surfaces and soils a method of supercritical fluid decontamination (SFD) is being intensively developed by this time [1,2,3,4]. This method is based on the property of gases in supercritical state, i.e. at pressure and temperature above critical point, to have density close to that of liquids providing high solubilizing ability and viscosity close to that of gases allowing decontamination of the objects of complex shapes. Supercritical carbon dioxide (SC CO₂) being nontoxic, available, cheap and possessing relatively low critical parameters (temperature >31°C, pressure >7.2 MPa) is the most frequently used fluid.

As a rule, common methods of decontamination are based on using organic or water solutions of decontamination reagents that result in formation of large volumes of secondary radioactive wastes. In case of SFD decontamination agents are dissolved in CO₂ or another fluid, which strongly reduces the volume of secondary radioactive wastes because supercritical fluid transforms into gaseous state on changing pressure or temperature, which allows easy removal of the “diluent” and separation of the dissolved compounds in compact form. Owing to these peculiar features SFD is a promising decontamination method.

The processes and equipment for surface decontamination in CO₂ solutions are developed in France [5,6,7,8], South Korea [1,9], Japan [2,3,10], Netherlands [11,12], USA [13], and Russia [4,14,15]. The first setup for working clothes washing in supercritical CO₂ (20-30 MPa, 50-70°C) was demonstrated in Los-Alamos National Laboratory (the United States) in 1996, and first dry-cleaner’s using liquid CO₂ was opened in 1998 (5-7 MPa, 20-40°C) [16]. Hence SC CO₂ can be used in industrial scale. However, supercritical process of decontamination requires rather expensive equipment able to work at high pressure. Studies performed at the Khlopin Radium institute (St. Petersburg, Russia) showed the possibility of development of inexpensive (cheap) decontamination process in CO₂ [17,18] or in ozone-friendly freon HFC-134a (1,2-1,4 MPa, 20-40°C) [19]. The aim of the work was to demonstrate feasibility of process for soil decontamination.

METHODS

The studies were performed using a pilot rig with natural circulation of carbon dioxide (Fig. 1) with an extractor volume of 200 ml and 5l (this unit is shown in Fig. 2).

First, the initial α -, β - and γ -ray activity of the samples was measured. At the experiments using laboratory setup, the samples studied were placed in an extraction cell $V=3,47$ ml, in which the required amount of water and complexons were added. Then CO₂ was supplied (7.0 MPa, 25°C), the cell was thermostated for 20-60 min, and then 35 ml of CO₂ were pumped through the cell for 40-120 minutes. In experiments at the pilot setups, the samples and complexons were placed into extractor. The setup was sealed and gaseous CO₂ was passed from a cylinder to a condenser, where CO₂ was liquefied at 5-8°C, and than it was supplied to the extractor by gravity. Decontamination took 1-4 hours with periodical agitation by changing direction of the CO₂ flow. Then, the samples were removed from the extractor and their final activity was determined.

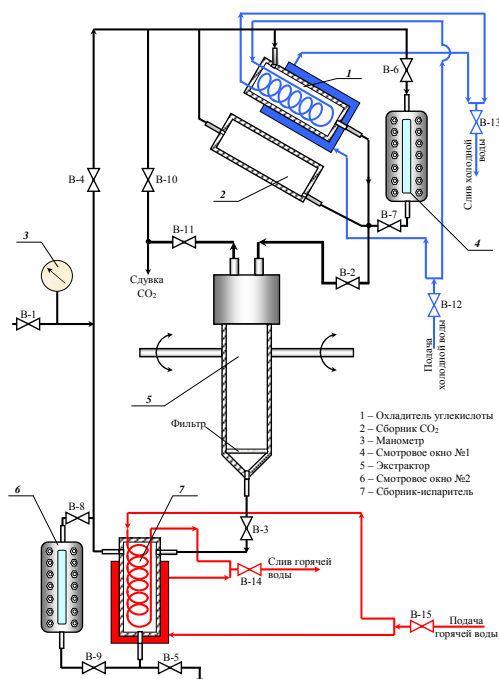


Fig. 1 – Hydraulic scheme of a pilot setup with natural circulation of CO₂



Fig. 2. Pilot setup with natural circulation of CO₂ ($V_{\text{extractor}} 5 \text{ l}$)

