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CHEMICAL ANALYSIS OF RADIOACTIVE MIXED LIQUID WASTES BY ALPHA/GAMMA SPECTROMETRY, ICP-OES AND ARSENAZO III

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ABSTRACT

Radioactive waste characterization is a very important step in radioactive waste management because it can influence subsequent stages, as waste conditioning, storage and disposal. This characterization must provide reliable information in order to satisfy some quality requirements based on chemical analysis of representative waste samples. This paper presents procedures adopted for characterization of thirteen different mixed liquid wastes stored at Waste Management Laboratory of Nuclear and Energy Research Institute, IPEN-CNEN/SP. The first action was the sampling of representative samples of each liquid storage package, followed by the alpha and gamma spectrometry, Arsenazo III and ICP-OES analysis. It was identified the radionuclides U, Pu, Cs and Am and others seven chemical elements. The results obtained will be used to perform the treatment of these wastes.

1. INTRODUCTION

A wide variety of radioactive liquid wastes are generated during the operation of nuclear facilities, in medicine, industry and research. Management of these wastes involves several stages, including primary characterization, which is important in order to guide subsequent stages, as wastes conditioning, storage and disposal.

In Brazil, the Radioactive Waste Management Department (RWMD) at the Nuclear and Energy Research Institute (IPEN-CNEN/SP) is responsible for storage and treatment of radioactive wastes generated in certain states in the country. National standard CNEN-NN-09 defines acceptance criteria for radioactive waste disposal and establish that liquid wastes must be immobilized in cement matrix [1].

Chemical and Radiochemical parameters control of these radioactive wastes during the management and quality assessment of the final package are important component of

radioactive waste management. Failure in these procedures can cause generation packages which do not comply with acceptance criteria of deposition or storage [2].

Some chemical species, however, interact with the cement and retard its hydration reactions, altering final durability and some properties of the matrix [3]. In fact, immobilization of some wastes is limited to approximately 5% (v/v) in order to prevent cement interactions and package degradation. The immobilization of these wastes would, consequently, generate large volumes and increase deposition costs [4]. In this context, waste characterization is an important tool to increase the percentage of waste volume in immobilization drums and decrease final volume of radioactive waste.

The objective of the present work was to assess the radiochemical and chemical inventory of radioactive liquid wastes stored at RWMD in order to guide the next steps of waste management.

2. MATERIALS AND METHODS

2.1 Radiochemistry Characterization

The radionuclide inventory was determined firstly by the history of the waste, followed by radiochemistry procedures. It was identified three elements, cesium, americium and plutonium. Measurement of ^{137}Cs and ^{241}Am was accomplished through a Gamma Spectrometry System (HPGe detector with beryllium window of 0.5 mm thickness). The detector shielding was composed of a lead wall (105 mm thickness), copper wall (2 mm), and lucite wall (4 mm). The activity concentration for ^{137}Cs and ^{241}Am was calculated through a specific energy photopeak of 661.66 and 59.54 KeV, respectively. The radiochemical procedure for the determination of isotopes of ^{238}Pu and ^{239}Pu was done according to the method described by Taddei and Silva [5]. This method involves sample dissolution (by HNO_3 and $HClO_4$), separation by ionic-exchange resin, electrodeposition and alpha-spectroscopy. Furthermore, uranium total was determined by Arsenazo III method, according to the method described by Silva et al [6], in order to compare its results with the one obtained at chemical characterization by ICP-OES.

2.2 Chemical Characterization

The instrument used in the present study was a Perkin Elmer ICP-OES Optimal DV 7000 and the instrumental operation conditions are showed below:

- R.F. Generator Frequency:40 MHz
- Plasma Torch:Standard 1 slit
- Injector:Standard 2 mm
- Detector:CCD
- Optic:Echelle
- View:Radial
- Power:1300 Watts
- Plasma Gas Flow:15 L/min
- Auxiliary Gas Flow:0,3 L/min

- Nebulizer Gas Flow:0,6 L/min
- Sample Flow Rate:1,5 mL/min

The radioactive liquid wastes, stored at RWMD in 20 liters glass bottles, were previously homogenized and the samples were collected with a disposable serological pipette and an automatic pipettor, and transferred to a polyethylene bottle of 220 milliliters.

