

RECOVERY OF ^{137}Cs FROM ACIDIC FISSION PRODUCTS SOLUTIONS

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A procedure for the isolation of ^{137}Cs from acidic fission products solutions, based on the use of silica gel and zirconium phosphate ion exchangers, is presented. The ^{137}Cs recovered by the ion-exchange process is converted to powder by coprecipitation of cesium with ammonium molybdophosphate. ^{137}Cs pellets have been prepared by compression of ^{137}Cs ammonium molybdophosphate powder using a hydraulic press. An important aspect of this procedure is that it does not require neutralization of the Purex waste.

INTRODUCTION

The radiochemical separation of ^{137}Cs is of great importance in the analysis of fission products mixtures. From considerations of fission yield, half-life and γ -rays energy, ^{137}Cs seems to be the nuclide of choice for use as radiation source, for measuring the burn up of reactor fuel as well as tracer for radiochemistry purposes.

In order to separate ^{137}Cs from other fission products chemical methods such as solvent extraction, precipitation

or ion exchange have been developed but in the majority of the papers published the recovery of the cesium involves neutralization of the radioactive solution.

The purpose of the work reported in this paper was the development of a procedure for recovering cesium from acidic fission products solutions, without previous neutralization of the radioactive solution, since the Purex waste solutions to be treated are strongly acidic /usually 4M HNO_3 /. The advantage of the acid process as compared to the process mentioned in the previous paragraph is the elimination of the neutralization of the feed solution since this neutralization step involves precipitation of gel-like cakes and dilution of the waste as well as the necessity of the addition of complexing agents to prevent precipitation of hydrolysable metals.

The ion-exchange method on inorganic exchange materials was selected to perform the required separation and zirconium phosphate /ZP/ is well known as an exchanger with strong affinity for cesium¹⁻³.

The first part of our studies has been reported earlier⁴. The adsorption behaviour of long lived fission products and uranium on ZP and silica gel columns were systematically studied. Experiments to determine the effects of various chemical variables such as composition of charge solution, nature and concentration of eluting agents, flow rate, concentration of uranium and quantity of exchanger upon adsorption of the elements mentioned were performed⁴.

Based upon these results, a flowsheet is presented which includes a first cycle to separate cesium from zirconium and niobium by sorption of ^{95}Zr and ^{95}Nb on silica gel. The second cycle allowed separation of cesium from uranium and from other fission products / ^{144}Ce , ^{90}Sr , ^{106}Ru / using ZP as selective sorbent for cesium.

After the recovery of ^{137}Cs from fission products mixtures, the next step was its solidification. The selection of an optimum process for the solidification of cesium has been studied earlier⁵. Several methods were considered such as evaporation, vitrification, adsorption on inorganic ion exchanger and coprecipitation with ammonium molybdophosphate. The latter was employed for the solidification of cesium.

EXPERIMENTAL

Radioactive tracers

Pellets of 2.5 g of U_3O_8 /natural isotopic composition/ was irradiated for 320 h under a thermal neutron flux of about $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ at the São Paulo swimming pool reactor and allowed to decay for 4 months. The irradiated uranium was dissolved in a 4M nitric acid solution. The solution so obtained was used after proper dilution to carry out the adsorption experiments. The main γ -ray emitter fission products present after a 4-month cooling time are ^{137}Cs , ^{95}Zr , ^{95}Nb , ^{106}Ru and ^{144}Ce . Carrier-free ^{90}Sr used as a tracer in these experiments was obtained commercially.

Composition of solutions

The studies reported here were made with a simulated low burn-up /500 MWdt⁻¹/ Purex waste. To an aliquot of the fission products mixture mentioned above containing uranium and radioactive tracers of the elements in study, a convenient volume of concentrated nitric acid as well as carriers of those elements were added in order to have a final 4M HNO_3 acidity and to bring the fission products concentration in the interval of 10^{-5}M to 10^{-4}M . Concentration of uranium was 0.1 g/l.

Flowsheet for recovering ^{137}Cs from acidic fission products solutions

A flowsheet for recovering ^{137}Cs from acidic fission products solutions is shown in Fig. 1.

