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RECUPERAÇÃO DO CÉSIO-137 DOS RESÍDUOS DE FISSÃO EM INSTALAÇÕES NUCLEARES

RECOVERY OF CESIUM-137 FROM FISSION PRODUCTS IN WASTES OF NUCLEAR REACTORS INSTALLATIONS

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INSTITUTO DE ENERGIA ATÔMICA

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ABSTRACT

A process for recovering cesium-137 from fission products wastes is described. The process is based on the entrainment of cesium by alum and it differs from the usual procedures in that the crystallization of alum is carried out in alcoholic medium and it is unnecessary to heat the solution and next cooling it down to crystallize the alum. Decontamination factors up 10^6 *is attained in one single cocrystallization, which is carried out in a very simple operation, and using six times less alum than that in the procedure where it is necessary to heat the solutions.*

INTRODUCTION

The importance of recovering fission products in the wastes of nuclear installations has ben largely stressed (9, 1, 8). These products are always encountered in nuclear power plants or in fuel elements reprocessing plants.

Although in a much smaller scale these problems also arise in swimming pool reactors as a consequency of corrosion or rupture of fuel elements or external contamination by U-235 on the fuel elements (5). Usually, the water of swmming pool reactors is kept circulating through an ion exchanger set in order to keep the amount of soluble ionic substances in the water as low as possible. When corrosion or rupture of fuel elements occurs the liberated fission products, mostly descendent of fission gases (kripton and xenon), will acummulate in the ion exchangers resins used for repurification of the water. By the time of regeneration of the resins the efluent from the regeneration solution is radioactive and cannot be disposed in public sewers.

As consequency of corrosion in some elements of the Brasilian Swimming Pool Reactor these problems were met (5), and in the process of treating the wastes coming from the resins an improved method for recovering cesium-137 was developed which showed to be of high yield, inexpensive and of simple execution.

The main processes of cesium recovery has been reviewed by Fisher and Ragenbass (1): precipitation by tetraphenyl boric acid, precipitation by ferrocyanide of nickel or iron, precipitation by phosphotungstic acid and co-crystallization with alums. This last process has been largely used as described by Rupp (8) and Gresky (3). Shortly, this method consists in adding ammonium or potassium alum to the cesium solutions, heating the mixture up to 80°C and then cooling it to room temperature in order to lower the solubility of the alum which separates from the liquid carrying the cesium.

The solubility of ammonium alum is not too low, being of the order of 150 grams per liter (4) at room temperature. This means that the filtered liquids are always being enriched in alum. The heating of the solutions in which the cesium is present makes the time of operation lenghty and it is a nuisance in cases where only ocasionally these wastes disposal treatments have to be carried out.

The process developed, and presented in this paper, to treat the efluent of radioactive resins, makes use of the low solubility of ammonium alum in a mixture of water and ethyl alcohol. In such solutions cesium is carried quantitatively by the ammonium alum separated from the solution. The operation is executed in only one step being unnecessary a second precipitation of alum in the filtered solution. The solubility of ammonium alum in the water-alcohol solution is about 3 grams per liter, only, as compared to 150 grams per liter when no alcohol is added to the efluent liquid. This means a quite small loss of alum, and expenses consequent of using alcohol are largely compensated by a much smaller amount of alum used in the procedures to be described in this paper (60 grams of alum per liter of cesium solutions, as compared to 360 grams per liter, in the procedure where supersaturation is achieved by heating the solution to 80°C and then cooling it down to room temperature). Because of not being necessary to heat the solution the operation is much simpler and rapid and the total price per operation is smaller for the present process.

A process had been developed to remove cesium-137 from methanol solution by Savolainem (10). It was not possible, for us, to localize this report directly, but in Gresky (3) it is mentioned that the operation facilities were quite complicated and that the recovery of cesium was only of 80 per cent.

