



Study of the physical properties of aluminothermic slags for the recovery of uranium and thorium

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ABSTRACT

NORM minerals generate, after metallurgical processing, radioactive slags that can be controlled by CNEN. Thus, it is necessary to establish a reprocessing route to make the material exemption. The route necessarily passes through the characterization of the slag from its physical properties. In this paper the results of the variation of the concentrations of U and Th oxides with the electrical, and magnetic properties of the slag, with their granulometry and with their density are presented. It has been observed that the metallurgical processing produces a slag with molecular connections between the oxides that constitute it. In this way, the separation of the oxides will only be possible with the leaching of the slag.

Keywords: NORM, uranium, thorium, columbite, tantalite, slags.

1. INTRODUCTION

There are minerals that, in addition to the element of interest, carry uranium and thorium isotopes. This type of material constitutes what the literature calls a naturally occurring radioactive material (NORM). An example of this type of material is the minerals subject to approval by the

Comissão Nacional de Energia Nuclear (CNEN). Among them is the columbite/tantalite (niobium-tantalum concentrate) [1].

Columbite/tantalite, in general, is processed by metallurgical processes to produce niobium-tantalum-iron alloys (FeNbTa) - which is a material free of regulatory control. As residue, a slag appears where the oxides of thorium (ThO_2) and uranium (U_3O_8) are concentrated [2]. This is generally arranged in piles, in trenches or other types of storage cells and must be stored in initial storage tanks for later adaptation and/or transfer to the Union. Therefore, the destination of this waste requires high investment in the design, commissioning, operation, and transfer [3].

In this article, the behavior of uranium and thorium oxides contents was studied through the tests of aluminothermic slag samples of FeNbTa: electrostatic separation, magnetic separation, gravimetric separation and granulometric studies (separation in sieves). Its initial objective is the characterization of the material in the function of physical properties. Thus, as it is the first part of a project that aims at uranium and thorium recovery, its purpose is to assist in the definition of a slag processing route.

2. MATERIALS AND METHODS

The studied slag is deposited in storage cells of the company premises as a case study. From time to time, the material is spread so that it does not reach a height that places the pile at risk of collapse. Thus, there is no chronological deposition and the only available information is the contents of niobium, tantalum, iron, tin, aluminum, silicon, uranium, and thorium oxides obtained by the company in the production of the alloys.

To obtain the samples, 130 kg of slag were collected at 25 points of the storage cells [4]. It was not possible to collect below the surface due to the impossibility of drilling the stack, as shown in Figure 1A. In Figure 1B, the appearance of the slag follows its processing.

Figure 1: In A, the appearance of a slag pile. In B, slag appearance.



Source: Author

2.1. Preparation of the sample

The preparation of the sample until obtaining the particle size suitable for the tests went through stages of crushing, grinding, homogenization and quarter sampling [5].

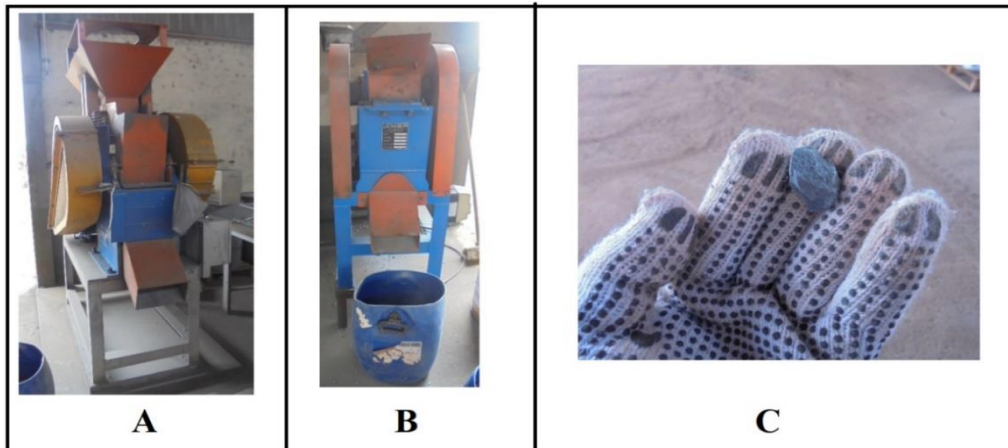
The crushing and grinding processes are processes of reducing the size (granulometry) of the rock or other material to adapt them to the next steps: take representative samples, processing, chemical analysis, for example. Basically, they are processes of mechanical fragmentation that use the different resistances of the materials to the forces of tension and compression [6].