A simulated Purex waste was made up to a volume of 500 ml solution 4N in nitric acid. This solution was passed through a silica gel column /1.0 cm diameter; height of the active charge was 50 cm/, originally conditioned by passing through it 250 ml of a 4M HNO_3 solution. The solution was percolated with a flow rate of 80 ml h^{-1} . After sorption of zirconium and niobium on silica gel the column was washed with 300 ml of water. From the silica gel column zirconium was eluted with 250 ml of 10M nitric acid solution whereas 100 ml of 4M HNO_3 -5% H_2O_2 mixture was used for elution of niobium.

For separating cesium from uranium, ruthenium, cerium and strontium, the effluent solution from the silica gel column as well as the effluent solution resulting from the washing operation /V = 800 ml; $[\text{H}^+] = 3\text{M}$ / were percolated through the ZP column /1.0 cm diameter and 60 cm of height, flow rate 25 ml h^{-1} /. The ZP column was previously conditioned with 200 ml 3M HNO_3 .

The column was washed with 200 ml of 3M nitric acid solution in order to remove uranium, cerium, strontium and ruthenium. All the elements, except cesium, were washed out from the column. Finally cesium was eluted with 600 ml of 6M nitric solution.

During the saturation and elution procedures aliquots of the solutions were collected and their activities measured using a multichannel analyzer coupled to a Ge/Li/ detector. ^{90}Sr was counted using a Geiger-Müller counter coupled to a scaler.

Uranium was determined by epithermal neutron activation analysis⁶ measuring the activity corresponding to the

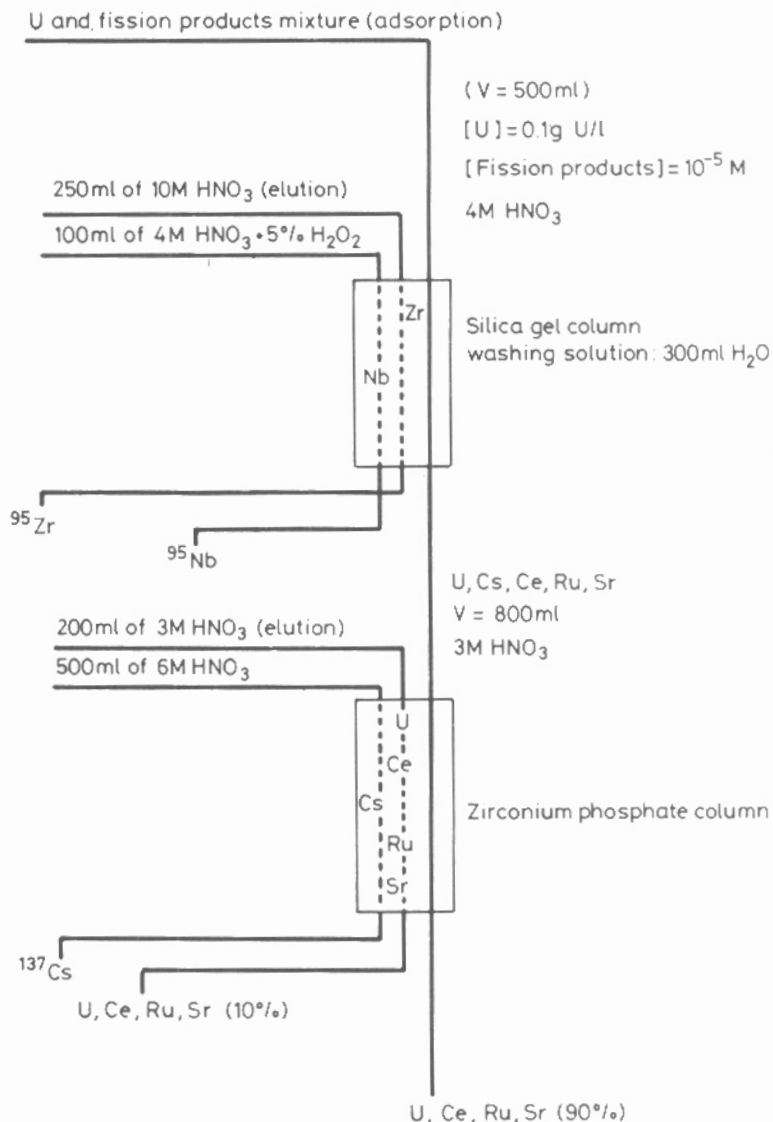


Fig. 1. Scheme of sequential recovery of ^{137}Cs from acidic fission products solutions

74.6 keV photopeak of ^{239}U . In this case use was made of a 7.5x7.5 cm well-type NaI/Tl/ scintillation detector coupled to a 400-channel analyzer.

