CLASSICAL METHODS OF CESIUM SEPARATION FOR ^{135}CS ACTIVITY EVALUATION

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Abstract

Two classical methods for separating cesium from aqueous samples were used by precipitating the element of interest with specific reagents whose selectivity is maintained by varying the pH within a certain range of values. These experimental studies can be applied to separate cesium radionuclides from both liquid waste and solutions obtained by mineralizing solid waste matrix (for example, spent resin produced during routine operations and maintenance activities at Romanian Cernavoda Nuclear Power Plant's PHWR-CANDU-6 Canadian type reactors). The two methods consist of: (1) precipitation of interfering elements (Co, Eu, Fe, Mn, Ni) as hydroxides, followed by alkaline-earth elements separation (Ca, Ba) as carbonates, and (2) precipitation and reprecipitation of Co, Eu, Fe, Mn, Ni, followed in sequence by precipitation and reprecipitation of Sr and Ca. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to evaluate the performance parameters (decontamination factors, decontamination efficiencies, recovery yield).

Keywords: *Cesium separation, Precipitation, Reprecipitation*

Introduction

The radioactive isotopes of cesium (^{134}Cs, ^{135}Cs, ^{136}Cs and ^{137}Cs) do not occur naturally; they exist as a result of human activity. The behavior of cesium radioactive isotopes in various media (soil, water, plants, human body and animals) transforms them into a potential hazard to the environment and people if it is not properly disposed. Radiocesium is easily absorbed by the soil and it is deposited to a depth of about 5 cm [1, 2]. The migration rate of cesium in groundwater is higher at lower pH levels, and some rocks (granite and basalt) tend to retain cesium, making it more difficult to detect in groundwater. The uptake of cesium radionuclides by plants continues at a linear rate throughout the growing season. It has been found that cesium concentrates in the roots, the lower part of the foliage, and the leaf veins. Cesium is almost completely absorbed from the gastrointestinal tract and concentrates mainly in soft tissues, particularly in muscles. The biological half-life of radiocesium in humans varies according to age, gender, and body weight, ranging from 50 to 150 days for adults, with a mean value of 101 days. Some studies were conducted to investigate one of the pathways of human exposure to radioactive cesium: plants – animals – humans. These investigations revealed a strong correlation between plant pollution and subsequent contamination of the human body [1].

The main fission products from thermal fission of ^{235}U are ^{135}Cs and ^{137}Cs. They can be found in the environment as a result of releases from nuclear power plants, fuel reprocessing facilities, nuclear accidents, and fallout from atmospheric weapons testing [3, 4]. The ^{135}Cs radioisotope is a pure β emitter (E_{max} = 210 keV) with a half-life of 2.2×10^6 years [1]. ^{135}Cs can be detected by the liquid scintillation counting (LSC) technique using efficiency tracing with ^{14}C [5, 6]. Due to interference from coexisting radionuclides, the LSC technique requires separation and purification of ^{135}Cs from the original sample matrix.

Methodology

In this experimental study, solutions containing Co, Eu, Fe, Mn, Ni ions (with a concentration of 1 g/L) and Sr, Ba, Cs ions (with a concentration of 5 g/L) were used. The mass concentration evaluation of the elements was performed by the inductively coupled plasma-optical emission spectrometric (ICP-OES) method.

Two sets of experiments were carried out to separate the Cs^+ chemical species, in order to evaluate the performance parameters: decontamination factors and efficiencies, chemical recovery yield of cesium. The algorithm for conducting the experiment is shown in Table 1.

Table 1. Algorithm for conducting experiments to separate cesium from the sample matrix

Set no.	*Sample aliquots*	*Sample composition*	*Algorithm for cesium separation*
1. double precipitation	P1, P2, P3, P4	Cs, Co, Eu, Fe, Mn, Ni, Sr, Ba	- Precipitation of interfering elements (Co, Eu, Fe, Mn, Ni) in the presence of NaOH solution, at pH= 8-9; - Precipitation of alkaline-earth elements (Sr and Ba) in the presence of Na_2CO_3 solution.
2. double precipitation/ reprecipitation	P5, P6, P7, P8	Cs, Co, Eu, Fe, Mn, Ni, Sr, Ba	- Precipitation of interfering elements (Co, Eu, Fe, Mn, Ni) in the presence of NaOH solution, at pH= 8-9; - Reprecipitation of interfering elements (Co, Eu, Fe, Mn, Ni) in the presence of NaOH solution, at pH= 8-9; - Precipitation of alkaline-earth elements (Sr and Ba) in the presence of Na_2CO_3 solution; - Reprecipitation of alkaline-earth elements (Sr and Ba) in the presence of Na_2CO_3 solution.