Thus, the collected slag was crushed to 25 mm with the use of two jaw crushers shown in Figure 2A and Figure 2B. The appearance of the slag after this step is available in Figure 2C. Subsequently, the crushed material was homogenized with a concrete mixer.

Subsequently, the sample was comminuted in a ball mill (see Figure 3) and again homogenized with the concrete mixer.

The last stage of sample preparation was its blocking using a Jones Equipment - see Figure 4. The following samples were obtained: a 3.0kg for electrostatic separation; 2.6kg for magnetic separation; 14,0kg for gravimetric separation; 2.0 kg for the granulochemical studies and the remainder, approximately 100 kg, has been archived for future studies [5].

Figure 2: Crusher used (A and B) and the appearance of the slag after the crushing step (C).



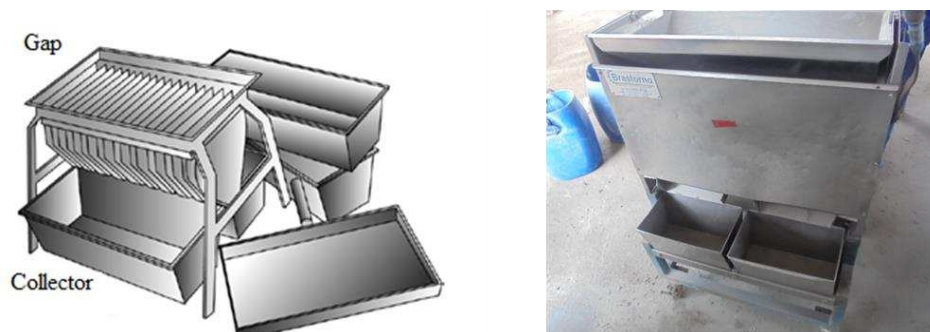
Source: Author

Figure 3: Ball mill used.



Source: Author

Figure 4: The left, Jones Equipment Scheme. The right, the equipment used.



Source: The left, [4]; the right, Author

2.2. Electrostatic separation

Electrostatic separation depends on the induction or polarization of charges in the constituent particles of the mineral and on the interaction of this charge with an external electric field. Conductive particles acquire a net electric charge and move towards the electric field. On the other hand, dielectrics move little [7]. Thus, the purpose of this test is to verify the concentration of U and Th as a function of the electrical properties of the slag.

The 3.0 kg sample was subjected to an electric field in an electrostatic separator/concentrator, according to Figure 5. The following products were obtained: conductors, non-conductors, and mixed (conductors and non-conductors).

Figure 5: *Electrostatic separator used. In A is deposited the non-conductors, in B the conductors and in C the mixed. The D, C, F buttons control the speed and voltage in the equipment.*



Source: Author.

2.3. Magnetic separation

Magnetic separation is based on the different response of minerals to an external magnetic field: particles that are attracted by the magnetic field, that is, with ferromagnetic or paramagnetic

behavior; particles that are repelled by the field, that is, with diamagnetic behavior [8]. The objective of this test is to verify the variation of the concentration of U and Th as a function of the magnetic properties of the material.

The sample of 2.7 kg was subjected to a magnetic separator/concentrator, according to Figure 6. The following products were obtained: magnetic, non-magnetic, and mixed (magnetic and non-magnetic mixture).

