STUDY OF ALUMINOTHERMIC SLAG LEACHING
FOR URANIUM AND THORIUM RECOVERY

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1. Introduction

The demand for sustainable energy grows every year, as it is necessary to generate growth, economic wealth, and quality of life while at the same time impacting the environment as little as possible, not compromising future generations. One option, for example, is the use of nuclear energy to reduce carbon emissions, one of the great villains that comes from economic growth [1].

For an even more significant reduction in the environmental impact, projects aimed at using waste from naturally occurring radioactive materials (NORM) for the recovery of uranium and subsequent use in the Nuclear Fuel Cycle are praiseworthy. One example is the Consórcio Santa Quitéria between the Indústrias Nucleares do Brasil (INB) and a fertilizer producer [2].

It is in this line that this article is proposed, that is, to present the results of leaching assays of a NORM residue to verify the possibility of recovering uranium and thorium. The material studied is an aluminothermic slag with the presence of U_3O_8 and ThO_2. It is a by-product of the metallurgical processing of columbite to produce niobium and tantalum ferroalloys. The facility carrying the processing has about 50.000 tons of this material stored in its unit [3].

The feasibility of recovery is appealing by reducing cost, and environmental liability for the company since the slag is a radioactive material that requires compliance with Comissão Nacional de Energia Nuclear (CNEN) standards - particularly the construction and maintenance of a repository [4]. In addition, it can be an increment to the nuclear fuel cycle with reduced cost compared to uranium mining, since the material does not need to be disassembled, presenting dimensions that would be sufficient to be used in smaller crushers and mills, for example [5]. Allied to this is that the uranium oxide content in the slag is higher than that found in Caetité-BA and Santa Quitéria-CE: 0.2% [6, p. 77] and 0.1% [7, p. 2160], respectively.

2. Methodology

The four process parameters, analysis, and equipment used are described below.

2.1. Sample granulometry

The slag was comminuted (crushed and ground) and then passed through 12 Tyler sieves to obtain two particle sizes: 100% smaller than 1000 µm and 100% smaller than 200 µm. One sample of each (head sample) was analyzed by X-ray bloom to determine the grade feed and the remainder quartered in 40 g aliquots for the assays.

2.2. pH control

Leaching is the removal of a soluble fraction of a solid material by employing a solvent that can be an acid or a base [8, p. 459]. It is a technique widely used in the production of uranium, zinc, rare-earth copper, and others [9, p. 158].

In this study, sulfuric acid (H_2SO_4) was chosen as the leaching agent, due to its traditional use for the extraction of uranium and thorium [10, p. 305, 11, p. 1612]. The concentration used was of 1 mol.L^{-1}.

The process parameter under study is the pH of the pulp being selected: pH = 1 and pH = 3.

2.3. Percentage of solids

The percent of solids, S%, represents the concentration of solids in a pulp. It is defined by Eq. 1, whereas m is the mass of solids (slag) and liquid (deionized water) [12, p. 47].

$$S_{\%} = \frac{m_{solid}}{m_{solid} + m_{liquid}} \rightarrow m_{liquid} = \frac{m_{solid}}{S_{\%}} - m_{solid} \tag{1}$$

Two percentages of solids were selected: 45% and 65%.

2.4. Assay time

The duration of each assay is another studied variable of the process. Periods of 6 h and 8 h were selected.

2.5. Determination of the number of assays

The number of assays, n, obeys the multiplicative principle of combinatorial analysis, that is:

$$n = granulometry \; x \; pH \; x \; percentage \; of \; solids \; x \; assay \; time \; x \; triplicates \tag{2}$$

$$n = 2 \; x \; 2 \; x \; 2 \; x \; 2 \; x \; 3 = 48 \; assays$$

The triplicate is the repetition of the assay, that is, each assay was performed three times.