Cesium separation by precipitation

The four aliquots (marked as P1, P2, P3, P4) were transferred to centrifuge tubes, and pH was increased at a value between (8…9) by adding 1M NaOH solution to precipitate transition ions (Ni^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Eu^{3+}), while the alkali and the alkaline-earth metals remained as a supernatant [7, 8].

Preliminary laboratory tests were performed to establish precipitation conditions: estimating the pH range and concentration of NaOH solution in order to obtain supersaturated solutions, which ensures interfering ions precipitation. The pH optimal value was calculated using the solubility product constants of the hydroxides as well as the precipitation chemical equations. In addition, knowing the molar concentration of ions in the sample, the solution volume and the solubility product constant, the minimal value of the NaOH solution concentration for initiating the precipitation process was calculated.

For example, the calculation mode for precipitation of $Co(OH)_2$ is: $Co^{2+} + 2HO^- \leftrightarrow Co(OH)_2$; $[HO^-] = a$ mol/L $\rightarrow [Co^{2+}] = a/2 \rightarrow [Co^{2+}]x[HO^-]^2 = K_{ps} \rightarrow a^2$ x a/2 = 2.5 x $10^{-16} \rightarrow [HO^-] = 7.94 \times 10^{-16} \rightarrow$ pOH = $-\log_{10}7.94 \times 10^{-6}$ $\rightarrow$ pOH = 5.1 $\rightarrow$ pH = 14 - pOH $\rightarrow$ *pH = 8.9*

The NaOH solution minimal concentration to initiate the precipitation process is: $[Co^{2+}]_{initial} = 1$ g/L $\rightarrow [Co^{2+}]_{initial} =$ 1/59 moli/L; $V_{Co\ ions\ solution} = 0.5$ mL; $V_{sample\ solution} = 7$ mL; $\rightarrow [Co^{2+}] = (0.5/7)\cdot(1/59)$ mol/L
$[Co^{2+}] \times [HO^-]^2 > K_{ps} \rightarrow [HO^-] > 4.54\cdot10^{-7}$ mol/L

The $Co(OH)_2$ precipitate solubility is: s = solubility of the Co^{2+}ions; $\rightarrow s\cdot(2s)^2 = K_{ps} \rightarrow s = 3.97\cdot10^{-6}$ moli/L.

The radiochemical procedure (precipitation of interfering elements - Co, Eu, Fe, Mn, Ni - as hydroxides, followed by alkaline-earth elements separation - Ca, Ba - as carbonates) is depicted in Figure 1.

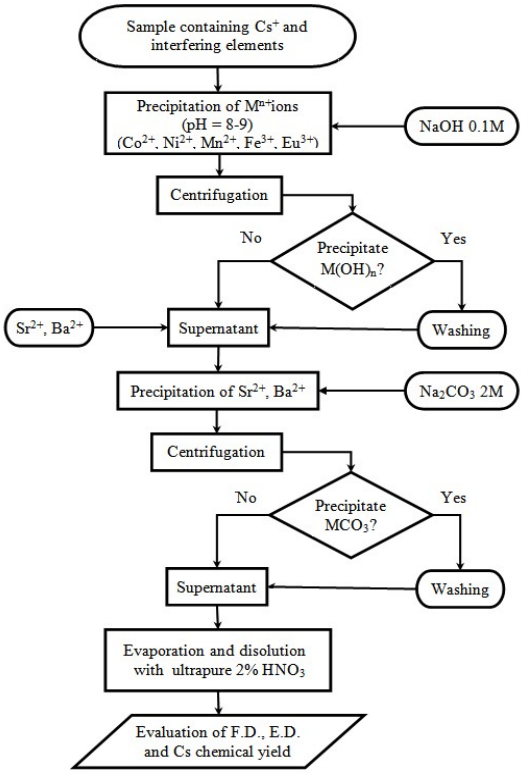


Fig. 1. Flow chart for Cs^+ separation using precipitation of transition elements as hydroxides, followed by alkaline-earth elements separation as carbonates

Figures 2 and 3 illustrate the precipitation process of transition elements as hydroxides, followed by alkaline-earth elements separation as carbonates.



Fig. 2. Precipitation with NaOH solution



Fig. 3. Precipitation with Na_2CO_3 solution

Cesium separation by precipitation – reprecipitation

A set of experiments was carried out to separate cesium by precipitation and reprecipitation of Co, Eu, Fe, Mn, Ni, followed in sequence by precipitation and reprecipitation of Sr and Ca, in order to increase the decontamination efficiency values. The radiochemical procedure is depicted in Figure 4.

