2017 International Nuclear Atlantic Conference - INAC 2017
Belo Horizonte, MG, Brazil, October 22-27, 2017
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR– *ABEN*

Agência Brasileira do ISBN
ISBN 978-85-99141-07-6

Study of the densification of uranium-erbium system

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ABSTRACT

The sintering process of UO_2-Er_2O_3 pellets has been investigated because of its importance in the nuclear industry and the complex behavior during sintering. The present study includes the development of nuclear fuel for power reactor in order to increase the efficiency of the fuel trough longer refueling intervals. The erbium is indicated for longer cycles, which means less stops to refueling and less waste.

In this work, we studied the use of erbium oxide by varying the concentrations in the range of 1-9.8%, which was added to UO_2 powder through mechanical mixing, aiming to check the rate of densification and a possible sintering blockage. The powders were pressed and sintered at 1700ºC under hydrogen atmosphere. The results show a sintering blockage in the UO_2-Er_2O_3 system that occurs in the range of 1500-1700ºC temperature. Dilatometric tests indicate a retraction of 21.87% when used Er_2O_3 at 1% mass concentration. This shrinkage is greater than is observed with higher concentrations or even without the addition of the burnable poison, providing us with a better degree of incorporation of the element erbium, resulting in pellets with density suitable for use as nuclear fuel.

1. INTRODUCTION

The trend in LWR reactors is to use bigger enrichments in ^{235}U to increase the reactivity of the nuclear fuel to prolong its useful life. With the increase in the reactivity of the reactor, it becomes necessary the use of devices to control the chain reaction.

The function of the burnable poison is basically to control the neutron population. To do so, the chemical element used for this function needs to capture neutrons resulting from the fission of uranium and isotope formed by nuclear reaction, doesn't/1/.

A way to add the burnable poison to fuel is using it in an integrated form. One of the possible burnable poisons is erbium, which is added in the form of powder of erbium oxide (Er_2O_3) to traditional fuel of UO_2. It is mixed mechanically to UO_2 powder. Thereby it is possible a long-term reactivity control, allowing the reduction of the global population of neutrons, being possible to position them in strategic regions of the reactor core.

Besides erbium, ZrB_2 and Gd_2O_3 are the other two burnable poisons used commercially in an integrated form in LWR reactors. The ZrB_2 is added to the fuel through the deposition of a thin layer on the surface of UO_2/2/.The Gd_2O_3 is the most traditional burnable poison used in reactors and also is mixed mechanically, maintaining greater resemblance to Er_2O_3.

The advantage of erbium about gadolinium is a low impact on fuel properties (thermal conductivity and melting point), due to the low concentration in fuel pellets and a good control of the moderator temperature coefficient. The disadvantage is mainly due to a penalty at the end of cycle/2/, which is due to a high neutron capture effect by the continuing ^{167}Erisotope formation. While gadolinium is recommended for up to 18 months cycles, the erbium can increase the lifetime of nuclear fuel from 18 to 24 months/3/, resulting in less refueling and less waste.

The isotope ^{167}Eris the main responsible for neutron capture, as it has a cross section of 654.80 barns for thermal neutrons. The other isotopes have less significant values. However, this isotope is continuously produced by neutron capture of the ^{166}Er isotope generating a penalty of reactivity/4/.The main isotopes of erbium are listed in table 1, along with abundance of each one.

Table 1- Cross section of isotopes of erbium/5/

Element	Natural isotope composition	Abundance (%)	Thermal capture cross-section (b)	Resonance capture integral (b)
$_{68}$Er	^{162}Er	0.1	29.18	574.83
	^{164}Er	1.6	13.25	144.71
	^{166}Er	33.6	20.81	110.00
	^{167}Er	23.0	654.80	3,906.60
	^{168}Er	26.8	2.78	40.56
	^{170}Er	14.9	5.91	58.57

In the years 70 the erbium (Er_2O_3) was studied as an alternative burnable poison in reactors LWR type. However, only in the years 80 the company Combustion Engineering (CE) conducted studies to effectively replace the gadolinium for this new burnable poison/6/.

The addition of burnable poison in the fuel pellets follow different routes in the literature, and can be made by mechanical mixing /3,7,8/, milling/8/ and coprecipitation/8,9/. These techniques suggest different degrees of homogeneity that interfere in the sintering mixture. The technique used by the INB (Nuclear Industries of Brazil) is the mechanical mixing of powders/10/. Its simplicity brings economic advantages, making the fuel element fabrication cheaper.