Figure 6: *Magnetic separator used. In A is deposited the non-magnetic, in B the magnetic and in C the mixed.*



Source: Author.

2.4. Gravimetric separation

The gravimetric separation is based on the different masses or densities of the particles that constitute a mineral. Thus, the purpose of this test is to verify the variation of the concentration of U and Th as a function of the density of the slag particles [4].

The equipment used was the flat table consisting of a rubber surface with V-shaped grooves that separate the material according to its mass: a part is directed to the sides being collected; the other part goes to the next table. In this way, the material is classified into concentrate (higher density

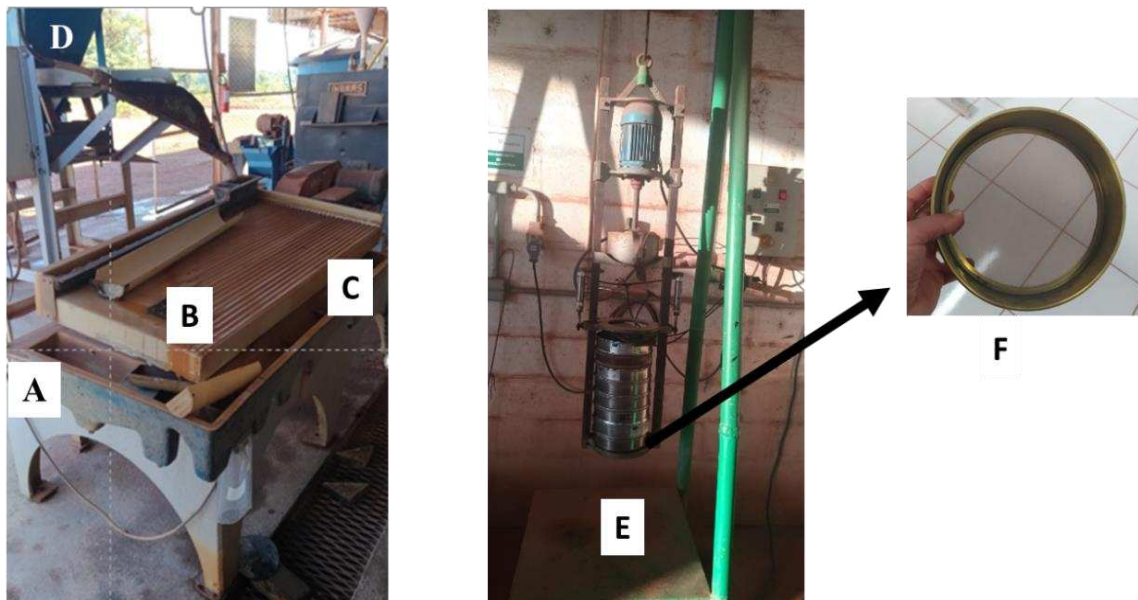
and/or mass), fine and mixed (mixture of concentrate and fines that have not been separated) [4] - see Figure 7.

2.5. Separation in sieves

Granulometry is a measure of the distribution of the different particles that make up a given mass. Thus, separation in granulometric sieves is a technique for separating and classifying minerals and/or materials according to the geometric size of the particles. Basically, the sample goes through a series of sieves with openings that maintain a relationship with each other, for example, the sieves that meet the Tyler Scale. This scale has a reference opening of $74\ \mu\text{m}$. The objective of this test is to verify the variation of U and Th contents as a function of the size of the slag particles [4].

In this work a set of sieves was used, according to Figure 7, for the separation in 14 different granulometries.

Figure 7: On the left, the table used in the gravimetric separation - in A, where the concentrate is deposited; in B the fines; in mixed C. To the center, set of sieves. To the right, detail of the sieves.



Source: Author.

2.6. X-rays fluorescence analysis (XRF)

All samples and products generated were analyzed using the X-ray fluorescence technique to obtain concentrations of U and Th oxides. The FRX technique is based on the analysis of the characteristic X-ray emitted by a molecule after its interaction with an incident X-ray [9].