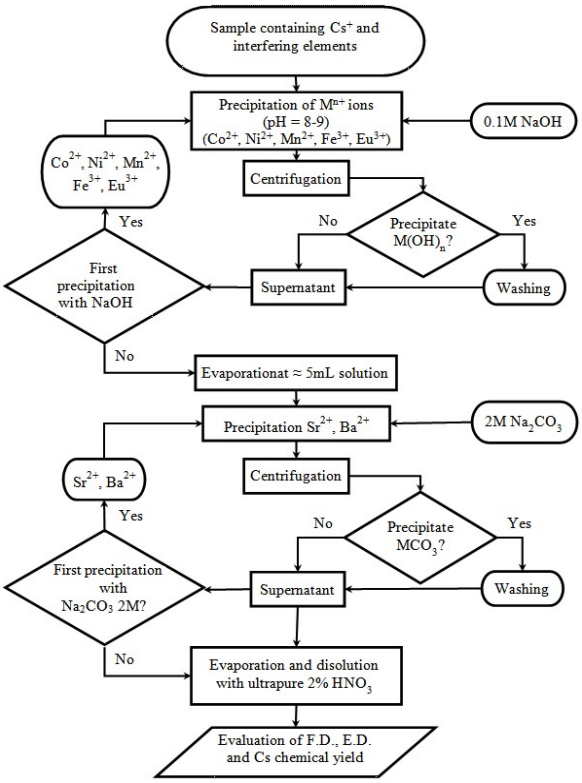


Fig. 4. Flow chart for Cs^+ separation using precipitation and reprecipitation of transition elements, followed in sequence by precipitation and reprecipitation of alkaline-earth elements

Results and discussion

Decontamination factors and efficiencies evaluation

Cs	*0.9999*	Ba	*0.9997*
Co	*0.9999*	Eu	*0.9999*
Fe	*0.9999*	Ni	*0.9997*
Mn	*0.9999*	Sr	*0.9987*

The recovery yield, Rec [%] for strontium is computed using Eq. Given below.

$$Rec = (m_{final}/m_{initial}) \cdot 100 \quad (1)$$

where: Rec = recovery yield [%]; m_{final} = mass of cesium in the purified fractions obtained by application of the two separation analytical methods [g]; $m_{initial}$ = mass of cesium in the initial samples (P1...P8) [g].

The decontamination factors and efficienciesare defined by Eqs. 2 and 3.

$$F.D = (m_{initial}/m_{final}) \quad (2)$$

$$E.D = 100 - [(m_{final}/m_{initial}) \cdot 100] \quad (3)$$

where: F.D.= decontamination factor; E.D.= decontamination efficiency [%]; m_{final} = mass of interfering elements (Co, Eu, Fe, Mn, Ni, Sr, Ba) in the purified fractions obtained by application of the two separation analytical methods [g]; $m_{initial}$ = mass of interfering elements(Co, Eu, Fe, Mn, Ni, Sr, Ba) in the initial samples (P1...P8) [g].

Performance parameters evaluation for cesium separation by double precipitation

The values of cesium recovery yield are reproducible for the four samples, spanning from 89.37 % to 91.27 %, with an average value of 90.25 %.

The values of decontamination factors are:

Co	2.68×10^2	Ba	1.06×10^2
Eu	2.21×10^3	Sr	1.14×10^2
Fe	1.12×10^3	Ni	3.62×10^3
Mn	1.85×10^3		

The variation of decontamination efficiencies corresponding to the interfering elements is shown in Figure 5.

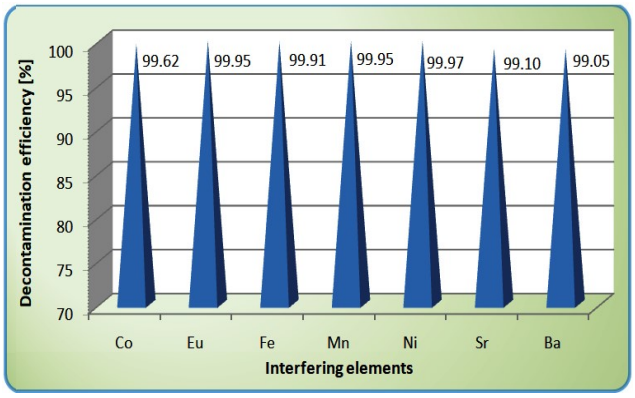


Fig. 5. Variation of decontamination efficiencies for double precipitation method

Performance parameters evaluation for cesium separation by double precipitation/reprecipitation

The values of cesium recovery yield are reproducible for the four samples, spanning from 77.33 % to 83.75 %, with an average value of 80.94 %.

The variation of decontamination efficiencies corresponding to the interfering elements is illustrated in Figure 6.

