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FAUSTO W. LIMA, ALCÍDIO ABRÃO, LAURA TOGNOLI AND CONSTÂNCIA PAGANO

Radiochemistry Division, Instituto de Energia Atômica, São Paulo

Reprinted from

UNITED NATIONS
PEACEFUL USES OF ATOMIC ENERGY

PROCEEDINGS OF THE SECOND INTERNATIONAL CONFERENCE,
GENEVA, SEPTEMBER 1958

PERGAMON PRESS
NEW YORK . LONDON . PARIS
LOS ANGELES
1959

Reprint from 2nd UN Geneva Conference.
Printed by Pergamon Press, London.

Fission Products in the Cooling Water of the Brazilian Swimming Pool Reactor

By Fausto W. Lima, Alcidio Abrão, Laura Tognoli and Constância Pagano *

The presence of fission products in the water of swimming pool reactors and in the water of critical assemblies has been observed by various authors.[1–4] Bolton *et al.*,[1] working on a critical assembly with plastic and unclad fuel elements, concluded that the activity found was attributable to several of the decay daughters of the noble gas fission products. The isotopes of krypton and xenon formed in the fission process, being gases, have freedom of motion in the fuel elements and those atoms which diffuse out of the fuel element during criticality dissolve in the water.

Moeller [2] showed that in the case of the Low Intensity Test Reactor (LITR) of the Oak Ridge National Laboratory, the presence of fission products in the water was due to uranium contamination on or near the surface of the fuel plates. During fabrication of the fuel elements, the enriched uranium–aluminum alloy was handled and worked in the same machinery where later the aluminum cladding was applied to the fuel. This procedure could lead to contamination of the outer surfaces of the cladding with the fuel itself.

Heat [3] concluded from studies of the Materials Testing Reactor that the major source of fission products in the cooling water in that reactor was fissionable material distributed on the surface of the reactor, such contamination resulting from rupture of fuel elements or failures of experiments containing fissionable materials.

Lustman [4] observed that diffusion of gaseous fission products through the aluminum cladding was the cause of the presence of fission products in the cooling water of the Pressurised Water Reactor. The diffusion phenomenon had been observed in uranium oxide–aluminum elements but not in metallic uranium.

The works mentioned in Refs. 1–4 indicate that the presence of fission products in the water might be ascribed to four possible causes: (*a*) contamination of the fuel element cladding with enriched uranium during fabrication; (*b*) pitting of the fuel element cladding; (*c*) diffusion of the uranium fission products into the cladding; (*d*) exposure to water of small samples of fissionable material used for experimental irradiation.

After the Brazilian Swimming Pool Reactor had operated for some time at various power levels up to 5 megawatts, a sample of the mixed bed resin, as well as of activated carbon, was taken from the tanks in the recycling water purification system. Preliminary tests were made to see if fission products had been collected in the resin or the carbon filter. These tests indicated that fission products had collected in the resin bed and in the activated carbon filter. No sample of fissionable material had been used for experimental irradiation and so cause (*d*) mentioned later should be excluded as a possible explanation for the presence of fission products in the resin bed. Cause (*a*) could also be eliminated since the elements had been subjected to a final acid cleaning after fabrication.[5] These elements had also been subjected to an alodizing [6] procedure to protect them against corrosion. This alodizing treatment consisted first in immersing each element for about 3 to 5 minutes in a degreasing bath at 85°C, made up of a solution of sodium metasilicate, sodium pyrophosphate and sodium hydroxide. Next the elements were rinsed in running demineralized water and then immersed in a deoxidizer bath made up of sodium silicofluoride and potassium dichromate. After being again rinsed in water the elements were given a final treatment in Alodine 1200 (a solution made up mainly of sodium chromate) [6] for about 2 to 3 minutes and then a final rinse in water; the pH of the Alodine solution was controlled at a value of 1.5 with nitric acid. Even if the acid cleaning of the elements after fabrication might not be effective for removal of contamination, the alodizing procedure should be sufficient for removal of any eventual contamination of the elements. Activation analyses were made of scrapped aluminum from the cladding of the elements. After irradiation, the samples of scrapped aluminum were dissolved in nitric acid and radiochemically analyzed for neptunium-239 by the method of Mahlman and Leddicote.[7] No positive results were found although samples of 50 milligrams had been irradiated.

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* Radiochemistry Division, Instituto de Energia Atômica, São Paulo.