Studies were performed using the samples of soils taken from 0.1-0.2 m depth. The samples were dried at 60°C for 4 h, and then were sifted through a sieve with mesh size of 0.5 mm to separate large fragments. Ozone-friendly Freon 134a (CF₃CFH₂, “Parys”, Russia). Hexafluoroacetylacetone HFA, Fluorochem, UK), tributyl phosphate (TBP), di-2-ethylhexylphosphoric acid (EHPA), octyl alcohol (OctOH), polyethylene glycol (PEG-600), and other reagents were supplied from Vekton Joint-Stock Company (Russia). Perfluorovaleric acid (PFVA) were purchased by PF GIPKh (Russia).

RESULTS AND DISCUSSION

Preliminary studies on treatment of real radioactively polluted soils using solutions of HFA and TBP or PEG-600 and PFVA in liquid CO₂ were carried on an enlarged pilot setup to specify the experimental conditions (Table 1 and 2). Depending on the type of soil nearly 20-50% Cs and 30-90% REE and TPE can be removed in a single-stage treatment. Two- or even three-stage treatment under these conditions allows to remove up to 99% Am and REE, but it is ineffective for Pu. The similar results were obtained using solutions of above complexons in liquid ozone-friendly freon HFC-134a.

Table 1. Decontamination of real contaminated samples of soil using solutions of PFVA in liquid CO₂ and HFC-134a (PFVA 500 μl, OctOH 500 μl, H₂O 100 μl, PEG-600 60 mg)

Soil samples	Cs extraction, %
Liquid carbon dioxide (7 MPa, 25 °C)	
Black loam, oversand (soil-vegetable layer)	19 ± 12
Quartz sand, light	53 ± 8
Liquid HFC-134a (1,2 MPa, 25 °C)	
Black loam, oversand (soil-vegetable layer)	21 ± 15
Quartz sand, light	58 ± 13

Possibility of simultaneous recovery of An-Ln and Cs-Sr fractions using TBP-EHPA-OctOH-water solutions in liquid CO₂ was shown previously in [17]. To compare the effectiveness of soil decontamination in CO₂ media, the sample of soil (black loam) was treated with water solutions in accordance with procedure given in [20, 21]. The data on recovery of Pu and Am with aqueous solutions of nitric acid and with solution of TBP-EHPA-octanol in carbon dioxide are shown in Fig. 3. The As seen, both methods provide nearly similar results, but in CO₂ solutions all the labile forms of Pu and Am are recovered 12 h instead of 72 h and the volume of secondary radioactive wastes is reduced by a factor

of more than 60. Analogous researches were performed to compare of effectiveness of Cs removal. It was found that nearly 45% Cs can be recovered from the sample in the single-stage treatment using solution of TBP-PFVA-PEG in CO₂. Treatment of the same sample with aqueous solutions of nitric acid also removed nearly 40% Cs. Hence, recovery coefficients of Cs, Am, and Pu using CO₂ as solvent for soil decontamination are similar to that obtained in aqueous solutions, simultaneously treatment duration can be decreased by a factor of 3, and the volume of secondary radioactive wastes can be reduced by a factor of 60.

Table 2. Removal of radionuclides from soils on treatment by HFA solutions in liquid CO₂ and HFC-134a, containing water and modifying agent (soil 3g, HFA 0.2 ml, H₂O 0.2 ml)

Soil sample	Modifying agent, ml		Content of radionuclides in soil after decontamination, %				
	py	TBP	²⁴¹ Am	¹⁵⁵ Eu	¹⁵⁴ Eu	¹⁴⁴ Ce	²³⁹ Pu
Liquefied carbon dioxide (7 MPa, 25 °C)							
Black loam, oversand (soil-vegetable layer)	0,2	---	27	59	18	45	83
	---	0,1	33	46	28	43	85
Quartz sand, light	0,2	---	53	69	73	47	79
	---	0,1	42	27	49	73	80
Liquefied HFC-134a (1,2 MPa, 25 °C)							
Black loam, oversand, (soil-vegetable layer)	0,2	---	31	67	20	50	88
	---	0,1	37	58	31	51	91
Quartz sand, light	0,2	---	59	77	78	52	89
	---	0,1	45	31	56	79	89

