Radiochemical Characterization of a waste stream at the Petten's High Flux Reactor: The Case of Ion Exchange Resins

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ABSTRACT

The High Flux Reactor (HFR) in Petten (NL) has been producing medical isotopes for several decades. Additionally, the HFR is used for many experiments including fuel/material tests. Over the years, Ion Exchange Resins (IER) that are used for the purification of the primary circuit and the basin have been replaced. Spent IER were accumulated and stored on site. Over time, the IER has become a historical waste issue that needs to be solved pragmatically as space to store them on site becomes scarce. This paper provides an overview of the characterization methodology needed to manage the Ion Exchange Resin wastes.

1. INTRODUCTION

The High Flux Reactor (HFR) is located on the nuclear site of Petten, in the north of the Netherlands. The reactor has been used, since its commissioning over fifty-five years ago for medical isotope production as well as for material/fuel research.

For most types of reactors, ion exchange resins (IER) are used to purify the primary water circuit and the water basin of soluble radionuclides. When the performance of the IER decreases, they are regenerated using acidic and basic media. After a few regeneration cycles, IER are considered spent and must be replaced. The spent IER is then discharged in containers and stored on site before (final) disposal.

Changes in waste processing and regulations in 1998 resulted in the accumulation of containers with spent IER. Since then, every other year two new batches of containers with spent IER (one anionic and one cationic) are added to the already large stockpile of waste containers.

In Table 1, the amount of containers accumulated is organized by batches according to its year of anionic IER replacement.

Table 1: Spent IER Contingent by year

Year of replacement/Batch	Amount of containers
2004	16
2009	19
2010	9
2011	10
2012	19
2014	22
2017	24
Total	119

The IER-containers need to be disposed of before the on-site storage facilities are full. A number of disposal options have been studied, from cementation to steam reformation processes. Incineration of the waste seems to be the most efficient and the most economically advantageous. To proceed in that direction, characterization of the spent IER was required. The IER can be anionic and cationic. The anionic ion exchange resins are the first to be characterized and treated as they are lower in activity.

A set of non-destructive analyses (gamma spectrometry) and of destructive analyses (beta-nuclide, total alpha, total beta) was developed.

The established characterization route is divided in three stages:

1. Establishing the degree of homogeneity within a batch by measuring Co-60 content.
2. Non-destructive analysis:
    a. gamma-spectrometry.
3. Destructive analyses for emitting nuclides:
    a. total-α/total-β via Liquid Scintillation Counter (LSC)
    b. Nuclide-specific analyses already implemented: H-3; Fe-55; Ni-63; Sr-90
    c. Nuclide-specific analyses to be implemented: C-14; Cl-36; Tc-99

In the following chapters the three stages are described in more detail.

2. CHARACTERIZATION STRATEGY:

The two main considerations are:

1. Acquiring representative data of the waste
2. Minimizing the amount of samples to be analyzed for cost-efficiency reasons

The following approach was then implemented:

1. Check the homogeneity within one container to eventually minimize the number of samples per container to one.
2. Check the homogeneity within a batch to eventually minimize the number of samples per batch to 3 or 4.
3. Perform the complete analyses (Non-destructive and destructive) on the 3 or 4 samples per batch.
4. Compile the results to obtain a complete characterisation of the spent IERs.

3. HOMOGENEITY AND REPRESENTATIVITY OF THE WASTE STREAM

The homogeneity or lack of homogeneity of the waste has serious implications on the amount of samples analyses that need to be performed. The HFR is used as a material test reactor and as an isotope producing reactor. The conditions to which the water is exposed to are not always constant and the procedure, even though repeated, is never exactly reproduced. The concept of nuclide vectors can *'a priori'* not be applied and requires validation testing: to apply a nuclide vector on a batch, the content should be homogeneous to a certain extent.

In the International Atomic Energy Agency (IAEA) publication, "Strategy and Methodology for Radioactive Waste Characterization", the following recommendation is found about the approach on homogeneity:

“[…]For stable waste streams, measuring one or more key nuclides and non-radioactive elements may be sufficient to check the homogeneity. For example, a simple and stable waste stream could be declared homogeneous if NDA measurements of 137 Cs and/or 60 Co made at different locations are within a 30% relative interval.[…]” [1]

NB: This value is calculated as follows: Considering a pool of results the average is calculated and 30% of the average is applied to determine the + and – range of acceptable results to validate the homogeneity conditions.

