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# Distribution of Plutonium Isotopes in Cooling Water from a PWR

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An investigation of plutonium isotopes in the primary cooling system of the Ringhals unit 2 (PWR) during normal operation has shown average concentrations of  $0.03 \text{ Bq}\cdot\text{l}^{-1}$  of  $^{238}\text{Pu}$  and  $0.02 \text{ Bq}\cdot\text{l}^{-1}$  of  $^{239+240}\text{Pu}$ . A major fraction of plutonium is associated with particles in contrast to dissolved plutonium in ionic form. The observed concentrations of plutonium isotopes in cooling water are characterized by log-normal distributions. The overall efficiency of the ion-exchange cleaning system with respect to plutonium in the primary circuit has been estimated as approximately 60%. During normal operation the ion-exchange cleaning system annually collects about 3 MBq of  $^{238}\text{Pu}$  and 2 MBq of  $^{239+240}\text{Pu}$ . The cleaning system efficiently removes plutonium particles with sizes in the range 0.05 to  $0.15 \mu\text{m}$  from the primary cooling water. Particles with sizes outside this range are removed less efficiently.

**KEYWORDS:** *Ringhals-2 reactor, plutonium isotopes, radioactive wastes, plutonium analysis, cooling water, ion-exchange resin, filters, filtration, removal, particulates, log-normal distribution, particle size*

## I. INTRODUCTION

In order to estimate potential future contaminations of the environment with transuranium elements from nuclear waste repositories and subsequent radiation doses to humans, it is necessary to know the inventories of these elements in the nuclear waste. The presence of transuranium elements, *e.g.* plutonium and americium, in the primary cooling water of nuclear reactors may arise from external uranium contamination of the fuel elements (tramp uranium) or from leaking fuel elements. This contamination will be retained to a large extent in the cleaning system of the primary cooling water (*e.g.* the cation- and anion-exchange resin bed). It is important to get information on the existing state of the transuranium elements in the cooling water whether they are dissolved or associated with particles in order to predict the fate of these

radionuclides in the nuclear reactor systems and in the radioactive waste.

The present paper describes the results of an investigation on the distribution of plutonium in the primary cooling water from Ringhals unit 2 (PWR) in Sweden. Radiochemical procedures were developed for the determination of plutonium in cooling water and ion-exchange resin. Samples of cooling water were taken during a six-months period from June 1991 shortly after restart of the unit following the scheduled annual shutdown. The results include the concentrations of plutonium at different locations in the reactor system, the inhomogeneous distribution of plutonium in the cooling water, the different sizes of the plutonium-carrying particles and the cleaning efficiency of the ion-exchange system to plutonium in the primary cooling

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water. Further detailed analytical results are given in Chen *et al.*<sup>(1)</sup>

## II. MATERIAL AND METHODS

### 1. Sampling Programme

Samples of cooling water from the primary circuit of unit 2 of the Ringhals power plant were collected at two sampling points, one before (RC) and one after (CV) the ion-exchange system. Sampling was carried out from 17 June to 2 December 1991. The sampling volumes were 0.1 l at the beginning but increased later to 1 l to obtain a higher sensitivity.

Preliminary results indicated that a significant proportion of the plutonium in the cooling water was associated with particles. In order to obtain information on the size distribution of these particles, the cooling-water samples were filtrated through membrane filters with pore sizes of 0.05, 0.15 and 5  $\mu\text{m}$ .

A total of 26 samples were collected at sampling point 'RC' and 29 samples were collected at 'CV'. Of these 55 samples, 38 were filtrated and thus analyzed both for the filter fraction and the filtrate solution.

