

Usage of Supercritical Fluids and Compressed Gases with the Purpose of Decontamination and Long Lived Radionuclides Recovery - 11293

V. Kamachev, Yu. Pokhitonov, D. Shafikov.
Khlopin Radium Institute, St. Petersburg, Russia

ABSTRACT

In the course of operation of nuclear processing plants and at termination of operation of various nuclear installations significant number of various objects (such as protecting cloths and shoes, tools, etc.) appears which surface is contaminated with radionuclide. As a rule, decontamination of these objects should be performed before their disposal or reuse. It should be noted that decontamination by common procedures, washing, or treatment with acidic (or alkaline) solutions of sequestering agents and oxidants yield large volumes of secondary aqueous radioactive wastes. Alternative procedure is decontamination in supercritical fluids and compressed gasses. This paper has been described the results of experiments on the use of compressed gases (carbon dioxide, ozone-friendly Freons) for decontamination of solid surfaces using both model and real contaminated solid objects including protecting cloths, tools, and soils. The effectiveness of the fibers decontamination by aqueous and non- aqueous procedures was compared. As shown, despite smaller effectiveness with respect to aqueous procedures, the large-scale decontamination in non- aqueous solutions seems rather promise. As the second task of this paper was to show the opportunity long-lived radionuclides recovery from substances obtained after radwaste solidification in polymer compositions.

INTRODUCTION

Common procedures to remove radioactive contaminations from the solid surfaces are often based on organic or aqueous solutions of appropriate reagents. This approach provides formation of the large volumes of secondary liquid radioactive wastes (LRW). The use of compressed (supercritical or liquid) gases as solvents for decontamination is a promising ways to reduce the volume secondary LRW.

At present, such decontamination technology, based on carbon dioxide in supercritical states, is developed in many laboratories throughout the world [1-5]. After termination of decontamination, process compressed gasses can by easily transformed into the gaseous state by decompression or heating, whereas contaminations can be obtained in the compact form. This will allow reducing the volume of secondary LRW by nearly a factor of 20 as compared to common decontamination procedures.

However, this technology requires rather expensive equipment to operate under high pressure (from 15 to 30 MPa). Our previous studies showed principal possibility of development of relatively cheap decontamination technology in liquid CO₂ or ozone-friendly Freon HFC-134a (CF₃-CFH₂) at 6-7 MPa or 1.0-1.2 MPa working pressure, respectively.

The use of compressed (supercritical or liquid) gases as solvents for decontamination is the important task but according our opinion this technology could be successful employ in some other fields somehow or other connected with waste management.

It is well known that the length of time specified for the waste save storage on numerous occasions depend on long-lived radionuclides content in waste. So if one succeeds in decrease long-lived radionuclides concentration in solid waste we can get opportunity to reduce time needed for the waste storage.

Taking in consideration reasoning above-mentioned we decided to carry out several experiments with solid samples of waste after solidification of solutions with special elastomeric polymers developed by Nochar[®] Corporation of Indianapolis, Indiana [11, 12].

It is also worth noting that Nochar's polymers are highly universal and can solidify aqueous solutions of various acidity and specific activity, organic liquids (diluent, extraction agents), various composition suspensions and sludges.

It is quite evidently, that using solutions solidification process with polymers has some restrictions. Among them the polymer matrices couldn't be used for long-lived radionuclides immobilization, such as transplutonium elements (TPE) as far as they demand the ultimate storage.

So the first goal of this work was to obtain experimental data on the decontamination effectiveness in the liquid gases as compared to the aqueous decontamination solutions.

And the second task of this paper was to show the opportunity long-lived radionuclides recovery from substances obtained after radwaste solidification in polymer compositions.

In other words it's the first attempt partitioning process usage with reference to solid products.

RESULTS OF EXPERIMENTS AND DISCUSSION

Study on the decontamination of the fabric surfaces.

Decontaminations tests were carried out using non- aqueous solvent ##. 1, 2 and 3:

Solution # 1: H₂O - 0.3 vol %; dioctylfluoroamylphosphoric acid (DOFAPA) 1.0 vol %, tributylphosphate (TBP) 1.0 vol% in liquid Freon HFC-134a.

