Characterization of Radioactive Spent Ion-Exchange Resins - 11144

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Abstract

This paper describes the sampling process, presents the initial results of analyses, and reports the method used to assess the homogeneity of spent ion-exchange resin collected as radioactive waste from the IEA-R1 research reactor water polishing system. Two batches of spent resins are stored in seven 200 L steel drums, the homogeneity of which was evaluated through results of distribution of $^{137}$Cs and $^{60}$Co concentrations, measured by gamma spectrometry of samples taken from different locations in the waste containers.

Keywords: spent ion-exchange resin, radioactive waste, homogeneity

1. Introduction

Spent ion-exchange resins replaced from the water re-treatment system of the IEA-R1 reactor are one of the most radioactive wastes collected by the Radioactive Waste Laboratory at the Nuclear and Energy Research Institute (IPEN-CNEN/SP). These are anion and cation Lewatit Mono Plus S100/MP500 mixed bed ion-exchangers purchased from Bayer Chemicals, and used in the reactor’s primary circuit water polishing system.

The IEA-R1 reactor is a 5 MW swimming pool reactor designed by Babcock and Wilcox, used for research and production of radioisotopes in São Paulo, Brazil. The first criticality in September 16, 1957 and the start of routine operation in January 25 of the next year make it the world’s fifth oldest research reactor with power above 1 MW still in operation [1].

The Radioactive Waste Laboratory is responsible for managing the radioactive wastes from IPEN-CNEN/SP’s operational and decommissioning activities. In addition, receives spent sealed radioactive sources and long-lived wastes with activities above clearance levels from users of radioisotopes for proper treatment. Its duties include: collecting, transporting, characterizing, treating, and storing the radioactive wastes in a form ready for disposal in a final disposal site. Although Brazil has not yet built this repository, waste acceptance criteria are already established and their requirements apply to waste packagings.

Since the IEA-R1 started operation, the ion exchange resin bed was replaced only two times: one in 1993, and one in 2003. One possible explanation for the longer period of usage of the first batch is the operation of the reactor mostly at 2 MW, in daily shifts of 8 hours, four days per week, with about two regeneration campaigns a year.

The waste management policy at IPEN-CNEN/SP is to keep radioactive discharges to the environment below regulatory limits and as low as reasonably achievable. However, the in situ waste management practice in the IEA-R1 building is still the original process of regenerating the resin beds when they are loaded and discharging the eluate into the sewage system, after a few days storage in a sampling and monitoring tank. With two redundant beds, regeneration takes place three to four times a year. When the exchanger is no longer capable of maintaining the quality of the reactor coolant system water, it is replaced and the spent bed is sent to the Radioactive Waste Laboratory for treatment as solid radioactive waste.
Both replaced batches were collected before the means to characterize and treat them properly were in place and, consequently, these wastes were kept under extended storage for decay. Spent resins were collected into polyethylene bags, inside eight 200 L drums and stored at the untreated waste storage room, without any further chemical or physical treatment. Now, the Radioactive Waste Laboratory is developing plans for immobilizing them [2]. A complete chemical and radioisotopic characterization is required as a first step of the treatment process.

The radioisotope composition of different spent resin drums is expected to vary because of high or low radioactive load after the last regeneration event and different decay times after withdrawal from the reactor, but also due to variations in the reactor operational conditions while the resin bed was in the reactor's water polishing system. Variation of operational conditions includes changes in operational plans such as duration of the weekly continuous operation schedule, thermal power history in each period, the extent of defects in fuel plates in the reactor core, etc.

In addition, the moisture content of packages may diverge largely, some drums containing much more water than the exchanger proper. The water contained in the slurry is expected to be only slightly radioactive because the resins concentrate the totality of the radionuclides that otherwise would be dissolved. However, a fraction of the activity may be in colloidal form, bound to small solid particles suspended in the slurry. Due to these facts and also due to differences in the specific mass of anion and cation resins, the concentration of radioactive species differs not only between different drums but also between top and bottom layers inside each drum, depending on the specific degree of segregation of cation and anion resin beads.