### 2. Radiochemical Procedures

The development of radiochemical procedures for the determination of plutonium in cooling water and ion-exchange resin was based on previous experience with the analysis of plutonium in environmental samples using a method of controlled valence developed after that of Talvitie<sup>(2)</sup>. The method of controlled valence<sup>(3)</sup> is based on a careful adjustment of the plutonium valences ( $\text{Pu}^{+3,4,5,6}$ ) throughout the various steps of the radiochemical procedure to ensure a high chemical yield as well as decontamination for other transuranium elements. The analyses of particulate plutonium were done by an initial complete decomposition of the particles (collected by filtration) in concentrated acids (HCl and  $\text{HNO}_3$ ) followed by the above mentioned method.

Due to the complex plutonium chemistry at  $\text{pH}=7$ , it was decided to carry out a laboratory test of the sorption of plutonium on

ion-exchange resins under conditions similar to those in the primary cooling water. The ion-exchange columns were first equilibrated with four column volumes of boric-acid solution containing  $6\text{ g}\cdot\text{l}^{-1}$   $\text{H}_3\text{BO}_3$  at  $\text{pH}=7$  after which the tracer  $^{242}\text{Pu}$  was added dissolved in 5-ml boric-acid solution. The columns were subsequently leached with 10 column volumes of boric-acid solution which were analyzed for plutonium. Finally, the columns were stripped for the sorped plutonium and assayed for the sorped fraction. Complete stripping of plutonium sorped on ion-exchange resin was achieved using concentrated acids (HCl and  $\text{HNO}_3$ ). This test procedure was applied for two cation-exchange columns ( $11\times 1.5$  cm Dowex-50 W, 100-200 mesh) and two anion-exchange columns ( $11\times 1.5$  cm AG 1-X4, 100-200 mesh).

### 3. Alpha-Spectrometry Procedures

After radiochemical treatment the samples were electroplated on stainless steel discs having a diameter of 19 mm; the active source area had a diameter of 16 mm. During counting each disc was mounted in a vacuum chamber under a silicon detector (surface barrier or ion implanted type) with an active area corresponding to a diameter of 12 mm. The source-detector distance was approximately 3 mm. The calibration of the detectors was carried out with sources made from standard solutions purchased from recognized vendors. The sources were prepared according to a technique outlined by Chen *et al.*<sup>(4)</sup> The counting efficiencies of the detectors ranged from 29% to 39%.

The samples were counted for 72 h or more and background counts made on blanks were recorded for similar time periods. The alpha spectra were evaluated by observing the total counts in the energy intervals for the relevant isotopes which cover the radiochemical tracer ( $^{242}\text{Pu}$  or  $^{236}\text{Pu}$ ),  $^{239+240}\text{Pu}$  and  $^{238}\text{Pu}$ . Detection limits were calculated from the background counts in the appropriate energy intervals by using a confidence factor of 4.65 to the standard deviation of the background count to obtain a 95% confidence level according to Currie<sup>(5)</sup>.

### III. RESULTS AND DISCUSSION

#### 1. Absorption of Plutonium on Ion-Exchange Resin

The results of the tests for the absorption of dissolved  $^{242}\text{Pu}$  on ion-exchange resins are shown in **Table 1**. Two sets of results are given for each type of ion-exchange resin. They show that about 76% of the dissolved plutonium is absorbed on the cation-exchange column and the remaining 24% passes through, while about 67% is absorbed on the anion-exchange column and the remaining 33% passes through. The valences of the  $^{242}\text{Pu}$  tracer (+3, 4, 5, 6) in  $\text{HNO}_3$  were equilibrated. At  $\text{pH}=7$ , the plutonium in each valence state is probably hydrolysed. The plutonium sorption on the ion-exchange resin might therefore be a physical adsorption rather than a chemical absorption.