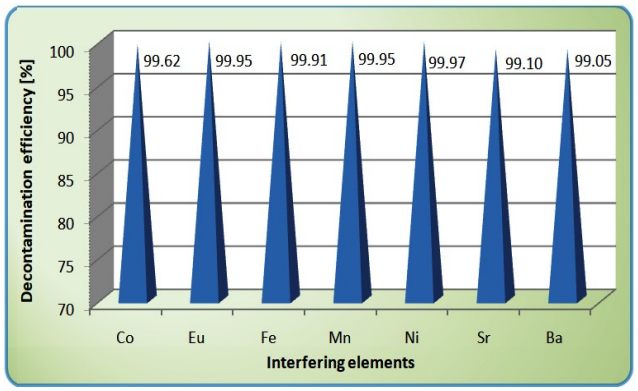


Fig. 6. Variation of decontamination efficiencies for double precipitation/reprecipitation method

The values of decontamination factors are comparatively presented in Table 2 along with the values obtained by the precipitation method.

Table 2. Decontamination factors of interfering elements corresponding to the two separation methods

	Decontamination factors	
Element	***Precipitation***	***Precipitation - reprecipitation***
Co	2.68×10^2	7.87×10^4
Eu	2.21×10^3	5.01×10^6
Fe	1.12×10^3	1.34×10^6
Mn	1.85×10^3	3.33×10^6
Ni	3.62×10^3	1.29×10^6
Sr	1.14×10^2	1.15×10^4
Ba	1.06×10^2	1.14×10^4

By applying the separation method by precipitation followed by reprecipitation, a significant increase in the decontamination factor values was observed in comparison to the precipitation method: 10^2 times for Co, Sr, Ba and 10^3 times for the other interferents (Eu, Fe, Mn, Ni).

Applicability of cesium separation methods

The experimental studies performed can be applied to the separation of radiocesium from spent resin produced during routine operations and maintenance activities at the Cernavoda NPP's PHWR CANDU-6 reactors [9].

Some research works [10-12] estimated the radiochemical content of β-γ (determined by γ spectral analysis), ^{63}Ni, and ^{90}Sr pure β (evaluated by liquid scintillation counting technique, after applying selective and quantitative separation methods) in the spent resin waste transferred from Cernavoda NPP (see Table 3). This waste was collected from a spent ion-exchange resin drum including the sieves of both the moderator and primary heat transport purification systems.

Table 3. Radiochemical composition of ion-exchange resins used in purification system at Cernavoda NPP

Radionuclide	Activity [Bq/g resin]
^{54}Mn	2.47 x 10
^{60}Co	1.18 x 10^3
^{134}Cs	4.47 x 10^2
^{137}Cs	2.81 x 10^4
^{63}Ni	1.17 x 10^3
^{90}Sr	5.97 x 10^2

The ratios between radiocesium activity (taking into account the cesium recovery yield) and the interfering radionuclides activities were calculated for the two separation methods using the initial activities of the interfering radionuclides and the decontamination factors values (presented in Table 2), and are presented in Table 4. Table 4 also contains the initial radiocesium activity to interfering radionuclide ratio.

According to Table 4, after applying separation methods, the interfering radionuclides activity is 10^3...10^9 times lower than that of radiocesium. Therefore, the two separation methods of radiocesium can be applied to spent resin samples.

Table 4. Initial and final ratios between radiocesium and interfering radionuclides activity in ion-exchange resins used in purification system at Cernavoda NPP

	Cs:^{54}Mn	***Cs:^{60}Co***	***Cs:^{63}Ni***	***Cs:^{90}Sr***
Initial	1.15 x 10^3:1	2.42 x 10:1	2.44 x 10:1	4.77 x 10:1
Double precipitation	1.93 x 10^6:1	5.85 x 10^3:1	7.97 x 10^4:1	4.92 x 10^3:1
Double precipitation/ reprecipitation	3.12 x 10^9:1	1.54 x 10^6:1	2.55 x 10^7:1	4.45 x 10^5:1

Conclusions

The results obtained by performing the two cesium separation and purification methods from aqueous samples reveal that both methods (double precipitation and double precipitation/ reprecipitation) are effective in separating cesium radionuclides from both liquid waste and solutions obtained by mineralizing solid waste matrix with the aim of quantifying ^{135}Cs activity.

The two cesium separation methodologies represent an effective tool for achieving very high decontamination factors of order 10^2 – 10^3 for the first method and 10^4 – 10^6 for the second method.

Cesium recovery yield values are reproducible for each separation method, ranging from 89.37 % to 91.27 % (with an average value of 90.25 %) for double precipitation method, and from 77.33 % to 83.75 % (with an average value of 80.94 %) for double precipitation/ reprecipitation method. Therefore, these methods can be applied to samples with low ^{135}Cs activity.

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