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Evaluation of the acid leaching technique for recovery of U_3O_8 and ThO_2 in niobium/tantalum slag

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ABSTRACT

This study presented the recovery of uranium oxide and thorium oxide from aluminothermic slag from the metallurgical processing of columbite – a niobium/tantalum mineral with the presence of U_3O_8 and ThO_2 – from a mining-industrial facility. The methodology consisted of sampling, comminution, and leaching using sulfuric acid. The head sample showed contents of (1.78 ± 0.14) % for U_3O_8 and (3.66 ± 0.04) % for ThO_2. The metallurgical recovery reached values above 80% for the uranium oxide and above 70% for the thorium oxide for pH < 1.5 and process time greater than eight hours.

Keywords: **uranium oxide, thorium oxide, metallurgical recovery.**

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1. INTRODUCTION

The availability and degree of energy use are linked to the socioeconomic development of countries. However its generation impacts the environment. Thus, matrix diversification is necessary to achieve sustainability [1]. In this perspective, the nuclear option is advantageous because it emits low carbon, has a low impact on water quality, has small soil occupation when compared to other matrices, accounts for and manages waste and rejects in all stages of the fuel cycle, generates and maintains jobs for decades. Its direct intake – uranium oxide – has only one purpose, which is energy production [2].

Still, in the context of sustainability, several authors are exploring an option to improve the cycle of nuclear fuel, which is the reuse of naturally occurring radioactive material (NORM). As uranium and thorium mineralize together with other elements such as niobium, tantalum, tin, mineral coal, phosphate, and rare earth, the industries that process them end up having as by-product NORM residues and rejects. This material constitutes a liability for industry, as in addition to the management requirements common to all industrial waste, there are also those related to safety and radiological protection [4,5,6,7,8].

Thus, by developing a process route that recovers the uranium present in the waste and tailings from mining-industrial facilities, it is possible to transform an environmental liability into an input for the fuel cycle, reduce the level of radiological safety necessary to contain the NORM and the necessity to build repositories for your safe storage.

Therefore, this study aims to evaluate the metallurgical recovery of uranium (U_3O_8) and thorium (ThO_2) oxides present in an aluminothermic slag from the production of niobium and tantalum ferroalloys – a residue/reject from the metallurgical processing of the columbite.

2. MATERIALS AND METHODS

This work had the following steps: sampling; sample preparation (comminution); leaching assays; determination of metallurgical recovery. The steps are detailed below.

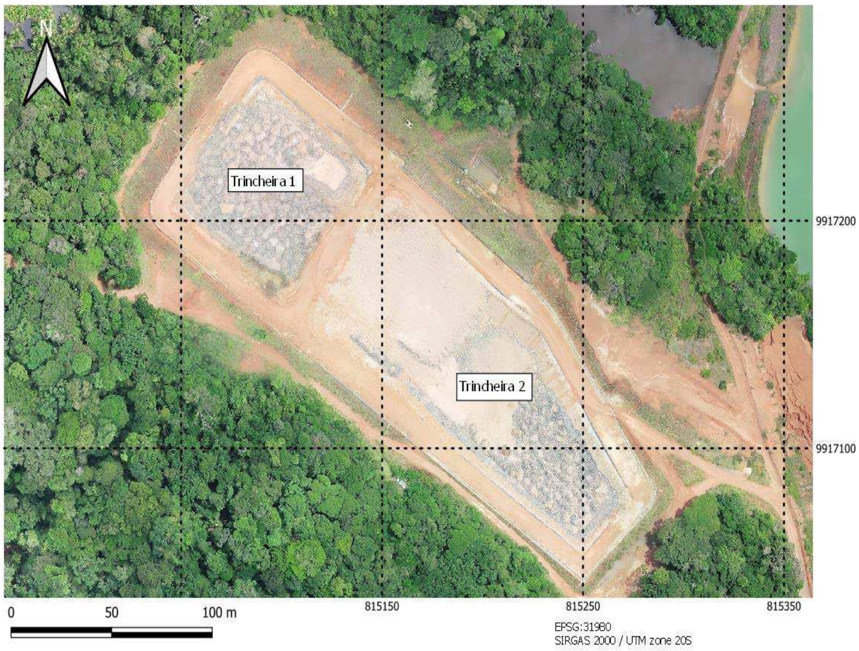
2.1. Aluminothermal slag

The waste used in this study comes from a mining-industrial facility located in the state of Amazonas, Brazil. The company produces niobium/tantalum ferroalloys from the pyrometallurgical processing of columbite (a mineral of niobium and tantalum that contains uranium and thorium in its composition) [10].

Columbite is inserted into furnaces with other inputs, such as barite, coal, and aluminum oxide. The carbothermic reduction takes place in the furnaces, resulting in the niobium/tantalum ferroalloy, which is commercialized, and in waste, including aluminothermic slag. This material is a NORM residue because, during the production process, uranium and thorium oxides migrate to this phase, which reaches an activity concentration higher than the level of exemption of radiological protection requirements [11, 12, 13].

The waste storage site is a licensed deposit located within the facility – see Figure 1 (“Trincheira 1” and “Trincheira 2”). Around 80.000 tons of slag [10] are deposited without chronological control of the material. Thus, piles are formed, as shown in Figure 2. where it is not possible to conduct probes for the sampling of the material.