Therefore, the sampling and characterization of each package were done adopting the premise that this waste is essentially a non-homogeneous material. Accordingly, samples were collected from two or three depths in the slurry of each drum.

Sampling of wastes must be carried out systematically using proven techniques since errors in waste composition may result in waste packages that are not in conformity with acceptance criteria for disposal, adversely affecting a repository. In addition, this work addressed increasingly strict requirements for quality and reliability of information about radioactive waste characteristics. It must be stressed that sampling activities had to be minimized to avoid high personnel exposures and because of the impossibility of remotely sampling spent resin drums under the current capabilities of the Radioactive Waste Laboratory.

Therefore, the sampling had to be planned carefully not only because of the radiation hazard but mainly because the sampling is one of the largest sources of uncertainty in the process of activity measurement. Homogeneity, representativeness, water content, and traceability of the sampling and measurements results were considered in sampling the waste.

These activities are part of a program to establish the protocols for sampling and analyzing the stored wastes, aiming at complying with regulatory requirements, gathering data to subsidize the definition of treatment processes, and finding scaling factors and correlation functions that allow calculate the activities of difficult to measure (DTM) radionuclides present in the wastes.

Scaling factor and correlation functions apply to reasonably homogeneous wastes, but as stated before, the spent resins can be considered non homogeneous waste in respect to radionuclides activity concentrations. However, the influence of some factors that affect homogeneity, for instance water content or decay time can be eliminated by correcting the results appropriately. The influence of factors that can not be eliminated, as reactor operation parameters for example, will be examined and the applicability of scaling factors for this waste eventually determined as a result of the work.
This paper describes the sampling process, presents the initial results of analyses and the assessment of homogeneity through the results of distribution of $^{137}\text{Cs}$ and $^{60}\text{Co}$ concentrations in the wastes, measured by gamma spectrometry of the samples, following the criterion recommended by IAEA [3].

2. Methods

2.1. Sampling

Sampling of spent resin drums was performed using a homemade thief sampler. A thief sampler consists of two slotted concentric tubes, the outer tube fitted with a conical pointed tip that permits the sampler to easily penetrate the material being sampled. It was made of PVC piping with three rectangular holes cut through both tubes each hole giving access to a chamber in the inner tube.

The sampling ports are opened or closed by rotating the inner tube. It allows taking samples simultaneously from bottom, middle, and top layers, thus allowing detecting stratification of the waste volume. The sizes of holes and inner chambers were such as to allow collecting a few tens of grams of waste in each port. Figure 1 (a) shows the sampler being inserted in the plastic bag of one waste drum and (b) a sample being transferred from the lower sampling chamber to a sample container.

Some drums contained the resins with low water content packed in as many as five separate polyethylene bags; in sampling these drums a scoop was used instead. Additional water samples from drums with large water content were taken with pipettes to allow measure activities in the resin proper and in the supernatant. Each sample contained about 30 grams (wet basis) of resin beads or water supernatant. All samples were then transferred to the analytical laboratory of the Radioactive Waste Laboratory.

2.2. Analysis

In the laboratory, three or four aliquots taken from each resin sample were dried in stove at 80°C for 24 hours, dry mass between 0.5 and 1.5 grams, and counted in polyethylene counting vials in geometries previously calibrated with certified standard sources. Aliquots were counted in Canberra Co-axial, Hyper-Pure P-type Germanium Detectors, models GX2020, relative efficiency of 20%, and GX4510, 45% relative efficiency. The peak to Compton ratio is 52.5:1. Energy calibration was done with certified Amersham $^{152}\text{Eu}$ and $^{210}\text{Pb}$ point sources. Eu-152 has well-defined photopeaks from 122 keV to 1,408 keV and $^{210}\text{Pb}$ presents a
photopeak in 46.5 keV, thus allowing calibration over the entire useful range of gamma energies of the equipment. The counting efficiency was determined by spiking 45 mm diameter x 3 mm thick cellulose filter discs with 51.78 Bq of $^{152}$Eu and 22.36 Bq of $^{210}$Pb drawn from Amersham calibrated solutions, and counting them inside the plastic containers used for counting the waste samples.