**Table 1** Relative amounts of plutonium absorbed on ion-exchange resin and in leachate solution

Column	Sample No.	Fraction absorbed on column (%)	Fraction in leachate (%)
Cation-exchange column	1	75	25
	2	76	24
Anion-exchange column	1	66	34
	2	67	33

#### 2. Plutonium in Cooling Water

The following example demonstrates the existence of particles associated with plutonium found in the primary cooling water. A 250-ml sample was collected the 26 June from the primary cooling water at location RC and split in two aliquots, No. 1 of 100-ml volume and No. 2 of 150-ml volume, after shaking to obtain uniformity. Aliquot No. 1 was assayed directly, whereas aliquot No. 2 was assayed after separation in two components by filtration. The results of the analyses are given in **Table 2**. Firstly, there is considerably (about twenty times) more plutonium in aliquot No. 1 than in aliquot No. 2 and secondly, the plutonium found in aliquot No. 2 is mainly retained in the filter. The large differences demonstrate that a significant fraction of the

plutonium in the cooling water is associated with particles.

**Table 2** Results of plutonium levels in a cooling water sample demonstrating non-uniform levels.

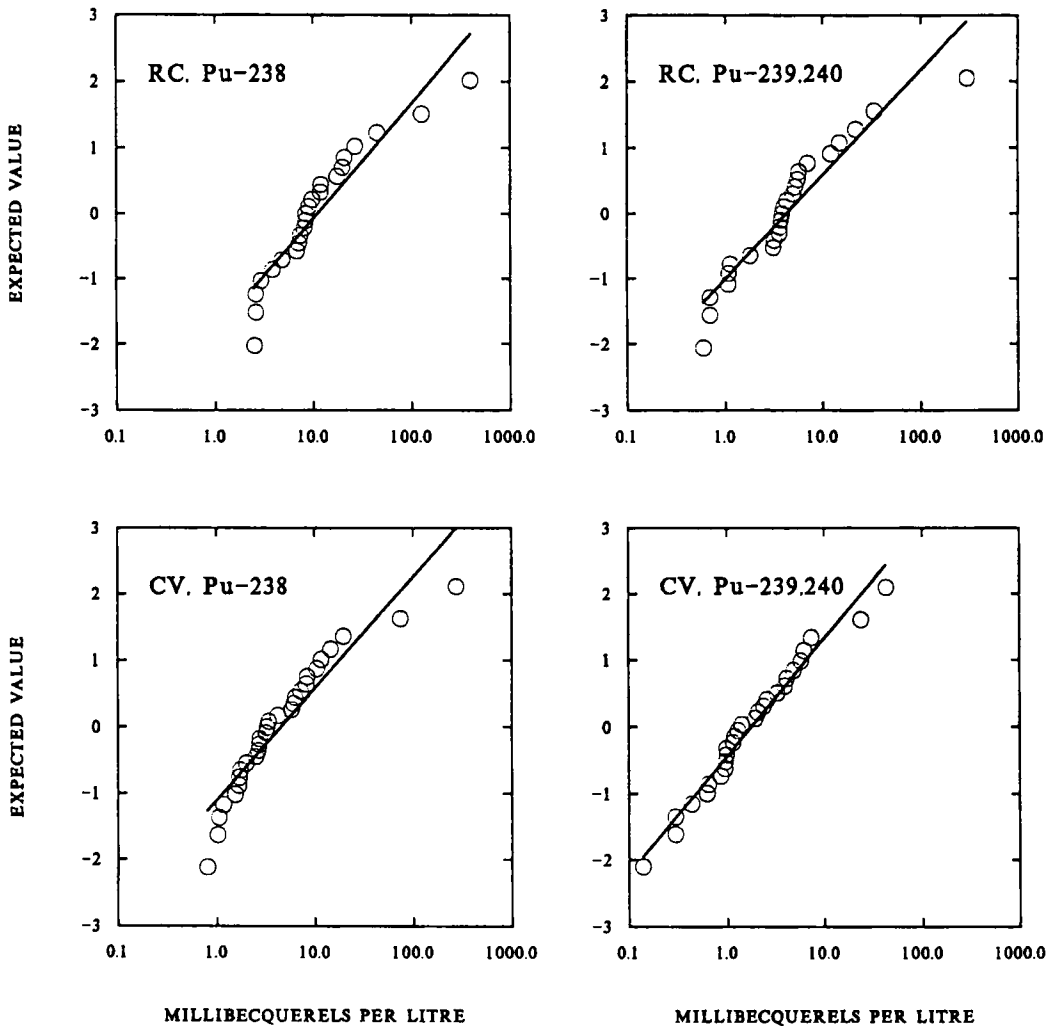
The sample was split in two aliquots after shaking to obtain uniformity. Aliquot No. 2 was filtered through Whatman glass-fibre filter type GF/F.