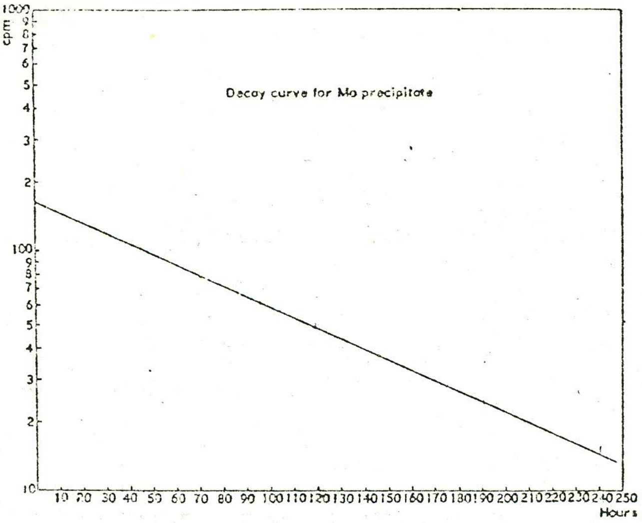

Figure 1

Causes (*a*) and (*d*) being eliminated, the presence of fission elements in the resin and carbon beds ought to be explained by diffusion of uranium or of fission products into the cladding (cause *c*) or by pitting of the fuel elements (cause *b*). This last one would indicate incipient corrosion of the fuel elements.

If the precursors of the fission products found were of gaseous nature only, such as krypton and xenon, the presence of these products would indicate that a diffusion mechanism might explain the phenomenon. However, if solid products formed directly in fission were found, this would indicate that corrosion had started in some or all elements, since no appreciable amount of uranium should be expected to diffuse through the cladding and out to the surface of the elements.

Such being the case, work was planned in order to look for fission products that would be directly formed as solids in fission. Of these, neodymium-147, zirconium-95, tellurium-132 and molybdenum-99 were chosen since their fission yields are high enough and they have half-lives convenient for work. However, the presence of molybdenum-99 would not be a definitive test since this isotope might also be formed by the (n, γ) reaction on Mo^{98} present in the stainless steel of the piping system. Moeller[2] found this isotope in his analysis and ascribed its presence to a probable dissolution of the steel. An evaluation of the amount of molybdenum-99 formed would indicate its mode of formation, since its fission yield is of the same order as that for barium-140, for instance. Approximately the same number of atoms of barium-140 and molybdenum-99 would be formed directly in fission.

The fission products with gaseous precursors which were looked for were barium, lanthanum, strontium, yttrium and cerium, their precursors being xenon or krypton. Lustman[4] observed that, in the case of uranium oxide–aluminum fuel elements, a considerable temperature gradient existed from the center to the outside of the fuel pellets. Although the temperature of the fuel elements in the Swimming Pool Reactor is not very high (around 40°C at 5 megawatts), isotopes of iodine which might be formed in fission were also looked for since this element is quite volatile.

THE WATER PURIFICATION RECYCLING SYSTEM

The water for the swimming pool reactor is first purified by a softener followed by an activated carbon filter and a mixed-bed ion-exchanger. Once the pool is filled, the water is recycled continuously through another set of carbon filter and mixed-bed ion-exchanger. The volume of the activated carbon in the recycling system is 17.6 cubic feet; the cationic and anionic resin occupy a volume of 4.65 cubic feet each, the cationic resin being of the strong acid type (sulfonic), and the anionic of the strong base type (quaternary amine). The total volume of the pool water is 272,000 liters. About 80 liters per minute is bypassed through the carbon filter and resin bed recycling system.

To collect samples for analysis, small columns of activated carbon and cationic and anionic resins were mounted in parallel with the large purification tanks. The volumes of carbon and resins in the small columns were 300 milliliters each. Water flowed through the series of three columns at a rate of about 2 liters per minute; samples of resins and carbon were taken for analysis at the end of each criticality experiment.

