ACTIVITY DETERMINATION OF THE DIFFICULT TO MEASURE RADIONUCLIDE $^{55}\text{Fe}$ IN OPERATIONAL RADIOACTIVE WASTE FROM THE ANGRA NUCLEAR POWER PLANT

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ABSTRACT

Pressurized Water Reactors, PWR, are responsible for converting nuclear energy from the nuclear reactions, in the core, into thermal energy by heat exchange with the water in the primary system and then into mechanical energy by the pressure increase from the heat exchange and at last, electrical energy, from the turbine rotation due to the resultant pressure. In a reactor such as described, cool water must flow through the Primary System (where the nuclear core is located) in order to allow heat exchange for electrical energy generation and also to refrigerate the core, providing it will not to be melted or causing any accident. Materials that make up the internal part of the primary system such as the walls or core coating may suffer effects like drag force due to the high water pressure or neutron activation due to the high levels of radiation. Therefore some of these nuclides that compose these materials are expected to be present in the core water and so, a filtration system is required to reduce these nuclides concentrations. At Angra Nuclear Power Plant two types of filtration systems are used, ion exchange resin, responsible for adsorbing these nuclides and a polymer-type filter responsible for withholding solid particles in suspension. After a while, these filters become saturated and must be replaced; once replaced, the old ones become Radioactive Waste of Low or Medium Activity. This study has evaluated the chemical yield of different procedures for $^{55}\text{Fe}$ determination by using anion exchange chromatography, to be further applied to determine the activity concentration in nuclear waste samples. The activity concentrations were determined by Liquid Scintillation Counting (LSC) and Gamma Spectrometry (GS). This project is part of a bigger objective that aims to fulfill several regulations from the Brazilian National Nuclear Energy Commission (CNEN) and the development of a repository for proper storage of radioactive waste materials.
1. INTRODUCTION

Radioactive waste are related to many possible origins, for example, the generation of electricity in nuclear power plants, fuel cycle and any other operation that may require a procedure including radioactive materials. In such operations, these wastes may possess a wide possibility range of radionuclides concentrations and activities and furthermore, in a wide variety of physical and chemical properties.

A common property of any radioactive material is the potential to cause damage related to the people and the environment and as expected, they must be managed in order to reduce any negative event [1].

During the process of energy generation in the PWRs, some events are expected due to the increased pressure and the high levels of radiation such as drag force and neutron activation in the materials that compose the pressure vessel. With such events, we may expect some of these materials’ nuclides to be present in the cooling water and so, this water becomes contaminated and must be treated to maintain a safe operation in the power plant, for this treatment a demineralization system is responsible for withhold these contaminants [2,3].

The demineralization system usually consists of three parts: 1) polymer-type filter; 2) Coal filter; 3) Ion exchange resin. As we can observe, each step, respectively, represents a thinner treatment, from a polymer-type filter, responsible for withholding particles in suspension until an ion exchange resin, which interacts in atomic level [3,4,5].

Some of these materials may not be easy to analyze and quantify, due to, mainly, three factors: non-gamma emission, low energy gamma emission or low intensity gamma emission. When we have a material with such properties of nuclides, we call them difficult to measure radionuclides, DMR.

In Brazil, law N° 10.308, from 20th November 2001, establishes rules for the final destination of radioactive waste produced in national territory, including the local selection, construction of facilities, operation, supervision, costs, indemnity, civil responsibility and final destination. Final destination of radioactive waste is also called a Repository, a place which is built to store these waste for undetermined time [6].

CNEN’s rule 6.09 establishes that all low or medium activity radioactive waste must be characterized with quantitative analysis in order to verify if they are within the limits configured by the regulations. Therefore all the content of these activity level materials must be known and reported [3].

Angra Power Plant reactors works according to the PWR system, so, they follow the process discussed above, except for the absence of a carbon filter. Its filtration system is composed of polymer-type and an ion exchange resin filters, after both get saturated, they must be replaced and so, generating low or medium radioactive waste as they are filled with radionuclides [5,7].

