CHARACTERIZATION OF RADIOACTIVE WASTES – SPENT ION-EXCHANGE RESINS AND CHARCOAL FILTER BEDS

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ABSTRACT

In the present paper we report the initial results of the work undertaken at the Radioactive Waste Management Laboratory (RWML), in São Paulo, Brazil, to develop sampling procedures and analytical methods applied to the characterization of radioactive wastes, specifically spent ion-exchange resins and charcoal filter beds generated at the IEA-R1 Research Reactor operated by the Nuclear Energy Research Institute (NERI). The work objectives are to characterize those wastes to comply with regulatory requirements, to generate data to support the development of treatment processes, and to improve characterization methods and laboratorial infrastructure.

1. INTRODUCTION

Since its first startup in September 11 1957 [1], the water treatment system of the IEA-R1 Research Reactor, operated by the Nuclear Energy Research Institute (NERI), in Sao Paulo, Brazil, periodically generates radioactive wastes constituted of spent ion-exchange resins and charcoal filter beds. Contact dose rates are in the range of tens of millisievert per hour and the total volume is about two cubic meters. These wastes are collected in 200 L steel drums with polyethylene liners and stored at the interim waste storage building of the Radioactive Waste Management Laboratory (RWML) awaiting for treatment and immobilization.

Both wastes must be solidified in a cement matrix by a process that is under development and for which a license application will be submitted to the regulatory authority. Meanwhile, the chemical and radiological characterization work is being done as a preparatory work for treatment and solidification process, to satisfy regulatory directives that require the specification of the radioactive content of each waste package [2].

The ion-exchange resins and the charcoal beds contain fission and activation products and may contain actinides as well.

RWML is conducting a program to develop analytical methods aiming at establishing the sampling and analytical protocols for characterizing radioactive wastes. The targets of the waste characterization program are three fold: 1) to comply with regulatory requirements concerning the radiological inventory of the wastes treated at the RWML facilities, 2) to

gather data that will support the definition of treatment and immobilization processes of those wastes, and 3) to find scaling factors that allow calculational methods to be employed in characterizing nuclear reactor wastes. Scaling factors and correlation functions are sometimes the only available methods for routine characterization of radioactive waste which contains difficult-to-measure radionuclides (DMR) [3]. The primary aim of the program is the formation of a laboratorial infrastructure and expertise on radioactive waste characterization, and establishing internal protocols for waste characterization at the RWML.

In the present paper we report the initial results of the ongoing research work on development of sampling procedures and analytical methods applied in the characterization of spent ion-exchange resins and charcoal filter beds.

2. METHODS

2.1. Sampling

Sampling of resin and charcoal granules was performed with a 'concentric three-slot tube thief', a device that consists of two tubes, one fitting closely inside the other, the bottom end of the outer tube fitted with a point, and with three oblong holes cut through both tubes in front of chambers in the inner tube. The holes are opened or closed by rotating the inner tube. See figure 1.
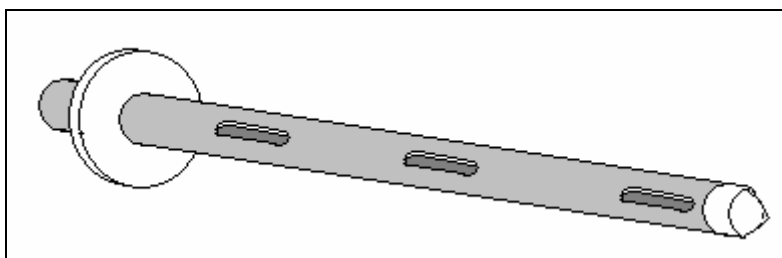

Figure 1 – concentric, three-slot tube thief sampler

Figure 2 and figure 3 illustrate the sampling procedure. First, insert the device into the waste material to the bottom of the drum, with the holes closed (Figure 2). Second, rotate the concentric tubes to the open position allowing the grains to flow into the sampling chambers. Third, rotate the tubes to the closed position and withdraw the sampler. Fourth, immediately place the sampling device over a sample collection sheet, release the samples by opening the holes and remove the samples with a spatula or spoon and place them in the sample container (Figure 3).

