SORPTION RECOVERY OF RADIONUCLIDES IN SUPERCRITICAL AND LIQUID CARBON DIOXIDE

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Introduction

The used of supercritical (SC) and liquid CO_2 for extraction of radionuclides seems rather promising owing to its advantages as compared to common organic solvents. One of the most important advantages is a possibility of preparing compact neat extract after evaporation of CO_2, this adventure makes attractive using of CO_2 as a solvent for radiochemical area. However, method of extract collection by CO_2 evaporation in some cases is not meeting the operation requirements. Therefore as a different way of extract collection may be selective recovery of heavy/radioactive metals on sorbents from CO_2 flow for decontamination processes to separate radioactive wastes from organics wastes. The data on sorption of radionuclides from CO_2 can be also of particular importance for some other technological procedures. Principle feasibility of this approach to the regeneration of fluid was demonstrated previously at the Khlopin Radium Institute [1].

Experimental

In this work studies on recovery of micro amounts of strontium and cesium from solutions in the form of complexes with perfluorovaleric acid (PFVA) and crown ether in liquid and SC CO_2 and of europium from solutions as complex with HFA and TBP liquid and SC CO_2 was carried out. For this purpose the following sorbents were used:

1. Activated carbon without pretreatment;
2. Synthetic zeolite NaA, preliminary dried at T ~ 300°C for 8 h;
3. Silica gel Silochrom II (microspheric silica gel, fraction 0.15-0.5 mm), preliminary dried at T ~ 300°C for 8 h.

The experiments were performed as follows: an aliquot (0.03-0.05 ml) of the solution of corresponding radionuclide was placed on a stainless steel disc and dried under the IR lamp. The compositions of the working solutions are listed below:

1. $CsNO_3$ in 0,1M HNO_3 with specific activity ~ 0,23 MBq/ml;

2. $Sr(NO_3)_2$ in 0,1M HNO_3 with specific activity ~ 0,31 MBq/ml;
3. $Eu(NO_3)_3$ in 0,1M HNO_3 with specific activity ~ 0,19 MBq/ml.

The resulting sample with known activity(A_{ini}) with the required reactants were placed in cell 3-1 and a weighed portion of the sorbent studied was poured without additional pressing in cell 3-2, which was closed from both sides with the standard filters (Keystone Co.) with external diameter close to the internal diameter of the cell. The scheme of sorption units and sorption sell are presented on Fig. 1 and 2. The view of sorption cell and sorption materials are presented on Fig. 3.