The characterization of this waste varies according to the radionuclides desired and the precision needed. These parameters are measured according to the identification and
quantification in order to acquire a database that provides enough information for handling and storing such materials.

Some of these radionuclides can be quantified directly through gamma spectroscopy due to their high energy or high intensity. Some of these nuclides are: $^{137}$Cs, $^{60}$Co, $^{57}$Co, $^{114}$Sb, $^{125}$Sb, $^{54}$Mn, $^{93}$Zr, $^{94}$Nb, $^{110m}$Ag, and they are classified as easy to measure radionuclides. However, some of the nuclides are difficult to measure, in other words, they fit in one of the three characteristics already described. In this case, a more intrusive technique is required. For this class of nuclides, preliminary complex chemical procedures are required in order to remove any material that may cause interferences [8]. Some of these nuclides are: $^3$H, $^{14}$C, $^{55}$Fe, $^{99}$Tc, $^{108m}$Ag and $^{93}$Zr.

The radiochemical separation is required for the total isolation of the radionuclide of interest is needed for the analysis. Some of the techniques applied are: precipitation, ion exchange chromatography and chromatographic extraction.

Once the nuclides of interest are isolated, analysis may take place. Particle or Gamma Spectrometric techniques may be used to acquire its activities. This analysis occurs through equipment sensible to alfa, beta or gamma radiation which provides the variable counts per second, CPS, obtained from the conversion of the particle or radiation energy into electrical impulse that may be interpreted by the computational system. In this study, the Liquid Scintillation Counting, LSC, and the Instrumental Neutron Activation Analysis, INAA, techniques were used.

This study analyzed the chemical yield of $^{55}$Fe using the analytical procedures: precipitation and ion exchange resin in standard reference materials aiming to apply these methodologies in numerous other samples. Furthermore, as a final objective, characterize the difficult to measure radionuclides: $^3$H, $^{14}$C, $^{99}$Tc, $^{108m}$Ag and $^{93}$Zr in order to fulfill the regulations required by the Brazilian nuclear commission for the construction of the first repository in Brazil.
2. METHODOLOGY

To verify the efficiency of the precipitation and ion exchange resin, two tests were applied, one of them using a standard Fe solution and the second one, using a complex sedimentary matrix reference material JSO-2 Geological Survey of Japan.

For the radiochemical separation procedure of Fe, precipitation using ammonium hydroxide (NH₄OH) and AG 1 – X8 ion exchange column were used as described below and shown in Figure 2.

2.1. Sample preparation

First, the sample must be in liquid state, so an acid attack is needed.

For the sedimentary matrix samples, 3 aliquots of approximately 0.5g were digested in a CEM’s high-power microwave Mars 6, using 12mL of reverse aqua regia. After this process, all the material, except for silica was dissolved. Each aliquot was transferred into a 150mL beaker and treated with 8mL (or until all the silica is dissolved) of fluoridric acid (HF). This process was taken over a heating plate on 150ºC.
As the standard Fe solution is already in a liquid state, no sample preparation was needed to proceed to the next steps.

The first radioactive waste samples chosen to be analyzed were the ion exchange resin samples, once they were already fully digested as part of a preliminary test by the Nuclear Waste Management Center (GRR) at IPEN. Twelve aliquots were prepared, each containing approximately 0.3g, digested using nitric acid (HNO₃) and hydrogen peroxide (H₂O₂), once dissolved; the samples were diluted with H₂O to a total of 2 liters. Afterwards the digestions, 10mL of each aliquot were used in this analysis. For this study, 3 samples were analyzed.

2.2. Precipitation

In this procedure, tracers for Fe, I and Ni and carrier for Fe were added in the 3 selected radioactive waste aliquots. (The addition of I and Ni tracers is due to a parallel analysis that will be conducted with the samples after the removal of the Fe for quantification purposes).

Ammonium Hydroxide (NH₄OH) was added in the samples in order to selectively precipitate the Fe (the volume of ammonium hydroxide varied according to the concentration of Fe in the sample); the orange precipitate evidences the presence of the iron hydroxide.