This sampler takes samples simultaneously from the bottom, the upper and the intermediate parts of the drums, thus allowing detecting any stratification of the waste volume.

Samples are indentified as bottom, upper or intermediate representing the layer from where they were withdraw. Some drums contained the wastes separated in as many as five polyethylene bags; a scoop was used instead in sampling of these drums.

Additional water samples from drums with large water content were taken with pipettes to allow discriminate activities in the resin or charcoal proper and in the supernatant water. About 30 grams of resins, charcoal or water supernatant were collected in each sample.

Figure 2 – Insert the sampler into the drum.

Figure 3 – Transfer samples to the container.

2.2. Radioisotopic content

Aliquots from each sample were taken and diluted to 100 mL in a standard counting glass vial. Gamma emissions were counted by 1000 seconds and analyzed in a Canberra gamma spectrometer with a 25% efficiency hiperpure germanium detector model GX2518, connected to an Accuspec multichannel analyzer card in a PC. Gamma spectrometry data were treated with the commercial software Gennie 2000.

2.3. Water content

Samples of fresh ion-exchange resins were used to establish a procedure to evaluate water content in the interstitial space between resin beads, in resin slurry. Samples of fresh, not radioactively contaminated resins of the same type of that used in the reactor water treatment system were used to establish a procedure for measurement of the water content of the active resins.

Resin slurry samples are weighted, the weight is registered as mass one, filtered for a few minutes in a buchner funnel and weighted again, the weight registered as mass two. The mass difference is assigned to interstitial water. Then, samples are dried to constant mass in an oven at 105 °C, weighted and the mass registered as weight three. The difference between mass two and mass three is assigned to the water absorbed inside the resin beads.

The height of the resin beads inside a flat bottomed flask with excess water, as measured with a ruler, is used to estimate the mass of resin in slurry inside a 200 L drum. The intent is to use the height of resin and the height of the water surface as a means to estimate dry resin mass and water content in the radioactive drums. Different heights of resin and excess water are measured and then their masses determined by the methods described before.

Samples of charcoal filter beds are going to be analyzed in respect to water content in the next step of the work and results will be reported in a future report.

3. RESULTS

3.1. Sampling

Forty eight samples of ion-exchange resins, charcoal filter beds, and water supernatant were drawn from the content of the 21 drums, each sample with about 30 g. From each sample, aliquots of about 1 g were used in the gamma spectrometry.

3.2. Radioanalysis

The following radionuclides were searched for by the gamma spectrometry: ^{54}Mn, ^{57}Co, ^{60}Co, ^{65}Zn, ^{85}Kr, ^{92}Nb, ^{94}Nb, ^{106}Rh, ^{106}Ru, ^{108m}Ag, ^{110m}Ag, ^{113}Sn, ^{125}Sb, ^{126}Sn, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{144}Pr, ^{154}Eu, ^{155}Eu. Results are shown in Tables 1 and 2.

In both waste streams, only Co-60 and Cs-137 were detected above 'minimum detectable activity' (mda) levels. All the other radionuclides of the list were below mda levels. Table 1 and table 2 show the activity concentrations of ^{137}Cs and ^{60}Co in each sample of ion-exchange resins and in each sample of charcoal filter bed respectively.

A reference laboratory analyzed the resin sample identified as 'drum 14 intermediate' and the charcoal sample identified as 'drum 15 intermediate'. Results were: 129 Bq(^{137}Cs).g^{-1} and 17950 Bq(^{60}Co).g^{-1} for resin sample, and 120 Bq(^{137}Cs).g^{-1} and 13830 Bq(^{60}Co).g^{-1} for charcoal sample [4]. Our results matched the results of the reference laboratory with deviations 1.5% and 9.8% for resins and 20% and 23% for charcoal. These biases are, most probably attributable to variations in the moisture content of each aliquot but may be due to a faulty calibration of our gamma spectrometer.