Figure 1: Deposit for slag storage



Source: Google Earth

The aspect of the slag can be seen in Figure 2. It generally has dimensions of less than one cubic meter, the most common size similar to that of a closed handle.

Figure 2: The aspect of the pile and the slag

2.2. Sampling and sample preparation

Figure 1 shows the sampling site: 130 kilograms of slag were collected at twenty-five points within the Storage Cell, spaced between 15 and 20 meters from each other. This procedure was adopted because of the impossibility to conduct probes in the repository and because the slag was deposited without chronological control.

After sampling, the slag went through a comminution stage. Initially, it was crushed and ground (50% less than 1.0 mm and 50% less than 0.2 mm) to obtain the necessary granulometry for leaching. Finally, the sample was homogenized and quartered to obtain the aliquots used in the assays – one of these, the head sample, was sent directly to the X-ray fluorescence analysis (XRF) to identify the initial contents of thorium uranium oxides. Figure 3 shows the equipment used: crushers; the ball mill; the Jones separator; the XRF analyzer (Rigaku, model ZSX Primus).

Figure 3: Equipment used in sample preparation.

crusher **ball mill** **Jones separator** **XFR analyzer**

2.3. Leaching and metallurgical recovery assays

The leaching assays aimed to verify uranium and thorium content variation in the obtained solid and liquid fractions.

The process variables were:

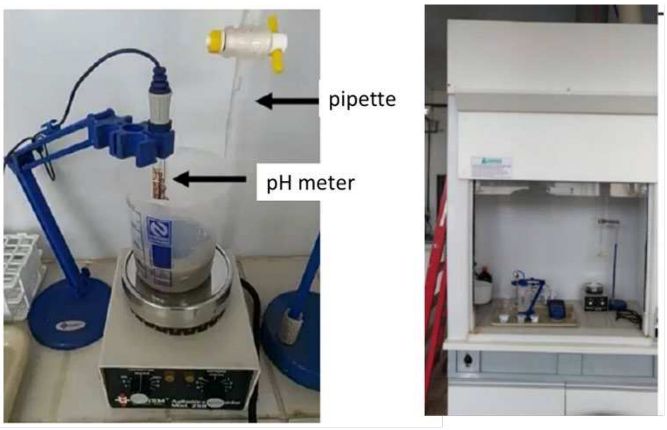
i) Percentage of solids. For pulp formation, two percentages of solids were selected: 20% and 40%.
ii) pH was controlled by adding sulfuric acid to the pulp. Five values for pH were used: 1; 1.5; 2; 2.5, and 3.
iii) Granulometry. Particle sizes of 1000 µm and 200 µm were prepared using the equipment in Section 2.1.
iv) Time. For this process variable, 6 h, 7 h, 8 h, and 9 h were selected as assay durations.

The pulp was prepared in a 250 mL beaker using 40 g of slag according to the granulometry selected for the test. As there are two different percentages of solids, 160 g of water were used for the 20% percentage and 60 g of water for the 40% percentage. Next, the pulp was placed on the magnetic stirrer for homogenization. Next, the pH was measured, and sulfuric acid was added through the pipette to obtain the desired value for each assay. Finally, the assay containing the set "granulometry-percentage of solids-pH" selected was placed under agitation during the processing time.

The equipment mentioned in the previous paragraph can be seen in Figure 4.

Thus, 160 assays were carried out, i.e., 80 assays in duplicate. At the end of each one, the pulp was filtered, dried, had its mass measured, and its contents of U_3O_8 and ThO_2 analyzed by FRX. Finally, using Equation 1. the metallurgical recovery, R, was obtained.

Figure 4: Equipment used in leaching assays.



magnetic stirrer and pH meter **experimental arrangement**

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

Where m_S and t_s are, respectively, the mass and content of the solid after leaching; m_{slag} and t_{slag} are, respectively, the mass and content of the slag before leaching. Note that the contents are for uranium and thorium oxides.

3. RESULTS AND DISCUSSION

3.1. Head sample

The XRF results, see Table 1. show significant levels of aluminum and silicon oxide.

Table 1: FRX result for the head sample.

Oxide	(% and uncertainty)	Oxide	(% and uncertainty)
SnO_2	0.036 ± 0.002	Nb_2O_5	1.62 ± 0.02
Fe_2O_3	0.91 ± 0.05	Ta_2O_5	0.56 ± 0.02
ZrO_2	2.96 ± 0.12	SiO_2	19.0 ± 1.0
U_3O_8	1.78 ± 0.14	Al_2O_3	53.0 ± 2.0
ThO_2	3.66 ± 0.04	Y_2O_3	0.54 ± 0.02