Aliquot No.	Treatment	Yield† (%)	$^{238}\text{Pu}$ ( $\text{mBq}\cdot\text{l}^{-1}$ )	$^{239+240}\text{Pu}$ ( $\text{mBq}\cdot\text{l}^{-1}$ )
1	No treatment	78	401	300
2	Filter paper	65	20	6.7
2	Filtrate	68	<0.6	0.4

† From  $^{242}\text{Pu}$  tracer

The results of the plutonium analyses of the cooling-water samples are shown in **Fig. 1**, which shows normal probability plots where the concentrations of  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$  are shown on logarithmic scales *vs.* a standard normal variable<sup>(6)</sup>. The vertical axes are scaled thus that the cumulative distribution function of a log-normal distribution will plot as a straight line. The results are approximately log-normally distributed as indicated by the lines fitted to the data. The data show higher levels before (RC) than after (CV) the ion-exchange system, and one-tailed Students *t*-tests carried out on the log-transformed data show that the differences are significantly larger than zero. For the  $^{238}\text{Pu}$  data the *t*-test shows that the difference is significant at the 5% level ( $t=1.83$ , 53 degrees of freedom), and for the  $^{239+240}\text{Pu}$  data the difference is significant at the 1% level ( $t=2.80$ , 50 df).

For the purpose of estimating the amount of plutonium retained in the cleaning system, **Table 3** gives the arithmetic mean concentrations of plutonium before and after the ion-exchange system. In addition to the arithmetic mean values calculated from the measured data, Table 3 includes the arithmetic mean values obtained from the log-normal distributions fitted to the observed data. While the arithmetic mean values from the observations depend strongly on the few large observations in each group, this is not the case for the



**Fig. 1** Normal probability plots of the concentrations of  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$  ( $\text{mBq}\cdot\text{l}^{-1}$ ) observed at the two locations RC before and CV after the ion-exchange system. The concentrations are shown on logarithmic scales *vs.* a standard normal variable. The log-normal distributions fitted to the data are shown as straight lines.

fitted distributions which represent the entire set of data in each group. It is noted that

the arithmetic mean values from the measured data are generally larger (within a factor 1.7) than those from the fitted distributions.

**Table 3** Arithmetic mean concentrations of plutonium isotopes in primary cooling water collected before and after the ion-exchange system ( $\text{mBq}\cdot\text{l}^{-1}$ )

	Data from measurements		Data from fitted distributions	
	$^{238}\text{Pu}$	$^{239+240}\text{Pu}$	$^{238}\text{Pu}$	$^{239+240}\text{Pu}$
Before (RC)	34	17	23	12
After (CV)	17	4.3	10	3.9

### 3. Plutonium in Ion-Exchange Resin

The data for the measurements from Table 3 show ratios between the levels after to those before the ion-exchange system varying from 0.25 for  $^{239+240}\text{Pu}$  to 0.50 for  $^{238}\text{Pu}$ ; for the sum of the three plutonium isotopes the ratio is 0.42. For the data from the fitted distributions the ratios are nearly the same, although the difference between the ratios

for  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$  is less pronounced. The data thus indicate a ratio of 0.4 of the plutonium levels after-to-before the cleaning system, corresponding to an average cleaning efficiency of the ion-exchange system for plutonium of about 60%.

The reason for the somewhat lower relative retention of  $^{238}\text{Pu}$  in the ion-exchange system than that of  $^{239+240}\text{Pu}$  is probably that the  $^{242}\text{Cm}$  inventory in the ion-exchange system acts as a secondary source of  $^{238}\text{Pu}$  to the primary cooling water at location CV. However, the present investigation has only considered isotopes of plutonium for what reason no observations have been made of the levels of curium isotopes in the primary cooling water.