The observed differences of concentrations between different strata of the same drum and between different drums deserve more explanation. Ion-exchange resins or charcoal filter beds were replaced in different occasions, accumulated different activities during the operational period, and have decayed by different times. This explains the larger differences between different drums. Errors in extracting aliquots with the same water content may account for the smaller differences observed in concentrations of samples of the same drum.

3.3. Water content

Oven-dried resin samples until constant weight were used to determine the water content of drained resins. Figure 4 shows the ratio of initial to final mass of all samples as a function of time at 105°C.

Results of water content of resins slurries are presented in Figures 5. Figure 5 (left) shows the regression line of data of resin height and resin mass, and Figure 5 (right) shows the regression line of data of water height and water mass.

Table 1. Gamma spectrometry of samples of spent ion-exchange resins.

Drum No.	Strata	Cs-137 (Bq.g^{-1})	Error (%)	Co-60 (Bq.g^{-1})	Error (%)
01	bag 1	21	9.4	441	8.3
01	bag 2	< mda	---	43	10
01	bag 3	20	10	380	8.3
01	bag 4	16	9.1	320	8.3
01	bag 5	25	8.2	427	8.2
03	bag 1	13	12	295	8.3
03	bag 2	15	9.7	328	8.3
03	bag 3	14	6.7	249	8.2
03	bag 4	16	7.8	295	8.2
10	bottom	1122	2.2	52378	8.0
11	bottom	168	5.3	31219	8.0
11	upper	< mda	---	6.5	9.9
12	bottom	166	5.1	21310	8.0
12	intermediate	1.6	16	194	8.1
14	upper	< mda	---	3.9	10
14	bottom	85	5.8	15361	8.0
14	intermediate	131	4.6	22505	8.0
16	bottom	490	2.3	26113	8.0
16	intermediate	528	2.3	28501	8.0

Table 2 – Gamma spectrometry of samples of charcoal filter beds

Drum No.	Strata	Cs-137 (Bq.g^{-1})	Error (%)	Co-60 (Bq.g^{-1})	Error (%)
02	bottom	41	6.8	2510	8.0
02	intermediate	59	5.0	2084	8.0
04	bottom	64	4.9	1820	8.1
05	bottom	14	9.8	513	8.1
05	intermediate	98	4.3	2394	8.0
06	bottom	28	9.1	1435	8.1
06	intermediate	59	5.0	1953	8.0
06	upper	1.0	18	13	9.3
07	intermediate	124	5.4	3639	8.1
07	bottom	115	4.1	3609	8.0
07	intermediate	109	4.3	3640	8.0
07	bottom	52	5.9	3272	8.0
08	bottom	92	4.3	3653	8.0
08	intermediate	75	6.0	2968	8.0
09	bottom	18	7.9	451	8.1
09	intermediate	81	5.3	2718	8.0
13	bottom	61	9.9	19908	8.0
13	upper	< mda	---	69	8.2
15	upper	2.1	11	82	8.1
15	intermediate	133	3.9	11281	8.0
15	upper	1.9	8.8	36	8.3
17	intermediate	105	6.9	23623	8.0
17	upper	2.1	11	78	8.1
18	upper	2.0	10	17	8.8
18	bottom	164	0.44	18234	8.0
19	upper	0.81	15	40	8.2
19	bottom	87	7.1	19480	8.0
20	upper	< mda	---	56	8.2
21	upper	0.73	24	52	8.3