EXPERIMENTAL

The repurification system for the water of the Brazilian Swimming Pool Reactor is composed of two sets of ion-exchangers and activated carbon stainless steel tanks. In each set there is one activated carbon tank followed by a mixed-bed ion exchanger; the mixed bed resins repurifies 6,000,000 liters of water between each regeneration. The total volume for regeneration solution, and washes of the resins after regeneration, is about 520 liters. During regeneration these volumes are collected in stainless steel tanks, ferric chloride is added to the solution and ferric hydroxide is precipitated by adding sodium hydroxide and sodium carbonate. The mixture is stirred and left for decantation; twenty four hours later the supernatant is separated from the precipitate which has collected a great part of fission products. At this stage the pH of the solution is about 10 and the majority of fission products is entrained with the precipitate; in the liquid remains cesium, traces of strontium as well as traces of rare earths and of ruthenium and sodium sulphate, which was formed when the resins were regenerated, in the concentration of about 38 grams per liter. This liquid, which has a gamma activity of 30 cpm/m1, counted in a well thallium activated NaI scintillator, was the source for all the experiments related in the present work. Experiments were carried out with volumes of 1, 2, 10 and 100 liters of solution.

PROCEDURE

To one liter of the filtrate from the carbonate hydroxide precipitation, sulphuric acid was added up to the and point of methylorange. At this stage 60 grams of ammonium alum were added and the liquid was stirred until dissolution of the alum giving a quite clear solution. The pH was ascertained to 3.6 with sulphuric acid and 250 milliliter of technical grade ethyl alcohol was added to the solution with continuous stirring. The temperature, in this operation, usually increased from 22°C to about 29°C; ammonium starts crystallizing and in about 10 to 15 minutes practically all alum that is not soluble in the mixture has separated from the liquid as a crystalline precipitate. This precipitate settles down well, is very easy to filter and its volume is about 3 per cent of the solution. The precipitate is filtered and the recovery of cesium in the precipitates is from 98 to 100 per cent with only one precipitation. Table I ilustrates a typical set of operations with one liter solution.

Table I - Cesium removal from one liter solution (Volume of alcohol added, 250 ml).

Experiment number	Ammonium alum grams added	Ammonium alum grams crystallized	pH	Agitation time (hours)	Standing time (hours)	Cs recovered percentage
1	20	0	3.70	1.0	24.0	0
2	30	3	3.70	1.0	24.0	0
3	40	14	3.70	1.0	24.0	13.5
4	50	24	3.70	1.0	24.0	97.5
5	60	35	3.70	1.0	24.0	99.5
6	60	37	3.70	1.2	2.0	100.0
7	60	25	3.90	1.5	16.0	98.0
8	60	34	3.70	1.5	16.0	98.0
9	60	34	2.10	1.5	16.0	100.0
10	60	29	1.75	1.5	16.0	98.0

This same process can be applied by using precipitated alum from a first decontamination and adding it to a fresh solution of cesium to be recovered, completing the amount of alum to 60 grams and repeating the process as previously described. Table II gives the results for the experiments carried out in this way. Experiment number one is started with 60 grams of alum which has already been used in a cesium recovery as described previously. Experiment number two is carried out by using the alum in the solution filtered from experiment number one (about 30 grams) and adding 30 grams of fresh alum, and so on. At the end of eleven operations the total amount of alum used was 360 grams and the amount of alum recovery was 58 grams, giving a comsumption of 302 grams of alum per 11 liters of solution of cesium. This same set of operation, without alcohol, can be carried out in accordance with Gresky (3), by using 350 grams of alum to start and the addition of 200 grams of alum per operation, heating the solution in each step to about 60° C and then cooling it down to 25°C. The total amount of alum to be used for the eleven recoveries would be 2,350 grams of alum of which 150 grams would be lost in each operation giving a total loss of 1,650 grams of alum per 11 liters of solution of cesium.

Table II — Cesium removal by a sequence of precipitation using in each experiments the alum crystallized in the previous one. Agitation time: one hour. Volume of alcohol added: 250 ml per liter of solution in each step. Initial mass of alum: 60 grams per liter; addition of 30 grams in each operation.

