

Long-lived radionuclides in residues from operation and decommissioning of nuclear power plants

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ABSTRACT

Radioactive residues, in order to be classified as Low-Level Waste (LLW), need to fulfil certain conditions; the limitation of the maximum activity from long-lived radionuclides is one of these requirements. In order to verify compliance to this limitation, the abundance of these radionuclides in the residue must be determined. However, performing this determination through radiometric methods constitutes a laborious task. In this work, ^{129}I concentrations, $^{239+240}\text{Pu}$ activities, and $^{240}\text{Pu}/^{239}\text{Pu}$ ratios are determined in low-level radioactive residues, including resins and dry sludge, from nuclear power plants in Spain. The use of Accelerator Mass Spectrometry (AMS) enables high sensitivities to be achieved, and hence these magnitudes can be re determined with good precision. Results present a high dispersion between the ^{129}I and $^{239+240}\text{Pu}$ activities found in various aliquots of the same sample, which suggests the existence of a mixture of resins with a variety of histories in the same container. As a conclusion, it is shown that activities and isotopic ratios can provide information on the processes that occur in power plants throughout the history of the residues. Furthermore, wipes from the monitoring of surface contamination of the José Cabrera decommissioning process have been analyzed for ^{129}I determination. The wide range of measured activities indicates an effective dispersal of ^{129}I throughout the various locations within a nuclear power plant. Not only could these measurements be employed in the contamination monitoring of the decommissioning process, but also in the modelling of the presence of other iodine isotopes.

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1. Introduction

Normal operation as well as the decommissioning of nuclear power plants routinely produce radioactive residues that can be fundamentally classified as High-Level Nuclear Waste (HLW) and Low-Level Nuclear Waste (LLW). LLW can be stored under less strict conditions than HLW. Under current Spanish regulations, in order to be classified as Low Level Waste, residues must conform to a number of conditions related to their specific activity, the half-life of the contained radionuclides, etc. Two of these conditions state that both alpha emitters and long-lived radionuclides can only be present in very low concentrations. Since some of these radionuclides cannot be detected at these levels by conventional radiometric methods, techniques of a more sensitive nature, such as Accelerator Mass Spectrometry (AMS), could be used in order to categorize the residue as LLW or even as standard residues [1–3]. These residues include a wide variety of materials resulting from various activities. For example, normal operation of a nuclear power plant produces evaporator concentrates from decontamina-

tion of liquids by evaporation, resins used for cleaning the reactor cooling water, and other liquids and sludge from the drying of the wet residues in containers and sinks.

Certain long-lived radionuclides of interest in these kinds of residues include ^{14}C , ^{55}Fe , ^{129}I and a number of actinides. In this work, we have determined ^{129}I in several of these materials; no mean feat of detection at low activities. ^{129}I is a highly significant radionuclide with regards to radioactive residues due to its long half-life and its mobility in the environment [4]. This radionuclide has also been determined in wipes from the José Cabrera nuclear power plant decommissioning operations used for the monitoring of surface contamination. The high sensitivity of AMS can help clarify the dispersal processes of volatile radionuclides such as I isotopes.

The Pu isotopes 239 and 240 have been determined in several of these samples. Although the total $^{239+240}\text{Pu}$ activity can be measured by alpha spectrometry without much difficulty, this is not the case for the ratio $^{240}\text{Pu}/^{239}\text{Pu}$ [5–7]. This ratio is dependent on the history of the residues, and hence on the fuel utilized, and could therefore provide a very suitable tool for the identification of accidental releases of radioactive material into the environment [8]. Through the monitoring of this parameter, it could also be possible to check the processes carried out at nuclear power plants and the status of the nuclear fuel.

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Table 1
 ^{129}I concentrations in low-level radioactive residues from Spain.

Sample	Type	Number of aliquots	Average ^{129}I concentration (10^9 ats/g)	Standard deviation or individual error (%)
R-AS-07-04	Resin	9	150	54.2
R-AS-08-01	Resin	10	30.5	88.2
VD-10-01	Resin	2	1.99 4.27	5.4 8.4
R-VD-9-01	Resin	3	30.1 27.4 54.8	6.4 6.8 2.6
R-VD-9-02	Dry sludge	2	21.3 18.1	2.3 2.3
R-VD-9-03	Dry sludge	2	14.1 12.0	4.4 5.6
IAEA-375	Env. soil	3	1.25 1.28 1.20	1.8 1.7 1.8

2. Methods

2.1. Radiochemical procedures

All samples were provided by ENRESA, the Spanish company responsible for the management of radioactive residues. Chemical preparation for ^{129}I determination is based on a microwave digestion method that has been described in detail elsewhere [9]. In short, about 6 ml of concentrated HNO_3 and 2 ml of iodine carrier (Woodward Iodine, 1 mg/ml) are added to 0.5 g of sample material and introduced into the MW oven at 200 °C for 20 min for digestion purposes. The iodine is then extracted into CHCl_3 and back-extracted into water. This operation is repeated three times. Finally, AgI is precipitated by the addition of AgNO_3 and pressed into the cathode after mixing with Nb powder.