Solution # 2: H₂O - 0.3 vol %, DOFAPA - 1.0 vol %, TBP - 1.0 vol % in liquid CO₂.

The aqueous decontamination solutions # 3 was used to compare the decontamination effectiveness of solution 1 and 2.

Solution # 3: decontaminant SF-3 (1 wt % in water).

The extraction composition DOFAPA - TBP (optimal concentration 1 vol % of each component in the solvent) provided efficient decontamination of actinide, lanthanide, Sr, and Cs salts, which are the most typical overall contaminants in radiochemical industry. Given composition was specially developed for treatment in liquid CO₂ or Freon containing 0,3-1 vol% water [6].

Decontaminant SF-3 is well-known rather efficient composition to remove radioactive contaminants from different surface and in some cases it can be used for overall decontamination. This composition is often used as 1 wt% aqueous solution at 20-40°C.

Decontaminant SF-3 involves sulfanole (15 wt %), sodium polyphosphate (35 wt %), and oxalic acid (50 wt %).

Our decontamination tests were carried out using the model samples of new cotton fabric "bleached" brand contaminated with europium, strontium, and cesium nitrate spiked with ¹⁵²Eu, ⁸⁵Sr, and ¹³⁷Cs, respectively.

In 24 h before contamination with radioactive contaminants given samples were treated with 0.2 M Na₂CO₃ solution for 3 min with intensive stirring, then subsequently washed with water and dried at 22-25°C for 18-20 h.

The square fragments (2.25 sm² area) were cut out from the fabric treated with sodium carbonate. Then, the solution of strontium, europium, and cesium nitrate in 0.1 M HNO₃ was dropped on center of the fragments in amount of 0.03 ml (3,8÷4,5*10⁷ Bq/l volume activity). Given solution volume entirely wetted a fabric fragment providing uniform distribution of radionuclide over the entire material surface. The samples prepared were dried at temperature 22-25°C for 18-20 h.

Decontaminations in the water media was carried out in the 100-ml flasks with continuous stirring on a magnetic stirrer (50-60 rpm) at 22.0±0.5°C.

The decontamination experiment involves both decontamination for 10 min and subsequent rinsing of decontaminated samples for 5 min using the same volume of pure solvent.

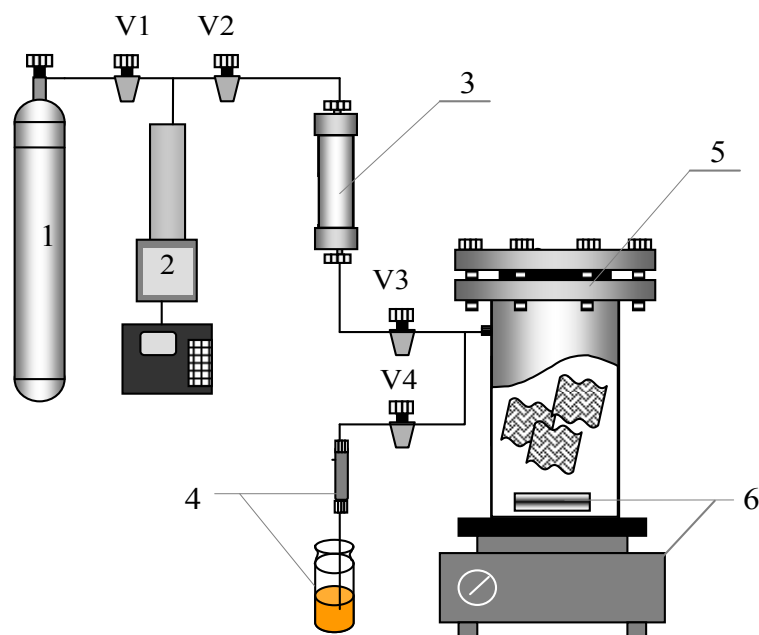
Three samples to be decontaminated were placed in the flask to be decontaminated, 50 ml of the appropriate solution nos. 3 was added, and then the experiment was performed with

stirring. The decontamination solutions were prepared in 24 h before experiments. After treatment the contaminated solution was removed from the flask and pure solvent was added to wash the samples. Then, the samples were dried at 22-25°C for 18-20 h before measurements of the final radioactive contaminations.

