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INTRODUCTION

There has been considerable research on the various fission products that can exist in the water of the swimming pool reactors, and by applying a new method of co-crystallization with ammonium alum, the special recovery of Cesium-137 from these products has been achieved [1]. Of the several methods studied for the recovery of Cesium-137 from fission products in nuclear installations, whether by "Crystallization and Co-crystallization" [2, 4, 5]; by "Precipitation and Co-Precipitation" [6, 7, 8, 9, 10, 11]; by "Ion-Exchange with Synthetic Resins" [9, 12, 13, 14, 15, 16]; and finally by "Extraction with Solvents" [17, 18], very few deal with the purification and concentration of Cesium-137 recovered by the several process developed.

In this paper various experimental conditions for the purification and concentration of Cesium-137 are dealt with, starting from its recovery by co-crystallization in the form of ammonium alum previously achieved by the procedure developed by Abrão, A., Lima, F.W. and Pagano, C., [1]. The composition of the crystallized compound containing Cesium-137 within the average range 10^{-20} to 10^{-22} Cesium moles per gram of ammonium alum can be found in table nº 1.

EXPERIMENTATION

For the purification and concentration of Cesium-137 from fission products, by the process of crystallization in alcoholic solution with ammonium alum [1], the experimental procedure was as follows:

- I. - Dehydration
- II. - Calcination
- III. - Leaching
- IV. - Purification by ion-exchange
- V. - Concentration

Prior to the dehydration and calcination procedures, a study on the thermo-gravimetric decomposition of the following ammonium alumns was made:

1.) Ch. P. ammonium alum
2.) Ch. P. ammonium alum crystallized in ethyl alcohol according to procedure [1].
3.) Stoichiometric mixture of Ch.P. Aluminum Sulphate and Ammonium Sulphate, crystallized in water at a temperature of 25°C.
4.) Ammonium Alum and Cesium-137, recovered by process [1].

The experimental results are shown on the graph of Fig. no. 1-A, values that allowed for a choice of temperature ranges of 25°C to 250 for dehydration and of 250°C to 800°C for calcination. Furthermore, it was found that the calcination residue totally retained the Cesium-137.

For the thermogravimetric investigation a thermobalance of the type TBM/A - Chevenard System SADAMEL, la Chaux-De-Fonds, (Switzerland), was used.

I. Dehydration

In order to eliminate humidity and crystallization water, the sample with an initial activity of 2875 pC per gram was submitted to a heating process at a temperature range of 20 to 100° C with an average temperature gradient increase of approximately 20°C an hour. Subsequently, heating at a constant temperature of 100°C for 2 hours continued until a constant mass was obtained, resulting in an average residue of the order of 67.65% of the original ammonium alum mass (Table 1). By this initial treatment, sharp losses by alum decay due to the abrupt increase in the volume of the sample are avoided. The total elimination of the crystallization water was achieved by submiting the previous residue to a temperature range of 100°C to 250°C with an average temperature gradient increase of 30°C per hour, following a five hour treatment. Eventually, heating at a constant temperature of 250°C for a 3 hour period was continued, the resulting anhydrous residue average being of the order of 53.92% (Table 1). By applying this dehydration procedure, the best results for the extraction of Cesium-137 by leaching with hydrochloric acid solutions were obtained.

II. Calcination

The activated dry alum resulting from the thermal treatment of total dehydration was submited to a process of chemical decomposition-reaction (1) by thermal effect at a temperature range of 250°C to 800°C maximum, with an average temperature gradient increase of 100°C per hour. Eventually, the sample underwent constant heating at a temperature range of 780°C - 800°C for a minimum 6 hours period.

$$Al_2(SO_4)_3\cdot(NH_4)_2SO_4\cdot 24H_2O \xrightarrow{\Delta} 24H_2O\uparrow + Al_2(SO_4)_3\cdot(NH_4)_2SO_4$$

(dehydration 20-250°C)

$$Al_2(SO_4)_3\cdot(NH_4)_2SO_4 \xrightarrow{\Delta} (NH_4)_2SO_4\uparrow + 3SO_3\uparrow + Al_2O_3 \quad (1)$$

(calcination 250-800°C)

The average constant residue obtained by calcination was of the order of 17.77% of the original alum sample (Table II). This residue contained the total aluminum in oxide form, Cesium-137 in sulphate form and all the other non volatile components at the temperature of the treated products obtained in the recovery of Cesium-137 [1]. By thermal treatment, ammonium sulphate commences volatilize constantly as from 500°C [20]. The aluminum sulphate decomposes into volatile sulphuric anhydride and aluminum oxide by heating as from 580°C [19], results that approach the experimental values obtained in the thermogravimetric investigation of different alums. For Cesium-137, as well as for sodium sulphate, thermic decomposition starts at temperatures higher than 800°C. The average activity loss of Cesium-137 shown in the calcination process is of the order of 3 parts per thousand (Table III), this value probably being due to statistical fluctuations of the measuring instruments rather than to actual loss of Cesium-137.