Cs-137, as a fission product, is too low to be easily measured in the batch resin samples. However Co-60 as an activation product was more reliable as a check on the homogeneity. Co-60 was measured directly after sampling by gamma spectrometry.

Homogeneity within a container

The content may not only be different between containers and batches but even within a container, heterogeneity might occur (see Figure 2 for a schematic view). For example, cobalt is mainly stable in water as oxidation state +2 [2] and potentially not bound to the resins, over time residual water would accumulate at the bottom of the container and end in a gradient concentration of Co-60. To check the internal homogeneity of a container, several samples were taken on selected containers corresponding to different zones of the container (see Figure 2). This internal container homogeneity test was performed on three different batches and in total on 7 containers (see Table 2).

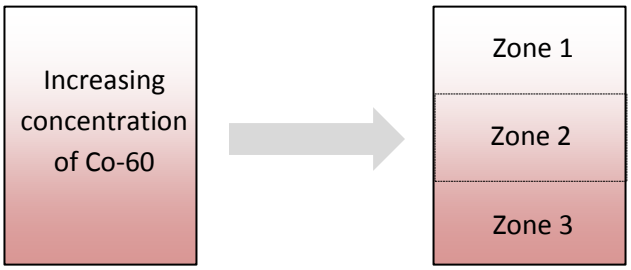

Figure 1: Potential inhomogeneity in the distribution inside a container (left) and sampling zone proposal for internal homogeneity check (right)

The sampling procedure is simple but requires preparation with regard to radioprotection. It is divided in 5 major steps:

1. Recovering of the container to be sampled from the storage facility and transporting it to the sampling area.
2. Sampling using a plastic tube (e.g. a large syringe) and collection in a 500mL PE bottle.
3. Closing of the container and transporting the container back to the storage facility.
4. Radiological control of the surface of the PE bottle.
5. Transport of the PE bottle to the laboratory for characterisation purposes (primarily gamma analysis).

In the case of the anionic resins, the dose rate is extremely low ranging from 8µSv/h (most of the containers sampled) to 110 µSv/h (for containers of the latest batch). Consequently, the handling

of the containers and the procedure did not require extra precautions. Overall, the procedure proved to be handled quickly and exposure was kept at a minimum. A picture of the filling up of the container when replaced and a picture of the sampling of the IER are shown in Figure 2.

Figure 2: Replacement of the IER (filling of the containers; left) and sampling of a IER filled container (right)

4. OVERVIEW OF THE SAMPLES TAKEN

Table 2: Overview of the samples taken

Batch	Total containers	Containers sampled	Container internal homogeneity check
2004	16	6	Yes, on 2 containers
2009	19	5	No
2010	9	4	No
2011	10	8	Yes, on 1 container
2012	19	9	Yes, on 4 containers
2014	22	7	No
2017	24	4	No

The internal homogeneity was checked on the 2012, 2011 and 2004 batches. The results were considered to be suitably consistent, therefore no more tests were performed.

5. DEMONSTRATING HOMOGENEITY WITHIN A BATCH

To demonstrate homogeneity within a batch (all the waste containers from a single resin exchange), the Co-60 activity was measured using gamma-spectrometry runs and results were reported per batch.

Seven batches (corresponding to the seven occurrences of IER replacement in the last 20 years) were analyzed and can globally be divided into three groups: Scattered results (Type I) but within the “homogeneity boundaries” (2 out of 7), variable (Type II) (2 out of 7) and homogeneous (Type III) (3 out of 7). The three groups are presented below.

- **Type I: scattered Co-60 activities:**

Table 3: Results for batch 2004

Container sampled	Co-60 (Bq/g)	Uncertainty (%)
1 (Zone 1)	7.95	5
1 (Zone 3)	8.09	5
2	8.86	5
3	13.00	5
4 (Zone 2)	12.20	5
4 (Zone 3)	11.40	5
5	12.00	5
6	8.24	5
Average	10.22	
Boundary (+/- 30%)	3.07	