There are thirteen types of radioactive liquid wastes stored at the department, each one with different characteristics. The samples dilutions, before ICP analysis, were performed taking into account the activity of each sample and radiological safety. The dilution factor was different from each sample and varied from 30 to 100, depending of the activity and radiochemical inventory. For each sample, it was prepared two diluted solutions in acid medium, using HNO_3 5% solution. At ICP equipment, there were made two measurements for each element.

3. RESULTS AND DISCUSSION

3.1 Radiochemistry Characterization

The radionuclide inventory was determined and it is showed in Tab 01. The three radionuclides was identified by theirs activity, and then, was calculated theirs concentration, in mg/L.

Table 1: Results of radiochemistry inventory of 13 liquid wastes

		^{241}Am	^{137}Cs	^{238}Pu	^{239}Pu
ID	Volume (L)	Concentration (mg/L)			
73	10	1.34×10^{-07}	-	2.91×10^{-06}	4.65×10^{-02}
74	20	9.05×10^{-04}	-	3.20×10^{-05}	4.60×10^{-01}
75	18	7.87×10^{-07}	5.00×10^{-09}	7.67×10^{-08}	1.04×10^{-04}
76	20	1.18×10^{-04}	-	1.03×10^{-05}	1.52×10^{-01}
77	20	3.15×10^{-07}	9.38×10^{-09}	6.23×10^{-08}	6.04×10^{-04}
78	8	-	1.41×10^{-08}	1.60×10^{-07}	9.44×10^{-05}
79	18	2.52×10^{-04}	9.70×10^{-08}	2.30×10^{-06}	3.45×10^{-02}
80	8	2.83×10^{-05}	1.13×10^{-07}	1.76×10^{-06}	2.51×10^{-02}
81	17	1.42×10^{-05}	2.66×10^{-08}	2.56×10^{-06}	3.78×10^{-02}
82	16	1.02×10^{-04}	-	1.97×10^{-06}	3.95×10^{-02}
83	8	-	2.97×10^{-08}	1.58×10^{-08}	1.71×10^{-04}
84	18	2.28×10^{-05}	-	5.59×10^{-08}	1.74×10^{-04}
86	10	1.73×10^{-06}	2.81×10^{-08}	9.59×10^{-08}	7.26×10^{-04}

3.2 Chemical Characterization

The chemical inventory was determined by ICP-OES. It was analyzed the concentration of calcium, chromium, cooper, iron, magnesium and zinc (Tab. 02) and thorium and uranium (Tab. 03). In Tab.03, it was showed the results of uranium determined by Arsenazo III method analysis, in order to compare the methods. Results of As, Be, Cd, Co, Li, Mo, Ni, Pb, Se, Sn, Sr, Ti, Tl, and V were not expressive (below detections limits) and it is not showed.

Table 2: Concentrations of Ca, Cr, Cu, Fe, Mg, Mn and Zn in radioactive liquid wastes