2.6. Leaching study procedures

Below are the procedures performed after obtaining the 40 g aliquots of slag.

i) Preparation of the pulp. Using Eq. 1, the mass of water added to the slag is determined to obtain the two percentages of solids. The pulp was prepared in a 250 ml beaker.

ii) Pulp homogenization. The beaker is placed on the magnetic stirrer until the pulp is homogenized (about 2 minutes).

iii) Addition of sulfuric acid. The pH meter probe is inserted into the pulp while adding sulfuric acid until the desired pH stabilization, as seen in figures Fig. 1 and Fig. 2 (pH =1 or pH = 3).

Figure 1: On the left, a fume hood with the equipment used in the assays. On the right, the pH meter and its probe.
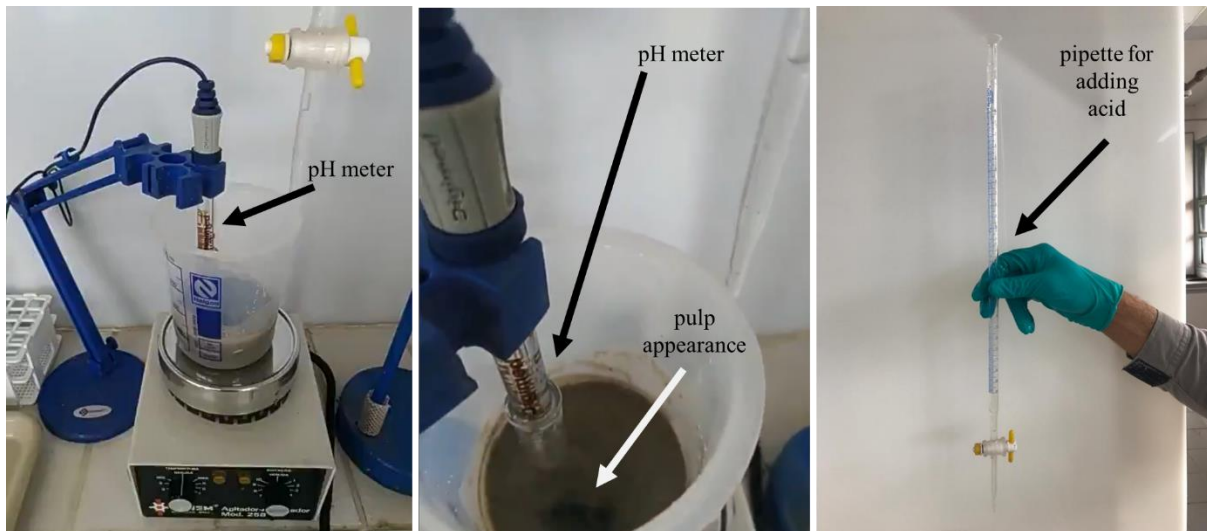

Figure 2: Some details of the experimental setup. On the left, the beaker is on the stirrer. In the center, the general appearance of the pulp. On the right, pipette for controlled addition of acid.

iv) pH monitoring. The setup must be kept on the magnetic stirrer throughout the assay (6 h or 8 h) to homogenize the pulp while the pH is monitored and controlled (see Fig. 2).

v) After completion of the assay, measure the mass in the beaker and the mass of the filter.

vi) Filter the pulp and dry the retained material.

vii) Measure the mass of material retained in the filter.

2.7. Analysis of the content retained in the filter and determination of the recovery of uranium and thorium oxides

As the objective is to study the recovery of uranium and thorium oxides, R, we opted for chemical analysis by FRX of the material retained in the filter, that is, the solid phase of the leaching and the use of Eq. 3:

$$R = 1 - \frac{m_s . t_s}{m_{slag} . t_{slag}} \tag{3}$$

where m_s, m_{slag}, t_s, and t_{slag} are the masses and concentrations of the solid after leaching and of the slag (solid before leaching), respectively.

Eq. 3 reflects the fraction of uranium and thorium transferred to the leaching: this is the reason for the subtraction of the unit since the expression only contains data for solids.

3. Results and Discussion

3.1. FRX analysis of the head sample

The result of the chemical analysis of the head sample is available in Table I. It is observed that there is no significant variation in the levels of uranium and thorium oxides between the particle sizes

Table I: Result of the FRX analysis of the head sample.