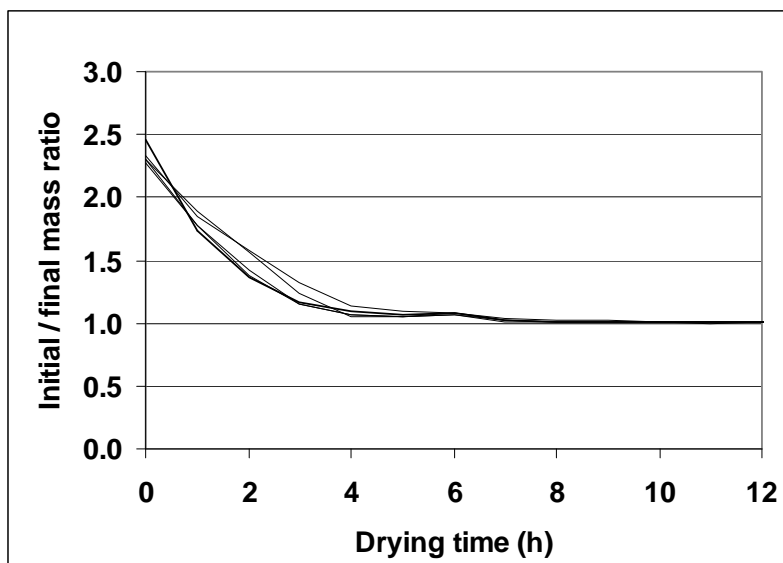**Figure 4 – Drying time of five drained resin slurries.**
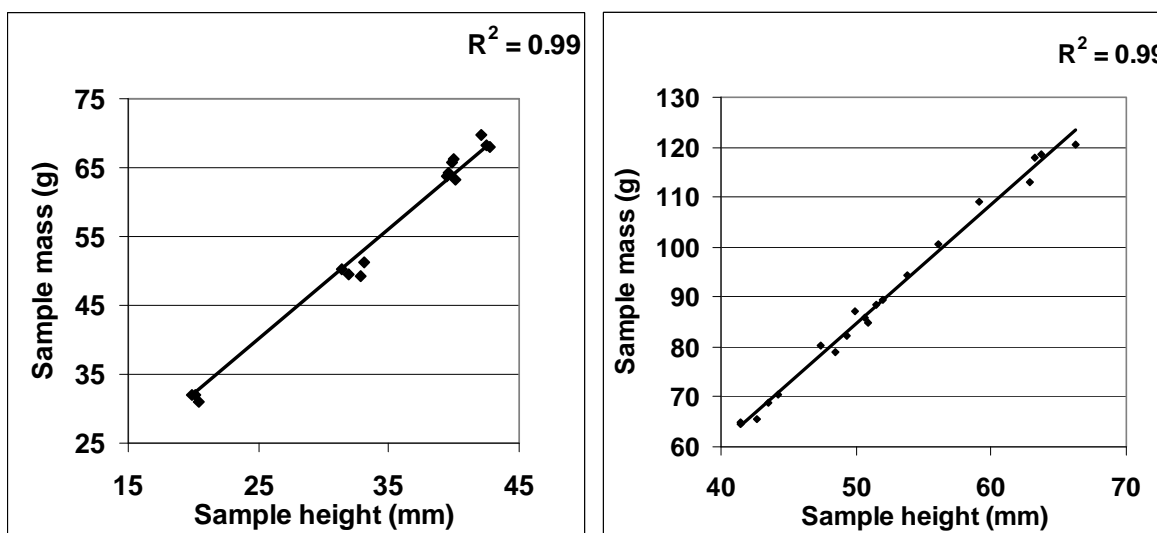

Figure 5 – Regression lines of data of resin (left) and water (rigth) heights and masses.

3. FINAL REMARKS

This paper reports the ongoing work on characterization of radioactive waste constituted of ion-exchange resins and charcoal filter beds from the IEA-R1 Research Reactor. This work is still in its beginnings and results presented here are preliminary and subject to further refinements and broadenings.

Results obtained thus far show progress in the learning of sampling methods and analysis methods for the characterization of slurries and wet solid radioactive wastes.

Further work will focus on improving detection capacity and accuracy and in establishing analytical protocols that eliminate systematic errors between determinations.

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