Experiment number	Standing time (hours)	pH	Cs recovered percentage –
1	16.0	3.35	100.0
2	0.3	3.70	100.0
3	0	3.70	100.0
4	0	3.65	100.0
5	16.0	3.60	99.5
6	0.5	3.32	100.0
7	0	3.36	100.0
8	0	3.64	99.0
9	1.0	3.60	99.1
10	0.3	3.60	98.0
11	15.0	3.50	100.0

Whatever is the method adopted, the sequential one where a crystallized alum with cesium-137 is re-used or that where only one precipitation is carried out one ends up by having the cesium-137 co-crystallized with the alum. This alum is filtered and the activity in the liquid is determined in a scintilometer and compared with the ativity of the same volume of liquid before the carrying of cesium by alum. Decontamination factors up to 10^6 have been obtained.

The crystallized alum is dissolved in hot water and ammonium hydroxide is added to the solution to precipitate aluminum hydroxide which is filtered. The solution is concentrated until elimination of ammonia, remaining ammonium sulphate and cesium sulphate. The ammonium salt can be removed by adding aqua regia and distilling ammonia gas.

The liquid in which the cesium sulphate is dissolved is passed through a anionic resin in hydroxide form. Cesium will come off in the efluent in the form of hydroxide. Excess ammonium is eliminated by boilling and the cesium hydroxide solution is neutralized with sulphuric acid and concentrate.

Aliquots of the solution were taken and sources for counting were mounted. Figure I is the gamma spectrum for the cesium compared with a spectrum of a standard cesium-137 as furnished by Tracerlab Inc. No gamma impurity was detected in the source obtained. Feather analysis of aluminum absorption curves indicated one beta component of 0.5 Mev and a harder one of 0.8 Mev. It is known (11) that aluminum absorption curves is not a highly precise method to indicate the 8 per cent 1.2 Mev beta component for cesium-137, which can be resolved only by beta ray spectrometry (7). It is interesting to notice that aluminum obsorption curve made by Glendenin and Metcalf (2) have the same shape as the ones presented in this paper, giving the 0.5 Mev beta component as determined by a Feather's analyzer, Figure 2.

The process can be summarised as following :

a) Neutralize the filtrate from the ferric hydroxide carbonate precipitation with sulphuric acid 1:1 up to the end point of methylorange.

b) Add 60 grams, per liter of solution, of ammonium alum

c) Add 250 milliliters of technical grade ethyl alcohol.

d) Separate the liquid from the settled crystals.

e) Add a fresh solution of cesium-137 to be removed.

f) Add 30 grams of alum, next 250 milliliters of alcohol. Repeat the procedure as required for the desired concentration.

Even if the concentration of cesium after some operations, reaches macro level the efficiency of the process is not hampered since the solubility of cesium alum is quite low in itself, (6).

DISCUSSION

It can be seen from Table I that there is no recovery at all when the amount of the alum is less than 30 grams per liter. With 50 grams per liter the entrainment of cesium is practically total. The results obtained when volumes of 2, 10 and 100 liters are handled are the same.

If the pH of the solutions is too high the amonium alum will crystallize very slowly; for this proportion of alcohol to the mass of alum the pH for a good entrainment should be in between 1.30 and 3.90. For these values of pH the loss of alum is very small being of the order of 3 per cent of the mass of the liquid separated from the crystallized alum, as compared with about 15 per cent for the process where no alcohol is used, with the solution being heated to 80°C and the amount of alum used is 350 grams of alum per liter of solution.

The yield of recovery of cesium in the precipitated alum is the same when the mass of alum is diminished and the volume of alcohol per liter of solution is increased. However, it is not convenient to increase the volume to much in benefict of a smaller amount of alum and the proportion of 60 grams of alum to 250 ml of alcohol per liter of solution was found to be a convenient one giving conditions, for routine work, easy to be carried out in waste disposal systems.

It might appear that although there is economy of alum the use of alcohol might raise the cost of the process. However, such is not the case since technical grade alcohol is quite inexpensive, specially in this country. Being not necessary to heat the solution before adding fresh alum to it and cooling it down to room temperature in each operation, the process with alcohol is very rapid and, in the whole, less expensive than the one in which the supersaturation of the solution is achieved by heat.

