PRESSURE AND TEMPERATURE INFLUENCE ON RADIONUCLIDE REMOVAL EFFICIENCY FROM DIFFERENT SURFACES

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INTRODUCTION

It is known that the efficiency of supercritical fluid extraction (SFE) of uranium depends on such factors as pressure, temperature, water presence and quantity of added complexones [1, 2, 3, 4, 5]. In the work the influence of these factors on plutonium and americium removal from Dacron, cotton and stainless steel samples was investigated. These materials were chosen for investigation as commonly occurring at radiochemical facilities. The samples were contaminated with plutonium and americium nitrates or oxides, because these chemical compounds are most often available on surfaces of materials to be decontaminated, on the one hand, and, on the other hand, essentially differ in their chemical properties.

I- MATERIALS AND METHODS

Hexafluoroacetylacetone was received from “Fluorochem”Co (Great Britain). Other reagents of analytical grade were obtained from “Vekton” Co (Russia). All reagents were used without additional purification. Isotopes of Am^{243} and Pu^{239} produced by “Isotop” Co (Russia) were used.

High-pressure syringe pump with cooled head (Grant-Instrument, Russia) and extraction cell made of stainless steel (3.5 ml, Keystone Scientific, USA) and coated by pyrolytic chrome were applied in experiments. Stainless steel, cotton and Dacron samples, as well as aliquots of complexone, modifier and water, were placed into extraction cell. Thereafter, CO_2 was forced into the cell, the cell was thermostatically controlled and kept for 20 min at preset pressures and temperatures (static extraction); then carbon dioxide was passed through the cell under the same pressure and temperature during 40 min (dynamic extraction). Extract was collected into methanol through capillary restrictor. Extracted and residual quantities of nuclides were determined by radiometry. The samples contaminated with plutonium (IV) and americium (III) were prepared by applying a solution aliquot on surfaces of the samples, then they were dried at 120^{o}C. The samples with plutonium and americium oxides on stainless steel surface were prepared by calcination of nitrate contaminated samples at 400^{o}C for two hours; the cotton and Dacron samples contaminated with Pu and Am oxides were prepared by rubbing into fabric the powder of Fe_2O_3 precipitated from Pu or Am-containing solution.

II- RESULTS AND DISCUSSION

Investigation of the pressure influence on decontamination efficiency by HFA solutions in CO_2 has shown that the removal degree of contaminants increases with pressure increase from 100 to 300 atm (Fig. 1); the results obtained are in good agreement with literary data about the pressure effect on metal extraction [2].

Another important factor of supercritical fluid decontamination process is concerned with the presence of water. The role of water in the process of supercritical fluid decontamination is widely discussed in scientific literature. It is known that the increase of added water amount up to a certain limit results in higher recovery of actinide nitrates and oxides. Further increase of added water does not practically affect the decontamination degree [1, 3, 5]. When investigating the water effect on supercritical fluid decontamination, it was found (Table 1) that the increase of added water amount in the range of its solubility in SC-CO_2 (to 1 % vol.) contributes to recovery of plutonium and americium. Further increase of added water amount has practically no influence on decontamination efficiency. The threshold value of water concentration for efficient radionuclide removal and the character of its influence on recovery degree allow to suggest the two most probable mechanisms of water effect: (i) water is needed to provide dissociation of ß-diketone and metal salt; (ii) water forms stable colloid solution in SC-CO_2 and metal complexes are extracted into SC-CO_2 in the form of micelles.