The activity of residue from the calcination is of 16,000 pC per gram, representing an increase 5.49 times higher in relation to the original alum; likewise, the average ratio of mass loss by calcination is 5.63 times inferior to the original alum (Table II). This provides the residue to be leached with hydrochloric acid solutions for the recovery of Cesium-137, together with the sodium sulphate and a small dissolution of aluminum oxide. Such a diluted solution will facilitate a better purification of Cesium-137 using ion-exchange resins.

The residue value by calcination of a Ch.P. ammonium alum is of the order of 12.46 % average and 12.67% for Ch.P. ammonium alum crystallized in the experimental conditions for recovery of Cesium-137 from fission products [1], values that differs from the 17.77 % average obtained in the treatment of alum for recovery of Cesium-137.

III. Leaching

The residue from calcination for an average activity of 16,000 pC per grams is leached with Molar-Hydrochloric Acid solutions, in the proportion of one gram calcined to 160 ml. of leaching solution, at a temperature range of 60°C to 80°C and with vigorous mechanical agitation for 15 minutes; 92% to 94% of Cesium-137 is extracted, which is separated by centrifugation or by decantation for 6 hours. The residue extracted can be washed with 80 ml. of the solution used for extraction, increasing the total recovery of Cesium-137 to the range of 96% to 98%, provided the washing is carried out under the same conditions as for the first extraction. The percentage variation of the Cesium-137 extraction from the residue, treated with hydrochloric acid leaching solutions of different concentrations, volume and temperature can be seen in Fig. 1. Hydrochloric acid treatment at higher concentrations and temperatures favours the extraction of Cesium-137, but increases the concentration of aluminum and hydrogen ions in the solution to be used as influent in the purification of Cesium-137 with an ion-exchange column.

The dissolution of the aluminum from the residue by leaching increases with the concentration of hydrochloric acid used as leaching liquid. Thus, at a temperature of 60°C to 80°C, the dissolution ratio is 8.3:1 and at a temperature of 20°C the relation is 20.3:1 for molar hydrochloric acid, as shown in Fig. 2.

The concentration of the sulphate ion in the leached solution varies slightly with the temperature and concentration of the hydrochloric acid used. Thus, in the 60°C to 80°C range the relation of total sulphate in the initial sample and that in the leached solution sample is 13.3:1, and at a temperature of 20°C it is 15.2:1, as shown in Fig. 3.

In the leaching solutions the presence of the ammonium ion is not detected, which indicates that the ammonium sulphate was totally eliminated by calcination. Aluminum, iron, sodium, cesium-137, chloride and sulphate ions showed positive reactions and the pH of the leached solution slightly lower. Leachings with solutions of different nitric acid and sulphuric acid concentrations provide results 2% to 5% lower than hydrochloric acid in Cesium-137 extraction, given the same agitation, temperature and concentration conditions.

IV. Purification With Ion-exchange

For the final purification of the leached solution containing Cesium-137, the ion-exchange procedure was applied , using strong cationic resin - Dowex 50, X-8-100-200 mesh, with an exchange capacity of 2.5 ± 0.15 millequiv. per ml. of humid resin.

The initial procedure consisted of retaining all cations in the column and eliminating all anions from the leached solution (influent), the latter having the following composition: 1.6, 2.4 and 10.0 millequivalents of aluminum sulphate and sodium ions respectively, the concentrations of Cesium-137 and iron ions being extremely low.

To study the distribution of the sodium ion, Na-24 was used as a tracer and Cesium-137 carrier-free. For the experiment 200 ml. of leached solution and a Dowex 50, X-8, 100-200 mesh column, with 3 ml. of resin was used and at an influent flow rate of 0.7-0.9 ml./min.

Under these conditions, the distribution of alkalies in function of the hydrochloric concentration in the influent was studied the experimental results of which are shown in Fig. 4. In accordance with curves shown, it is apparent that the maximum optimum concentration of hydrochloric acid in the influent must be 0.0206 M in order to retain the total cations, including Cesium-137, with 100% efficiency.