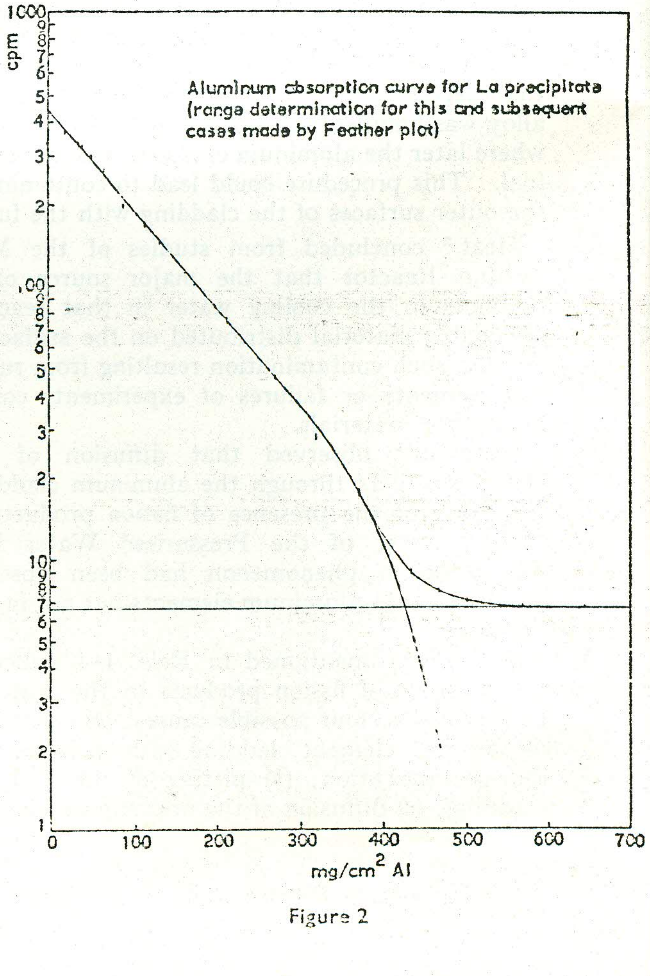

Figure 2

Samples were also taken from the large tanks after about four million liters of water had been repurified. In this latter case only radioactive species with half-lives larger than about ten days were looked for.

EXPERIMENTAL PROCEDURES

Samples of resin were eluted with 2 to 6N hydrochloric acid or with 1:1 nitric acid. Carbon samples were ignited and the ashes analyzed or, as in the case of the search for iodine, the carbon was washed with 0.5M potassium sulfite solution whose pH was maintained at 10 with sodium carbonate. Suitable carriers were added to the solutions and chemical separations were carried out; the amount of added carriers varied from 5 to 20 milligrams per 100 milliliters of solution.

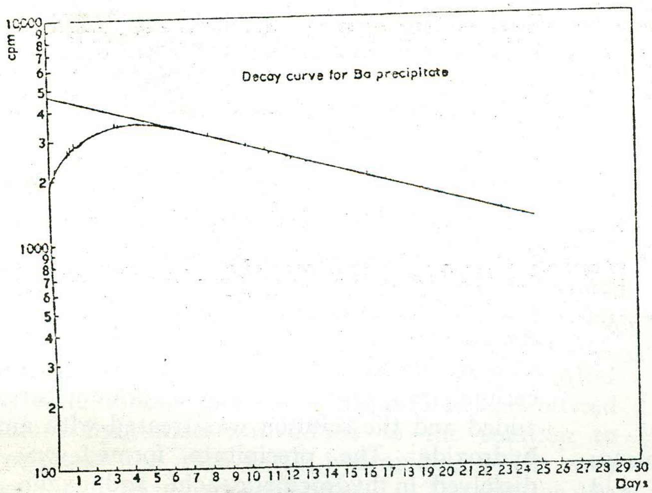

Figure 3

CHEMICAL SEPARATIONS

After every critical experiment the small columns were dismounted, eluted and analysis was made on the eluate. The chemical separation processes to be described are typical for every experiment.

Fission Products with Gaseous Precursors

Barium and Lanthanum

After the reactor had been operating for 6 hours at one megawatt, five grams of dried cationic resin was taken from the small columns and eluted with 200 milliliters of 2N hydrochloric acid solution. Carriers were added for Fe, Y, Cu, Ca, Sr, Ba, La, Mg, Zn and I and the solution was saturated with potassium sulphate. The precipitate of barium and strontium as well as of the double sulphate of lanthanum and potassium was filtered off. The precipitate was treated with 1:3 hot hydrochloric acid to dissolve lanthanum and the filtrate was left standing for two hours to settle any barium sulfate that might have passed through the filter and then filtered again. The solution of lanthanum was made 0.3N in hydrochloric acid, lanthanum was precipitated as oxalate and mounted for counting. Half-life determinations and aluminum absorption curves were made of the precipitate (Figs. 1 and 2). The curves indicate the presence of lanthanum-140.

