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PRELIMINARY ASSESSMENT OF THE CONTENT OF RARE EARTH ELEMENTS, URANIUM AND THORIUM IN TANTALITE AFTER PROCESSING WITH MICROWAVE

Sumair G. Araújo, Liliane Landini, Gabriel R. Zeferino, Vera L. R. Salvador, Marcos A. Scapin

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP, Brazil
sgaraujo@ipen.br, llandini@ipen.br, Gabriel_20111914@hotmail.com, vsalvado@ipen.br, mascapin@ipen.br

ABSTRACT

The microwave application of (MW) was studied with the aim of verifying the potentiality in the processing of tantalite containing compounds of rare earth elements (REEs), uranium and thorium (radioactivity level was below the background). The samples were prepared powdered and had, as initial composition, mainly: Ta_2O_5 (24.20)%, La_2O_3 (18.00%), CeO_2 (6.30%), Nd_2O_3 (2.35%), Pr_6O_{11} (1.99%), Y_2O_3 (1.57%), ThO_2(0.11%) and U_3O_8(0.035%). They were processed in the microwave batch reactor (2.45GHz, 2kW). After the processing, the results of characterization by X-Ray Fluorescence (FRX), Scanning Electron Microscopy (SEM) and Energy-Disperse X-Ray Spectroscopy (EDS) showed that the content of the main compounds of REEs, besides Th and U were: La_2O_3 (9.38%), CeO_2 (20.00%), Nd_2O_3 (6.29%), Pr_6O_{11} (3.58%), Y_2O_3 (2.57%), ThO_2(0.33%) and U_3O_8(0.036%). This occurred in the samples prepared with distilled water and irradiated with 15bar of H_2. These preliminary tests were promising, but more experiments are needed, since many variables may still be explored and laboratory infrastructure is available for this purpose, at IPEN-CNEN/SP. As the demand for the use of REEs is rapidly increasing, due to the various applications (for example, as neutron moderators in nuclear reactors, special magnets, TV screens, cell phones and computers, catalysts, missiles, electric vehicles, wind and solar energy, among others), future studies would make it possible to add value and improve the quality of this ore. Finally, microwave technology could be used as an alternative for the reuse of these elements contained in mineral exploration residues.

1. INTRODUCTION

The Brazilian Ministério da Ciência, Tecnologia, Inovações e Comunicações (MCTIC) elaborated a national strategy for the period of 2016-2022, including several government agencies, among them Comissão Nacional de Energia Nuclear (CNEN), as well as large entities industrial representatives, academics, service sector and civil society in general. In the mineral resources sector, support was emphasized in the development of productive chains of strategic minerals, such as rare earth, citing that there was resumption of your production in Brazil and in research and technological development for reduction of oxides, production of metal alloys and manufacturing of high-tech products based on these elements. In this context, the rare earth appear as the concept of strategic minerals associated with scarce minerals, essential or critical for the country, as well as for those which have competitive advantages for the economy [1].
The rare-earth elements (REEs) include those known as lanthanides (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium), besides the yttrium and

scandium. Generally, these elements occur associated with other minerals, some of them radioactive elements (uranium and thorium), and whose separation is not simple. The international market has been led by China since 2005, and from 2014 several countries, among them Brazil, have started to invest in exploration and production of the elements present in rare earth. Their exploitation is a major challenge and is related to the domain of all the stages and technological routes for the production cycle (from geological research in exploration to production of rare-earth oxides and finished materials). The rare-earth elements do not occur in the free state in nature and usually are associated with tantalite (Fe, Mn) Ta_2O_6 and Columbite (Fe, Mn) Nb_2O_6, besides the monazite, and the ytriotantalite [2].

As the demand for the use of REEs is rapidly increasing, due to the various applications (for example, as neutron moderators in nuclear reactors, special magnets, TV screens, cell phones and computers, catalysts, missiles, electric vehicles, wind and solar energy, among others), future studies would make it possible to add value and improve the quality of this ore [3, 4].

In this context, several researches have been done worldwide in order to seek new technologies and the most economically viable resources, to use the rare earth elements.
As the various studies were carried out at IPEN with microwave technology (recycling / recovery / reuse of elastomers, , immobilization of radioactive waste, petroleum hydrotreating biodiesel production) [5-9], the idea came up to conduct studies by using the microwave technique in order to verify their potentiality in the processing of tantalite that contains compounds of rare earth elements, uranium and thorium. Furthermore, this type of research and development is included in one of the guidelines of the CNEN [10].