For the elution of the sodium and cesium retained in the column, as also for the iron and aluminum ions, a solution of hydrochloric acid 0.229 M was used as eluent, as shown in Fig. 4, conditions in which the best distribution of sodium and cesium ions are obtained. For this experiment, a cationic column (2.1 cm, i.d. x 25 cm, x 18 cm,) containing 43 ml. of resin was used. The eluent solution was percolated with a velocity of 1.3 to 1.5 ml/min. and Na-24 was used as tracer for sodium; Fig. 5 shows the results.

To desorb the sodium from the column, elution with eleven column volumes was necessary, Cesium-137 collecting between 14 and 33 column volumes. Iron, aluminum and the other ions that might form part of the solution were totally retained in the column, hydrochloric acid solutions higher than 0.6 Molar being used as an eluent.

V. Concentration

The eluate from the column containing the total Cesium-137 in the form of chloride and having a small excess of HCl, was concentrated at low temperature in a steam bath. The gamma-ray spectrum of the concentrated solution shows no impurities of other radioisotopes compared with a standard source spectrum (RT-2 Model, 0.447 C, N. Chicago Co.) of Cesium-137.

The final activity of the recovered Cesium-137 depended on the amount of crystallized ammonium alum containing Cesium-137 used in the purification and concentration process, providing a final product that was found to be 96% to 98% of the initial processed alum.

CONCLUSION

The procedure studied in this paper for the extraction, purification and concentration of Cesium-137 from ammonium [1], has allowed us to obtain this radioisotope in the activity and purity required for use in research that is carried out in different scientific fields.

The dehydration and calcination procedure has allowed for the activity increase of the sample in a ratio 5.49 times average (Table II), as also to retain the total Cesium-137 residue, with a maximum loss average of 3 pC/thousand (Table III). By leaching, 96% to 98% of the Cesium-137 retained in the calcined residue is recovered (Fig. 1); and by purification with ion-exchange resin, a separation of Cesium-137 is obtained from other metallic and non-metallic elements, radioactive or not, found in the original solution, with a yield near to 100% of separation efficiency.

The gamma-ray spectrum of the recovered Cesium-137 showed no contamination of other radioisotopes.

The technique studied also allows for the separation of Cesium-137 in extremely low concentration of sodium, ammonium, aluminum, iron and sulphate that may be found in initially high concentrations. Thus, the concentration, purification and if necessary analytical determination, can be carried out in safety.

In accordance with the general procedure investigated, a general flow sheet is suggested for the extraction, purification and concentration of Cesium-137 from its crystallization as ammonium alum as shown in the diagram (Fig. 7).

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SUMMARY

This paper studies the various experimental conditions for the concentration and purification of Cesium-137, starting from its recovery by co-crystallization in the form of ammonium alum. Cesium-137 was concentrated and purified from fission products by crystallization in alcoholic solution with ammonium alum. Cesium-137 was recovered from the alum following a flow sheet including: dehydration, calcination, leaching, purification by ion-exchanger and concentration.

A study on the thermo-gravimetric decomposition of the ammonium alum containing Cesium-137 was made which permitted to conclude that there is no loss of cesium when the alum was dehydrated to 250°C and calcined from 250 to 800°C. The residue (aluminum oxide) containing the totality of Cs-137 was leached with 1 M HCl, 92-94% of Cs-137 being extracted. Finally, Cesium-137 was purified by ion-exchanger technique. The Cesium-137 obtained was highly radiochemically pure.

<u>RÉSUME</u>

Dans ce travail on étudie les conditions expérimentales pour concentrer le Cesium-137, à partir de sa récupération par co-cristallisation sous la forme d'alun d'ammonium.

Le Cesium-137 a été concentré et purifié à partir des produits de fission par cristallisation alcoolique avec de l'alun d'ammonium.

Le Cesium-137 a été récuperé de l'alun suivant un schéma qui comprend les etapes suivantes: déshydration, calcination, lixiviation, purification par résine échangeuse d'ions et concentration.

On a fait l'étude thermogravimétrique de la décomposition de l'alun d'ammonium qui contenait le Cesium-137. Cette étude a permis de constater qu'on ne perd pas le Cesium-137 quand l'alun est déshydraté jusqu'a 250°C et ensuite calciné de 250 a 800° C. Le résidu (oxyde d'aluminium) contenant la totalité du Cesium-137 a été lessivé avec de l'acide chlorhydrique 1 N, et 92-94% du

Cesium-137 a été extrait.