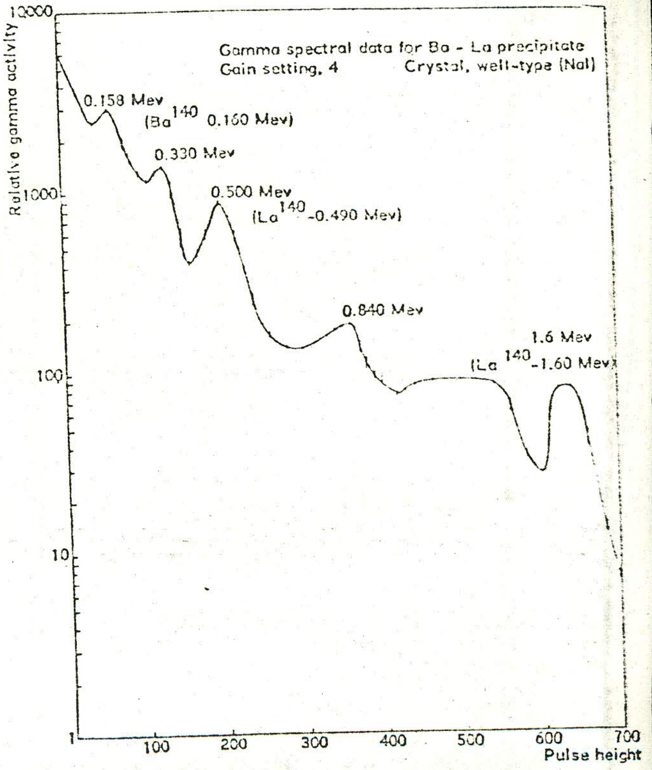

Figure 4

Barium was analyzed by precipitation of barium chromate in acetic acid media after isolation of the alkaline earths group, having previously eliminated the groups of metals of insoluble sulfides as well as the insoluble hydroxides. Figure 3 gives the decay curve and Fig. 4 the gamma spectral data for the barium sulfate precipitate. This set of curves indicates the presence of barium-140 and lanthanum-140.

Yttrium

Yttrium was analyzed in the filtrate from th barium sulfate and lanthanum sulfate precipitates The solution was made 0.3N in hydrochloric acid anc

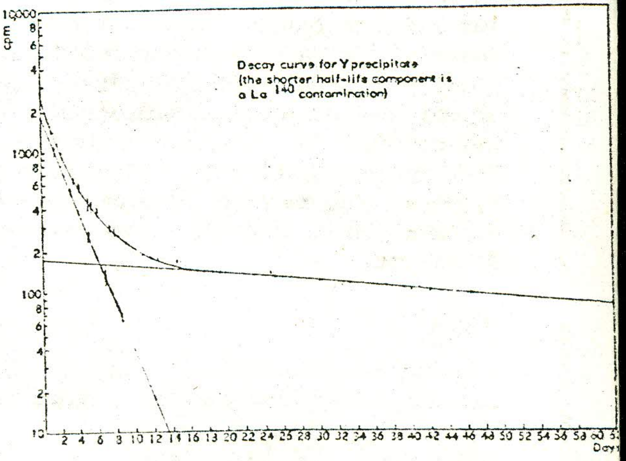

Figure 5

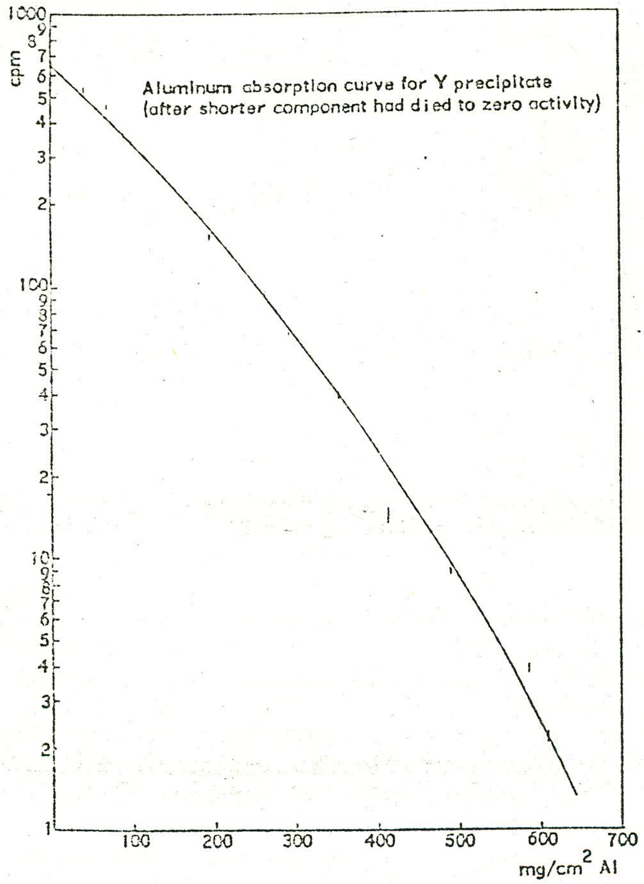

Figure 6

oxalic acid was added to precipitate yttrium oxalate; this was filtered, washed with diluted oxalic acid and mounted for counting. Half-life determination and the aluminum absorption curve indicated the presence of yttrium-91 (Figs. 5 and 6).