3. RESULTS AND DISCUSSION

Table 1 presents the results of the electrostatic test. It is verified 63.5% of the slag mass behaved as conductive; 9.0% as mixed and 27.6% as non-conductive. However, the levels of U and Th oxides showed little variation - see Figure 8A.

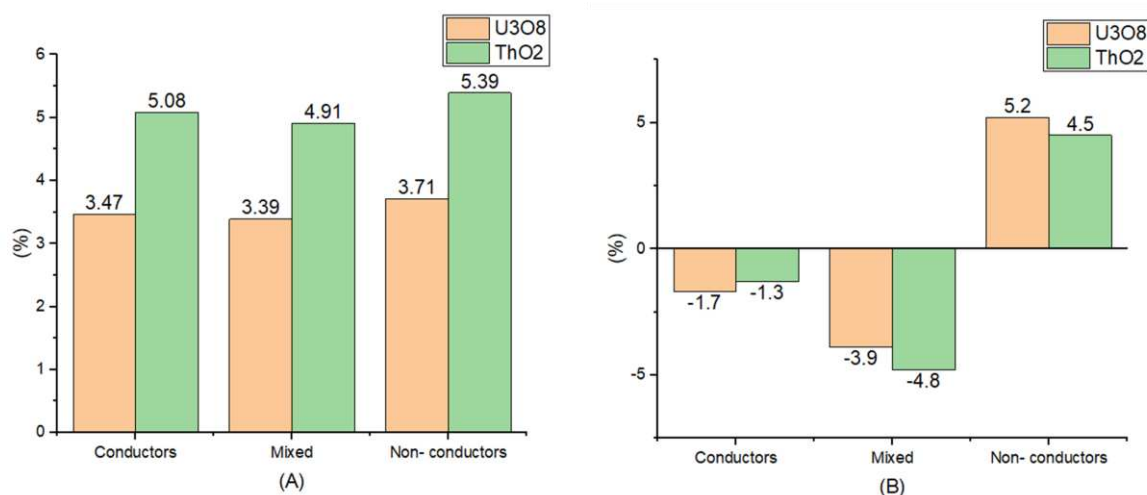
Table 1: Results of chemical analysis (XRF) of slag after electrostatic separation.

| Description | Mass (g) | Mass (%) | SnO ₂ (%) | Fe ₂ O ₃ (%) | ZrO ₂ (%) | U ₃ O ₈ (%) | ThO ₂ (%) | Nb ₂ O ₅ (%) | Ta ₂ O ₅ (%) | SiO ₂ (%) | Al ₂ O ₃ (%) | Y ₂ O ₃ (%) |
|------------------------------|----------|----------|----------------------|------------------------------------|----------------------|-----------------------------------|----------------------|------------------------------------|------------------------------------|----------------------|------------------------------------|-----------------------------------|
| Conductors | 1957 | 63.48 | 0.19 | 2.38 | 6.75 | 3.47 | 5.08 | 5.78 | 1.17 | 21.75 | 51.67 | 1.59 |
| Mixed | 275.9 | 8.95 | 0.18 | 1.84 | 7.79 | 3.39 | 4.91 | 4.16 | 1.15 | 26.73 | 61.06 | 1.89 |
| Non-conductors | 850.3 | 27.58 | 0.20 | 1.23 | 7.05 | 3.71 | 5.39 | 3.55 | 1.06 | 25.05 | 58.06 | 14.40 |
| Calculated head ¹ | 3083 | 100 | 0.19 | 2.02 | 6.93 | 3.53 | 5.15 | 5.02 | 1.13 | 23.11 | 54.28 | 5.15 |

In Figure 8B, it was verified that there was no significant change in the U₃O₈ contents in relation to the calculated head: a reduction of 1.7% for the part that behaved as a conductor, a decrease of 3.9% for mixed and increase of 5.2% conductors. For ThO₂ the behavior was similar: reduction of 1.3%, decrease of 4.8% and an increase of 4.5% for conductors, mixed and non-conductive, respectively.