The sintering temperature is also another factor that influences the behavior of the pellet. In the literature, are used temperatures ranging between 1650ºC/7/ and 1760ºC/10/. Despite the thermal cycle of the INB using this last value, there is evidence in the literature of formation of solid solution to 1700° C, through the mechanical mixture of powders of UO_2 and Er_2O_3/3/.

The commercial use of the percentage by weight of Er_2O_3 varies between 1wt% and 2.5wt%/2/, however there are studies for fuels using this burnable poison at rates of 2%, 4%, 8% and 12%, and in situations in which the pellets containing the burnable poison were not present in all the rods of the reactor, it was used proportions up to 16%/11/. The results

obtained indicate that there is a clear advantage in the use of erbium, enriched with the isotope ^{167}Er, both in terms of initial reactivity rate, as in the penalty at end of cycle/4,11/.
Another proposal that exists in the literature is the use of 9.8% of erbium in nuclear fuel, isotopically separated in ^{166}Er (5.8%) and ^{167}Er (4.0%). At this ratio, using enrichment at19.8%, the k factor stands at 1.05, and can be used as nuclear fuel/12/

2. EXPERIMENTAL

The analyses performed by the scanning electron microscope show the morphological characteristics of the particles. Figure 1 shows the morphology of UO_2 powder that typically comes from AUC (Ammonium Uranyl Carbonate), with particles with rounded corners/10,13/. Er_2O_3 powder already presents a different morphology, as shown in Figure 2, where you can see particles with smaller size, irregular, with angular corners, forming cohesive crystals.

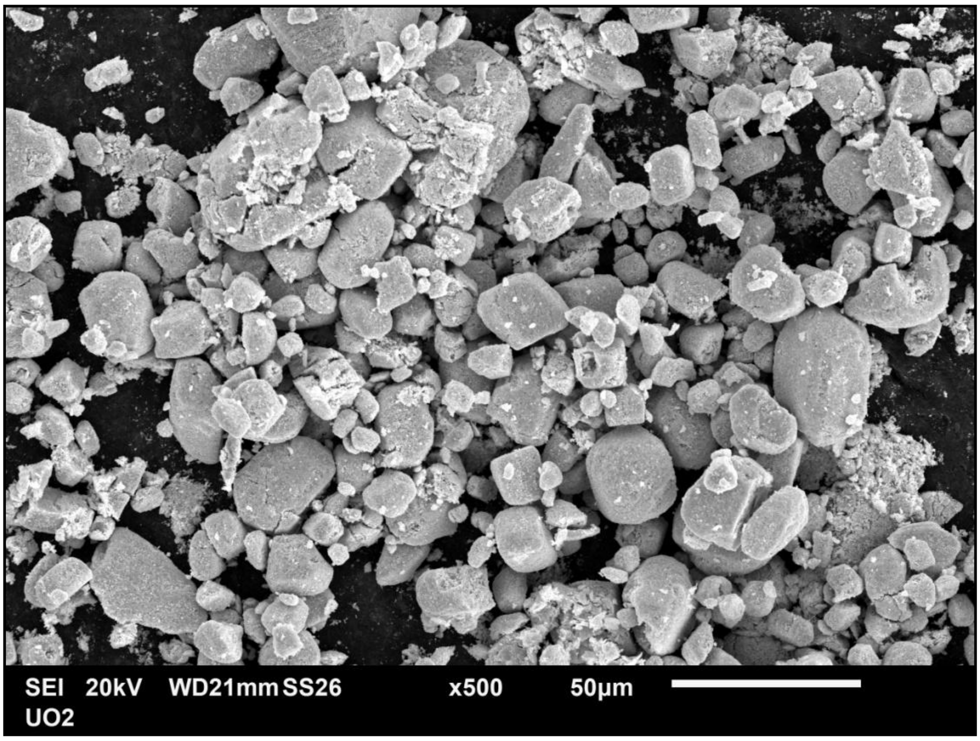

Figure 1: UO_2 powder morphology

Granulometric analyses of powders by laser indicate that the size of up to 50% of the particles of UO_2 is 30.04 µm, while Er_2O_3 particles are 11.04 µm. The difference between the sizes of particles helps the process of compaction, since the smaller particles may occupy gaps left between larger particles.