The microwaves are non-ionizing electromagnetic energies, with frequencies in the range of 300MHz to 300GHz. The values of 915MHz, 2.450MHz, 5.800MHz and 22.125MHz are accepted for use in scientific and industrial installations, but the most used is 2.450MHz value. They are used for selective heating of materials, whose molecular structures may be affected, depending on their dielectric properties. Therefore, it is possible to process materials and initiate chemical reactions in several compounds. The efficiency of microwave heating is based on the direct conversion of energy, which is directly released into the material, i.e. heating starts from interior of the material body. The need to heat the vessel walls that contains the sample is eliminated, as compared to the occurred in the traditional heating methods, and the speeds of the process are highers, i.e., the reaction times can be much smaller. Thus, one of the favorable results can be energy saving compared to traditional heating, in certain processes [11-13].

2. . EXPERIMENTAL

2.1. Microwave Processing

The processing of the samples, this work was carried out in a batch reaction unit, with microwave and conventional heating (electric), installed at IPEN-CNEN/SP; with the following characteristics: volume up to 1L; operation only with conventional electric heating (MC) up to 500°C, only heating with microwave (MW) of 2.45GHz and frequency performance up to 2kW (continuous) and up to 8kW (pulsed) or both combined (MC and MW); H_2 gas pressure up to 200bar; sample agitation until 1200 revolutions per minute (rpm); controled and automated security system, allowing on-line monitoring of process variables (incident and reflected waves, power, reaction time, temperature, pressure, agitation speed); information on the progress of the process, in a clear and easy viewing, with screens, navigation procedures for alarms, to major historical events and trends graphs; collections of samples can be performed at any stage of the process [8].

2.2. Materials

The samples used in this work were based on tantalite from the northeastern region of Brazil with associated rare earth elements, with thorium and uranium (radioactivity level was below the background). They were prepared powdered (granulometry 60-100mesh) and had, as initial composition, mainly: Ta_2O_5 (24.20)%, Fe_2O_3 (19.00)%, La_2O_3 (18.00%), CeO_2 (6.30%), TiO_2 (6.12%), Nb_2O_5 (5.18%), MnO (5.71%), P_2O_5 (2.94%), Al_2O_3 (2.78%), Nd_2O_3 (2.35%), Pr_6O_{11} (1,99%), ZrO_2(1.85%), Y_2O_3 (1.57%), ThO_2(0.11%) and U_3O_8(0.035%). The samples containing 5g of tantalite were mixed with distilled water and nitric acid – Merck, purity of 65% (bulk concentrations of 0% and 25%).

2.3 Experimental Procedure

The samples were processed in the microwave batch reactor (2.45GHz) at IPEN-CNEN/SP, with stirring rate 600rpm, MW power of 2kW, reaction time 15min., reaction initial temperature of 100°C and they were conducted in the presence of hydrogen gas (initial value -15bar) or air pressure. The samples were collected and sent for analysis, before and after processing.

2.4. Characterization Techniques

The solid samples were characterized by Energy Dispersive X-Ray Fluorescence (EDXRF - Shimadzu - model 720), for elemental analysis (15kV – for Na to Sc and 50kV – for Ti to U, until 1mA, 5mm collimator; count time 100s); Scanning Electron Microscopy (SEM - Tabletop SEM, model TM 3000, Hitachi - 15kV, resolution 30nm) for morphological analysis integrated to Energy Disperse Spectroscopy (EDS - Quantax EDX, Bruker) for to identify the qualitative composition of the sample at specific points in the image [14, 15].

3. RESULTS

3.1 Chemical Composition of the samples

The results of EDXRF analysis for the main chemical compositions of the samples can be seen in Table1 (“R” samples– solid residue after processing with MW). The content of uranium remained around the same value as the original sample. In the thorium case it increased more than 180% in the sample treated only with water and 15bar of H_2. In Table 1 the quantitative results are presented for the “1R”, “2R”, “3R” and “4R” samples determined by EDXRF.