Opening (um)	% retained	U_3O_8	ThO_2
1000	0	-	-
850	23,3	1,76	3,65
600	17,2	1,78	3,62
425	9,2	1,78	3,69
300	7,5	1,77	3,68
200	9,6	1,75	3,67
180	7	1,76	3,66
150	8,6	1,75	3,64
105	7,7	1,78	3,66
75	4,5	1,79	3,65
53	3,4	1,79	3,67
44	1,4	1,76	3,66
<44	0,6	1,77	3,63
Head - 100% < 1000		$1,77 \pm 0,01$	$3,66 \pm 0,02$

3.2. Leaching result - Chemical analysis of the solid

Fig. 3 shows the appearance of the slag after leaching, filtering, and drying the pulp.

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Figure 3: The appearance of the slag after leaching, filtering, and drying.

The results of the chemical analysis of solids after leaching are summarized in Table II. As they were performed in triplicate, there were three results from each group "granulometry - pH - % solids - time," so the values are given as the mean followed by the respective standard deviation.

Table II: Result of chemical analysis (FRX) of the solid after leaching, filtering, and drying.

Group	Granulometry (μm)	pH	Solids (%)	Time (h)	m_{liquid}[1] (g)	m_{solid}[2] (g)	U_3O_8 (%)	ThO_2 (%)
01	200	1	45	4	48,9	36,2	1,1 ± 0,1	2,4 ± 0,3
02	200	1	45	8	48,9	37,9	1,0 ± 0,1	2,1 ± 0,1
03	200	1	65	4	21,5	35,2	1,0 ± 0,4	2,1 ± 0,2
04	200	1	65	8	21,5	34,1	0,6 ± 0,1	1,3 ± 0,1
05	200	3	45	4	48,9	35,2	1,3 ± 0,3	2,9 ± 0,5
06	200	3	45	8	48,9	33,1	1,1 ± 0,5	2,5 ± 0,2
07	200	3	65	4	21,5	37,2	1,2 ± 0,1	2,7 ± 0,1
08	200	3	65	8	21,5	36,4	1,0 ± 0,1	2,0 ± 0,3
09	1000	1	45	4	48,9	36,1	1,2 ± 0,1	2,4 ± 0,2
10	1000	1	45	8	48,9	39,1	1,0 ± 0,1	2,2 ± 0,1
11	1000	1	65	4	21,5	36,1	1,2 ± 0,1	2,3 ± 0,1
12	1000	1	65	8	21,5	32,5	1,0 ± 0,1	2,1 ± 0,1
13	1000	3	45	4	48,9	33,9	1,3 ± 0,3	2,9 ± 0,4
14	1000	3	45	8	48,9	37,9	1,2 ± 0,2	2,6 ± 0,2
15	1000	3	65	4	21,5	32,4	1,3 ± 0,2	2,8 ± 0,3
16	1000	3	65	8	21,5	33,1	1,2 ± 0,1	2,5 ± 0,3

[1] Determined by Eq. 1.
[2] Solid mass after leaching, filtering, and drying.

Complementing the results, Fig. 4 shows the histogram with the distribution of the chemical analysis of U_3O_8 and ThO_2 of the solids of the 48 assays performed.