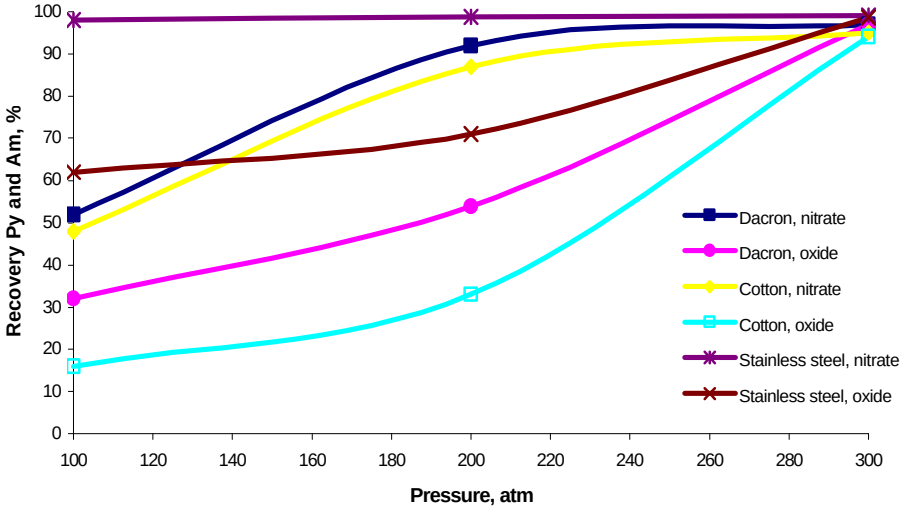

Fig. 1 Pressure effect on decontamination of Dacron, cotton, and stainless steel by ß-diketone solutions in SC-CO_2 (30 µl HFA, 30 µl Py, 10 µl H_2O)

Table 1 Effect of water presence on decontamination in SC-CO_2 (30 µl HFA, 30 µl Py, 300 atm, 60°C)

Material and contaminants	% recovery with various additions of water				
	0	10 µℓ	30 µℓ	70 µℓ	100 µℓ
Dacron, Am and Pu nitrate	$42_{\pm4}$	$44_{\pm6}$	$55_{\pm3}$	$72_{\pm7}$	$77_{\pm9}$
Dacron, Am and Pu oxide	$27_{\pm7}$	$32_{\pm7}$	$57_{\pm2}$	$56_{\pm6}$	$57_{\pm11}$
Cotton, Am and Pu nitrate	$37_{\pm6}$	$53_{\pm7}$	$63_{\pm3}$	$66_{\pm4}$	$70_{\pm7}$
Cotton, Am and Pu oxide	$39_{\pm12}$	$40_{\pm11}$	$49_{\pm8}$	$54_{\pm8}$	$63_{\pm9}$
Stainless steel, Am and Pu nitrate	$40_{\pm9}$	$61_{\pm9}$	$62_{\pm8}$	$62_{\pm11}$	$72_{\pm13}$
Stainless steel, Am and Pu oxide	$27_{\pm6}$	$32_{\pm4}$	$53_{\pm5}$	$53_{\pm7}$	$61_{\pm14}$

Results of experiments on determination of temperature effect on contaminants removal from surfaces of selected materials are presented in Table 2. The range of investigated temperatures was limited to 40 and 80°C, because the critical temperature of CO_2 is 31°C [6,7], and at temperature above 80°C there is observed thermal destruction of both complexes and some ß-diketones [3, 4].

The obtained data have revealed that the recovery of plutonium and americium from surfaces of Dacron and stainless steel samples increases with temperature rise; plutonium and americium nitrates therewith are removed more efficiently than their oxides. However, in the case of cotton surface the increase of temperature to 70-80°C causes the noticeable decrease in recovery degree of both nitrates and oxides of actinides. The nature of this effect is not clear and calls for further investigation. The influence of added complexone amount on decontamination efficiency was investigated as well (Fig. 2).

Table 2 Temperature effect on decontamination in SC-CO_2 medium (30 µl HFA, 30 µl Py, 300 atm, 60°C)

Material and contaminants	Recovery at various temperature, %				
	40 ??	50 ??	60 ??	70 ??	80 ??
Dacron, Am and Pu nitrate	$34_{\pm5}$	$38_{\pm8}$	$44_{\pm14}$	$69_{\pm7}$	$81_{\pm7}$
Dacron, Am and Pu oxide	$18_{\pm3}$	$24_{\pm5}$	$32_{\pm3}$	$40_{\pm7}$	$42_{\pm9}$
Cotton, Am and Pu nitrate	$58_{\pm7}$	$53_{\pm9}$	$53_{\pm6}$	$50_{\pm6}$	$40_{\pm4}$
Cotton, Am and Pu oxide	$21_{\pm9}$	$35_{\pm4}$	$40_{\pm5}$	$42_{\pm11}$	$36_{\pm5}$
Stainless steel, Am and Pu nitrate	$65_{\pm6}$	$61_{\pm12}$	$63_{\pm9}$	$62_{\pm4}$	$72_{\pm6}$
Stainless steel, Am and Pu oxide	$35_{\pm11}$	$32_{\pm7}$	$32_{\pm8}$	$37_{\pm5}$	$41_{\pm2}$