Data acquisition and spectral analyses was performed with the Genie 2000 software from Canberra Industries. To lower the counting errors due to high detector dead time, same aliquots of about 1 g were used in the gamma spectrometry.

The following radionuclides were searched for in samples: $^{54}$Mn, $^{58}$Co, $^{60}$Co, $^{65}$Zn, $^{92}$Nb, $^{94}$Nb, $^{106}$Rh, $^{108}$Ag, $^{110m}$Ag, $^{126}$Sn, $^{125}$Sb, $^{126}$Sb, $^{134}$Cs, $^{137}$Cs, $^{154}$Eu, $^{155}$Eu, $^{211}$Am.

Aliquots were counted for 60 minutes with lower detection limits between 2 and 8 Bq per one gram of resin, under the above counting conditions.

The homogeneity criterion recommended by IAEA [3] is to measure the concentrations of $^{60}$Co and/or $^{137}$Cs in samples taken from different locations in the waste volume, and verify whether results are within a 30% relative interval, for a simple and stable waste stream to be declared homogeneous.

3. Results

Nineteen samples of ion-exchange resins and water supernatant were drawn from the content of the 7 drums. The two drums that contained the ‘1993 batch’, with apparently dry resins packed into four and five plastic bags, yielded nine samples. Each of the five ‘2003 batch’ drums contained the resins in a single polyethylene bag and yielded seven samples of resin and three supernatant water samples. Samples with about 30 g were drawn and from each sample, aliquots of about 1 g were used in the gamma spectrometry.

All resin aliquots contained $^{60}$Co and $^{137}$Cs in relevant quantities and all other gamma emitters below minimum detectable limits. A complete analysis of alpha, beta, and gamma emitters is underway following the methods described by Tavcar et al.[4] and will be reported later. Table 1 shows the average concentration plus/minus standard deviation (68% confidence interval) of $^{60}$Co and $^{137}$Cs activities, in the n indicated aliquots of each sample, corrected for decay to the date of discharge from the reactor.

<table>
<thead>
<tr>
<th>Waste container Id.</th>
<th>No. of Aliquots</th>
<th>$^{60}$Co concentration ± 1 sd [Bq.g$^{-1}$]</th>
<th>$^{137}$Cs concentration ± 1 sd [Bq.g$^{-1}$]</th>
<th>$^{60}$Co to $^{137}$Cs ratio ± 1 sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drum 1</td>
<td>bag 1</td>
<td>3</td>
<td>5767 ± 113</td>
<td>63 ± 2.2</td>
</tr>
<tr>
<td></td>
<td>bag 2</td>
<td>3</td>
<td>486 ± 10</td>
<td>4.0 ± 0.23</td>
</tr>
<tr>
<td></td>
<td>bag 3</td>
<td>4</td>
<td>5232 ± 100</td>
<td>58 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>bag 4</td>
<td>3</td>
<td>5643 ± 102</td>
<td>62 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>bag 5</td>
<td>3</td>
<td>7255 ± 94</td>
<td>69 ± 2.2</td>
</tr>
<tr>
<td>Drum 3</td>
<td>bag 1</td>
<td>3</td>
<td>3300 ± 67</td>
<td>35 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>bag 2</td>
<td>4</td>
<td>3488 ± 61</td>
<td>37 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>bag 3</td>
<td>4</td>
<td>3976 ± 94</td>
<td>40 ± 5.0</td>
</tr>
<tr>
<td></td>
<td>bag 4</td>
<td>4</td>
<td>3784 ± 59</td>
<td>39 ± 1.4</td>
</tr>
<tr>
<td>Drum 10 bottom</td>
<td></td>
<td>4</td>
<td>211074 ± 3768</td>
<td>3095 ± 113</td>
</tr>
<tr>
<td>Drum 11 bottom</td>
<td></td>
<td>3</td>
<td>104897 ± 2081</td>
<td>442 ± 21</td>
</tr>
<tr>
<td>Drum 12 bottom</td>
<td></td>
<td>3</td>
<td>89935 ± 1785</td>
<td>445 ± 23</td>
</tr>
<tr>
<td>Drum 14 bottom</td>
<td></td>
<td>4</td>
<td>53651 ± 987</td>
<td>219 ± 16</td>
</tr>
<tr>
<td>middle</td>
<td></td>
<td>4</td>
<td>87382 ± 1431</td>
<td>350 ± 21</td>
</tr>
<tr>
<td>Drum 16 bottom</td>
<td></td>
<td>4</td>
<td>142109 ± 2010</td>
<td>1785 ± 62</td>
</tr>
<tr>
<td>middle</td>
<td></td>
<td>4</td>
<td>154400 ± 2571</td>
<td>1950 ± 64</td>
</tr>
</tbody>
</table>