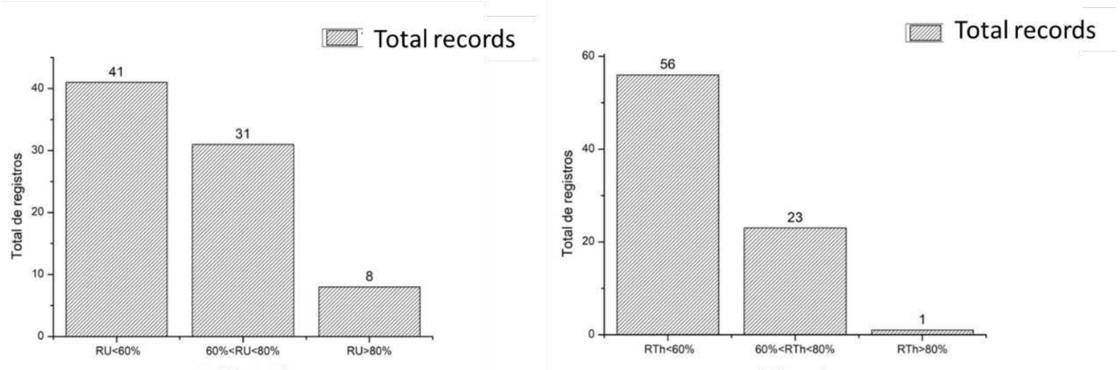
The first may be linked to the process of obtaining ferroalloys since aluminothermy uses Al_3O_2 (aluminum oxide) as input, and, in this type of processing, aluminum migrates to the waste [14]. The SiO_2 (silicon oxide) is very commom in slags – typically between 15% and 20% [15].

The uranium oxide content draws attention: about six times higher than the levels in Caetité (Bahia); 18 times higher than the Santa Quitéria Project (Ceará); and larger than most major deposits in the world. This result alone is not enough to establish the use of waste as an alternative to mining since its quantity is limited, but it already shows that there is potential to be explored [2, 9, 16].

3.2. Leaching assays - influence of the process parameters

Figure 5 presents the distribution of recoveries of uranium and thorium oxides in three classes: recovery below 60 % ($R < 60$ %); recovery between 60 % and 80 % ($60\ \% < R < 80$ %); and recovery above 80 % ($R > 80$ %). U_3O_8 presented the highest number of records in class $R > 80$ %. For both oxides, the most representative class was $R < 60$ %.

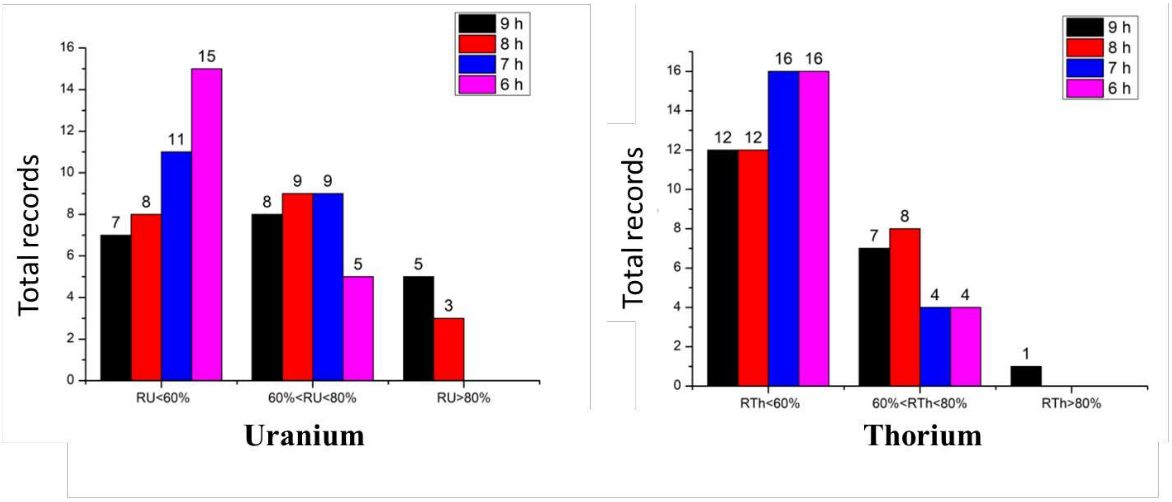
Figure 5: Results of leaching assays - distribution of metallurgical recovery.



Uranium **Thorium**

Time had a very significant influence on metallurgical recovery, as according to Figure 6, the greatest recoveries correspond to times greater than or equal to 8 h for both oxides. The contact between the slag particles and sulfuric acid allows the dissociation of the residue and the transfer of uranium and thorium to the lye. Thus, a longer time can potentiate this effect.

Figure 6: Results of leaching assays – influence of time.



On the other hand, there is a time from which the solution becomes saturated, and that is when the balance between solid and liquid fractions occurs [17,18]. This was not observed in this study, possibly due to the choice of parameters. Nevertheless, it can be inferred that it is more than eight hours – in Section 3.5, which presents the results as a function of time, this statement becomes more evident.

Also, concerning Figure 6, there are records with recoveries below 80% at all times. This result shows that the other process parameters also influence leaching and metallurgical recovery [17].

The influence of pH is shown in Figure 7. There is a marked predominance for records greater than 80 % for pH =1 – especially for uranium. This role of pH was expected since the lower values potentiate the formation of ions that are transferred to the lye [6,17,18]. On the other hand, the observation of recoveries lower than 80 % for pH = 1 corroborates the statement made for time, that is, that the other parameters also influence leaching and metallurgical recovery.

The influence of granulometry is shown in Figure 8. A relevant role of this parameter was not observed due to the uniformity of the distributions. This result was not expected since the larger particles represent larger surfaces that facilitate leaching and, consequently, metallurgical recovery [14, 17, 19].

Figure 7: Results of leaching assays – influence of pH.