3.3. Result of uranium and thorium recovery

Applying the data from Table I and Table II in Eq. 3, the recovery of uranium and thorium oxides for each group in the leachate is obtained. The results are shown in Fig. 5, which presents the graph with the comparison between the results obtained in the groups.
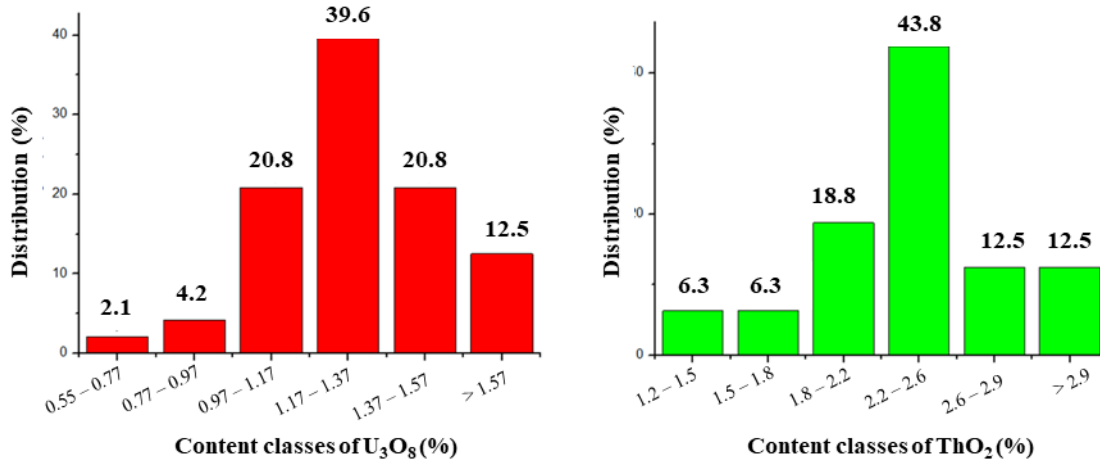
Figure 4: Distribution of contents in the solid after leaching, filtering, and drying. On the left, uranium oxide; on the right, thorium oxide.
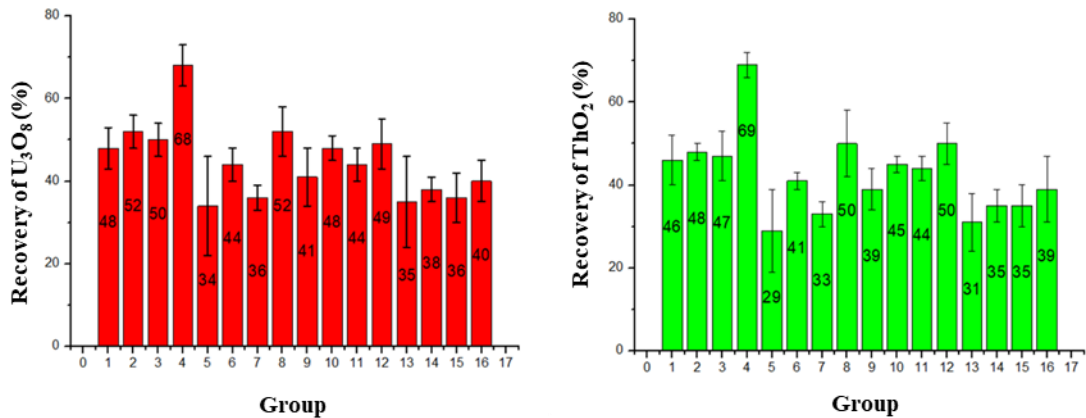

Figure 5: Comparison between recoveries. On the left, uranium oxide; on the right, thorium oxide.

It is observed that the group with the best recovery performance was group 4 with 200 μm particle size, pH = 1, percentage of solids of 65%, and leaching time of 8 h for both U_3O_8 and ThO_2.

4. Conclusions

The 48 assays carried out show that the optimal parameters for slag leaching are close to 200 μm particle size, pH = 1, solids percentage of 65%, and leaching time of 8 hours.

By analyzing the data in Fig. 5, it is also noted that the main factors for recovery are pH and leaching time. Thus, for future studies, further assays with pH ranging between 0.5 and 1 are proposed, and time between 7 and 9 hours. Other variables such as temperature, pressure, and acid concentration are also interesting to be explored.

5. Future work

In addition to the investigation of other parameters mentioned in the previous item, the search for techniques for separating U and Th contained in the leachate is future work. An alternative widely used in hydrometallurgy is the use of solvent extraction techniques that are based on the different solubility in

immiscible liquids of the elements of interest [8, pp. 510-3]. There are works, for example, with leaching of rare earth elements containing uranium and thorium that use amines as extractants [13, p. 499].

Acknowledgements

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