The extraction and purification of the plutonium from the radioactive residues is performed in three main steps: the spiking of the samples with about 2 pg of ^{242}Pu ; the leaching with concentrated HNO_3 for 20 min at 200 °C in pressurized closed vessels in a microwave oven (MW); and chemical purification of the plutonium using TEVA[®] ion chromatography resins, as explained in [10]. Aliquots containing less than 10 mBq of $^{239+240}\text{Pu}$, as determined by previous alpha-spectrometry analysis, were processed for the AMS determinations, in order to prevent severe contamination of the ion source. The MW digestion is employed to prevent exposure of personnel to radioactive vapours. The Pu, as PuO_2 , is then dispersed in an iron oxide matrix mixed with Nb powder in a 1:2 mass ratio, and pressed into appropriate Al cathodes for the AMS determinations.

2.2. AMS measurements

Measurements are carried out at the 1 MV AMS facility at the Centro Nacional de Aceleradores in Sevilla (CNA, Spain). ^{129}I is measured at charge state 3^+ and at 1 MV terminal voltage. Characteristic currents at the low energy side are between 1 and 5 μA of $^{127}\text{I}^-$, transmission is approximately 9% and machine background values are typically $^{129}\text{I}/^{127}\text{I} \cong 3 \times 10^{-13}$. Greater detail is given in [11]. For the samples described in this paper, uncertainties are in the majority of cases between 5% and 10% (1σ).

Details about the Pu AMS measurement technique at the CNA can be found in [12]. Briefly, plutonium isotopes (^{242}Pu , ^{239}Pu , ^{240}Pu) are extracted from the Cs sputter ion source as PuO^- , stripped to Pu^{3+} in Ar gas at a terminal voltage of 670 kV, and finally counted using the total energy signal provided by a gas ionisation chamber. In order to completely destroy the molecules

surviving the stripping process in the 3^+ charge state and with the same M/q ratio as Pu isotopes in 1^+ and 2^+ charge states, the stripper gas pressure was increased by a factor of 3 compared to that corresponding to the maximum optical transmission (3×10^{-2} mbar, measured in the middle of the stripper channel), with a 25% loss of ions due to scattering events (from 16% to 12%, as measured for $^{232}\text{Th}^{16}\text{O}^-/^{232}\text{Th}^{3+}$ [12]). The plutonium isotopes were injected sequentially into the detector by making use of the so-called “Slow Sequential Injection” analysis system developed by High Voltage Engineering Europe (Amersfoort, Netherlands) by means of changing the bouncer of the low-energy magnet, the terminal voltage and the electrostatic deflector. Pulsing times of 5 s were dedicated to ^{242}Pu , of 20 s to ^{240}Pu and of 15 s to ^{239}Pu . On average, every sample was measured for about 25 min, divided into 5-min steps. The final instrumental error of the measurement was approximately 2%, as determined from the evolution of the standards. This external error is mainly due to current variations from the ion source. The ^{239}Pu and ^{240}Pu concentrations in the original samples are finally quantified by considering the amount of ^{242}Pu spike added to the samples in a first stage (isotope dilution method).

3. Results and discussion

Tables 1 and 2 show the results for the ^{129}I concentrations, the $^{239+240}\text{Pu}$ activities, and $^{239}\text{Pu}/^{240}\text{Pu}$ ratios measured in various kinds of LLWs, respectively. ^{129}I concentrations are calculated by assuming that the amount of ^{127}I present in the sample is negligible compared to the added carrier. If that is the case, the ^{129}I concentration can be found to be the product of the added ^{127}I carrier multiplied by the isotopic ratio measured by AMS. For ^{129}I analysis, at least two aliquots were independently prepared for AMS measurement for each sample, depending on the amount of sample available. For the determination of Pu isotopes, three aliquots of each sample were prepared.