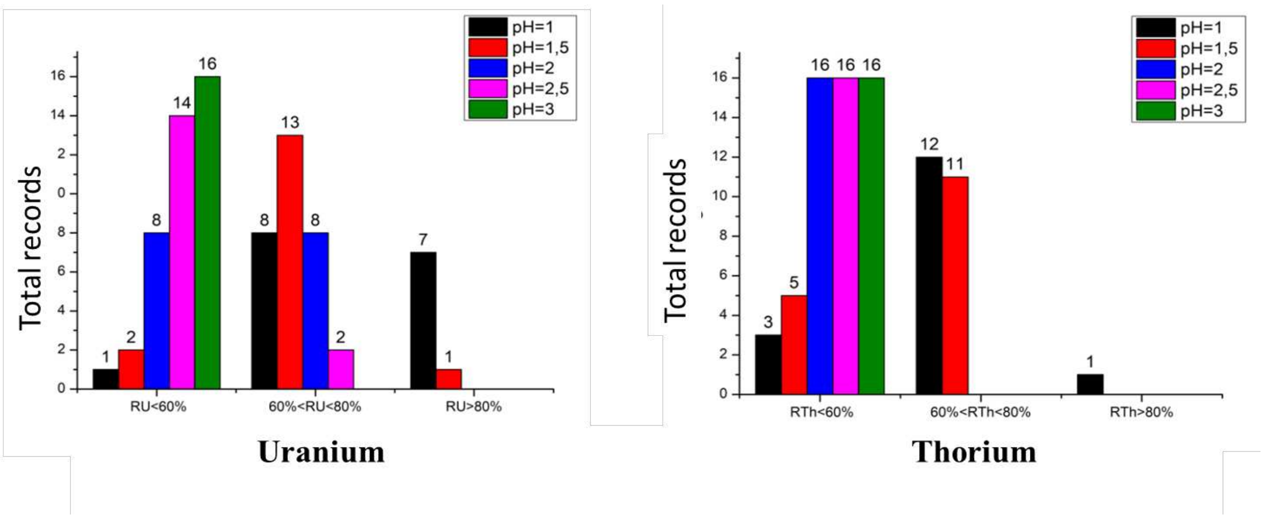
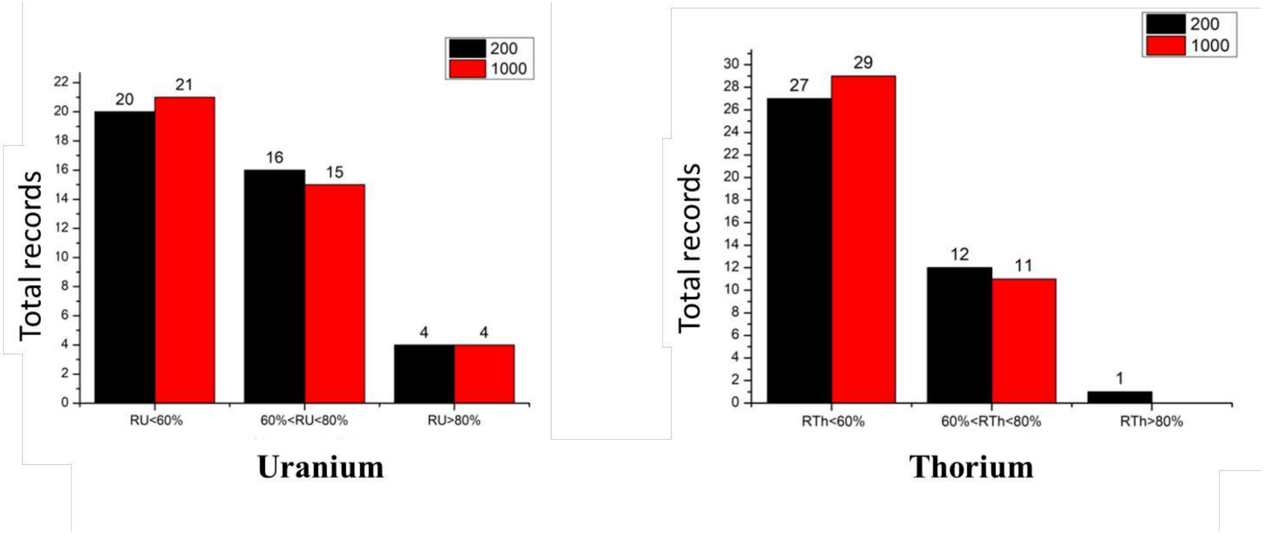


Figure 8: Results of leaching assays – influence of granulometry.



Thus, the distributions observed in Figure 8 may be related to the following:

i) operational procedure itself, i.e., the fact that we have four competing process parameters;