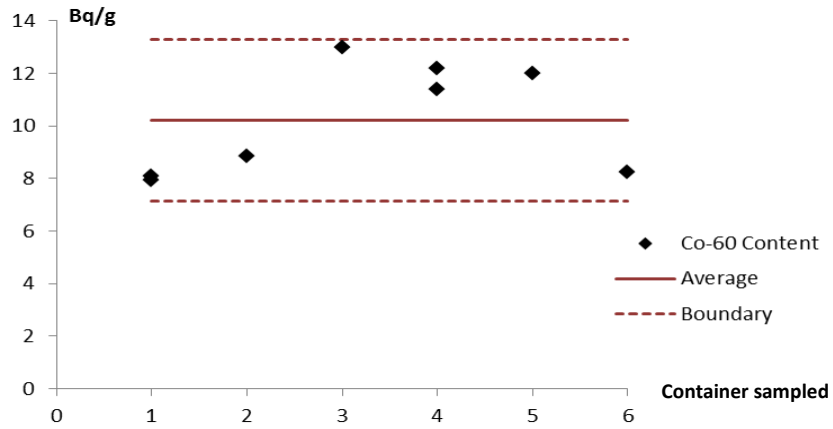

Figure 3: Graphic representation of batch 2004 (scattered batches).

Conclusion and remarks:

Despite scattered results, the measured values are within the boundaries and the batch is classified as homogeneous. Anyhow, for more conservatism, the results obtained in the later analysis for the container represented by sample number 3 for the other radionuclides will be applied to the rest of the batch.

- **Type II: "variable":**

Table 4: Results for batch 2010

Container sampled	Co-60 (Bq/g)	Uncertainty (%)
1	21.6	4
2	19.2	4
3	17.7	4
4	9.79	4
Average	19.5	
Boundary (+/- 30%)	5.9	

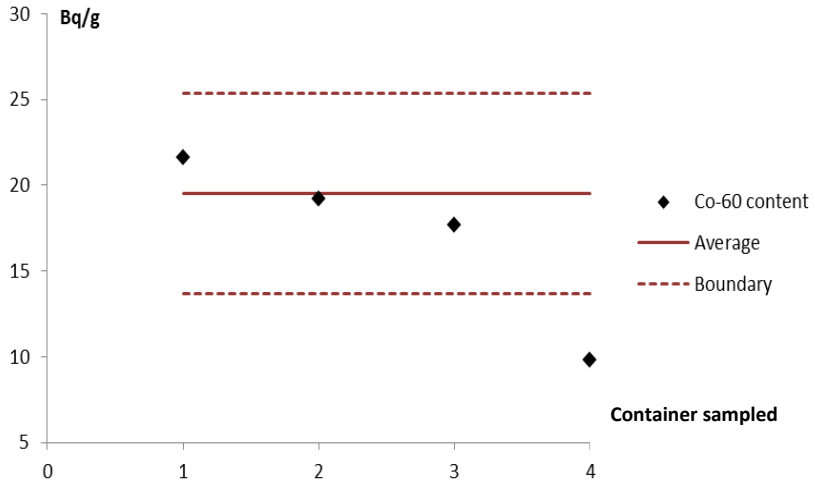

Figure 4: Graphic representation of batch 2010 (a variable gradient batch).

Conclusion and remarks:

The sample from container 4 is taken from the last container of a batch and contains residual water with little resin. Therefore, the average value calculated ignores this last value. Still, for more conservatism, the results obtained from the analysis of other radionuclides within the batch will be applied to this container (namely other gammas emitting radionuclides and H-3; C-14; Cl-36; Fe-55; Ni-63; Sr-90).

- **Type III "homogeneous":**

Table 5: Results of homogeneous batch 2012

Container sampled	Co-60 (Bq/g)	Uncertainty (in %)
1 (Zone 1)	24,8	4
1 (Zone 2)	26,0	4
1 (Zone 3)	27,5	4
2	24,2	4
3	24,4	4
4 (Zone 1)	25,3	4
4 (Zone 2)	24,7	4
4 (Zone 3)	25,6	4
5	25,8	4
6	26,6	4
7	25,4	4
8 (Zone 1)	23,7	4
8 (Zone 2)	24,4	4
9 (Zone 1)	26,2	4
9 (Zone 2)	25,0	4
9 (Zone 3)	25,6	4
Average	25,3	
Boundary (+/- 30%)	7,6	