Yttrium was also analyzed by taking the eluate from the resins and adding the same carriers as for barium. Silver nitrate was added to the solution to precipitate iodine, the silver iodide was filtered, the solution was made 0.3*N* in hydrochloric acid and a stream of hydrogen sulfide was passed through it. The insoluble sulfides were filtered, the solution was boiled to eliminate hydrogen sulfide and nitric acid was added to oxidize ferrous ion to ferric ion. Ammonium hydroxide was next added to precipitate iron, yttrium and lanthanum hydroxides, which were then filtered and dissolved in nitric acid. The solution was neutralized with sodium hydroxide, made up to 0.3*N* in hydrochloric acid, and oxalic acid was added to precipitate yttrium and lanthanum; the precipitate was mounted for counting. The presence of yttrium-91 was confirmed (Figs. 5 and 6).

Iodine

Iodine was analyzed by taking the eluate from an anionic resin which had been standing for about 10 days after the critical experiment. The resin was eluted with 2*N* hydrochloric acid. Carriers were added as before and iodine was precipitated as palladium iodide which was counted. Half-life determination indicated the presence of iodine-131.

Iodine was also found in the activated carbon filter. The activated carbon was treated with 0.5*M* potassium sulfite and the pH was maintained at about 10 with sodium carbonate. After this treatment the carbon was separated from the solution, which was then made acid with nitric acid, and iodine precipitated as silver iodide. The presence of iodine-131 was confirmed by this procedure (Fig. 7).

Strontium

Strontium was analyzed in the filtrate of the barium chromate precipitate. The filtrate was treated with sulfuric acid and ammonium sulfate or, alternatively, with sodium sulfate. The strontium sulfate was filtered and mounted for counting. Figures 8 and 9 indicate the presence of strontium-89.

Although the fission yields for strontium-89 and strontium-90 have approximately the same values, the activity due to Sr^{90} is negligible as compared to Sr^{89} owing to the much larger value for the half-life of Sr^{90}.

Cerium

Cerium was analyzed in the ashes of activated carbon which had been standing for about one month after a critical experiment. The ashes were melted with sodium hydroxide and potassium nitrate in an iron crucible and leached with water. The insoluble part was dissolved in hydrochloric acid; neodymium, cerium, iron, aluminum and chromium carriers were added and the solution was treated with ammonium hydroxide. The precipitate formed was filtered, dissolved in hydrochloric acid, and oxalic acid was added to precipitate the rare earths. The precipitate was ignited, dissolved in nitric acid and potassium iodate was added to precipitate the ceric ion. The ceric iodate was filtered and mounted for counting in a single-channel gamma spectrometer; a photopeak found at 0.142 Mev indicated that the cerium isotope present might be cerium-141. Half-life determination was made at this photopeak and a value of 31.9