Finalement ce Cesium-137 a été purifié à l'aide de résine échangeuse d'ions. La pureté radiochimique du Cesium-137, ainsi obtenu est très haute.

RESUMO

Êste trabalho estuda as várias condições experimentais para a concentração e purificação de Cesium-137, partindo de sua recuperação por co-cristalização na forma de alúmen de amônio. Cesium-137 foi concentrado e purificado a partir dos produtos de fissão por cristalização de solução alcoólica com alúmen de amônio. Cesium-137 foi recuperado do alúmen num esquema que inclui as seguintes etapas: desidratação, calcinação, lixiviação, purificação por troca iônica e concentração.

Foi feito o estudo termogravimétrico da decomposição do alúmen de amônio contendo Cesium-137 que permitiu concluir não haver perda dêste radioisótopo quando o alúmen é desidratado até 250°C e calcinado de 250 a 800°C. O resíduo (óxido de alumínio) contendo a totalidade do Cesium-137 foi lixiviada com HCl 1M, tendo sido extraído 92-94% do Cesium-137. Finalmente o Cesium-137 foi purificado por troca iônica. O Cesium-137 obtido tem pureza radioquímica altamente elevada.

TABLE No. 1

DETERMINATION		AMMONIUM ALUM-CESIUM (x)		Ch. P. AMMONIUM ALUM	
No.	ANALYSIS	PERCENTAGE average	DEVIATION average	PERCENTAGE average	DEVIATION average
1	Loss of water (humidity at the temperature of 20°C.	0.04	0.00	0.00	0.00
2	Loss of crystallization water at the temperature of 100°C.	32.35	± 0.05	33.50	± 0.04
3	Loss of crystallization water at the temperature of 250°C (xx)	46.08	± 0.08	47.68	± 0.05
4	Total aluminum	5.86	± 0.15	5.88	± 0.04
5	Total Sulfate	42.15	± 0.19	42.24	± 0.06
6	Total Ammonium	4.13	± 0.04	4.17	± 0.03
7	Insoluble in 2 M HCl at a temperature of 80° - 100°C	0.37	± 0.01	0.00	0.00
8	Other compounds such as: Na_2SO_4, Cs_2SO_4, $Fe_2(SO_4)_3$	1.18	± 0.02	0.00	0.00
9	TOTALS	99.77	± 0.48	99.97	± 0.18

(x) Recovery by the process of Abrão, A., Lima, F.W., Pagano, C. [1]

(xx) In the total percentage water loss by crystallization at a temperature of 250° the losses of water humidity at a temperature of 20° C and crystallization water at a temperature of 100° C are included.

TABLE No. III

LOSS OF CESIUM-137 BY CALCINATION

DET.No.	ACTIVITY IN pC		
	CRYSTALLIZED ALUM	TOTAL LOSS	LOSS IN PARTS PER 1000
1	7520	23	3
2	7920	19	2
3	2940	19	6
4	3000	21	7
5	4125	5	1
6	5160	7	1
7	5355	19	4
8	5580	23	4
9	7620	7	1
10	6430	2	0
Average	5565	15	3

TABLE No. II

CALCINATION ACTIVITIES AND RESIDUES

DET.No.	ACTIVITIES IN pC per gram			CALCINATION RESIDUE		RATIO OF MASS LOSS BY CALCINATION	
	Alum NH_4-Cs	Calcined Residue	Ratio of Increased Act.	Alum 1 (x)	Alum 2 (xx)	Alum 1 (x)	Alum 2 (xx)
1	2767	15250	5.52	17.50	12.67	5.72	7.89
2	2750	14610	5.27	17.55	-	5.70	-
3	2700	14380	5.33	17.48	-	5.72	-
4	3170	17380	5.48	17.75	-	5.64	-
5	3210	18000	5.61	17.90	-	5.59	-
6	2745	16450	5.98	17.95	-	5.57	-
7	2740	16400	5.88	17.80	-	5.62	-
8	2910	16550	5.68	17.65	-	5.66	-
9	2700	14420	5.35	18.05	-	5.54	-
10	3010	16680	5.55	18.03	-	5.55	-
Average	2875	16012	5.57	17.77	12.67	5.63	7.89

(x) Recovery of Cesium-137 with ammonium alum [1].

(xx) Pure crystallized ammonium alum under same experimental conditions [1].

Alum 1 = ammonium-cesium-137 - Alum Alum 2 = Ch, P. ammonium Alum.