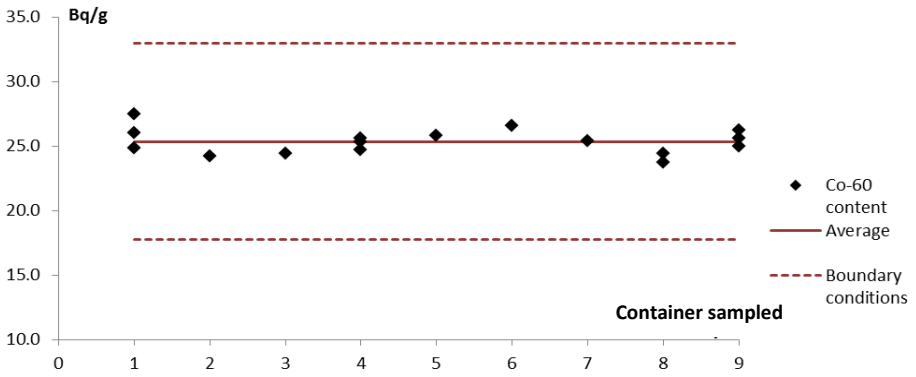

Figure 5: Graphic representation of one of the homogeneous batches

Conclusion:

Different zones have been sampled in containers 1, 4, 8 and 9. The results given in Table 5 show a homogeneous behavior. The nine containers sampled in this batch behave homogeneously.

- **General conclusion and further remarks:**

For all the batches, values are within the 30% boundaries, except for one container in one batch with a very low Co-60 level. Homogeneity has thus been determined for these batches.

6. SECOND STAGE: EVALUATION OF NUCLIDE CONTENT VIA NON-DESTRUCTIVE ANALYSIS

NB: The method developed and results presented below are simplified for commercial and confidentiality reasons.

NB2: In total more than 50 samples have been treated for gamma spectrometry, only the general conclusions will be discussed in the following paragraph.

Gamma spectrometry:

Gamma spectrometry is the primary analysis performed. The same conditions are applied for all the samples: geometry and quantity of IER are strictly identical. A HP Ge detector N-type is used for detection and the software *Genie 2000*® is used for the calculation and analysis of the spectra.

The main gamma emitting nuclides found in anionic resins are Co-60 and Sb-125. Traces of europium isotopes and for one batch a cadmium contamination (Cd-109 and Cd-113) were also found.

Total alpha and total beta:

Results on total alpha/total beta activity are obtained by measuring the resins in a gel suspension with a LSC and by evaluating the overlap between the alpha and beta emitting particles.

The overlapping alpha and beta response is solved with the following protocol. During the

measurement, quenching corrections and cross-talk corrections between alpha- and beta-particles are performed by the LSC. However, there are order of magnitude differences between the alpha and beta activity, and a correction for the error in the quantification needs to be applied. Due to overwhelming beta activity compared to the alpha activity, beta-particles are read as alpha-particles. Pure alpha and beta sources, adsorbed onto blank resins, are used to determine the error in the quantification for the activity level of the sample and correction are applied.

On a general level, almost no alpha emitting particle content is detected , typically less than 2 Bq/g, whereas the of beta activity ranges from 200 Bq/g for the oldest batch up to 15,000 Bq/g for the freshest one.

7. THIRD STAGE: NUCLIDE CONTENT EVALUATION VIA DESTRUCTIVE ANALYSIS

NB: The method developed and results presented below are simplified for commercial and confidentiality reasons.

The recurring beta-emitting nuclides identified during waste characterization are: H-3; C-14; Cl-36; Fe-55; Ni-63, Sr-90; Tc-99 [3]. Over the past year, detection methods for Fe-55, Ni-63 and Sr-90 have been developed at NRG and will get ISO 17025:2005 certified in the near future. The method to measure H-3 is already ISO17025 accredited.

In about a year, NRG developed a strategy to measure most of the nuclides using the same samples and by applying co-precipitation and column separation techniques. A general description of the procedure is given Figure 6.