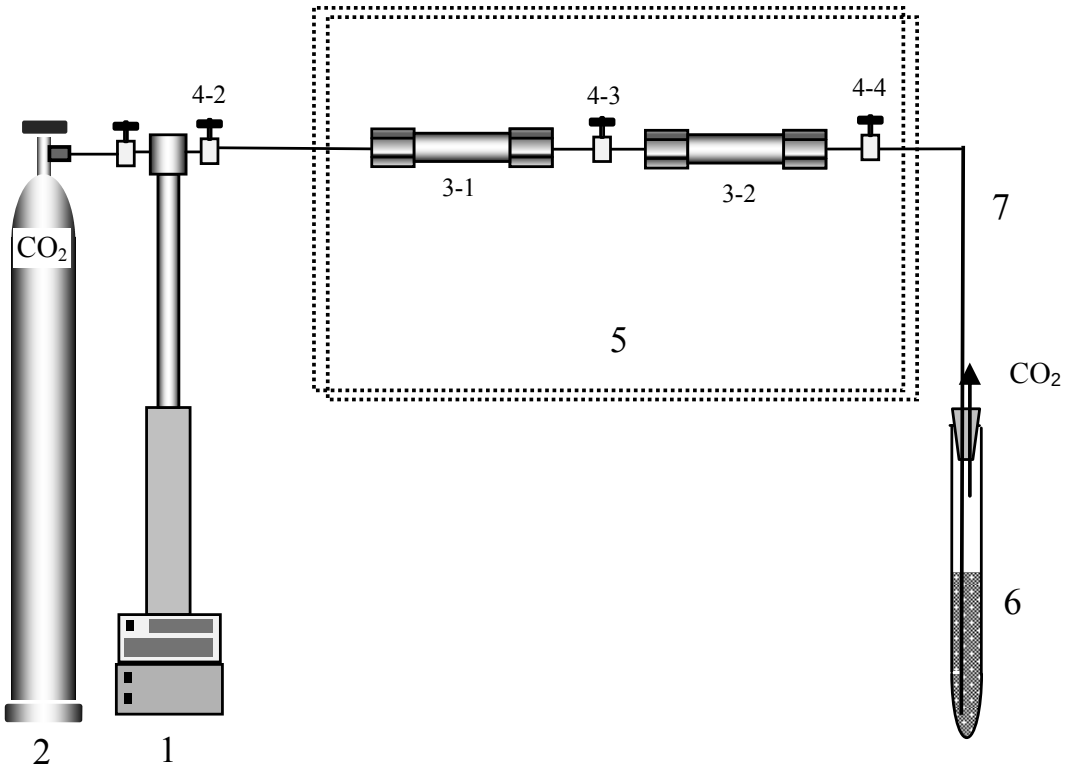

Fig. 1. Scheme of the sorption unit.

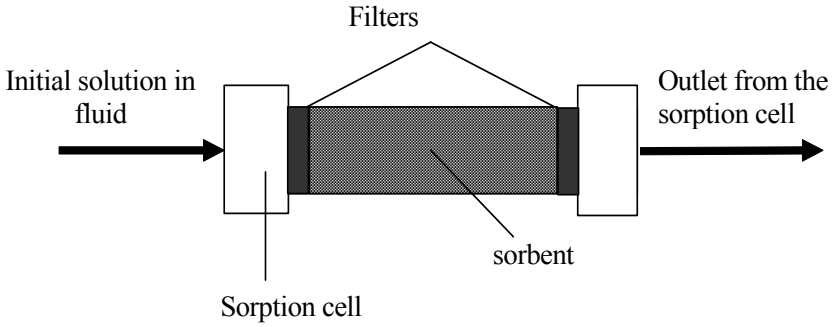

Fig. 2 Sorption cell.

Both cells were placed in a temperature controlled water bath. Using high-pressure pump 1 (open closed valve 4-3) cell 3-1 (10.0 ml volume) was filled with CO_2 from cylinder 2 up to required pressure at given temperature. The system was kept at given conditions for 30-45 min (static extraction). Then, valve 4-3 was opened and the system was pumped with nearly 10 cell volumes of CO_2 (~100 ml). The pumping rate was controlled by restrictor 7 (internal diameter 100 mkm) and valve 4-4 (1.0-1.5 ml/min). Then CO_2 with dissolved complex was transmitted through the sorption cell 3-2 filled with corresponding sorbent, and bubbled through the trap solution 6 (ethanol or chloroform, 25 ml). After the experiment termination the cell was ventilated, dismantled, then the sorbent was recovered and the content of radionuclides was analyzed:

1. on the surface of the stanless steel disc by measuring of the residual β- or γ-ray activity of radionuclides in question -A_{res};
2. in the extraction cell 3-1 by analysis of the chloroform washing solution– A_{sol};
3. on the sorbent by sampling after drying of certain weight/volume on a support – A_{sorp}.
4. in trap 6 by measuring of an aliquot of the trap solution on the stainless steel support – A_{trap}.

Fig. 3. Cells for radionuclides 3.1 (10.5 ml) and for sorbent 3-2 (10.2 ml) and sorbents: А – zeolite NaA, Б – silica gel Silochrom II, В – activated carbon.

After analysis of radionuclide dissolved and adsorbed on corresponding material we calculated the effective coefficients of extraction $E_{ext}=(A_{ini}-A_{res})/A_{ini}*100\%$ and sorption и сорбции $E_{sorb}=A_{sorp}/(A_{ini}-A_{res})*100\%$. The results are listed in Tables 1 and 2.

Table 1. Sorption of cesium and strontium complexes with PFVA -dicyclohexil-l8-crown-6 (DCH18C6) and europium complex with HFA-TBP in liquid CO_2 (7 MPa, 22°C) on various sorbents (extraction cell volume 10.0 ml, sorption cell volume 10.4ml).