Solidification of ^{137}Cs

The solution resulting from the elution operation of ZP column containing cesium was divided in three fractions of 200 ml. 3 g of ammonium molybdate and 1 g of ammonium monohydrogen phosphate were added to each fraction. The solutions were heated to 60 °C and the precipitate was digested at that temperature for 1 h under occasional stirring. The solutions were filtered and the precipitate was washed with distilled water and dried at about 100 °C.

Preparation of ^{137}Cs pellet

In order to obtain 2 mm thick ^{137}Cs pellet, the powder of ^{137}Cs -ammonium molybdophosphate /250 mg/ and 50 mg of teflon were placed in a steel die of 6 mm diameter and it was compressed at about 10.000 pounds, by using a hydraulic press. The pellet was sintered at 350 °C for 2 h in an electric furnace to obtain the ^{137}Cs pellet.

RESULTS AND DISCUSSION

For the sorption experiments carriers of the elements in study were added in order to bring the fission products concentration to levels corresponding to the Purex waste. However, it must be pointed out that the flowsheet proposed in this work can be applied to the recovery of cesium from fission products mixtures when they are carrier free.

To test the suitability of ZP and silica gel exchangers for many cycles of operation as well as to verify the yield and purity of cesium obtained by using the flowsheet of Fig. 1., the columns packed with these exchangers were subjected to 8 sorption-elution cycles. The results have shown that these exchangers are sufficiently stable

in contact with radioactive solution and nitric acid solutions. The recovery percentage of cesium was 90% and its radiochemical purity, checked by γ -rays spectrometry, was equal to 98%.

The flowsheet such as the one presented here can be applied to remove cesium directly from acidic fission products solutions. It is advantageous in comparison with that procedures that requires neutralization of the waste, since the neutralization step involves precipitation of gel-like cakes which are troublesome and the formed precipitate carries appreciable quantities of cesium.

Besides the recovery of ^{137}Cs , the flowsheet indicated in Fig. 1. allows also the separation of ^{95}Zr and ^{95}Nb isotopes from the fission products solutions, by sorption of these radioisotopes on the silica gel column.

In a further work the effluent solution from the ZP column, containing uranium, cerium, ruthenium and strontium, will be treated to separate ^{90}Sr , which is utilized as beta radiation source.

At least 95% of cesium can be solidified by coprecipitation with ammonium molybdophosphate. The ^{137}Cs pellet is of high radiochemical purity since most of the fission products were removed on silica gel and ZP columns. The recovery of ^{137}Cs and its utilization as tracer or as radiation sources / ^{137}Cs pellet/ is rather important in the waste treatment program.

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REFERENCES

1. F. Girardi, R. Pietra, E. Sabbioni, J. Radioanal. Chem., 5 /1970/ 141.
2. C.B. Amphlett, L.A. McDonald, J.S. Burgess, J.A. Maynard, J. Inorg. Nucl. Chem., 10 /1959/ 69.
3. I.J. Gal, O.S. Gal, Proc. U.N. Intern. Conf. Peaceful Uses of Atomic Energy, Geneva, 28, 24, 1958.
4. I.I.L. Cunha, L.G. Andrade e Silva, XVI Congresso Latino-Americano de Quimica, Rio de Janeiro, Brasil, 1984.
5. I.I.L. Cunha, L.G. Andrade e Silva, I Congresso Geral de Energia Nuclear, Rio de Janeiro, Brasil, 1986.
6. L.T. Atalla, F.W. Lima, J. Radioanal. Chem., 20 /1974/ 607.