3.1. ^{129}I and Pu isotopes in normal operation residues

There are very few results concerning ^{129}I concentration or activities in similar samples in the literature. Suarez et al. [13] presented a method of gamma counting for the determination of this radionuclide in ion exchange resins and evaporator concentrates in 1996. However, all the presented values corresponded to samples previously spiked with a certain ^{129}I activity. For these samples, total activities between 0.11 Bq (7.9×10^{13} ats) and 1.84 Bq (1.3×10^{15} ats) were measured. More recently, Park et al. [14]

Table 2
 $^{239}\text{Pu} + ^{240}\text{Pu}$ activities and $^{240}\text{Pu}/^{239}\text{Pu}$ ratios in low-level radioactive residues from Spain.

Sample	Type	$^{239}\text{Pu} + ^{240}\text{Pu}$ activity (mBq/g)	Error (%)	$^{240}\text{Pu}/^{239}\text{Pu}$ (atom/atom)	Error (%)
R-TR-08-02	Dry sludge	7.06	1.4	0.1059	3.0
R-AS-07-04	Resin	49.95	1.2	0.2475	2.5
		25.89	1.4	0.2453	2.8
		37.30	1.3	0.2471	2.7
		30.07	2.0	0.2457	2.7
R-AS-08-01	Resin	15.85	1.4	0.2226	3.5
		1.90	3.5	0.1938	9.5
		10.82	2.0	0.2381	2.8
		13.53	2.5	0.2288	3.3
		2.58	5.1	0.2406	6.4
AS-06-03	Resin	50.31	1.6	0.3508	2.4
		67.85	1.5	0.3565	2.3
		22.60	25.8	0.3585	34
R-CO-09-05	Resin	1050.2	1.3	0.3445	2.1
		1348.8	1.6	0.3658	2.6
		1307.4	1.8	0.3668	2.4
VD-10-01	Resin	8.80	0.20	0.2908	3.1
		7.09	0.19	0.2911	3.6
		7.89	0.38	0.2607	6.3

measured ^{129}I in cement and paraffin samples used for solidifying liquid waste by a gas proportional counter. ^{129}I concentrations ranged between 5.4×10^{13} and 8.1×10^{13} ats/g in cement while in paraffin they varied between 2.6×10^{13} and 7.6×10^{13} ats/g. The minimum detectable activities were calculated to be about 5.0×10^{13} and 2.6×10^{13} ats/g, respectively. Unfortunately, a direct comparison with our results is impossible, as they correspond to different types of samples. However, these values are several orders of magnitude over the typical ^{129}I concentration levels found in this work, thereby demonstrating the higher sensitivity of Accelerator Mass Spectrometry compared with counting methods for ^{129}I detection.

Although the uncertainties of individual measurements of ^{129}I concentrations for each sample are typically between 2% and 15%, it is interesting to see that the differences between aliquots are significant in a number of cases. A similar effect can be appreciated for the $^{239+240}\text{Pu}$ activities measured (Table 2), especially in the case of resins. However, results for Pu isotopic ratios are much more similar between aliquots. These effects can be interpreted as evidence of a strong inhomogeneity in the materials, particularly in resins. It can be explained by the fact that resins originating from several purification processes are mixed in containers before being transported to the LLW storage facility. The total $^{239+240}\text{Pu}$ activity in the resins must be directly related to the volume of liquid that has been filtered through them and to the original concentration of Pu in this liquid.

The samples showing higher $^{239+240}\text{Pu}$ activities could have been studied by either alpha counting or AMS. However, AMS offers two advantages: the possibility of obtaining unambiguous information on the $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio; and the use of a simpler radiochemical procedure, due to the near absence of matrix effects.

Concerning the Pu isotopic ratios, different $^{240}\text{Pu}/^{239}\text{Pu}$ ratios are found for different samples: between 0.225 and 0.359 for resins; and a single value of 0.1059 for dry sludge. The ratios obtained for the resins are very different to those expected for other contamination sources. According to Taylor et al. [15], the expected values of this ratio depend on the origin of the material, with ratios above approximately 0.22 found in nuclear reactors. ^{239}Pu is produced in nuclear reactors from ^{238}U via neutron capture and subsequent beta decay of the resulting ^{239}U ($T_{1/2} \sim 23.47$ min). As well as being fissile, ^{239}Pu undergoes neutron capture within nuclear reactors, thereby producing ^{240}Pu and generating the heavier isotopes