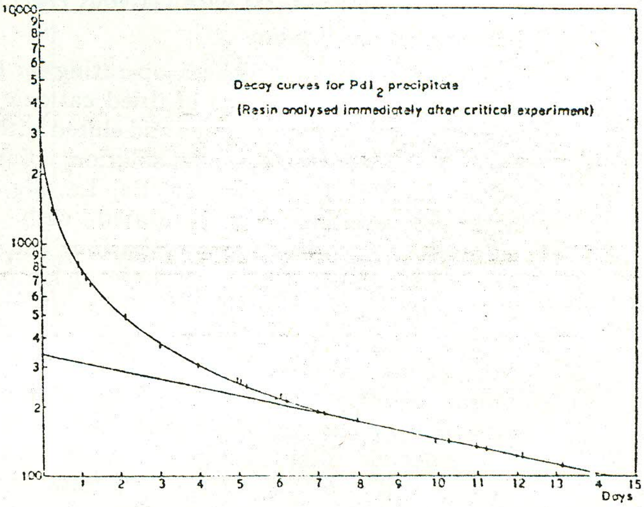

Figure 7

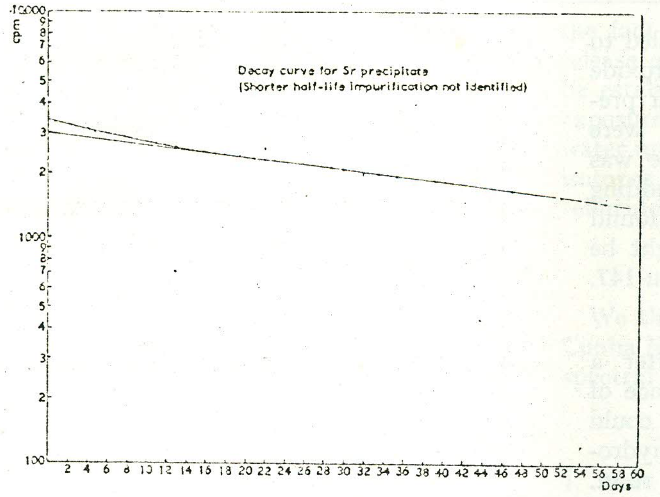

Figure 8

days was found, which confirms the presence of cerium-141 (Fig. 10).

Fission Products Formed Directly as Solids in Fission

Neodymium

Neodymium was looked for in the activated carbon as well as in the resin beds. Twelve hours after a critical experiment at one megawatt for six hours, the activated carbon and resins were taken for analysis. The same treatment as indicated previously for cerium was applied to the carbon. After the ceric iodate had been precipitated and filtered sodium hydroxide was added to the solution to precipitate the rare earth hydroxides, which were then dissolved in hydrochloric acid. The solution was made 0.3N in acid and oxalic acid was added to precipitate the rare earth oxalates, which were filtered, ignited and dissolved in hydrochloric acid and the solution passed through a cationic resin in ammonium form where the rare earths were absorbed. After this column, with the resins in the rare earth form, a second column was attached with a cationic resin saturated with copper; both columns were of 10 centimeters length and 8 millimeters diameter. The resins were then eluted with a solution at 10 grams per liter of ethylenediaminetetraacetic acid at a pH of 8.7 according to the procedures given by Spedding, Powell and Wheelwright.[8] Neodymium fractions were collected after almost all copper had been eluted, the oxalates of each fraction were precipitated and mounted for counting and no activity was found either in a Geiger counter or in a gamma-scintillometer, even when all neodymium fractions were redissolved, reprecipitated and mounted again for counting.

When the neodymium was looked for in the resin eluate the same procedure [8] was applied, but a scavenging of activities other than rare earths was made. To the eluate, carriers of iron, copper, barium, cerium, neodymium and praseodymium were added; the solution was made 0.3N in hydrochloric acid and hydrogen sulfide gas was passed through it; the preci-