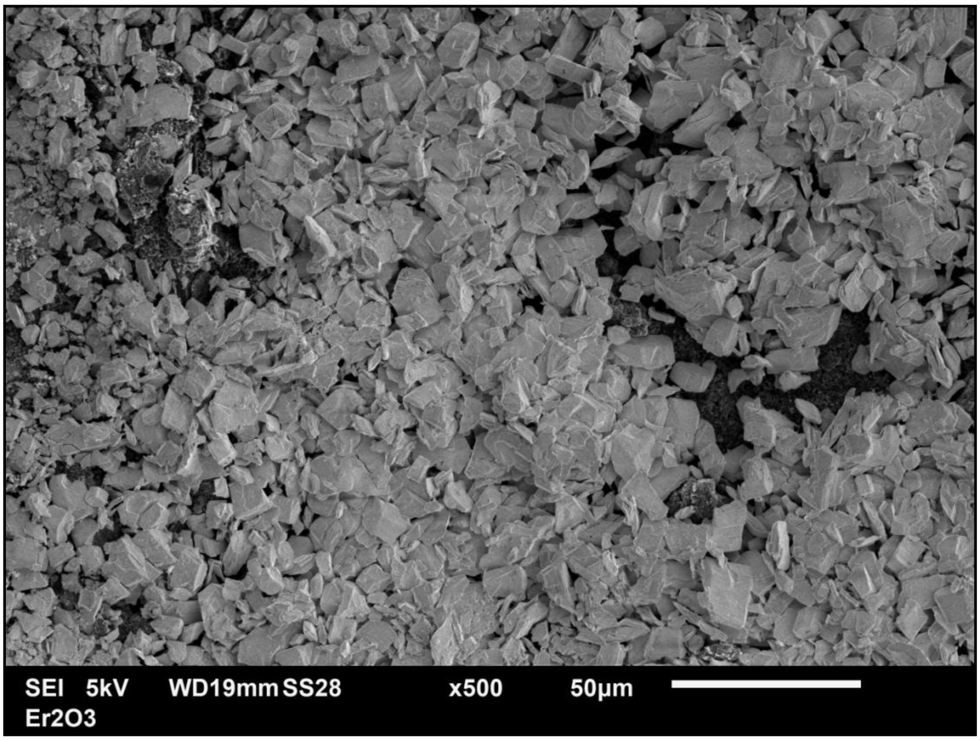

Figure2: Er_2O_3 powder morphology

The UO_2 powder was ceded by the INB and follows their quality parameters. Table 2 shows the chemical impurities presented in the material, analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) in the INB laboratory /10/.

Table 2: chemical impurities in UO_2 powder

Impurities (µg/gU)	F	Al	Ca	B	Fe	Ni	Si	Gd
Specification limits	≤ 100	≤ 250	≤ 25	≤ 0.5	≤ 100	≤ 50	≤ 100	≤ 1
UO_2	5.312	1.777	4.212	< 0.2	15.24	0.421	6.916	0.2

As shown in table 2, the contaminants are within the specification used by the INB, can be used for making pellets without changing the chemical properties due to low presence of other chemical elements. Other chemical analyses are performed to evaluate the UO_2 powder, according to table 3.

Table 3: chemical properties of the UO_2 powder

Analysis	Value	Specification
O/U ratio	2.0818	2.08 - 2.30
U quantity (wt%)	87.574	≥ 86.8
Enrichment (^{235}U wt%)	4.137	4.10 - 4.15
Humidity (wt%)	0.15	≤ 0.4

The O/U ratio, uranium quantity, enrichment and humidity were also within the parameter set by the INB, allowing establishing that there is no chemical aspect that makes the material unfeasible.

Physical analyses of UO_2 powder ensure good compactibility of the green pellet, as well as a good sinterability. It were characterized the specific surface area, density and flowability. The results are presented in table 4.

Table 4: physical properties of UO_2 powder

Analysis	Valor	Specification
Specific surface (m^2/g)	5.0	2.5 - 6.0
Bulk density (g/cm^3)	2.2	2.0 - 2.6
Flowability (s/50g)	4.6	≤ 10

Physical analyses are within the specification, validating the material for the manufacture of fuel pellets.