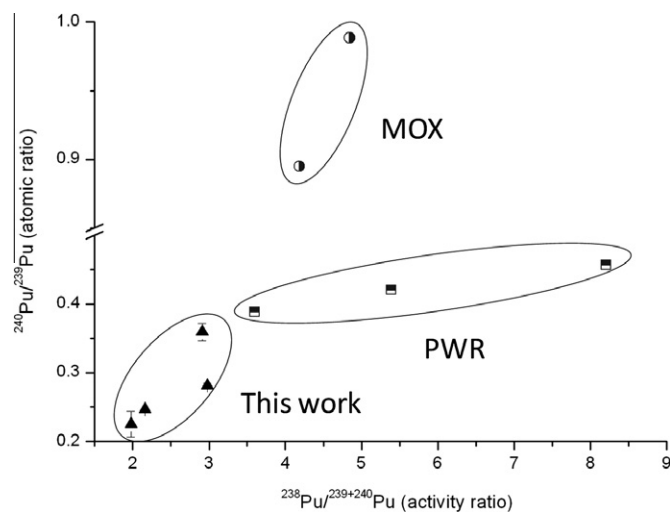


Fig. 1. $^{240}\text{Pu}/^{239}\text{Pu}$ vs. $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratios in LLW samples from Spanish nuclear power plants compared to nuclear fuel values from [15]. MOX–PWR reactors show similar $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratios than PWR but different $^{240}\text{Pu}/^{239}\text{Pu}$ ratios. For the three groups of samples, a positive correlation is suggested. For the samples in this group, a linear fitting results in $^{240}\text{Pu}/^{239}\text{Pu} = 0.04 (0.12) + 0.093 (0.048) * ^{238}\text{Pu}/^{239+240}\text{Pu}$ ($r^2 = 0.482$).

of Pu through successive neutron capture. The $^{240}\text{Pu}/^{239}\text{Pu}$ ratio therefore depends on the composition of the source material and the subsequent irradiation history of the material. Since similar chemical behaviour can be expected from both isotopes, the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio in LLW is expected to reflect the history of the source material, showing higher ratios for fuel of a greater irradiation. This would explain the difference between the $^{240}\text{Pu}/^{239}\text{Pu}$ ratios in our samples. For example, in our results, samples labelled AS correspond to the same nuclear power plant. Although there are just three different samples, an increase in the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio is seen when the total $^{239+240}\text{Pu}$ activity rises. Furthermore, for the samples R-CO-09-05, R-TR-08-02, and VD-10-01, which correspond to different nuclear plants, high $^{239+240}\text{Pu}$ activities are related to high ratios, and low $^{239+240}\text{Pu}$ activities are related to low ratios. However, it remains impossible to establish any unambiguous conclusion from this correlation due to the small number of results.

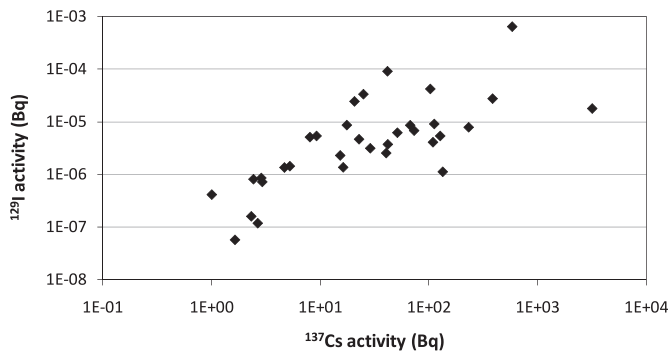


Fig. 2. ^{129}I vs. ^{137}Cs activities in wipes from the José Cabrera nuclear power plant (Spain). A strong variability in both magnitudes can be observed.

Unfortunately, only three samples could be prepared and measured for both ^{129}I and Pu isotopes: R-AS-07-04, R-AS-08-01, and VD-10-01. This renders it unfeasible to obtain much information on the relationship between these radionuclides. However, the highest ^{129}I activities also seem to be related to high $^{239+240}\text{Pu}$ activities and $^{240}\text{Pu}/^{239}\text{Pu}$ ratios.