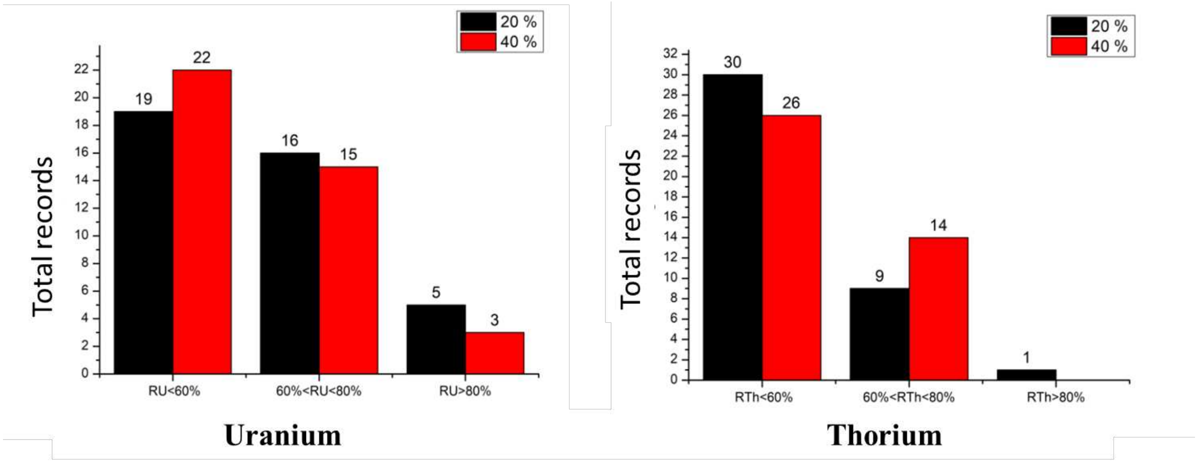
ii) selected dimensions (200 μm and 1000 μm) – a greater or lesser slag comminution may be required;

iii) physical structure of the waste - according to the physical tests, it was not possible to obtain concentrated products according to the physical properties;

iv) specific surface area of the slag – a parameter that considers the material's porosity and texture [20, 21], but which was not the target of this study.

The influence of the percentage of solids is presented in Figure 9. It is observed that the parameter of 20 % of solids obtained the highest number of records in the classes with the highest recoveries.

Figure 9: Results of leaching assays - influence of solids percentage.



Uranium **Thorium**

These results were not expected since the higher the availability of solids, the better leaching [14, 17]. On the other hand, some authors presented results in which the percentage of solids was not relevant [22].

3.3. Leaching assays – recovery of uranium and thorium oxides

For the evaluation of leaching tests, the results were grouped into a configuration of "pH-granulometry-percentage of solids", as shown in Table 2.

The “Assays” column presents the results in ascending order of time, i.e., the first of each group was submitted to a leaching time of six hours, the second to seven hours, the third to eight hours, and the fourth to nine hours. These data were used for the graphs of recovery versus time.

As noted in Section 3.4, the most relevant parameters in this study were pH and time. Thus, Figure 10 and Figure 11 present, respectively, the results for pH =1 and for pH = 1.5. The others were not presented because from pH = 2. Metallurgical recoveries are concentrated in the R classes < 80 %.

Table 2: Grouping of leaching assays for analysis of metallurgical recovery.

Grupo	pH	Configuration (pH-granulometry-solid %)	Assays
1	~ 1.0	1 – 200 – 20	63. 5, 18, 70
2	~ 1.0	1 – 200 – 40	1. 79, 65, 6
3	~ 1.0	1 – 1000 – 20	55, 52. 40. 39
4	~ 1.0	1 – 1000 – 40	69, 26, 48, 44
5	~ 1.5	1.5 – 200 – 20	73. 53. 11. 41
6	~ 1.5	1.5 – 200 – 40	31. 22. 8, 13
7	~ 1.5	1.5 – 1000 – 20	47, 75, 17, 66
8	~ 1.5	1.5 – 1000 – 40	58, 21. 9, 72
9	~ 2.0	2.0 – 200 – 20	29, 56, 64, 14
10	~ 2.0	2.0 – 200 – 40	45, 46, 51. 15
11	~ 2.0	2.0 – 1000 – 20	77, 24, 32. 28
12	~ 2.0	2.0 – 1000 – 40	43. 50. 76, 2
13	~ 2.5	2.5 – 200 – 20	61. 37, 80. 78
14	~ 2.5	2.5 – 200 – 40	20. 33. 30. 7
15	~ 2.5	2.5 – 1000 – 20	16, 34, 49, 36
16	~ 2.5	2.5 – 1000 – 40	68, 25, 57, 54
17	~ 3.0	3.0 – 200 – 20	62. 10. 59, 42
18	~ 3.0	3.0 – 200 – 40	4, 12. 35, 19
19	~ 3.0	3.0 – 1000 – 20	27, 23. 74, 67
20	~ 3.0	3.0 – 1000 – 40	71. 3. 38, 60

The pH = 1 groups had the best metallurgical recovery performance (R_{U3O8} or R_{ThO2}), as shown in Figure 10. Among these, Assay 70 stands out in Group 1 with R_{U3O8} = (82.9 ± 0.2) % and R_{ThO2} = (81.6 ± 0.2) %. The other process parameters in this group were granulometry 200 μm; and 20% solids.