If we assume our observations to be representative for one years operation, we may estimate the inventories of plutonium in the ion-exchange system based on a mean flow rate of cooling water from the primary system through the ion-exchange system of  $6.6 \text{ l}\cdot\text{s}^{-1}$ . The annual inventories of the plutonium isotopes in the ion-exchange system are given in **Table 4**, where the results are calculated from the plutonium levels before the ion-exchange system for both the observed data and the fitted data, and a cleaning efficiency of the system of 60%. The overall results are that the annually accumulated inventories in the ion-exchange system during normal operation may be estimated as approximately 2 MBq of  $^{239+240}\text{Pu}$  and 3 MBq of  $^{238}\text{Pu}$ .

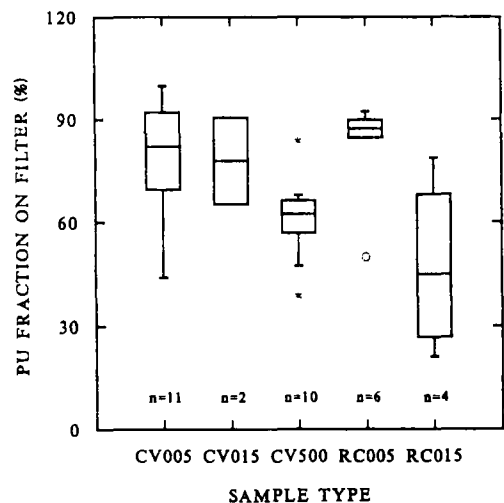
**Table 4** Inventories of  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$  (MBq) in the ion-exchange system after one years operation estimated from measured data directly and from data fitted to the observations

Data from measurements		Data from fitted distribution	
$^{238}\text{Pu}$	$^{239+240}\text{Pu}$	$^{238}\text{Pu}$	$^{239+240}\text{Pu}$
4.2	2.1	2.8	1.5

#### 4. Size of Plutonium Particles

The distributions of the data show that plutonium in the cooling water is associated with particles both before and after the ion-

exchange system. If the fraction of the plutonium associated with particles after the ion-exchange system was insignificant compared to the dissolved fractions, one would expect normal rather than log-normal distributions of the concentrations at location CV. For the samples where detectable levels of  $^{238}\text{Pu}$  were found in the filtrate solution, the fractions of plutonium activity on particles were calculated. The  $^{238}\text{Pu}$  data were used for this purpose since they consistently show higher levels than those of  $^{239+240}\text{Pu}$ . They also constitute a more complete set since several  $^{239+240}\text{Pu}$  results from the filtrate solutions were below the limits of detection. **Figure 2** summarises the plutonium particle fractions in box-and-whisker plots for each of five groups that represent the two locations, RC and CV, and three pore sizes of 0.05, 0.15 and  $5 \mu\text{m}$  (e.g. the label CV015 means results from the location CV for the filter size  $0.15 \mu\text{m}$ ). The box-and-whisker plots give the median values, and



**Fig. 2** Box-and-whisker plot of the plutonium particle fractions for five groups of data that represent the two locations (RC and CV) and three filter pore sizes of 0.05, 0.15 and  $5 \mu\text{m}$ .

The plot shows the median values, upper and lower quartiles; the whiskers extend to the points within 1.5 times the interquartile range; extreme points beyond this range are shown as individual values (\*, o). The number of observations in each group is indicated ( $n$ ).

the upper and lower quartiles; the whiskers extend to the points that lie within 1.5 times the interquartile range; extreme points beyond this range are plotted as individual values<sup>(7)</sup>.