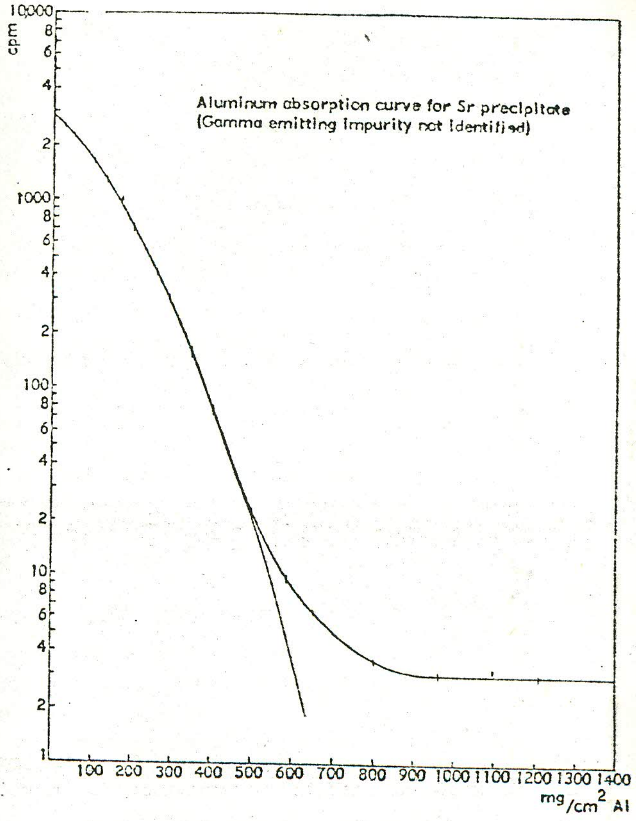

Figure 9

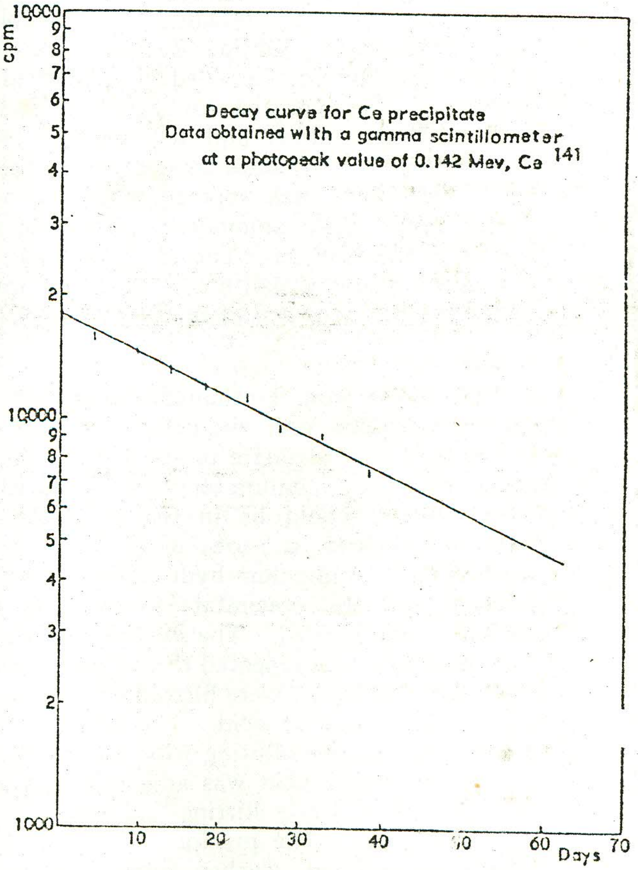

Figure 10

pitate formed was filtered, the solution was boiled to eliminate the hydrogen sulfide, ammonium hydroxide was added to it and the iron and rare earth precipitates were filtered off. The hydroxides were redissolved and the same procedure as before was followed to separate neodymium by the Spedding method. Also, in this case, no activity was found in a Geiger or gamma-scintillometer that might be ascribed to the 11.6-day half-life of neodymium-147.

Tellurium

Tellurium was looked for immediately after a critical experiment so that the eventual presence of the isotope tellurium-131 of half-life 77 hours could be checked. The resins were eluted with $2N$ hydrochloric acid until no activity was left in the resin. From a total volume of 450 milliliters an aliquot of 200 milliliters was taken and 50 milligrams of tellurium as potassium tellurite was added. The solution was heated to about 80°C and a stream of sulfurous acid was passed through it to reduce the tellurium in the tellurite to metallic tellurium. The tellurium was filtered, washed, mounted and counted with no positive result concerning activity, either in a Geiger counter or in a gamma-scintillometer.

Molybdenum

To the eluate of the resins, carriers for iodine, bromine, iron, zinc, barium, magnesium, lanthanum and molybdenum (as molybdate) were added. Acetic acid and ammonium hydroxide were added to the solution and the molybdenum was precipitated as lead molybdate by adding lead acetate. The precipitate was filtered, dissolved in nitric acid and the solution was evaporated to dryness. Hydrochloric acid was then added and the solution was again evaporated, the procedure being repeated three times. Lead molybdate was reprecipitated as before by adding acetic acid, ammonium hydroxide and lead acetate to the solution. The precipitate was mounted for counting and a half-life of 66 hours was found, indicating the presence of molybdenum-99 (Fig. 11).

Zirconium

Carriers for iron, lanthanum, strontium, barium, yttrium, calcium and zirconium (zirconyl chloride) were added to the eluate of the resins. In order to ensure that the zirconium-96 that might exist at tracer concentration would be in the same form as the zirconium carrier, a series of chemical treatments were made. Ammonium hydroxide was added to the solution and the precipitate formed was dissolved without being filtered. The solution was then boiled. The procedure was repeated three times. Finally the insoluble hydroxides were filtered off and dissolved in hot 1:1 hydrochloric acid. The solution was made to 50 milliliters by diluting with water, 10 milliliters of 16% mandelic acid was added, the solution was heated at 80°C while stirring and then left standing for 30 minutes. The precipitate of zirconium mandelate was filtered, washed with 3% mandelic acid and mounted for counting. No activity was found in a Geiger counter or gamma-spectrometer.