Table 1: Results of EDXRF analysis (chemical composition)

Compound	"1R" sample*	"2R" sample*	"3R" sample*	"4R" sample*
Ta_2O_3	25.0±3	24.0±2	13.0±1	7.0±0,7
Nb_2O_5	7.1±0,7	5.6±0,6	3.0±0,3	1.6±0,2
Al_2O_3	1.7±0,2	1.4±0,1	3.5±0,4	5.3±0,5
TiO_2	3.2±0,3	3.0±0,3	3.8±0,4	5.6±0,6
Fe_2O_3	16.0±2	16.0±2	15.0±2	18.0±2
P_2O_5	4.5±0,5	4.5±0,5	6.4±0,6	5.6±0,6
CeO_2	6.4±0,6	18.0±2	20.0±2	18.0±2
La_2O_3	6.2±0,6	5.5±0,6	18.0±2	15.0±2
Pr_6O_{11}	1.4±0,1	1.5±0,2	3.6±0,4	3.3±0,3
Nd_2O_3	2.6±0,3	6.0±0,6	6.3±0,6	4.9±0,5
Y_2O_3	1.4±0,1	1.3±0,1	2.6±0,3	2.6±0,3
U_3O_8	0.037±0,004	0.030±0,003	0.036±0,004	0.030±0,003
ThO_2	0.023±0,002	0.11±0,01	0.31±0,03	0.27±0,03

*percentage value

According to the results shown in the Table 1, it is verified that the treatments applied to the "1R" and "2R" samples does not change the chemical composition, since the levels of Ta, Nb, Fe, Ti, and Al are practically the same.

As the EDXRF technique is more sensitive, to heavier elements and with decreasing Ta and Nb contents ("3R" and "4R" samples) that must be present in the solubilised part of the samples, it can be observed in the residue that the rare earth contents had a significant increase.

In "3R" sample the concentrations of Ce, La, Pr and Nd had an increase around 2.5 to 3 times with respect to "1R" sample and the Y in the order to 1.8 times. The U content remained constant while the content of Th had an increase of the order of 13.5 times, which indicates a good condition of treatment for their separation. In adittion, "4R" sample conditions proved to be good for Ti extraction.

In Figs. 1 to 4 are shown the images obtained by scanning electron microscopy [SEM – samples (a)] and the microanalysis spectra, obtained by energy dispersive spectroscopy [EDS-samples (b)], for samples "1R", "2R", "3R" and "4R", respectively.

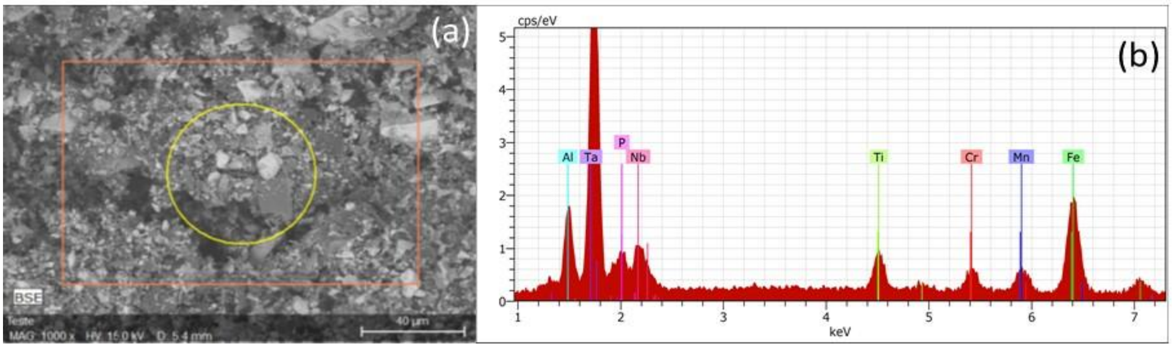

Figure 1: Sample "1R" – results of SEM and EDS.

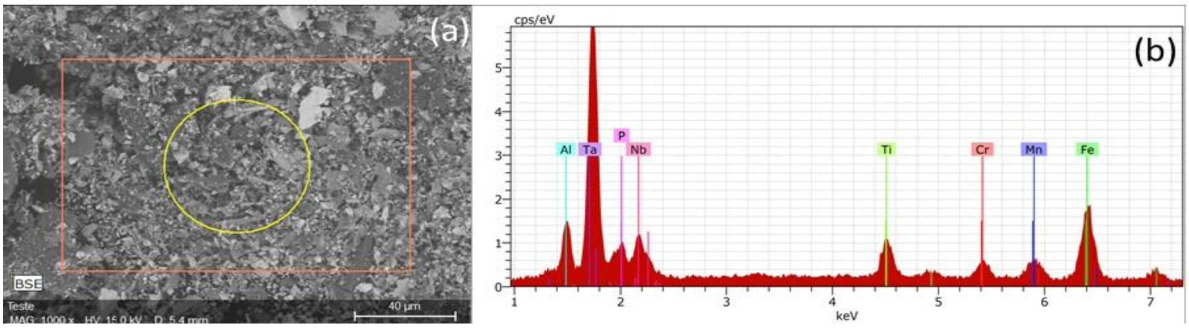

Figure 2: Sample "2R" – results of SEM and EDS.