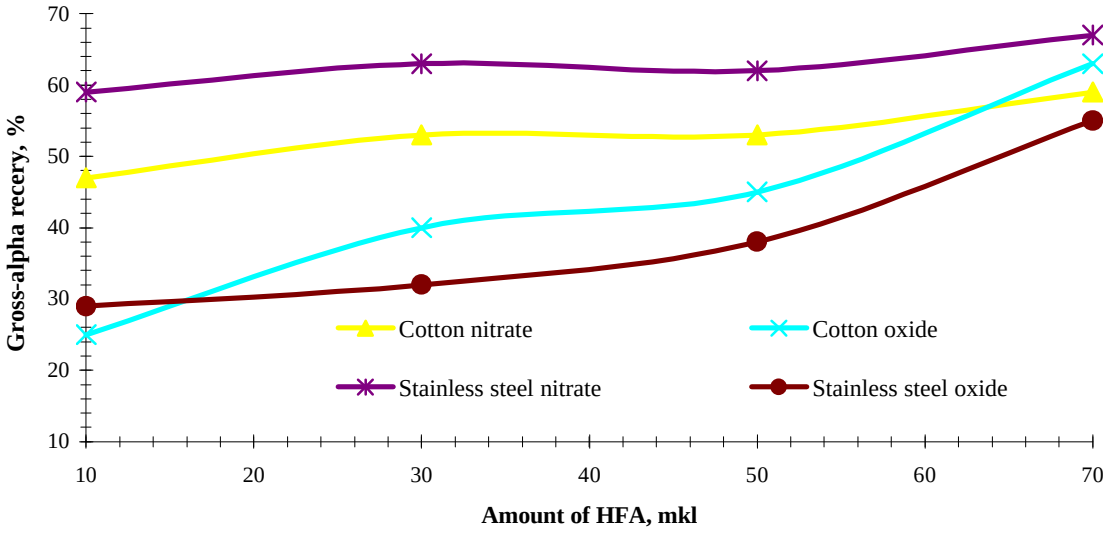

Fig. 2 Effect of added HFA amount on decontamination of Dacron, cotton and stainless steel by ß-diketone solutions in SC-CO_2 (30 µl Py, 10 µl H_2O, 300 atm, 60 °C)

The obtained data have confirmed that for efficient decontamination the HFA concentration in SC-CO_2 should be within 1.0 – 3.0 %vol. (around 30 – 100 µl under the experimental conditions); this is determined by the necessity of attaining the required decontamination degree. Since the required decontamination factor is not attained at concentration below 1.0 %vol., at concentration above 3 %vol. the consumption of expensive complexone increases unjustifiedly.

CONCLUSION

1. It has been demonstrated that at constant pressure the recovery degree of plutonium and americium from Dacron and stainless steel surfaces increases with temperature rise; plutonium and americium nitrates are removed better than their oxides. However, in the case of cotton the temperature increase to 70-80^{o}C results in considerable decrease of recovery degrees of both nitrates and oxides.
2. It is found that the recovery degree of actinide oxides from cotton and stainless steel surfaces monotonically increases with increasing the HFA complexone concentration in SC-CO_2, whereas the HFA concentration affects the removal degree of actinide nitrates only slightly. The obtained data show that for affording the efficient decontamination the HFA concentration in SC-CO_2 should be in the range of 1.5 – 3.0 % vol..
3. It is shown that the increase of added water amount to a certain limit leads to increasing the recovery degree of actinide nitrates and oxides and the further increase of added water amount does not practically affect the decontamination factors.
4. The conducted studies have made it possible to determine the conditions for efficient removal of actinide nitrates and oxides from surface of different materials: SC-CO_2 at pressure 300 atm, at temperature 50-70^{o}C, 0.3 – 1.0 % vol. H_2O, 1.5 – 3.0 % vol. HFA and 1.5 – 2.0 % vol. Py.

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