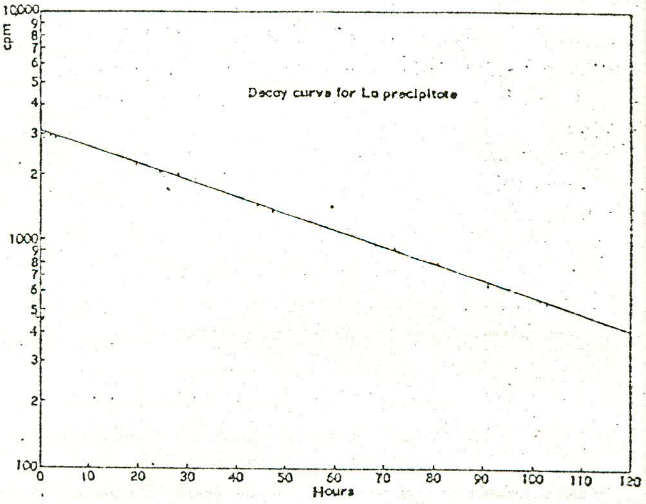

Figure 1λ

DISCUSSION

All radioactive nuclides found, with the exception of molybdenum-99 and iodine isotopes, had precursors that were formed as gases in fission. Barium-140 and lanthanum-140 are descendants of xenon-140 whose fission yield is 6.1%; yttrium-91 is a descendant of krypton-91 with a fission yield of 5.9%; strontium-89 descends from krypton-89 whose fission yield is 4.6%; cerium-141 descends from xenon-141 whose fission yield is 5.7%.

The other radioactive isotopes looked for have relatively high fission yields (Nd^{147}, 2.6%; Te^{132}, 3.6%; Zr^{96}, 6.4%; Mo^{99}, 6.2%) and half-lives convenient for this type of work. It follows that the concentration of the nuclides that might exist in the resins or activated carbon would not be appreciably decreased by decay during the various steps of the work. However, with the exception of molybdenum-99, none of the nuclides was found in the various analyses performed.

The mode of formation of molybdenum-99, besides the fission of uranium-235, is a (n, γ) reaction on molybdenum-98. Moeller [2] had already observed the formation of this radioactive isotope, and attributed its presence in the water to the dissolution of the steel in the pipe system. The presence of this isotope in the water of the Brazilian reactor might also be explained by the dissolution of the steel and not by the release of molybdenum-99 formed directly in fission. If the molybdenum-99 found in the resin bed were of fission origin its amount should be of the same order of magnitude as barium-140, lanthanum-140, yttrium-91 and cerium-141 since their fission yields are about the same. However, semiquantitative tests made on the products eluted from resins which had been used on the same critical experiment showed that the amount of molybdenum-99 was about 100 times less than the isotopes of the same fission yield; it was even less than iodine-131 whose fission yield is only 2.8%.

The negative results for neodymium-147, tellurium-132 and zirconium-96 indicate also that the mode of formation of molybdenum-99 is by a (n, γ) reaction and not by fission. Otherwise one would expect to find also neodymium-147, tellurium-132 and zirconium-96, since their releasing mechanism from the fuel elements would be the same, all being solid isotopes.

Bolton *et al.*[1] found that the contamination in critical assembly rooms was due to descendants of gaseous fission products whose half-lives were relatively large, such as Kr^{88} (2.8 hours) and Xe^{138} (17 minutes). Owing to their long half-life as compared to other isotopes of krypton and xenon, these would have time to diffuse through the fuel elements, dissolve in the water and later come into the atmosphere. Gaseous isotopes of very short half-lives would not have time to escape from water into the air. However, in the present work, fission products were found in the resin beds and carbon filters whose gaseous precursors had very short half-lives. These were, for instance, Ba^{140} and La^{140} descending from Xe^{140} (16 seconds); Y^{91} descending from Kr^{91} (10 seconds); Ce^{141} descending from Xe^{141} (3 seconds). The only possible explanation for the presence of these isotopes in the resins and in the carbon filters is that, although the half-life of their precursors is not large enough to permit their escape from the water to the atmosphere, it is possible that certain amount of gases diffuses through the elements and dissolves in the water and the gases decay completely to their solid descendants. However, it seems that gaseous diffusion cannot be the only cause for the presence of some fission products in the water, since iodine isotopes formed in fission were also found. Lustman[4] had already called attention to the fact that the real mechanism of fission product release might need a considerable amount of work to be established with certainty. It is not likely that exposure of enriched uranium in the elements to the water might be the cause of iodine isotopes; otherwise isotopes such as neodymium-147, zirconium-95 and tellurium-132 should also have been found.

ACKNOWLEDGEMENTS

We thank Mr. Silvio Bruni Herdade and Mr. Ivan Cunha Nascimento for obtaining many of the gamma-spectral counting data.

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