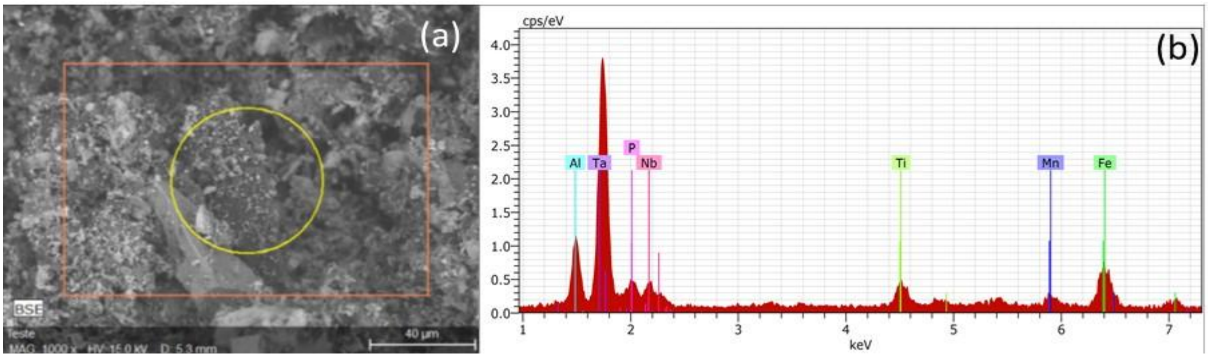

Figure 3: Sample "3R" – results of SEM and EDS.

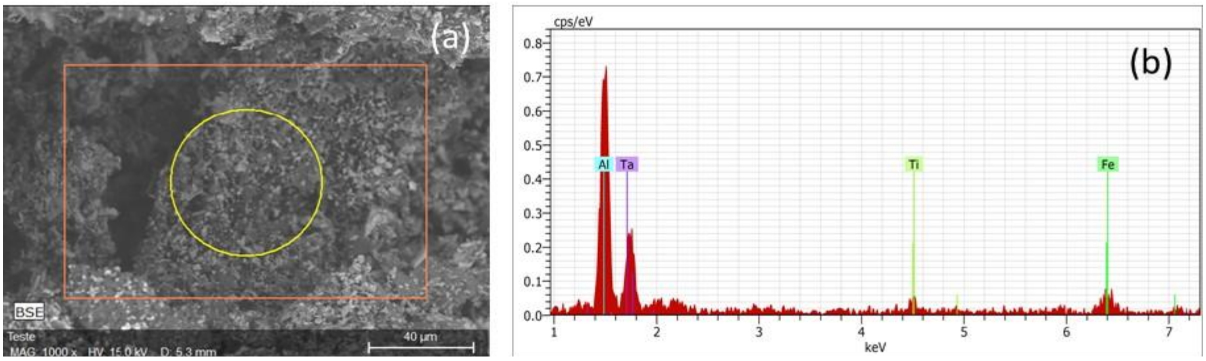

Figure 4: Sample "4R" – results of SEM and EDS.

It can be seen by Figs. 1 and 2, that the "1R" sample treated with acid and water and the "2R" sample treated with acid, water and hydrogen gas did not present modifications in particle size – Figs. 1 (a) and 2 (a). In terms of chemical composition, the elements Al, Ta, P, Nb, Ti, Cr, Mn and Fe were maintained, in the same proportions, shown in Figs. 1(b) and 2(b). At first, there is indication that the presence of hydrogen gas, with the value employed, provided no benefit.

According to Figs. 3 and 4, it can be seen that the "3R" sample treated with water and hydrogen and the "4R" sample treated only with water showed a significant decrease in particle size as compared to "1R" and "2R" samples, with "4R" sample having the smallest particle size. Thus, it can be verified that the treatment applied to the "4R" sample was the most efficient for the extraction of the elements Ta and Nb (this element was not detected in this sample). The results are confirmed by the EDS analyzes shown in Fig. 4 (b), in which there was a significant decrease of the Ta element.

The results show that the treatments applied for the "1R" and "2R" samples do not change the chemical composition, since the contents of Ta and Nb are are practically the same. It means that H_2 gas has not caused any effect on the content of these elements. These results are corroborated with those obtained by EDXRF.

