



Study of aluminothermic slag leaching for uranium and thorium recovery

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ABSTRACT

The need for energy by modern society is increasing. On the other hand, it is necessary to reduce costs and environmental impact. In this perspective, the recovery of uranium present in industrial waste from the processing of naturally occurring radioactive material (NORM) appears as a possible complement to the mining stage of the Nuclear Fuel Cycle. NORM's uranium recovery can reduce environmental liabilities and mineral processing costs (especially blasting, crushing, and grinding). The industrial residue of this study, a type of aluminothermic slag, comes from the metallurgical processing of columbite (niobium and tantalum mineral) and has a content, measured by X-ray fluorescence, of 1.78 % of U₃O₈. This content is higher, for example than those found in Lagoa Real-BA (0.2 % in rock) and Santa Quitéria-CE (0.1 % in rock). Another material that will be studied is ThO₂, which is also present in the slag with a content, measured by X-ray fluorescence, around 3.66 %. The process parameters analyzed were pH of the solution, time, granulometry and percentage of solids. The metallurgical recovery of U₃O₈ reached a maximum value of 71,3 % with pH = 1, time of 8 hours, 65 % percentage of solids, and 200 µm of granulometry. The metallurgical recovery of ThO₂ reached a maximum value of 69,7 % with pH = 1, time of 8 hours, 65 % percentage of solids, and 200 µm of granulometry.

Keywords: uranium oxide, thorium oxide, leaching.



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. MATERIALS AND METHODS

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 14 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 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 Equation 1, whereas m is the mass of solids (slag) and liquid (deionized water) [12, p. 47].

$$S\% = \frac{m_{solid}}{m_{solid} + m_{liquid}} \rightarrow m_{liquid} = \frac{m_{solid}}{S\%} - m_{solid} \quad (1)$$

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 4 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:

$$n = \text{granulometry} \times \text{pH} \times \text{percentage of solids} \times \text{assay time} \times \text{duplicates} \quad (2)$$

$$n = 2 \times 2 \times 2 \times 2 \times 2 \times 3 = 48 \text{ assays}$$

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 $(40,00 \pm 0,01)$ g aliquots of slag.

i) Preparation of the pulp. Using Equation 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 Figure 1 and Figure 2.



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

Source: the authors.

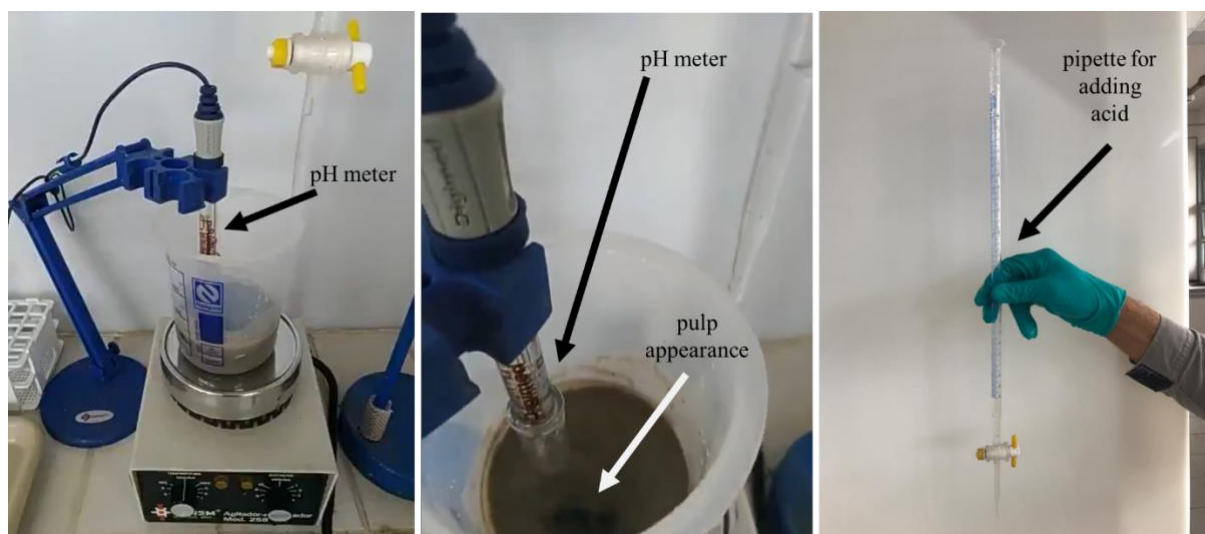


Figure 2: Some details of the experimental setup. On the left, the beaker is on the stirrer. In the center, the general appearance of the pulp. On the right, pipette for controlled addition of acid. Source: the authors.