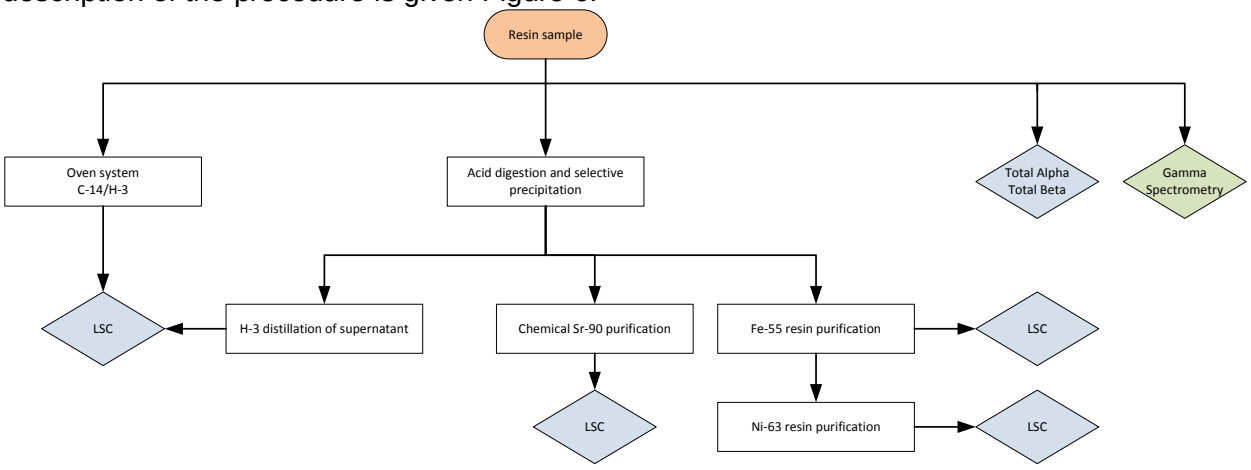

Figure 6: Overview of the characterization route for resins samples

Sample preparation and specific measurements:

The desired radionuclides (except potentially for C-14) are located on the surface of the resins, for further measurements it is then required to have those radionuclides transferred from the surface into solution. Two approaches are possible:

- Leaching: Milder conditions and “lighter” chemistry,
- Total destruction of the IER with a combination of acidic and oxidative media.

The second approach was chosen after a few tests, mainly due to uncertainties about the conditions in which the IER would be found. The destruction setup includes the use of strong acids. Resins beds are heated in concentrated sulphuric acid and concentrated nitric acid is

added at a later stage to oxidize the beds. A photo of the setup of the destruction of the IER is shown Figure 7.

Figure 7: Setup for the IER destruction

The main drawback of the total destruction is the matrix in which the nuclides of interest are, making the precipitation/separation/purification path more complex. In the analysis protocol, we choose a cascade of selectivity to recover the nuclides of interest from the resins. To achieve this, a selection of precipitation, filtration and specific selective column are used.

Internal standard methods are used to calculate the recovery rate of the treatment. This means two analysis are carried at the same time, using the exact same amount of material from the sample, one of them being spiked with an internal standard of a known content. The recovery rate is calculated and can be applied on the targeted sample to determine the desired content.

Measurements:

The results collected in the measurements are given below in Table 6 showing excellent results for this representative container.

Table 6: Recovery measurement for the concerned nuclides

Nuclide	Internal standard added [Bq]	Internal standard recovered [Bq]	Recovery [%]	IER activity [Bq/g of resin]
H-3	582	474	81	744
Sr-90	672	493	73	10
Fe-55	1992	1455	73	5172
Ni-63	679	388	57	5

Further method developments and quality control:

Currently the Tc-99 method using a similar path is under development at NRG.

Additionally, a pyrolyser was acquired for measurement of C-14 and Cl-36. Development of the method will occur in the first half of 2018. At the moment, these measurements are performed by other labs.

Parallel to the method developments, the compliance and accreditation of some methods to the norm ISO 17025:2005 (or the updated 2017 version) is the primary goal of the whole characterization in the quality assurance domain.

8. CONCLUSION

The analysis and characterization of the IER coming from Petten's nuclear reactor were necessary steps for NRG to allow their waste treatments. By developing the necessary radiochemical techniques in a challenging time frame, NRG not only obtains excellent results on the different batches of IER but also demonstrates its capacity to overcome some of the long lasting challenges within waste management. The breakdown of the main issue into smaller independent issues, as well as the early stage involvement of all the different stakeholders was and still is a key component of the success of this project.

The practical case of IER is representative of the issues currently encountered by many waste producers. The approach developed by NRG is foreseen to fit with various types of waste streams, from various sources, allowing in the long term to standardize the approach on waste management not only at NRG and in the Netherlands but also internationally, for the rest of the nuclear community.

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[3] An introduction to nuclear waste immobilization, second edition, chapter 12, 2014, M.I. OJOVAN; W.E.LEE