^{238}Pu activities had been previously measured in some of the measured samples. When plotting the ratio $^{238}\text{Pu}/^{239+240}\text{Pu}$ against the ratio $^{240}\text{Pu}/^{239}\text{Pu}$, a positive correlation can be found (Fig. 1). It is therefore possible to conclude that alpha spectrometry could give as much information as AMS through the measurement of the $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratio. However, a complete characterization of the fuel status through the measurement of Pu isotopes can only be made if both ratios are measured. For example, $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratios in Pressurized Water Reactors (PWRs) and Mixed Oxide Fuel Reactors (MOX–PWR) can be similar [16]. In contrast, $^{240}\text{Pu}/^{239}\text{Pu}$ ratios are lower in PWRs. This can also be seen in Fig. 1, where a comparison is made between the Pu isotopic ratios in our samples and samples measured by Yamana et al. [16]. Higher $^{240}\text{Pu}/^{239}\text{Pu}$ ratios indicate that the fuel has been used for a longer time. The $^{238}\text{Pu}/^{239+240}\text{Pu}$ ratio cannot provide any discrimination between MOX and PWR fuel. However, together with the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio, a total characterization becomes possible. At the same time, the measured $^{240}\text{Pu}/^{239}\text{Pu}$ results for our samples suggest that they have been contaminated by a relatively short use of fuel.

3.2. ^{129}I in wipes from decommissioning activities

In addition to the samples described, a total of 33 wipes from the José Cabrera nuclear power plant decommissioning process are prepared for total ^{129}I activity measurement. These are routinely sampled in order to control possible contamination of surfaces during the dismantling process. Fig. 2 shows these results plotted against ^{137}Cs activity. Although a direct comparison cannot be made since this sampling is not completely systematic, all the wipes were taken in a similar way. The most remarkable conclusion from this figure is therefore the wide range of ^{129}I activities measured, from 5.65×10^{-8} Bq (4.0%) to 6.4×10^{-4} Bq (3.8%). About 80% of the measured values were between 0.1 and 25 μBq . This means that there is an effective and inhomogeneous dispersal of ^{129}I across the various zones of the nuclear power plant, probably in a gaseous form. This conclusion can be extrapolated to shorter-lived iodine radioisotopes and could lead to a map of iodine radioisotope deposition in the plant after a longer study.

As expected, there is a positive correlation between ^{129}I and ^{137}Cs in the wipes, although their activities are not proportional. Indeed, there is a wide range of $^{129}\text{I}/^{137}\text{Cs}$ activity ratios, from 3.3×10^{-8} to 1.3×10^{-5} . However, about 85% of the ratios are be-

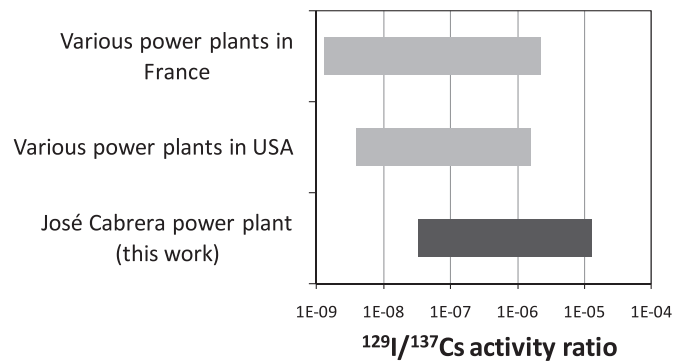


Fig. 3. Comparison between $^{129}\text{I}/^{137}\text{Cs}$ ratios in wipes from the José Cabrera nuclear power plant (Spain) and model calculations in various power plants from France and USA [8].

tween 5×10^{-7} and 100×10^{-7} . It is possible to compare these ratios to those calculated by Hwang and Lee [17] in test resins from various nuclear power plants in USA and France by means of mathematical models (Fig. 3). Wide ranges of this ratio are found for these plants as well, but on average they appear to be one order of magnitude lower than our results in wipes.

4. Conclusions

It has been shown that Accelerator Mass Spectrometry is a powerful tool for the characterization of low-level residues from nuclear power plants, both from normal operation and decommissioning. This enables the determination of the concentrations of long-lived radionuclides that must remain below certain specified levels in these materials in order to qualify for the LLW classification. Furthermore, the evaluation of activities and isotopic ratios of radionuclides, such as ^{129}I , ^{240}Pu , and ^{239}Pu , provides data on the origin and the history of these residues. They can provide information about the type of fuel used, its burning level, and about other processes in operation in the nuclear power plants.

Finally, the measurement by AMS of ^{129}I contamination monitoring of materials during decommissioning has also been found to be a highly useful tool and could be employed to monitor the dispersal of other I isotopes inside nuclear power plants, as well as contamination monitoring.

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