4. CONCLUSIONS

After the processing, for the main compounds of REEs, besides Th and U, the changes were: La_2O_3 (9.38%), CeO_2 (20.00%), Nd_2O_3 (6.29%), Pr_6O_{11} (3.58%), Y_2O_3 (2.57%), ThO_2(0.33%) and U_3O_8(0.036%). This occurred in samples prepared with water and processed with H_2. However, it was observed, as the same, that without H_2 the results were very close, indicating that the use of hydrogen gas and acid could be excluded. This can lead to a cleaner and environmentally processing.
All the studied variables affected in some way the content and morphology of some elements, even if in a discreet way.
These preliminary tests were interesting because they demonstrated that microwave technology can be a promising alternative to the processing of these types of materials. Even so, few tests have been performed and many variables can still be explored for process of separating elements. In the case of continuity of the tests, these results will serve as a starting point, including comparing the same equipment, the heating with microwave, traditional or both together, once it was designed for this purpose, that is available at IPEN-CNEN/SP .

This technology can bring benefits, especially in the reduction of leaching time, the metals extraction improvement (increase in the recovery of valuable metals) and consequently, there may be reduction of capital and operating costs. This is an advantage of processing with microwave when compared to traditional methods.

REFERENCES

1 "Estratégia Nacional de Ciência, Tecnologia e Inovação 2016 – 2022", http://www.finep.gov.br/images/a

finep/Politica/16_03_2018_Estrategia_Nacional_de_Ciencia_Tecnologia_e_Inovacao_2016_2022.pdf (2016)
2 "Minerais - Terras Raras", http://www.defesanet.com.br/tecnologia/noticia/17223/Minerais-Terras-Raras/ (2014).
3 A. R. Jha, *Rare Earth Materials - Properties and Applications*, CRC Press – Taylor & Francis Group, Boca Raton & USA (2014).
4 "Minerais Estratégicos e Terras-Raras", https://www2.camara.leg.br/a-camara/estruturaadm/altosestudos/temas/pdf/minerais-estrategicos-e-terras-raras (2014).
5 L. Landini, S. G. Araújo, A. B. Lugão, H. Wiebeck, "Preliminary analysis to BIIR recovery using the microwave process". European Polymer Journal, v. 43, pp. 2725–2731 (2007).
6 "Estudo do reaproveitamento da borracha de cloropreno pela aplicação da tecnologia de microondas", http://www.teses.usp.br/teses/disponiveis/85/85134/tde-27112007-151344/pt-br.php (2007).
7 "Estudo da imobilização de rejeitos radioativos em matrizes asfálticas e resíduos elastoméricos utilizando a técnica de microondas", http://www.teses.usp.br/teses/disponiveis/85/85134/tde-13062008-154046/pt-br.php (2007).
8 "Method and Apparatus for Microwave Assisted Processing of Feedstocks", https://patents.google.com/patent/US20080264934 (2008).
9 S. G. Araujo, L.Landini, V.L.R. Salvador, M.A. Scapin, B.F. Massanares, A.B. Urbaninho, "Estudo da viabilidade de produção de biodiesel, a partir de óleos vegetais e catalisadores de resíduos de frutos do mar, em uma unidade reacional de hidrogenação em batelada, assistida por micro-ondas e aquecimento convencional", *23º Congresso Brasileiro de Engenharia e Ciência dos Materiais*, Foz do Iguaçu, Brazil, November 04-08 (2018).
10 "Plano de Orientações Estratégicas 2019-2022", http://www.cnen.gov.br/images/cnen/documentos/acesso_a_informacao/Plano-de-Orientacoes-Estrategicas.pdf
11 K. E. *Haque*, "Microwave energy for mineral treatment processes —a brief review", *Int. J. Miner. Process*, **v.57,** pp.1-24 (1999).
12 D. L. Rakhmankulov, S. Y. Shavshukova, F. N. Latypova, V. V. Zorin, "Laboratory and Industrial Applications of Microwave Techniques", *Russian Journal of Applied Chemistry*, **v.75 (9)**, pp. 1377-1383 (2002).
13 L.Landini, S.G. Araújo, A.B. Lugão, "Application of microwave technology in rare earth elements – a short inquiry", *International Nuclear Atlantic Conference*, Santos, Brazil, September 30 to October 5 (2007).
14 G. R.; Lachance, C. Fernand, *Quantitative x-ray fluorescence analysis. New York*, NY: John Wiley & Sons (1994).
15 "Aplicação da difração e fluorescência de raios X (WDXRF): ensaios em argilominerais", http://www.teses.usp.br/teses/disponiveis/85/85134/tde-07052007-161852/pt-br.php (2003).