The results from Fig. 2 show large variabilities among the plutonium particle fractions. Nevertheless, there is a clear tendency that the filters with smaller pore sizes retain larger fractions of the total plutonium activity in the cooling-water samples. The median values for the plutonium particle fractions are considered more representative than the mean values due to the large variability; the median values are given in **Table 5**. From these values and the arithmetic mean concentrations in Table 3, the average concentrations

**Table 5** Median values of fractions (%) of <sup>238</sup>Pu activity on particles in primary cooling water, determined for different filter pore sizes (μm) and the two sampling locations

Pore size (μm)	Location RC	Location CV
0.05	87 %	82 %
0.15	45 %	78 %
5.0		62 %

of <sup>238</sup>Pu in the primary cooling water have been estimated as a function of particle size. Based on these data, estimates have been made of the particle-size distributions of the <sup>238</sup>Pu activity at locations RC and CV including adsorption on the ion-exchange resin. These estimates are shown in **Table 6** which gives the estimated concentrations in mBq·l<sup>-1</sup> and in percent relative to the total concentration at RC of 23 mBq·l<sup>-1</sup>. The values from Table 6 indicate that a significant fraction (about 40%) of the plutonium activity before the ion-exchange system is associated with particles of sizes in the range 0.05 to 0.15 μm. This contrasts to the situation after the ion-exchange system, where the data indicate that the plutonium activity associated with particles in this size range is insignificant. The ion-exchange cleaning system thus seems to work efficiently for plutonium particles of sizes in the range 0.05 to 0.15 μm. The retention of plutonium particles larger than 0.15 μm or less than 0.05 μm in the ion-exchange system seems to be not quite as efficient.

**Table 6** Estimated distributions of <sup>238</sup>Pu activity in primary cooling water at locations RC and CV and in ion-exchange resin as a function of particle size.

The percentages refer to the total concentration at RC.

Particle size (μm)	Location RC		Location CV		Adsorbed on ion exchange resin	
	(mBq·l <sup>-1</sup> )	(%)	(mBq·l <sup>-1</sup> )	(%)	(mBq·l <sup>-1</sup> )	(%)
>0.15	10.4	45	7.8	34	2.6	11
0.05-0.15	9.6	42	0.4	2	9.2	40
<0.05	3.0	13	1.8	8	1.2	5
Total	23	100	10	43	13	57

#### IV. CONCLUSIONS

An investigation of the levels of plutonium isotopes (<sup>238</sup>Pu and <sup>239+240</sup>Pu) in the primary cooling water of the Ringhals unit 2 (PWR) in 1991 during normal operation has shown average concentrations of 0.03 Bq·l<sup>-1</sup> of <sup>238</sup>Pu and 0.02 Bq·l<sup>-1</sup> of <sup>239+240</sup>Pu in samples collected before the ion-exchange cleaning system. In samples collected after the ion-exchange cleaning system the average levels were found at

0.02 Bq·l<sup>-1</sup> of <sup>238</sup>Pu and 0.004 Bq·l<sup>-1</sup> of <sup>239+240</sup>Pu. The results show distinct non-uniform distributions of plutonium in the primary cooling water; the observed concentrations may be characterized by log-normal distributions.

The efficiency of the ion-exchange cleaning system with respect to plutonium in the primary cooling water has been estimated as approximately 60%, and the annually collected plutonium activities in the ion-exchange system during normal operation have been esti-

mated as about 3 MBq of  $^{238}\text{Pu}$  and 2 MBq of  $^{239+240}\text{Pu}$ .

The inhomogeneous distribution of plutonium in the primary cooling water is due to the fact that a major fraction of the plutonium activity is associated with particles. Filtration of cooling-water samples through filters of different pore sizes has given information on the distribution of the activity as a function of the size of the plutonium particles. The results show that the ion-exchange system efficiently removes the plutonium particles of sizes in the range 0.05 to 0.15  $\mu\text{m}$  from the primary cooling water. The removal by the ion-exchange system of plutonium particles larger than 0.15  $\mu\text{m}$  or less than 0.05  $\mu\text{m}$  is less efficient.

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