- iv) pH monitoring. The setup must be kept on the magnetic stirrer throughout the assay (4 h or 8 h) to homogenize the pulp while the pH is monitored and controlled (see Figure 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 metallurgical recovery of uranium and thorium oxides

As the objective is to study the metallurgical 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 Equation 3:

$$R = 1 - \frac{m_s \cdot t_s}{m_{slag} \cdot t_{slag}} \quad (3)$$

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.

Equation 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 1. It is observed that there is no significant variation in the levels of uranium and thorium oxides between the particle sizes.

Table 1: Result of the FRX analysis of the head sample.

Opening (μm)	% retained	U_3O_8	ThO_2	Opening (μm)	% 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	1,76	3,67	200	0	-	-
180	7	1,76	3,66	180	21,2	1,78	3,65
150	8,6	1,79	3,64	150	26	1,79	3,68
105	7,7	1,78	3,66	105	23,3	1,76	3,66
75	4,5	1,79	3,65	75	13,7	1,77	3,67
53	3,4	1,79	3,67	53	10,4	1,8	3,69
44	1,4	1,76	3,66	44	3,7	1,78	3,66
<44	0,6	1,79	3,63	<44	1,8	1,77	3,65
Head - 100 % < 1000		$1,78 \pm 0,01$	$3,66 \pm 0,02$	Head - 100 % < 200		$1,78 \pm 0,01$	$3,66 \pm 0,01$

According to table 1, 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. As the slag deposit has 50 thousand tons, the amount of U_3O_8 is around 890 tons (1.78 % of 50,000 tons).

3.2. Leaching result - Chemical analysis of the solid and metallurgical recovery

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



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

Source: the authors.

The results of the chemical analysis of solids after leaching and the results of the metallurgical recovery of uranium and thorium oxides (Equation 3) are summarized in Table 2. 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 2: Result of chemical analysis (FRX) of the solid after leaching, filtering, and drying.

Granulometry (µm)	pH	Solids (%)	Time (h)	m_{liquid}^1 (g)	m_{solid}^2 (g)	U_3O_8 (%)	ThO_2 (%)	U_3O_8^3 Recovery (%)	ThO_2^3 Recovery (%)
200	1	45	4	$48,9 \pm 0,4$	$36,2 \pm 0,6$	$1,1 \pm 0,1$	$2,4 \pm 0,3$	$44,1 \pm 0,1$	$40,7 \pm 0,1$
1000	1	45	8	$48,9 \pm 0,3$	$39,1 \pm 0,3$	$1,0 \pm 0,1$	$2,1 \pm 0,1$	$45,1 \pm 0,1$	$43,9 \pm 0,2$
200	3	65	8	$21,5 \pm 0,1$	$36,4 \pm 0,6$	$1,0 \pm 0,1$	$2,0 \pm 0,3$	$48,9 \pm 0,1$	$50,3 \pm 0,1$
1000	1	45	4	$48,9 \pm 0,6$	$36,1 \pm 0,6$	$1,2 \pm 0,1$	$2,4 \pm 0,2$	$39,2 \pm 0,1$	$40,8 \pm 0,1$
200	3	65	4	$21,5 \pm 0,7$	$37,2 \pm 0,7$	$1,2 \pm 0,1$	$2,7 \pm 0,1$	$37,3 \pm 0,1$	$31,4 \pm 0,2$
1000	1	65	4	$21,5 \pm 0,4$	$36,1 \pm 0,1$	$1,2 \pm 0,1$	$2,3 \pm 0,1$	$39,2 \pm 0,1$	$43,3 \pm 0,1$
200	3	45	8	$48,9 \pm 0,1$	$33,1 \pm 0,9$	$1,1 \pm 0,5$	$2,5 \pm 0,2$	$48,9 \pm 0,2$	$43,5 \pm 0,3$
1000	3	45	4	$48,9 \pm 0,2$	$33,9 \pm 0,6$	$1,3 \pm 0,3$	$2,9 \pm 0,4$	$38,1 \pm 0,1$	$32,8 \pm 0,1$
200	1	65	8	$21,5 \pm 0,8$	$34,1 \pm 0,8$	$0,6 \pm 0,1$	$1,3 \pm 0,1$	$71,3 \pm 0,1$	$69,7 \pm 0,1$
1000	3	65	4	$21,5 \pm 0,1$	$32,4 \pm 0,4$	$1,3 \pm 0,2$	$2,8 \pm 0,3$	$40,8 \pm 0,1$	$38,0 \pm 0,1$
200	1	45	8	$48,9 \pm 0,2$	$37,9 \pm 0,8$	$1,0 \pm 0,1$	$2,1 \pm 0,1$	$46,8 \pm 0,1$	$45,6 \pm 0,1$
1000	1	65	8	$21,5 \pm 0,9$	$32,5 \pm 0,1$	$1,0 \pm 0,1$	$2,1 \pm 0,1$	$54,4 \pm 0,1$	$53,4 \pm 0,2$
200	3	45	4	$48,9 \pm 0,2$	$35,2 \pm 0,1$	$1,3 \pm 0,3$	$2,9 \pm 0,5$	$35,7 \pm 0,1$	$30,3 \pm 0,1$
1000	3	65	8	$21,5 \pm 0,6$	$33,1 \pm 0,1$	$1,2 \pm 0,1$	$2,5 \pm 0,3$	$44,2 \pm 0,2$	$43,5 \pm 0,1$
200	1	65	4	$21,5 \pm 0,6$	$35,2 \pm 0,8$	$1,0 \pm 0,4$	$2,1 \pm 0,2$	$50,6 \pm 0,2$	$49,5 \pm 0,1$
1000	3	45	8	$48,9 \pm 0,1$	$37,9 \pm 0,9$	$1,1 \pm 0,2$	$2,4 \pm 0,2$	$41,4 \pm 0,1$	$37,9 \pm 0,1$