¹ Weighted average of the oxides contents by the mass of the products.

Figure 8: In A, the variation of the contents of the U and Th oxides with the electrostatic separation of the slag. In B, the variation of the U and Th oxides contents of the calculated sample head and electrostatic separation products.



Source: Author.

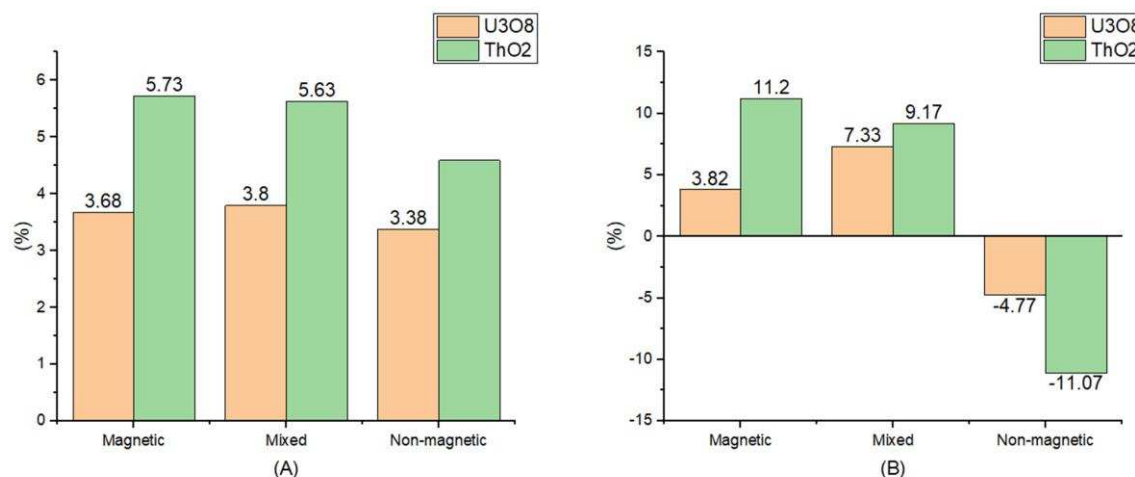
Table 2 presents the results of the magnetic test. It is verified that 39.1% of the slag mass behaved as magnetic; 11.6% as mixed and 49.2% as non-magnetic. However, the levels of U and Th oxides showed little variation - see Figure 9A.

Table 2: Results of chemical analysis (XRF) of slag after magnetic separation.

| Description | Mass (g) | Mass (%) | SnO ₂ (%) | Fe ₂ O ₃ (%) | ZrO ₂ (%) | U ₃ O ₈ (%) | ThO ₂ (%) | Nb ₂ O ₅ (%) | Ta ₂ O ₅ (%) | SiO ₂ (%) | Al ₂ O ₃ (%) | Y ₂ O ₃ (%) |
|--------------|----------|----------|----------------------|------------------------------------|----------------------|-----------------------------------|----------------------|------------------------------------|------------------------------------|----------------------|------------------------------------|-----------------------------------|
| Magnetic | 1012.77 | 39.1 | 0.20 | 1.94 | 8.35 | 3.68 | 5.73 | 6.00 | 1.26 | 23.16 | 48.10 | 1.59 |
| Mixed | 300.62 | 11.6 | 0.19 | 0.87 | 8.49 | 3.80 | 5.63 | 3.89 | 1.02 | 21.21 | 52.80 | 2.10 |
| Non-magnetic | 1273.75 | 49.2 | 0.18 | 1.00 | 5.87 | 3.38 | 4.59 | 3.29 | 0.91 | 20.40 | 58.73 | 1.65 |
| Calc. head | 2587.14 | 100 | 0.19 | 1.35 | 7.14 | 3.54 | 5.16 | 4.42 | 1.06 | 21.57 | 53.88 | 1.68 |

Figure 9B shows the variation of the U and Th oxides of the magnetic test in relation to the calculated head. In the case of U₃O₈, there was an increase of 3.82% for the magnetic; increase of 7.33% for the mixed and decrease of 4.77% for the non-magnetic. For ThO₂: increase of 11.2% for the magnetic; an increase of 9.17% for the mixed and reduction of 11% for the non-magnetic.