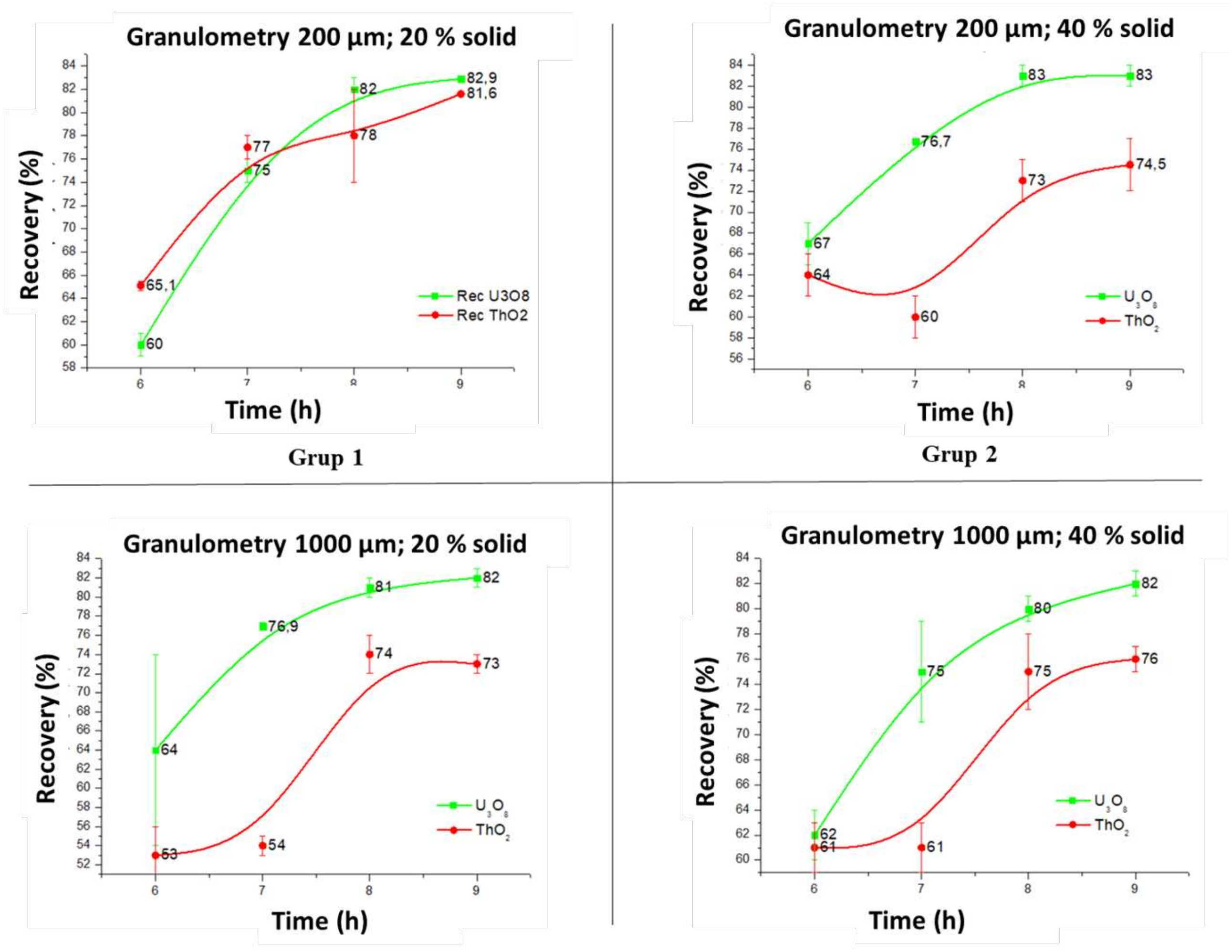
Other relevant results, this time in Group 2 (pH = 1; granulometry 200 µm; and 40% solids), are Assay 6 and Assay 65 – both with R_{U3O8} = (83.0 ± 1.0) %. It is added that Assay 65 was carried out in eight hours. Thus, recovery of over 80 % was achieved in less than nine hours – which may represent, in an operational phase, savings in inputs.

According to Figure 11. although the number of records greater than 80% of the pH groups = 1.5 is lower than the pH groups = 1 here, there were also highlights:

i) Group 5 – thorium oxide had, in Assay 41 (pH = 1.5; t = 9 h; granulometry of 200 µm; 20 % solids), a recovery of R_{ThO2} = (76 ± 1.0) %;

ii) Group 7 – uranium oxide had, in Assay 66 (pH = 1.5; t = 9 h; granulometry of 1000 µm; 20 % solids), a recovery of R_{U3O8} = (81 ± 4,0)

Figure 10: Results of leaching assays - pH groups = 1.