¹ Determined by Equation 1. ² Solid mass after leaching, filtering, and drying. ³ Determined by Equation 3.

Complementing the results, Figure 4, 5, 6, and 7 shows the metallurgical recovery of the group "granulometry - pH - % solids - time". Thus, "200-1-45", for example is 200 μm granulometry, pH = 1, 45 % solids percentage.

According to the graphs, the main parameters for metallurgical recovery are time and pH. For pH = 1 and t = 8 h, for both oxides, the best results occurred.

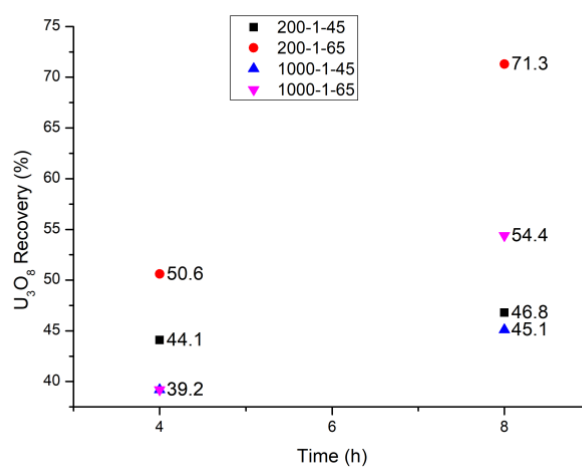


Figure 4: U_3O_8 metallurgical recovery: pH = 1.
Source: the authors.

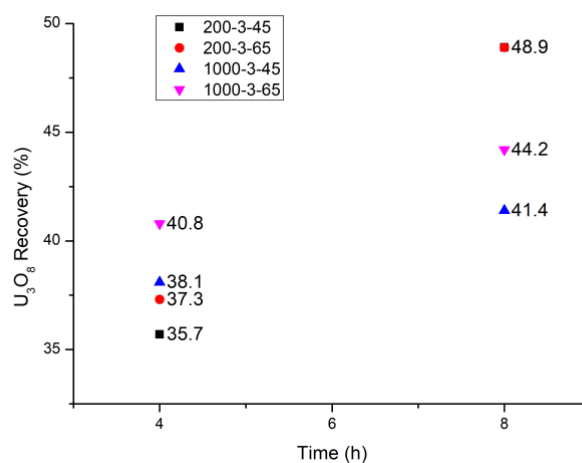


Figure 5: U_3O_8 metallurgical recovery: pH = 3.
Source: the authors.

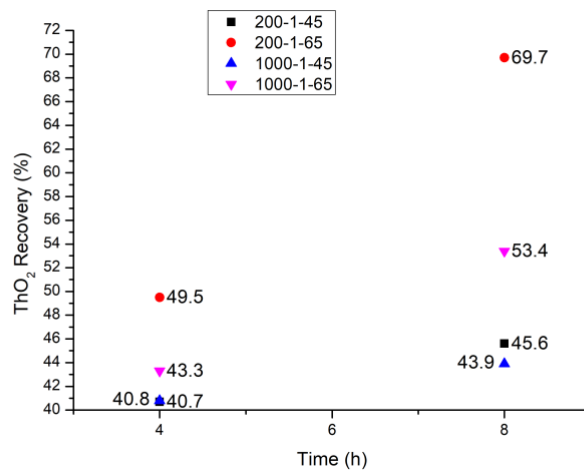


Figure 6: *ThO₂ metallurgical recovery: pH = 1.*
Source: the authors.