Table 1 – Mean concentration of $^{60}$Co and $^{137}$Cs in dry aliquots of spent resin samples.
These results were used to evaluate the homogeneity of this waste stream in respect to stratification inside the same container, or between different containers from the same batch, and between the batches collected in 1993 and 2003. Figure 2 shows a plot of concentrations measured in each sample and the ±30% boundary around the mean concentration of each drum or group of drums, used as a criterion of homogeneity.

Differences between the results of 1993 and 2003 activities, corrected for the date of discharge from the reactor, are unexpectedly large. Also, in each batch, two distinct groups are consistently identified, indicating some source of inhomogeneity in the waste stream. The differences are larger for $^{137}$Cs in the two groups of the ‘2003 batch’, which is evidenced by the ratios of $^{60}$Co to $^{137}$Cs activities shown in the last column of the table 1 and in the graph of Figure 3. The causes of this unexpected difference need further investigation.

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**Figure 2** – Average activity concentrations of $^{60}$Co and $^{137}$Cs in samples from each waste container of spent ion-exchange resins, as indicators of homogeneity of the waste stream.

**Figure 3** – Ratio of the activities of $^{60}$Co and $^{137}$Cs in samples from each waste container.
Results of activity concentrations in samples from the same drums of the ‘1993 batch’ are very close and likewise the results of samples from the ‘2003 batch’ are almost completely fenced by the ±30% boundary in each of the two groups of containers.

Finally, it was found one order of magnitude lower concentrations of both $^{60}$Co and $^{137}$Cs in bag 2 of the drum No. 1.

4. Discussion and conclusions

The differences of concentrations between different strata, or between different bags, in the same drum are small as expected. However, the differences between some drums of the same batch may indicate segregation of anion/cation beads during the transfer of the slurry from the resin tank to the waste containers. This hypothesis will be examined by analysis of radioisotopes in anionic form present in each group of samples.

As pointed earlier, different concentrations between different batches of spent resins was expected as a result of differences in the operational parameters of the reactor operation during the two corresponding periods. However, the large observed disparity is most probably the result of regeneration of the resin beds before transfer to the waste containers. The reactor operators justified the regeneration of resins prior to discharging them, as a means to reduce exposures during handling of the waste drums. Evidence for this explanation is the similar ratios of $^{60}$Co and $^{137}$Cs concentrations, taking into account that both radioisotopes are produced by distinct processes in the reactor core.

The outlier results obtained with sample from bag 2 of drum No. 1 will be further examined in order to determine the reason for the low activity concentration found in that container.

The assessment of the homogeneity of this waste stream made it possible to better understand its nature and properties and, also important, allowed to further examine the possibility of using scaling factors or correlation functions to estimate the activities of difficult to measure radioisotopes in this or in other waste streams.

References