Grup 1

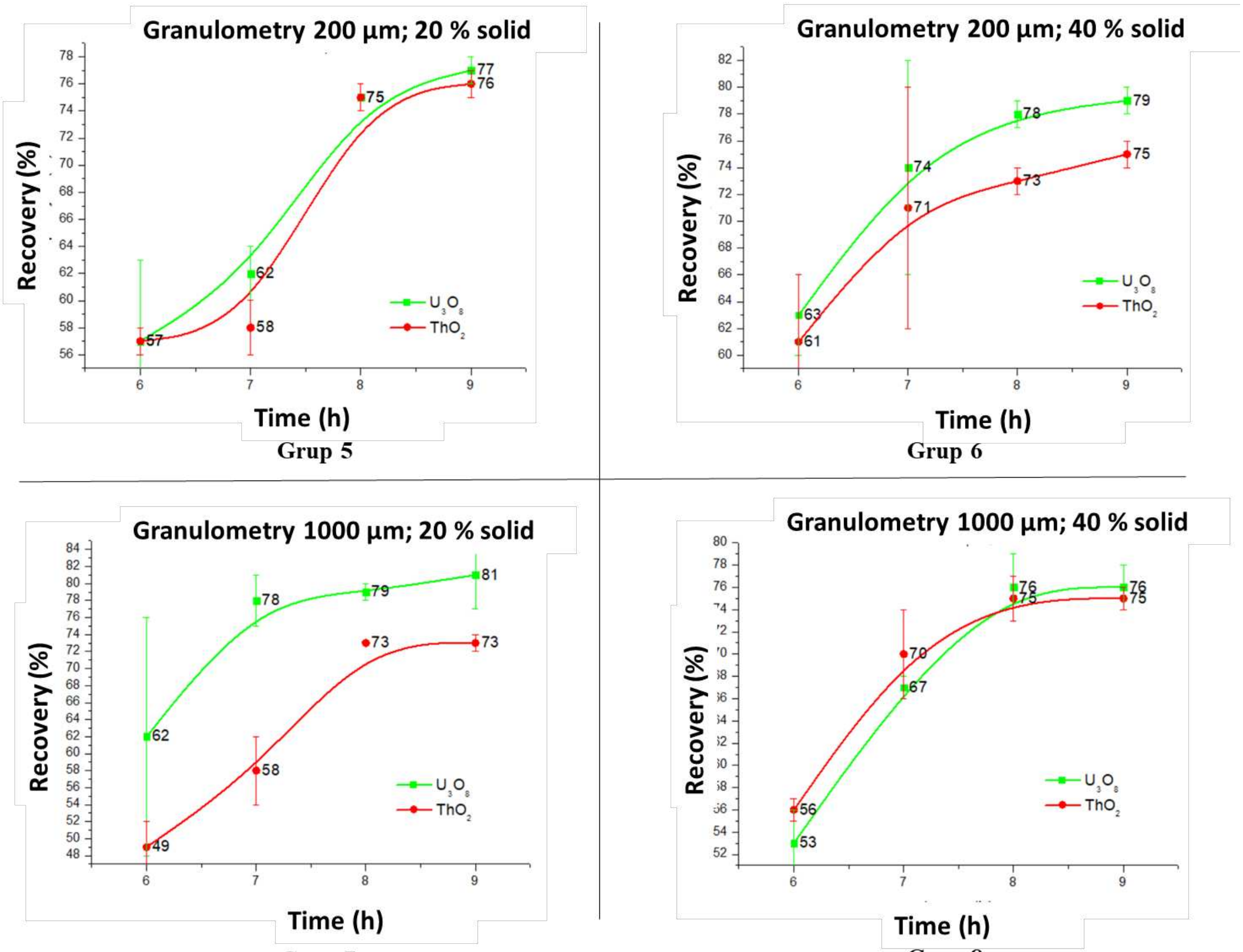
Grup 2

Grup 3

Grup 4

The reason for the notes in the preceding paragraphs is that a higher pH may imply, at an operational stage, an increase in the economy of supplies.

Figure 11: Leaching assays results - PH groups = 1.5.



Grup 5

Grup 6

Grup 7

Grup 8

4. CONCLUSION

The head sample presented higher levels of uranium oxide and thorium oxide than those of Caetité, Santa Quitéria, and the main deposits in the world [7,9,23]. Thus, despite the limitation in the feed mass, since there are only 80,000 tons of slag in the tank, it has potential – either as a complement to the fuel cycle or due to the reduction of liabilities.

It was observed that the main parameters for leaching were pH and time – the highest recoveries obtained were at pH less than or equal to 1.5 and times greater than or equal to eight hours. The following stand out: Assay 70 (pH = 1; t = 9 h; granulometry 200 µm; and 20% solids) for both U_3O_8

and ThO_2 (R > 80 %); Assay 6 (pH = 1; t = 9 h; granulometry 200 μm; e 40 % solids) and Assay 65 (pH = 1; t = 8 h; granulometry 200 μm; and 40 % solids)) for uranium oxide (R > 80 %); Assay 41 (pH = 1.5; t = 9 h; granulometry 200 μm; 20 % solids) for thorium oxide (R > 75 %); and Assay 66 (pH = 1.5; t = 9 h; granulometry 1000 μm; 20 % solids) for U_3O_8 (R > 80 %).

As a future study, it must be verified the influences of particle dimensions since granulometry was not fundamental in this study, contrary to what the literature pointed [14, 19, 24].

It is also necessary to check what is the ideal leaching time. In this study, it was found that it is around eight or nine hours. However, it is necessary to establish it with greater precision to establish the time from which leaching is balanced.

In conclusion, from a sustainability perspective, it is necessary to think about future generations. That is, to reduce and reuse the waste in general. Thus, the option of processing slag, provided it meets the requirements of radiological protection and safety, is justifiable because it can increase the cycle of nuclear fuel since the metallurgical recovery has exceeded 60 % in many cases. In addition, processing can at least reduce a liability that requires the construction, operation, and control of deposits with radioactive material whose half-life is of the order of the age of the Earth (U-238) or even the universe (Th-232).

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REFERENCES

[1] WNA. Molten Salt Reactors. **World Nuclear Association**, 2018. Available at: <https://www.world-nuclear.org/information-library/current-and-future-generation/molten-salt-reactors.aspx>. Accessed in: 20 July 2019.

[2] WNA. The Nuclear Debate. **World Nucear Association**, 2020. Available at: <https://www.world-nuclear.org/information-library/current-and-future-generation/the-nuclear-debate.aspx>. Acesso em: 14 August 2021.