Figure 9: In A, the variation of the contents of the U and Th oxides with the magnetic separation of the slag. In B, the variation of the U and Th oxides contents of the calculated sample head and magnetic separation products.



Source: Author.

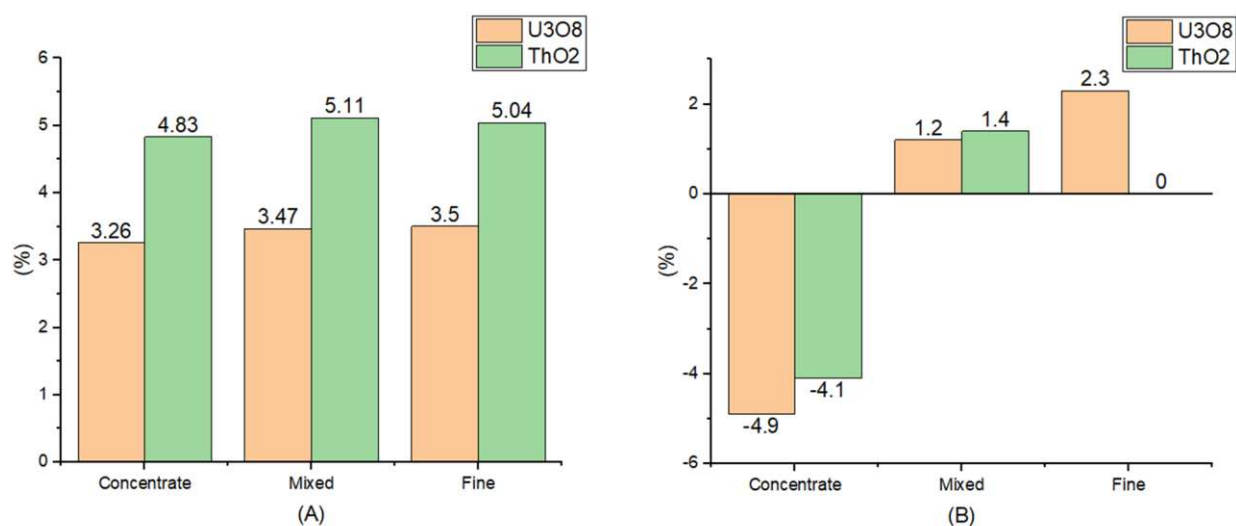
Table 3 presents the results of the gravimetric test. It is verified that 22.6% of the slag mass behaved as a concentrate (higher density); 64.5% as mixed and 12.9% as fines (lower density). However, the levels of U and Th oxides showed small variation again - see Figure 10A.

Table 3: Results of chemical analysis (XRF) of slag after gravimetric separation

| Description | Mass (g) | Mass (%) | SnO ₂ (%) | Fe ₂ O ₃ (%) | ZrO ₂ (%) | U ₃ O ₈ (%) | ThO ₂ (%) | Nb ₂ O ₅ (%) | Ta ₂ O ₅ (%) | SiO ₂ (%) | Al ₂ O ₃ (%) | Y ₂ O ₃ (%) |
|-------------|----------|----------|----------------------|------------------------------------|----------------------|-----------------------------------|----------------------|------------------------------------|------------------------------------|----------------------|------------------------------------|-----------------------------------|
| Concentrate | 3.26 | 22.6 | 0.19 | 3.36 | 6.15 | 3.26 | 4.83 | 8.51 | 1.34 | 19.81 | 51.11 | 1.44 |
| Mixed | 9.32 | 64.5 | 0.17 | 1.14 | 7.14 | 3.47 | 5.11 | 3.53 | 1.03 | 23.05 | 53.80 | 1.57 |
| Fine | 1.87 | 12.9 | 0.20 | 1.41 | 7.17 | 3.50 | 5.04 | 4.10 | 0.91 | 24.67 | 51.50 | 1.51 |
| Calc. head | 14.45 | 100.0 | 0.18 | 1.68 | 6.92 | 3.43 | 5.04 | 4.73 | 1.08 | 22.53 | 52.89 | 1.53 |