Nuclide $A_{исх.}$(Bq)	Reactants/ (mkmole)	Sorbent (g)	$A_{res,}$ Bq	$A_{sorp,}$ Bq	$A_{trap,}$ Bq	E_{exp}, %	E_{sorp}, %
^{137}Cs/ (738)	PFVA (32) DCH18C6 (58) H_2O (278)	Carbon (2,5)	511	210	0,02	31	92
^{137}Cs/ (799)	PFVA (32) DCH18C6 (58) H_2O (278)	Silica gel (2,2)	500	290	0,01	37	97
^{137}Cs/ (1020)	PFVA (32) DCH18C6 (58) H_2O (278)	Zeolite (6,7)	752	275	0,01	26	102
^{90}Sr/ (930)	PVFA (32) DCH18C6 (58) H_2O (278)	Carbon (2,4)	603	284	0,02	35	87
^{90}Sr/ (1025)	PFVA (32) DCH18C6 (58) H_2O (278)	Silica gel (2,3)	652	350	0,01	36	94
^{90}Sr/ (993)	PFVA (32) DCH18C6 (58) H_2O (278)	Zeolite (6,7)	555	450	0,01	44	103
^{152}Eu/ (5500)	HFA (212) TBP (110) H_2O (556)	Carbon/ (2,5)	2011	3180	0,02	63	91
^{152}Eu/ (5405)	HFA (212) TBP (110) H_2O (556)	Silica gel (2,4)	2225	3150	0,01	59	99
^{152}Eu/ (5666)	HFA (212) TBP (110) H_2O (556)	Zeolite (6,6)	2600	3075	0,01	54	100

Table 2. Sorption of cesium and strontium complexes with PFVA -DCH18C6 and europium complex with HFA-TBP in SC CO_2 (25 MPa, 60°C) on various sorbents (extraction cell volume 10.0 ml, sorption cell volume 10.4ml).

Nuclide A $_{исх.}$(Bq)	Reactants/ (mkmole)	Sorbent (g)	$A_{res,}$ Bq	$A_{sorp,}$ Bq	$A_{trap,}$ Bq	$E_{exp,}$ %	$E_{sorp,}$ %
^{137}Cs (852)	PFVA (32) DCH18C6 (58) H_2O (278)	Carbon 2,1	100	700	0,02	88	93
^{137}Cs (770)	PFVA/32 DCH18C6/58 H_2O/278	Silica gel (2,3)	52	711	0,03	93	99
^{137}Cs (780)	PFVA (32) 18C6 (58) H_2O (278)	Zeolite (6,7)	15	777	0,01	98	102
^{90}Sr (930)	PFVA (32) DCH18C6 (58) H_2O (278)	Carbon (2,6)	50	920	0,01	95	105
^{90}Sr (977)	PFVA (32) DCH18C6 (58) H_2O (278)	Silica gel (2,6)	67	970	0,01	93	107
^{90}Sr (985)	PFVA (32) DCH18C6 (58) H_2O (278)	Zeoilte (6,1)	12	985	0,01	99	101
^{152}Eu (5423)	HFA (212) TBP (110) H_2O (556)	Carbon (2,2)	55	5200	0,01	99	97
^{152}Eu (5603)	HFA (212) TBP (110) H_2O (556)	Silica gel (2,2)	45	5550	0,02	99	100
^{152}Eu (5500)	HFA (212) TBP (110) H_2O (556)	Zeolite (6,0)	32	5580	0,02	99	102

Conclusion

Thus, by the example of corresponding complexes of cesium, strontium, and europium, our experimental results show principle possibility of treatment of the fluid solvent to remove dissolved radionuclides using appropriate sorbents among sorbents studied, the highest sorption properties were observed for zeolite, however, we assumed that silica gel is also rather promise sorbent for the technology developed. The sorption effectiveness's were more than 90 % for all cases.

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1 D. Shafikov, V. Kamachev, A. Murzin, V.Babain, A. Shadrin. «Sorption of radionuclides from complexone solutions in liquid CO_2» Radiochimica Acta, v.94, N1, 87-90 (2006)