One impurity that might possible come out with the cesium-137 would be strontium-89 and strontium-90, since some traces of these two isotopes might pass in the filtrate from the ferric hydroxide-carbonate precipitate. For this reason the 1.46 Mev beta rays from strontium-89 (53 days), 0.61 Mev. beta ray strontium-90 (28 years) and the 2.229 Mev beta rays from yttrium-90 (64.8 hours, strontium-90 descendent) were looked for in the aluminum absorption curves and none of them were found. The activity determined every day for about four months showed the absence of any beta impurity with a half-life of 53 days that might be ascribed to strontium-89; the absence of strontium-89 indicates no contamination by strontium-90 and its descendent yttrium-90, obviously. No rare earths and ruthenium contamination was found as can be seen by the gamma spectrum in Figure I.

The removal of cesium by the crystallized alum is very rapid and agitation time from half-one hour on, gave always the same percentage of recovery. The standing time does not affect the results and filtration made immediately after half-one hour of agitation on, and any time up to 24 hours gave the same results, Table I and II.

The procedure worked out well for cesium present at tracer or at macro concentration.

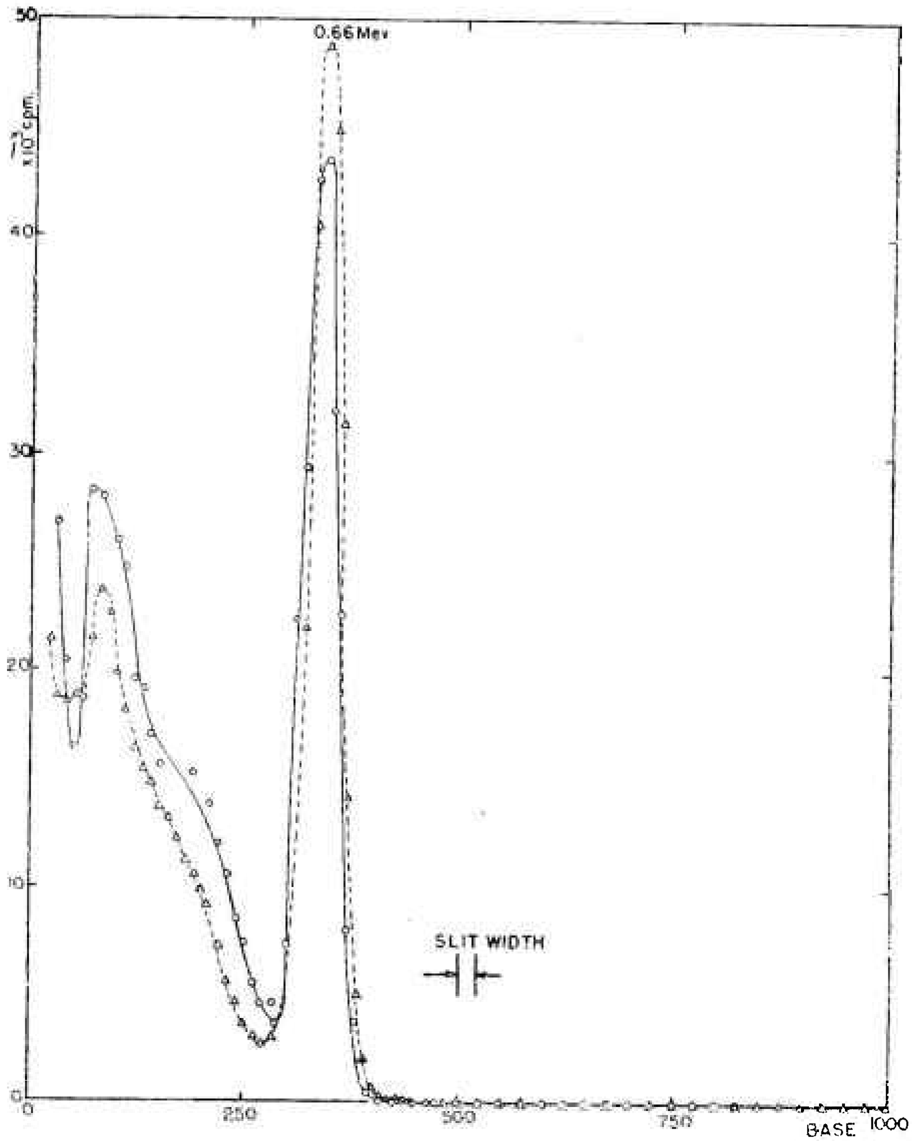

Figure I — Gama ray spectra for Cs-137 separated in alum (dashed lines) and a standard Cs-137 (full-line).

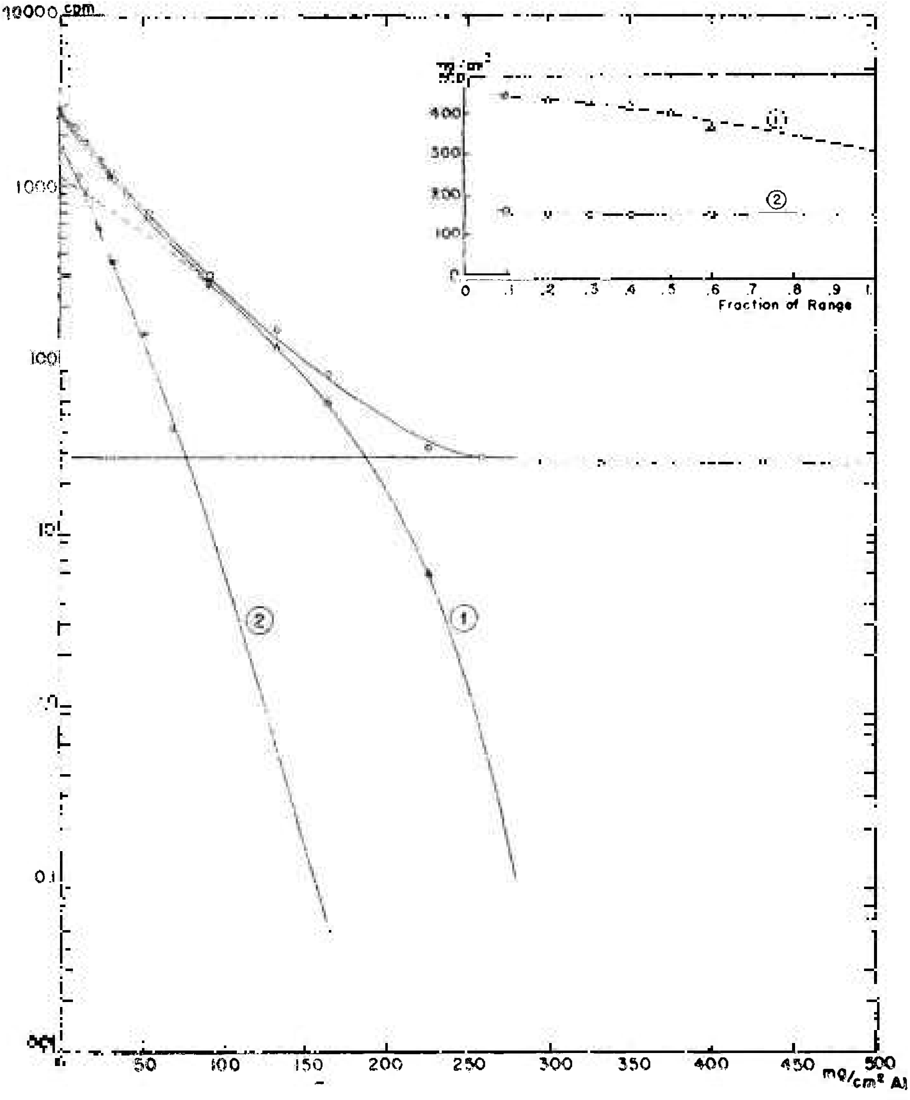

Figure II — Aluminum absorption curve and Feather's analysis for Cs-137 separated in alum.

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