Figure 10B shows the variation of the U and Th oxides of the gravimetric test concerning the calculated head. In the case of U₃O₈, there was a reduction of 0.5% for the concentrate; increase of 0.1% for the mixed and increase of 0.2% for the fines. For ThO₂: reduction of 0.4% for concentrate; increase of 0.1% for the mixed and there was no change for the fines.

Figure 10: In A, the variation of the contents of the U and Th oxides with the gravimetric separation of the slag. In B, the variation of the U and Th oxides contents of the calculated sample head and gravimetric separation products.

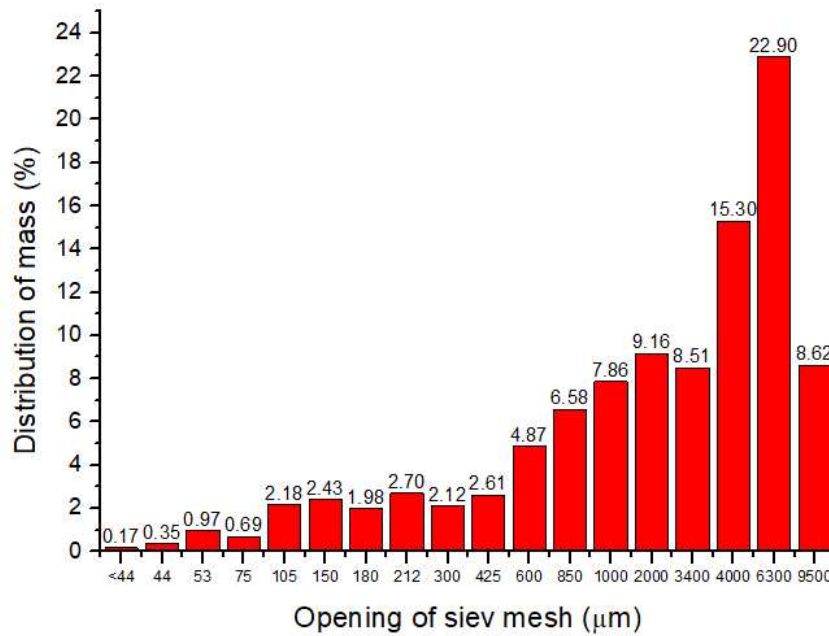


Source: Author.

In the sieving test (separation in sieves) 18 granulometries were obtained. The percentage distribution of mass is shown in Figure 11. It was verified that mass predominated in the largest granulometries: 6300 μm (22.9%) and 4000 μm (15.3%).