The manufacture of fuel pellets used in this work followed the production process of powder metallurgy. The raw material used is UO_2 powder, manufactured by direct reduction of AUC. The ADS (aluminum distearate) was used as a solid lubricant, at a rate of 0.2%. These two materials are traditionally used by the INB[/10/]and were ceded by this company. The erbium will be added to the mix, in the form of oxide (Er_2O_3) in proportion by weight of 1.0%, 2.5%, 4.0% and 9.8%.

Mixed powders of UO_2-Er_2O_3 were weighed and mixed in a container in the form of a tube, with braided wires in its interior, favoring the breaking of agglomerates. After closing the container, this was positioned in a turbula type homogenizer and the mixture was homogenized during 1 hour.

The theoretical density (TD) of the mixture depends on the concentration of the components. For the calculation of the theoretical density of the mixture was used the equation:

$$\text{TD} = \frac{100}{\left(\frac{x}{10.96}+\frac{y}{8.64}+\frac{0.2}{5.35}\right)}$$

Where x is the mass fraction of UO_2 and 10.96 g/cm^3 is its TD[/8/]. The mass fraction of Er_2O_3 is represented by the letter y and 8.64 g/cm^3 is its TD[/11/]. Also 0.2% is the mass fraction of ADS used as a lubricant and 5.35 g/cm^3 is its TD[/14/].The compaction was performed in uniaxial form in a floating matrix by a hydraulic press. The compaction pressure ranged between 3.0 and 3.6 tf/cm^2, depending on the concentration of Er_2O_3 used. Table 5 presents the results obtained in the manufacture of the green pellets.

Table 5: green density of the pellets

Mixture	Green density(g/cm^3)	TD of the mixture (g/cm^3)	% TD
UO_2 pure	5.55	10.95	50.68
UO_2.1.0%Er_2O_3	5.50	10.92	50.37
UO_2.2.5%Er_2O_3	5.47	10.87	50.32
UO_2.4.0%Er_2O_3	5.50	10.83	50.78
UO_2.9.8%Er_2O_3	5.39	10.67	50.52

In this study, the sintering was performed by using a dilatometer, Setaram brand, Setsys model. The atmosphere used was of pure hydrogen. The sintering program used a heating rate of 5°C per minute, until the temperature of 1700°C, in which the pellet stayed for 3 hours. The cooling occurred at a rate of 20°C per minute until the shutdown of the equipment.

3. RESULTS AND DISCUSSION

Figure 3 shows the curves of sintering obtained. Note that the shrinkage of the pellets with 1.0%, 2.5%, 4.0% and 9.8% by weight of Er_2O_3 was decreasing. The pellets with Er_2O_3 concentration of up to 4.0% had greater retraction than the pellet of UO_2 pure. Only the pellets with 9.8% had a smaller retraction.

In every curves was evidenced a sintering blockage, which was observed in works studying the densification of the UO_2-Gd_2O_3 system[/7,13,15/]. In these works, the blockage is characterized by a visible inflection in the sintering curve. At UO_2-Er_2O_3 system this inflection is less pronounced, and is best evidenced for high concentration erbium oxide.