The sample was filtered in order to withhold the iron hydroxide. The eluent is stored for future analysis of other radionuclides.

Chloridric Acid (HCl) was used to solubilize the iron hydroxide withheld in the filter and collected in a beaker. The bright yellow solution evidences the presence of the iron chloride.

The obtained Fe solution was dried in a heating plate under 150ºC. This procedure is necessary to adapt the samples for the characteristics needed for the next step.

2.3. Ion Exchange Resin Procedure

In an AG 1 – X8 ion exchange column, Fe in chloride form tends to be adsorbed. For this procedure, 30mL of HCl 9M were added to the dry aliquots and mixed in order to achieve a total solubilization. This final solution was transferred to the column in order to adsorb the Fe, the portion of the sample that didn’t interact with the resin was separated for future analysis of different nuclides.

HNO₃ 8M was used to desorb the Fe from the resin. 40mL of the acid was transferred to the column and the resultant solution was collected. The volume of nitric acid needed may vary according to the column dimensions.

2.4. LSC Analysis

The resultant solution from the previous procedure was dried and summed with H₂O to a total of 5mL. This aqueous solution of iron nitrate was mixed with the scintillation cocktail in a quartz vial, for iron quantification, Perkin Elmer’s Ultima Gold AB scintillation cocktail was used in the proportion of 1:3 resulting in 5mL of sample in aqueous solution and 15mL of scintillation cocktail. This final cocktail was mixed and set aside wrapped in an aluminum foil, to prevent contact with the light, for 1 day. At last, activity concentration was acquired.
2.5. Neutron Activation Analysis

For both standard Fe solution and RM materials, neutron activation analysis was used in order to determine the concentration of Fe after the separation procedures in order to acquire a yield based on the known concentrations in those materials.

For the radioactive waste, neutron activation analysis was used to determine the final concentration of the tracer added in the first step of the analysis in order to determine proportionality, once both tracer and sample losses of Fe tend to be the same. After activity concentration acquired by LSC, a 5mL aliquot of each sample was separated for neutron activation analysis calculus of yield. Each of the separated aliquots was dried inside a plastic vessel (dimensions: radius:5mm; height:5mm). The vessel was irradiated for 8 hours under a neutron flux of 1~5 \times 10^{12} n/cm^2/s in order to calculate the final concentration of Fe tracer in the sample and fulfill the variables to calculate the concentration in the radioactive waste sample.

The concentration of the samples may be acquired using the Equation 1 which relates the obtained activity from the equipment and sample mass.

\[
C_a = C_p \times \frac{m_p \times A_a}{m_a \times A_p}
\]

Where:

- \(C_a\) = Element concentration in the sample
- \(C_p\) = Element concentration in the standard
- \(M_a\) = Sample Mass
- \(M_p\) = Standard Mass
- \(A_a\) = Activity (cps) of the element in the sample
- \(A_p\) = Activity (cps) of the element in the standard

All the samples were analyzed in a hiper pure Ge detector (HPGe) from Canberra Industries, for 2 hours each. Detector was connected to electronics responsible for converting electrical signals from the detector into computational data. CAX Program was used in order to acquire each activity respectively to each energy according to a pre established calibration [9].

3. RESULTS AND DISCUSSIONS

Once samples and reference materials were analyzed, chemical yields (for RM samples and Standard Fe Solution) and Activity Concentration (for ion exchange resin) were acquired.

For Chemical Yields, the obtained concentration of the analysis was compared to the literature values in order to acquire the yield to be further applied to the radioactive waste samples.