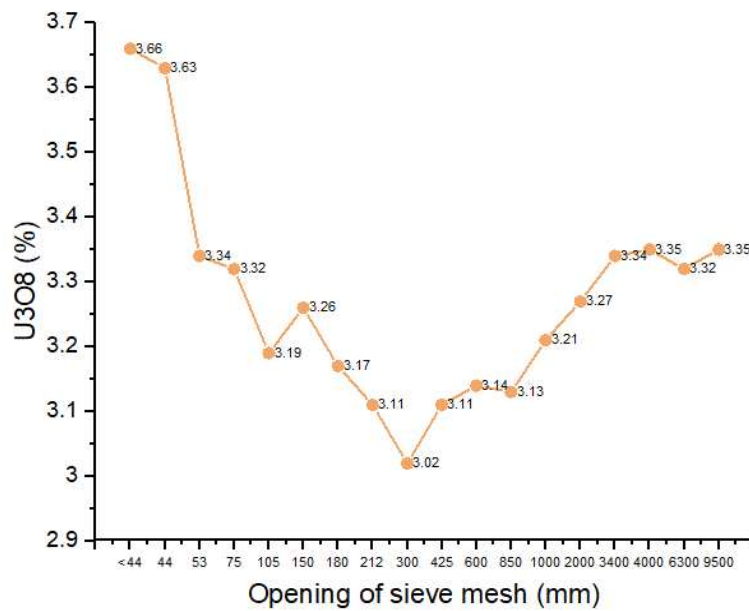
Concerning the distribution of oxides contents, a similar behavior was observed to the other tests: no significant predominance in any of the granulometries for both U₃O₈ (see Figure 12) and ThO₂ (see Figure 13).

Figure 11: Mass distribution as a function of slag granulometry.

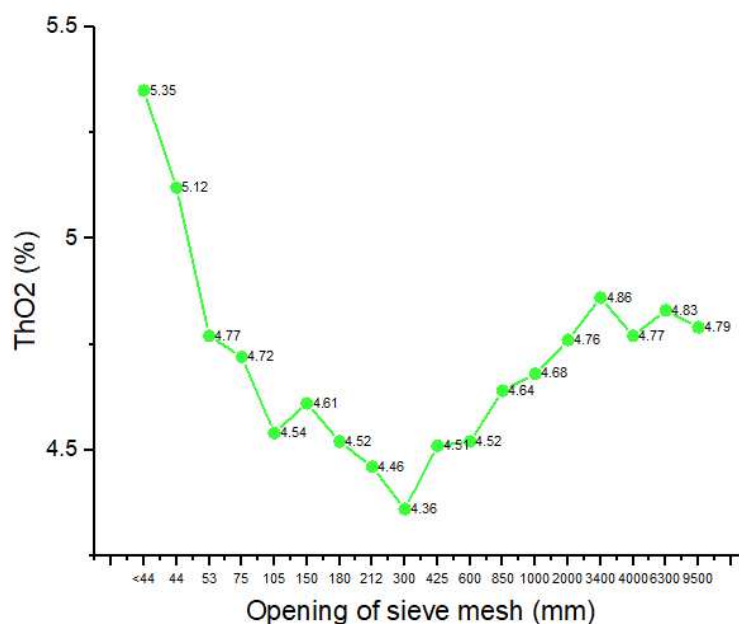


Source: Author.

Figure 12: Variation of the U_3O_8 contents with the granulometry



Source: Author.

Figure 13: Variation of the ThO_2 contents with the granulometry

Source: Author.

4. CONCLUSION

With the tests carried out, it was observed that the concentration of uranium and thorium oxides remained practically unchanged regardless of the electrical, magnetic, density/mass and particle size of the slag. This is probably due to the process of production of ferroalloys: the metallurgical treatment produces as waste a slag with molecular connections between the oxides that constitute it. In other words, it can be stated that physical procedures will not be able to concentrate the slag in "high" and "low" uranium and/or thorium contents. Thus, it will be necessary to evaluate a leaching step (acid attack) for the release of uranium and/or thorium contained.

This paper is part of the initial stage of a project that aims at the recovery of uranium and thorium from the slag of iron alloys of niobium and tantalum. Thus, these tests have shown that it will be necessary to evaluate a leaching step for the release of uranium and or thorium.

Another point observed but not recorded in this article was that slag might represent an investment opportunity since the contents of all the metals of interest of the company (niobium,

tantalum and tin) occur in concentrations higher than that found in rock [2]. Thus, the viability of a process that recovers the metals and the uranium-free and thorium-free can assist in the transformation of a radioactive residue into a mix of highly valued oxides.

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