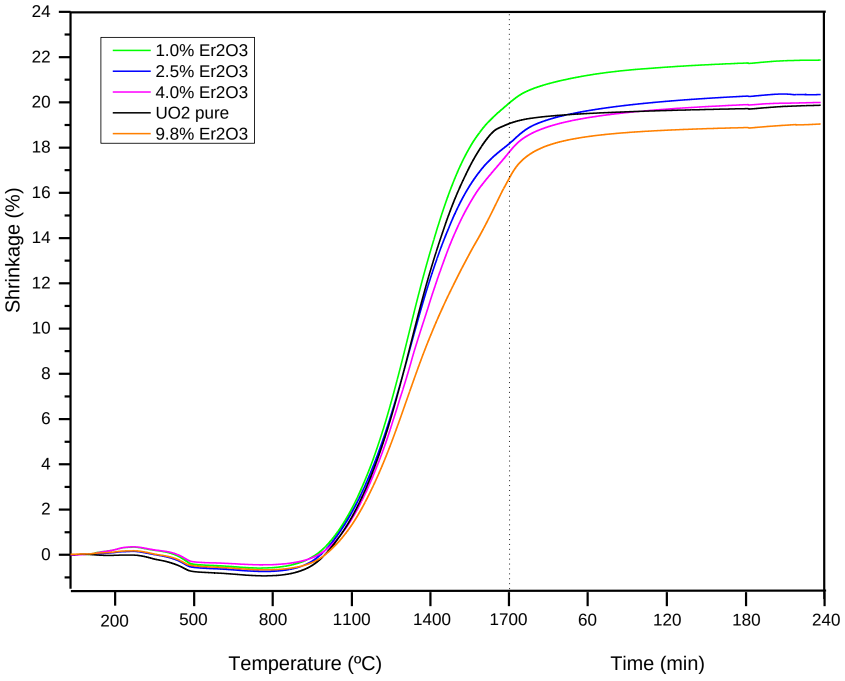

Figure 3: Sintering curves

A proposed explanation for the sintering blockage in the UO_2-Gd_2O_3 system is the occurrence of the Kirkendall effect[/7/]. Caused by the difference between gadolinium diffusivity in the crystalline structure of UO_2 and that of uranium in the crystalline structure of Gd_2O_3. This difference creates pores at high temperature, which hardly are eliminated in the later stages of sintering, causing the inflection in the sintering curve. Probably this same mechanism is occurring in the UO_2-Er_2O_3 system.

Erbium can be considered to have the same effect as gadolinium when it solubilizes in the crystalline structure of UO_2, where Gd^{3+} cation replaces U^{4+}. In this process, for electronic neutralization, it causes the oxidation of U^{4+} to U^{5+}. As the higher valence uranium ions have a lower atomic radius, this change causes an increase in diffusivity and, consequently, an increase in sintering[/9/].

The atomic radius of the Er^{3+} cation is slightly larger than the U^{4+}, according to table 6, making the lattice period of the crystalline structure of UO_2 increase with the formation of the solid solution $(U,Er)O_2$, but the oxidation of the U^{4+} cation by U^{5+} causes that the sum of these events leads to a smaller lattice period, decreasing the volume of the unit cell and increasing the density. However, the density of the compound decreases, since the substitution occurs by a lighter atom, where one event prevails over the other[/16/].

Figure 4 shows the ratio of pellet density to Er_2O_3 concentration, where the pellet without this compound is considered 0%. The relationship is practically linear, where there are probably two events contributing to the reduction of density, the first being the porosity formation by the Kirkendall effect, shown through the inflection of the sintering curves, and then the decrease of the mass of the crystalline structure, by the entrance of the E^{3+}cation, despite increased retraction of the pellets relative to the UO_2 pellet.

Table 6: Atomic radius[/16/]

Cation	U^{4+}	U^{5+}	Er^{3+}	Gd^{3+}
Atomic radius (nm)	0.1001	0.0880	0.1004	0.1053

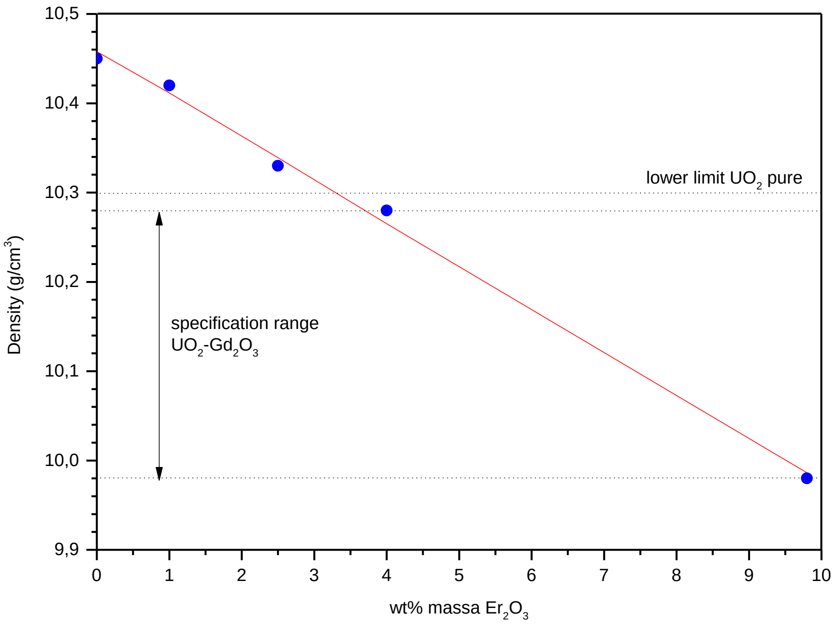

Figure 4: Density x percentage by weight of Er_2O_3

The density specified for the fuel pellet $(U,Gd)O_2$ is in the range of 9.98 g/cm^3 to 10.28 g/cm^3. If the pellets studied are compared to this specification, it can be concluded that pellets with a mass fraction of between 4.0% and 9.8% of Er_2O_3 can be produced, as shown in figure 4. Already the pellets with 1.0% and 2.5% had density within the specification of UO_2 pure (94% DT - lower limit)[/15/].