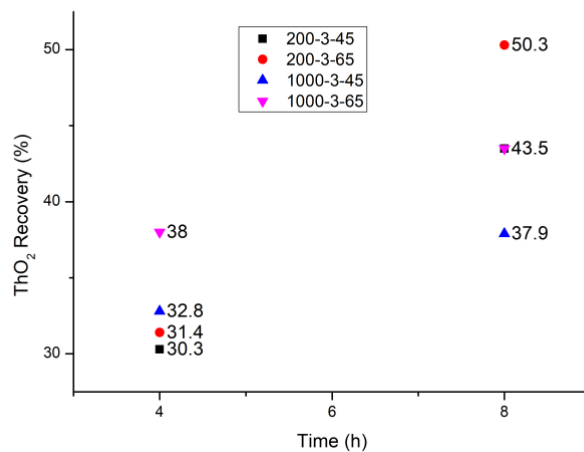


Figure 6: *ThO₂ metallurgical recovery: pH = 3.*
Source: the authors.

The pulp with a solids percentage of 65 % presented better results in the metallurgical recovery than the pulp with 45 % of solids. This contrasts with what is generally observed, that is, the lowest percentages are linked to better leaching results and, consequently, to better metallurgical recoveries [6, 7, 8].

The metallurgical recovery obtained with a granulometry of 200 μm had a better performance when compared to the metallurgical recovery of granulometry of 1000 μm . This is related to the fact that smaller granulometry allows better leaching - the reduction of the dimension increased the contact between sulfuric acid and the oxides [9, 10, 11].

Despite this, the result obtained with the granulometry contrasts with Table 1, where the size of the slag particles did not affect the levels of U_3O_8 and ThO_2 measured by XRF. Thus, it appears that leaching is a necessary process for the metallurgical recovery of slag.

The best results for the metallurgical recovery of the oxides occurred for the parameters 200 μm of granulometry, $\text{pH} = 1$, percentage of solids of 65 % and time of 8 h. For U_3O_8 , the recovery was 71.3 % (see Figure 4). For ThO_2 , the recovery was 69.7 % (see Figure 6).

The highest results obtained with $\text{pH} = 3$ were in the order of 50 % (see Figure 5 and 7) for both oxides. Although these values are much lower than those obtained with $\text{pH} = 1$, they should not be discarded, since the higher pH implies a lower consumption of acid. This can be interesting from an economic point of view, as it represents a lower cost.

4. CONCLUSION

After granulometric separation of the slag and analysis of the products by XRF, the result obtained for the U_3O_8 content is 9 times higher than that of Caetité-BA [6, p. 77] and 18 times higher than that of Santa Quitéria [7, p. 2160]. The amount of uranium stored in the deposit is around 890 tons of U_3O_8 .

After the leaching tests, it was found that the main factors for metallurgical recovery were time and pH . In contrast to the literature, in this study, a higher percentage of solids resulted in greater leaching and metallurgical recovery. And the smaller granulometry implied greater metallurgical recovery.

The best metallurgical recovery results were 71 % for U_3O_8 and 69 % for ThO_2 . For these results, the process parameters were 200 μm , $\text{pH} = 1$; 65 % solids; and time of 8 h.

In recoveries with $\text{pH} = 3$, the metallurgical recovery was lower, being around 50 % for U_3O_8 and ThO_2 . These values can still be attractive considering that higher pH implies a lower amount of acid.

Thus, the recovery of uranium and thorium oxides can represent an opportunity to reduce the radiological risk of slag - an industrial waste - and reduce the need to build deposits of radioactive material or even provide an increase in the Nuclear Fuel Cycle.

For future studies it is necessary to investigate the relationship between the percentage of solids and leaching; investigate other leaching times, other solids percentages, other pH values and other granulometry values; perform the leaching using other process parameters such as, for example, pressure, other types of acid, use of oxidizing agents; evaluate the cost involved in inputs and processes.

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 [7, pp. 510-3]. There are works, for example, with the leaching of rare earth elements containing uranium and thorium that use amines as extractants [12, p. 499].

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