The decontamination experiments using the solutions based on liquid CO₂ or Freon HFC-134a were performed on a laboratory setup shown in Fig 1. Given solutions were stirred with a magnetic stirrer (50-60 rpm) at 22.0±0.5°C.

Three samples to be decontaminated were introduced into the 50-ml stainless steel decontamination chamber 5, which was placed on the magnetic stirrer, and then the required amount of the reagents were added in chamber for reagent dissolution 3. Then, the setup was sealed and the chamber for reagents dissolution (3) was pressurized with Freon (up to 1.2 MPa) or CO₂ (up to 7 MPa) to prepare the decontamination solutions. In chamber (3) the required reagents were dissolved in compressed gases.

After dissolution valve V3 was opened and decontamination chamber 5 was filled with solution nos. 1 or 2. The decontamination process was performed for 10 min. Then, the pressure was released and the chamber was decompressed up to atmospheric pressure using a decompression device 4. The decontaminated samples were removed from chamber 5 and the chamber walls were washed with ethanol and then dried with a flow of warm air. Then, the samples were placed into chamber 5 for washing with pure compressed HFC-134a or CO₂ for 5 min.



- 1 - Cylinder with compressed gas;
- 2 - High pressure pump;
- 3 - Chamber for reagents dissolution;
- 4 - Decompression device;
- 5 - Decontamination chamber;
- 6 - Magnetic stirrer;
- V1÷4 - Valves.

Fig. 1. Laboratory setup.

After washing of decontaminated samples the chamber was decompressed up to atmospheric pressure through decompression device 4, the decontaminated samples was taken from the chamber and the final content of radioactive contaminants was measured.

The initial and final contents of radionuclide on the sample surface were determined by radiometric analysis. The average value of three successive measurements of the content of radioactive contaminants on the sample surface (A, Bq) was determined; the measurement error (δ_{OTH}) was no more than $\pm 5\%$.

The mutual effect of radionuclide in the course of the decontamination process was not taken into account because all the experimental procedures were performed with the trace amounts of radionuclide in strongly diluted solutions ($<10^{-4}$ Ml), and the molar excess of the solvent to each complexing agents and to each radionuclide was greater by a factor of at least 1000.

For each decontamination solutions the decontamination factor (Kd) was calculated using the following expression:

$$Kd = A_{initial} / A_{final},$$

where $A_{initial}$ and A_{final} are the initial and final activity of the sample, Bq.

The measurement error of the decontamination factor was calculated using the results of three parallel experiments and only the experimental errors were taken into account.

The experimental data obtained are summarized and presented below in the Table I.

TABLE I. Comparison of decontamination effectiveness' in liquefied CO₂, HFC-134a and water.

Decontamination solution	Eu		Sr		Cs	
	Recovery, %	Kd	Recovery, %	Kd	Recovery, %	Kd
# 1	67 \pm 6	3 \pm 0,3	84 \pm 6	6 \pm 0,3	88 \pm 7	8 \pm 0,8
# 2	58 \pm 5	2,5 \pm 0,5	68 \pm 6	3 \pm 0,3	75 \pm 4	4 \pm 0,2
# 3	91 \pm 5	11 \pm 0,5	97 \pm 4	45 \pm 2	99 \pm 6	362 \pm 22

Comparison of the decontamination coefficient given in the table showed that decontamination in non-polar or low polar media (solution nos. 1 and 2) is less efficient than that in the aqueous solutions (solution nos.3). At the same time the decontamination effectiveness by the solutions of complexing agents in non-polar or low polar solvents (liquid CO₂ HFC-134a) are almost comparable.

All the solutions studied are characterized by one general feature; it was found that cesium is most efficiently removed from the fabrics the removal of strontium is less efficient, whereas the removal of europium from the fabric is rather difficult. Previously it was found fact that even small amounts of water improve the effectiveness of decontamination solutions [5, 7]. All the above data and the fact that water in Sc fluids and compressed gasses occurs in the form of micro- or even nanoemulsion [8, 9] suggest that especially formation of micro- or nanomicelles is a key factor to improve decontamination effectiveness in non- and low polar solvent.

At present the data on the mechanism of the Ionic complexation in the reverse microemulsion are scarce, but certain studies in this direction will probably promote development of the effective and low waste decontamination technology in non- aqueous solvent.