The Table 1 shows the obtained results for Standard Fe Solution Samples Concentrations (Ca), Concentration Error (Eca), Standard Value (StdValue) and standard error (Std E) in order to acquire a chemical yield for the precipitation and ion exchange procedure.
Table 1: Fe concentrations obtained in the Standard Fe Solution analysis

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>Ca (ppm)</th>
<th>Eca</th>
<th>StdValue(ppm)</th>
<th>Std E</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>10701.40</td>
<td>452.87</td>
<td>10005</td>
<td>50</td>
<td>106.96</td>
</tr>
<tr>
<td>C2</td>
<td>9362.30</td>
<td>396.20</td>
<td>10005</td>
<td>50</td>
<td>93.58</td>
</tr>
<tr>
<td>C3</td>
<td>9325.02</td>
<td>100.04</td>
<td>10005</td>
<td>50</td>
<td>93.20</td>
</tr>
<tr>
<td>C4</td>
<td>10734.35</td>
<td>115.16</td>
<td>10005</td>
<td>50</td>
<td>107.29</td>
</tr>
</tbody>
</table>

For a simple matrix sample, in this case Standard Fe Solution, precipitation and ion exchange resin procedures showed chemical yields between 93% and 106% which represents a positive conclusion about usage of these methodologies in further analysis of the radioactive samples.

Table 2 shows the obtained concentrations (Ca), concentration error (Eca), Standard Reference Concentration (StdValue), Standard Error (Std E) and Yield for the RM Samples.

Table 2: Fe concentrations obtained in RM Samples analysis

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>Ca (ppm)</th>
<th>Eca</th>
<th>StdValue(ppm)</th>
<th>Std E</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JSO2-1</td>
<td>5786.87</td>
<td>1969.98</td>
<td>73080</td>
<td>630</td>
<td>79.21</td>
</tr>
<tr>
<td>JSO2-2</td>
<td>36369.46</td>
<td>1191.27</td>
<td>73080</td>
<td>630</td>
<td>49.75</td>
</tr>
<tr>
<td>JSO2-3</td>
<td>59959.83</td>
<td>1001.81</td>
<td>73080</td>
<td>630</td>
<td>81.55</td>
</tr>
</tbody>
</table>

Through these data acquired, samples 1 and 3’s average will be applied in the chemical yield for the samples in Table 3. Results obtained in the sample 2 seems to be qualified as an outlier. Further JSO2 Reference Material will be analyzed in order to double check this event and solve this variant.

Table 3 shows the obtained activities from the Radioactive Waste Samples analyzed in disintegrations per minute (DPM), followed by the activity concentrations obtained through the Equation 2, in Becquerel (Bq) which comprehends the obtained activity, sample mass, in grams, and the chemical yield acquired in the analytical procedures using standard materials.

\[
C_a = \frac{A_a}{60 \times m_a} \times y
\]  

Where:

- \( C_a \): Activity concentration
- \( A_a \): Activity in Bq
- \( m_a \): Sample initial mass
- \( y \): Chemical yield for the procedure

Table 3: Activity concentrations obtained from Ion Exchange Resin Samples

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>DPM</th>
<th>DPS (Bq)</th>
<th>Mass(g)</th>
<th>Yield</th>
<th>Ca (Bq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IER-1</td>
<td>329388,4</td>
<td>5489,807</td>
<td>0,035629</td>
<td>0,803809</td>
<td>123851,6</td>
</tr>
<tr>
<td>IER-2</td>
<td>279194,4</td>
<td>4653,24</td>
<td>0,036926</td>
<td>0,803809</td>
<td>101293,3</td>
</tr>
<tr>
<td>IER-3</td>
<td>224160,2</td>
<td>3736,003</td>
<td>0,032101</td>
<td>0,803809</td>
<td>93550,64</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

The procedures applied in Standard materials have shown a high chemical yield, demonstrating, in these preliminary tests, to be reliable in terms of analytical procedures for Radioactive Samples. Further tests will be applied in order to discover the origin of the outlier value in sample JSO2-2 seeking a totally reliable procedure to be further applied in a larger group of samples and different matrices of operational nuclear waste from Angra Nuclear Power Plant. This project aims to establish several methodologies in order to acquire the safest and most reliable procedure for DMRs, more tests will be developed for $^3$H, $^{14}$C, $^{99}$Tc, $^{108m}$Ag and $^{93}$Zr.

REFERENCES