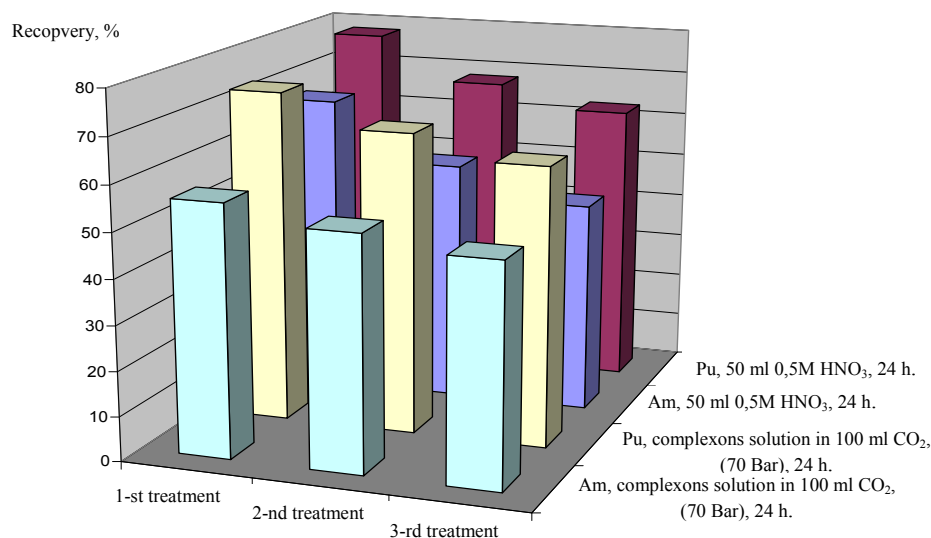


Fig 3. Recovery of Pu, Am from the loam sample with aqueous solutions of nitric acid and complexons solutions (TBP 0.2 ml, EHPA 0.2 ml, OctOH 0.2 ml, and water 0.2ml) in liquid CO₂

Our experimental data confirmed the possibility of simultaneous removal of An-Ln and Cs-Sr fractions. However, the effectiveness of removal of actinides and REE using HFA, TBP, pyridine, and water solutions in liquid CO₂ is significantly higher. Hence, it was of particular interest to study the possibility of removal of these fractions by two successive treatments of the sample: first with solution of HFA, TBP, pyridine, and water in liquid CO₂, and then with solution of PFVA, TBP, OctOH, and PEG-600 in liquid CO₂ after that. To demonstrate the possibility of soil decontamination, the loam samples were treated with solutions of HFA and pyridine in CO₂ or with solutions of PFVA, TBP, OctOH, and PEG-600 in CO₂, and then successively with the same solutions. The experiments showed that radioactive contamination of soils can be reduced by a factor of 1,5 (Table 3). As for Am, Cs and γ -ray activity, their coefficient of decontamination reach 1.8. In our experiments treatment of the soil samples (500 g) was

performed using 120 ml of organic compounds.

Table 3. Decontamination of the loam sample on the enlarged pilot setup (70 atm, 25°C, soil sample (500 g), total activity 80 $\mu\text{Sv/h}$)

Content	Decontamination coefficient		Residual contamination, $\mu\text{Sv/h}$
	Am	Cs	
HFA 30 ml, pyridine 30 ml, H ₂ O 30 ml	1,5	1,3	58
PFVA 10 ml, TBP 10 ml, OctOH 10 ml, PEG-600 10 ml, H ₂ O 10 ml	1,5	1,6	48
Successive using above solutions	1,8	1,8	42

CONCLUSIONS

Using real radioactively-contaminated soil samples, it was found that decontamination with complexation solutions in liquid CO₂ is more efficient than that using aqueous solutions of salts or acids. Solutions of complexions in liquid CO₂ allow to reduce the volume of secondary radioactive wastes by more than a factor of 50.

Principal possibility of using CO₂ and ozone-friendly freon HFC-134a as solutions for decontamination was demonstrated.

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