[3] DOE. Quadrennial Technology Review 2015. **United States Department of Energy**, 2015. Available at: <https://www.energy.gov/quadrennial-technology-review-2015>. Accessed in: 15 agosto 2021.

[4] HORE-LACY, I. Production of byproduct uranium and uranium from unconventional resources. In: HORE-LACY, I. **Woodhead Publishing Series in Energy Number 93 - Uranium for Nuclear Resources, Mining and Transformation to Fuel**. 1ª. ed. Duxford – United Kingdom: Elsevier, 2016. Cap. 9, p. 239-251.

[5] WANG, L. ET AL. Recovery of rare earths from wet-process phosphoric acid. **Hydrometallurgy**, Amsterdam, December 2009. 41-47.

[6] ZHANG, J.; ZHAO,. **Separation Hydrometallurgy of Rare Earth Elements**. New York: Springer International Publishing, 2016.

[7] IAEA. **IAEA-TECDOC-1849 - Uranium Resources as Co- and By-products of Polymetallic, Base, Rare Earth and Precious Metal Ore Deposits**. Viena: International Atomic Energy Agency, 2018. Available at: <https://www-pub.iaea.org/MTCD/Publications/PDF/TE-1849web.pdf>.

[8] FUKUMA, H. T.; FERNANDES, E. A. N.; QUINELATO, A. L. Distribuição de Radionuclídeos Naturais nos Produtos da Fabricação de Ácido Fosfórico com Rocha Fosfática de Itatiaia - Ceará. **Repositório do IPEN - International Nuclear Atlantic Conference - INAC 2002.** São Paulo, 2002. Available at: <https://www.ipen.br/biblioteca/cd/inac/2002/ENAN/E03/E03_046.PDF>. INAC/ENAN-2002.

[9] IAEA. List of Uranium Deposits - UDEPO. **IAEA.org - NUCLEUS**, 2020. Available at: <https://infcis.iaea.org/UDEPO/Deposits>. Accessed in: 26 December 2021.

[10] SAP AG. **SAP SE - System Applications and Products in Data Processing**. Walldorf: SAP AG, 2021. Versão 6.0. Suporte Package 11. Software de gestão de estoques da empresa.

[11] CNEN. **Posição Regulatória 3.01 / 001:** 2011 - Critérios de exclusão, isenção e dispensa de requisitos de proteção radiológica. Rio de Janeiro: Comissão Nacional de Energia Nuclear, 2011.

[12] MOURA, V. V.; PEREIRA, C. **Mineradoras e Metalurgias NORM**. Anais da Quarta Semana de Engenharia Nuclear e Ciências das Radiações. Belo Horizonte: UFMG. 2018. p. 572-8.

[13] RIO, M. A. P. **Indústrias de Mineração Não Nucleares e o Aumento da Exposição à Radiação Natural**. Tese (Doutorado em Ciências). Rio de Janeiro: UERJ, 1999.

[14] GUPTA, C. K. **Chemical Metallurgy**. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, 2003.

[15] SANO, N. et al. **Advanced Physical Chemistry for Process Metallurgy**. Tokyo: Academic Press, 1997. ISBN 978-0126189209.

[16] INB. INB Home > Nossas Atividades > Urânio > Recursos. **INB Home**, 2021. Available at: <https://www.inb.gov.br/Nossas-Atividades/Ur%C3%A2nio/Recursos>. Acessed in: 27 December 2021.

[17] HABASHI, F. **A Textbook of Hidrometallurgy**. Saint-Foy: Métallurgie Extractive Québec, Enr., 1993.

[18] NALIVAIKO, K. et al. Characterization and processing of radioactive uranium containing waste sludge by sulfuric acid leaching. **Journal of Environmental Chemical Engineering**, Amsterdã, v. 10. n. 1. janeiro 2022. ISSN 2213-3437.

[19] DUTRA, I. C.; LEITE, V. D. Influência da granulometria e do pH no processo de dessorção de amônia em torres de recheio. **Revista DAE**, São Paulo, p. 25-37, janeiro 2015.

[20] MULAZZANI, R. P.; GUBIANI, P. I. **Modelo de estimativa da área superficial específica do solo por meio da curva granulométrica**. XI Reunião Sul-Brasileira de Ciência do Solo - Qualidade do Solo & Ambiente de Produção. Frederico Westphalen: Sociedade Brasileira de Ciência do Solo. 2016. p. 1-3.

[21] CESSA, R. M. A. et al. Área Superficial Específica, Porosidade da Fração Argila e Adsorção de Fósforo em dois Latossolos Vermelhos. **Revista Brasileira de Ciências do Solo**, São Paulo, v. 33. n. 5, p. 1153-1162. 2009. ISSN 1806-9657.

[22] IBRAHIM, M. E. et al. Processing of the mineralized Black Mica for the recovery of uranium, rare earth elements, niobium, and tantalum. **Hydrometallurgy**, Amsterdam, v. 197, novembro 2020.

[23] IAEA. IAEA.org - NUCLEUS List of Thorium Deposits - ThDEPO. **IAEA.org - NUCLEUS**, 2020. Disponivel em: <https://infcis.iaea.org/THDEPO/Deposits>. Accessed in: 26 December 2021.

[24] VAN DER SLOOT, H. A.; HEASMAN, L.; QUEVAUVILLER, P. H. Harmonization on Leaching. **Extraction Tests**, Amsterdam, p. 281-285, 1997.