The effect of the addition of Gd_2O_3 on UO_2 has smaller retraction and decreases the density more, according to the literature[/7,13,15/], compared to this study. Probably by the value of the atomic radius of Gd^{3+} in relation to Er^{3+}, according to table 6, since its entry in the crystalline structure causes the lattice period to increase and erbium has greater diffusivity.

In Figure 5, the retraction rate of the mixtures is shown, where it can be seen that, except for the mixture with 1.0wt% by weight of Er_2O_3, all were smaller than the UO_2 pure, between the temperatures of 900ºC and 1500ºC. In the mixture with 1.0wt% Er_2O_3, as there is a low mass fraction of Er_2O_3, there is an increase in the sintering rate, which indicates a good homogeneity of these particles by the mixture. As the mass fraction of Er_2O_3 is increased, this homogeneity decreases, causing the particles to act as larger agglomerates, potentiating the Kirkendall effect.

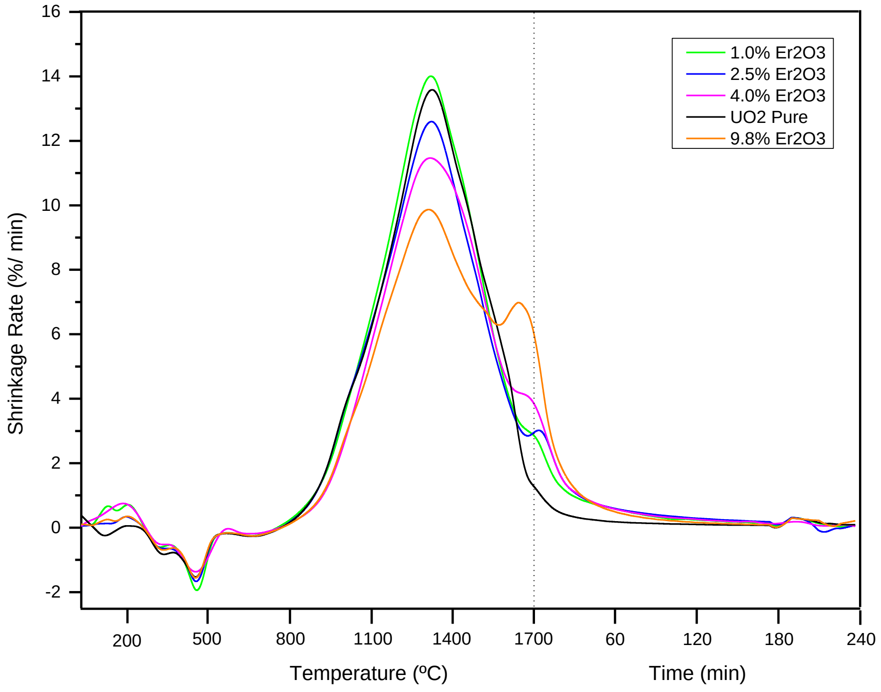

Figure 5: Shrinkage rate of the sintering curves

The sintering curves show an inflection of the curve near the temperature of 1700°C. Probably this inflection is due to the entrance of the erbium into the crystalline structure of UO_2, in greater volume, as in the case of gadolinium[/7/]. This phenomenon becomes clearer when observed the derivative of the sintering curves, which express the shrinkage rate. At about 1700°C, the entry of the erbium into the larger crystalline structure causes a new retraction peak. This new retraction peak increases as the Er_2O_3 concentration increases and is mainly due to the formation of the U^{5+}cation, when the Er^{3+} cation replaces the U^{4+}. The combined actions result in the curves shown in figure 3 and 5, showing the preponderance of the Kirkendall effect in the mixture.