	Concentrations in mg/L (mean ± standard deviation)						
ID	Ca	Cr	Cu	Fe	Mg	Mn	Zn
73	10.9 ± 0.1	3.8 ± 0.2	#	2.1 ± 0.2	#	#	0.3 ± 0.0
74	15.0 ± 1.3	6.8 ± 0.7	#	189.4 ± 17.2	#	#	2.5 ± 0.1
75	42.7 ± 3.0	1.9 ± 0.1	#	31.9 ± 3.7	54.6 ± 1.5	0.9 ± 0.0	2.9 ± 0.2
76	8.3 ± 0.3	2.3 ± 0.1	#	38.6 ± 2.5	0.8 ± 0.1	#	0.7 ± 0.0
77	23.7 ± 0.3	1.7 ± 0.1	#	22.2 ± 0.5	7.1 ± 0.3	1.1 ± 0.0	6.4 ± 0.2
78	15.0 ± 0.9	2.0 ± 0.1	1.5 ± 0.1	2.6 ± 0.3	#	#	4.9 ± 0.4
79	36.5 ± 3.0	1.8 ± 0.0	#	207.5 ± 20.6	15.3 ± 1.0	16.0 ± 0.2	10.5 ± 0.8
80	28.8 ± 2.4	3.6 ± 0.2	2.1 ± 0.1	1517.3 ± 94.6	4.2 ± 0.4	5.2 ± 0.3	5.5 ± 0.0
81	10.3 ± 0.6	1.9 ± 0.2	1.6 ± 0.0	2.5 ± 0.1	2.3 ± 0.2	#	1.6 ± 0.2
82	13.2 ± 0.5	2.0 ± 0.2	#	14.7 ± 0.3	0.9 ± 0.0	#	1.8 ± 0.1
83	72.2 ± 2.3	5.1 ± 0.1	0.4 ± 0.0	134.4 ± 11.6	19.8 ± 2.4	7.0 ± 0.6	6.3 ± 0.1
84	126.4 ± 11.1	2.2 ± 0.1	#	102.5 ± 10.8	85.6 ± 9.0	0.6 ± 0.0	#
86	74.6 ± 5.4	4.7 ± 0.4	0.4 ± 0.0	137.3 ± 6.5	20.3 ± 1.4	6.8 ± 0.1	8.7 ± 0.1

Table 3: Concentrations of Th and U (ICP and Arsenazo III methods) in radioactive liquid wastes

	Concentrations in mg/L (mean ± standard deviation)		
ID	Th	U (ICP)	U (Ar)
73	0.6 ± 0.0	8.3 ± 0.8	10.1 ± 0.7
74	21.4 ± 1.9	516.6 ± 52.3	508.0 ± 53.0
75	22.9 ± 1.3	120.7 ± 1.5	106.7 ± 6.9
76	10.7 ± 1.0	334.5 ± 32.2	253.6 ± 4.9
77	2.3 ± 0.2	4.6 ± 0.4	3.2 ± 0.2
78	168.2 ± 13.0	214.8 ± 11.6	186.0 ± 10.5
79	21.0 ± 0.8	59.7 ± 2.1	48.0 ± 3.3
80	116.7 ± 10.6	217.2 ± 15.8	360.2 ± 8.5
81	3.1 ± 0.2	155.5 ± 17.3	168.6 ± 10.9
82	1.8 ± 0.1	32.6 ± 3.2	44.6 ± 4.0
83	16.5 ± 0.2	233.6 ± 25.6	239.6 ± 4.4
84	11.6 ± 1.0	13.4 ± 0.4	15.0 ± 1.6
86	14.5 ± 1.3	192.6 ± 16.2	271.6 ± 13.0

All wastes analyzed showed radionuclides in quantities exceeding the exemption limits specified in Norma CNEN-NE-6.05 (*Gerência de Rejeitos Radioativos em Instalações Radioativas*) [7] which characterize them as radioactive waste. In general, the samples analyzed are heterogeneous and the elements in higher concentrations are U, Th and Fe.

The uranium concentrations obtained by ICP-OES and Arsenazo III were close, indicating that both techniques are effective for determination of uranium in radioactive wastes. However it is noteworthy that the ICP-OES technique possesses the advantages of being faster, has less steps and lower reagent consuming.

4. CONCLUSIONS

In Brazil, the project of the national repository is under development and acceptance criteria for final disposal have not been established yet. However, the results obtained will be useful to determine primary conditions to waste immobilization and storage. The techniques adopted were efficient for characterization of these radioactive waste and they may be adopted for analysis of others liquid wastes stored in the RWMD and of those that will be received in the future.

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