Study on the long lived radionuclide recovery from the solidified polymer compounds.

The studies on TPE, REE and short-lived radionuclides (e.g. Cs) petitioning/decontamination from the polymeric matrixes aged to about 30-35 days.

The following decontamination compositions hexafluoroacetylacetone (HFA) – TBP - H₂O and dioctafluoroamylphosphoric acid (DOFAPA) –TBP - H₂O were used for TPE, REE and Cs recovery into media of liquefied HFC-134a and sc CO₂. The results of the experiments are presented on Fig.2 and 3.

According to the data obtained (Fig. 1) the increase of the samples aging from 1,5 to 30-35 days provide considerably increase in the recovery degree from 16 to 71 % and from 14 to 68 % for TPE and REE respectively in the medium of sc CO₂.

It was detected that the TPE and REE recovery process in medium of liquefied HFC-134a has comparable efficiency to that of similar process in sc CO₂ as well.

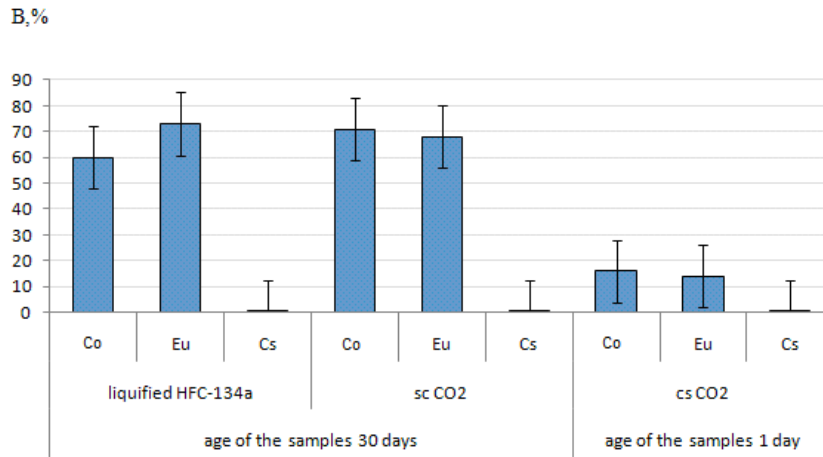


Fig 2. Co and Eu recovery from solidified samples in the media of sc CO₂ (30,0 MPa, 40 °C) and liquefied HFC-134a (1,2 MPa, 25 °C). Duration of the treatment 20 min, weight of the samples 0,18-0,21 g. Decontamination composition: 1 vol. % HFA – 1 vol. % TBP – 0,3 vol. % H₂O.

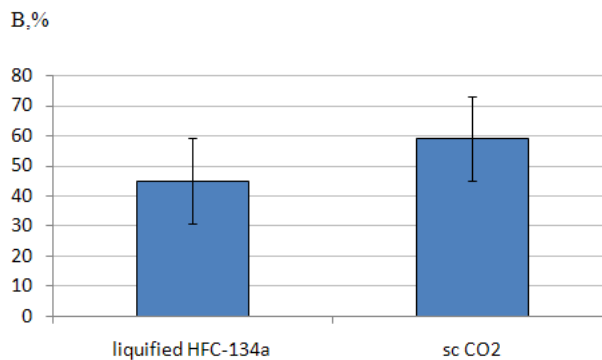


Fig 3. Cs recovery from solidified samples in the media of sc CO₂ (30,0 MPa, 40 °C) and liquefied HFC-134a (1,2 MPa, 25 °C). Duration of the treatment 20 min, weight of the samples 0,18-0,21 g. Decontamination composition: 1 vol. % DOFAPA – 1 vol. % TBP – 0,3 vol. % H₂O

CONCLUSION

- Our experimental data on radionuclide recovery from the fabric surface in the media of compressed gases suggest the possibility of development of low waste nonaqueous technology for decontamination, which would provide deactivation of various materials with low level of radioactive contamination at moderate operation pressures.
- The set of experiments performed with compressed gases and with the purpose Eu (as analog of transplutonium elements) and Cs recovery from solid waste have demonstrated principle possibility long-lived and short-lived radionuclides partitioning. Recovery degree for cesium in this case was less then 0.1 %.

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