4. CONCLUSION

An investigation was carried out on the sintering behavior of fuel UO_2-Er_2O_3. From the experimental results presented, you can highlight the erbium acts as a densifying agent,

forming denser fuels inserts that mixtures made with UO_2-Gd_2O_3. The results demonstrate the applicability of this fuel poison in an integrated manner to traditional fuel of UO_2.
The sintering block appears in the UO_2-Gd_2O_3 system with mixing UO_2-Er_2O_3, but less intense. This allows use of the fuel content UO_2-Er_2O_3 LWR reactors.

ACKNOWLEDGMENTS

This project also had the support of INB (Nuclear Industries of Brazil), for the shipment of raw material, and CAPES / Eletronuclear for the financing.

REFERENCES

1. DUDERSTADT, J. J.; HAMILTON, J. L. Nuclear Reactor Analysis. New York: John Wiley & Sons, Inc., 1976.
2. INTERNATIONAL ATOMIC ENERGY AGENCY. Characteristics and use of urania-gadolinia fuels. IAEA-TECDOC-844. Vienna, Austria: IAEA, 1995.
3. DEHAUDT, Ph., LEMAINGNAN, C., CAILLOT, L., MOCELLIN, A., EMINET, G. New UO_2 fuel studies. Nuclear Reactor Directorate. International Atomic Energy Agency (IAEA). IAEA-TECDOC-1036. France. 1998.
4. FRANCESCHINI, F., PETROVIC, B., Use of isotopically modified erbium to improve fuel cycle economics in IRIS. 5th International conference on nuclear options in countries with small and medium electricity grids. Croatia. 2004.
5. BARCHEVTSEV, V., ARTISYUK, V., NINOKATA, H., Concept of erbium doped uranium oxide fuel cycle in light water reactor. Tokyo Institute of Technology. Journal of nuclear science and technology. Vol. 39, nº. 5, p. 506-513. 2002.
6. PORTA, J., ASSON, M. Alternative poison? Stabilization additive? What future? Progress in Nuclear Energy. Elsevier. Vol. 38, p. 347-350. 2001.
7. DURAZZO, M., SALIBA-SILVA, A. M., URANO DE CARVALHO, E. F., RIELLA, H. G., Sintering behavior of UO_2-Gd_2O_3 fuel: pore formation mechanism. Journal of Nuclear Materials. 433. 334-340. 2013.
8. PALANKI, B., Fabrication of UO_2-Gd_2O_3 fuel pellets. Journal of Materials Science and Chemical Engineering. 4, 8-21. 2016.
9. DURAZZO, M., OLIVEIRA, F. B. V., URANO DE CARVALHO, E. F., RIELLA, H. G., Phase studies in the UO_2-Gd_2O_3 system. Journal of Nuclear Materials. 430. 183-188. 2010.
10. COSTA, D. R., EZEQUIEL, F. J., GONZAGA, R., BERNARDELLI, S. H. Individual Influence of Al_2O_3 and Nb_2O_5 on Grain Growth of UO_2 Sintered Pellets Manufactured an INB. International Nuclear Atlantic Conference. Associação Brasileira de Energia Nuclear - CNEN. Brazil. 2013.
11. RENIER, J. P. A., GROSSBECK, M. L., Development of improved burnable poisons for commercial nuclear power reactor. OAK Ridge National Laboratory. U. S. Department of Energy. 2001.
12. BARCHEVTSEV, V., ARTISYUK, V., NINOKATA, H., Concept of erbium doped uranium oxide fuel cycle in light water reactor. Journal of nuclear science and technology. Vol. 39, nº. 5, p. 506-513. 2002.
13. SERAFIM, A. C., Estudo de Densificação do Combustível Urânio - 7% Gadolínio (Gd_2O_3) nanoestruturado. Master´s thesis. IPEN. 2016.

14. Aluminum distearate propetiers: https://www.americaelements.com/aluminum-distearate-300-92-5. Accessed in 07.2017
15. SANTOS, L. R., DURAZZO, M., URANO DE CARVALHO, E.F., RIELLA, H. G., Effect of $Al(OH)_3$ on the sintering of UO_2-Gd_2O_3 fuel pallets with addition of U_3O_8 from recycle. Journal of Nuclear Materials. 493. 30-39. 2017.
16. FEDOTOV, A. V., MIKHEEV, E. N., LYSIKOV, A. V., NOVIKOV, V. V., Theoretical and experimental density of $(U,Gd)O_2$ and $(U,Er)O_2$. Atomic Energy. Vol 113, nº 6. 2013.