

BERYLLIUM PROJECT: DEVELOPING IN CDTN OF URANIUM DIOXIDE FUEL PELLETS WITH ADDITION OF BERYLLIUM OXIDE TO INCREASE THE THERMAL CONDUCTIVITY

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ABSTRACT

Although the nuclear fuel currently based on pellets of uranium dioxide be very safe and stable, the biggest problem is that this material is not a good conductor of heat. This results in an elevated temperature gradient between the center and its lateral surface, which leads to a premature degradation of the fuel, which restricts the performance of the reactor, being necessary to change the fuel before its full utilization. An increase of only 5 to 10 percent in its thermal conductivity, would be a significant increase. An increase of 50 percent would be a great improvement. A project entitled "Beryllium Project" was developed in CDTN - *Centro de Desenvolvimento da Tecnologia Nuclear*, which aimed to develop fuel pellets made from a mixture of uranium dioxide microspheres and beryllium oxide powder to obtain a better heat conductor phase, filling the voids between the microspheres to increase the thermal conductivity of the pellet. Increases in the thermal conductivity in the range of 8.6% to 125%, depending on the level of addition employed in the range of 1% to 14% by weight of beryllium oxide, were obtained. This type of fuel promises to be safer than current fuels, improving the performance of the reactor, in addition to last longer, resulting in great savings.

1. INTRODUCTION

The nuclear fuel currently based on pellets of uranium dioxide is very safe and stable. They have no dangerous reaction by coming into contact with the cooling water of the reactor due to a possible failure of the fuel coating, have a high melting temperature and excellent power to retain fission products. However, they have a relatively low thermal conductivity that generates an elevated temperature gradient between the center and its lateral surface. This leads to a premature degradation of the fuel, which restricts the performance of the reactor, and it's necessary to replace the fuel before it is fully utilized.

A project, entitled "Beryllium Project", was performed at CDTN – *Centro de Desenvolvimento da Tecnologia Nuclear*, which aimed to develop a new type of uranium dioxide nuclear fuel pellets with the addition of beryllium oxide (BeO) to increase its thermal conductivity. These fuel pellets will present consequently a lower gradient of temperature, and promises to prevent this premature degradation that occurs in conventional fuel, increasing the useful life of the fuel, resulting in great savings. This project was based on the work done by Purdue University researchers, led by Alvin A. Solomon, and funded by the Department of Energy United States (NERI Project - Nuclear Energy Research Initiative - Project Number 02-180) [1,2,3]. They used uranium dioxide powder self milled to generate spherical particles. We used microspheres of UO₂ produced in CDTN by the process developed by Firma HOBEG/Germany, belonging to the Group NUKEM, to manufacture fuel elements for high temperature gas cooled reactors, a process absorbed and transferred to CDTN during the "Program of Research and Development on the Thorium Utilization in PWRs" [4,5,6]. With such microspheres, pellets were manufactured without the addition of BeO, to serve as reference for the calculation of the thermal conductivity increases, and pellets with additions of 1wt% up to 14wt% of BeO. The thermophysical properties of these pellets were measured using the laser flash method and thus, the improvement in thermal conductivity caused by the gradual increase in the amount of BeO was evaluated. The methodologies used and the obtained results are presented.

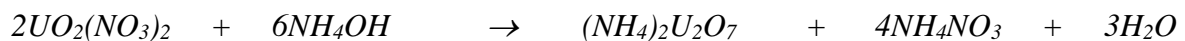
2. METODOLOGY

2.1. UO₂ Microspheres Fabrication – Sol-Gel Process

The microspheres of uranium dioxide (also called kernels), were produced by sol-gel process developed by Nukem / Hanau / Germany to produce fuel elements for High Temperature Gas Cooled Reactors. But it has been adapted to fabricate (Th,U)O₂ fuel pellets for pressurized water reactors [7,8,9,10,11].

By this process, to an aqueous solutions of uranyl nitrate is added polyvinyl alcohol (PVA) as an auxiliary material to increase the solution viscosity and carbon black as pore former to lowering the mechanical strength of the microspheres in order to make easier their desintegration during pressing. Finally, to avoid agglomeration of the carbon black that can cause obstruction of the equipment nozzle, tetrahydrofurfuryl alcohol (THFA) or ethanol is added to the feed solution. Using mechanical vibration of an electromagnetic vibration system, the feed solution is forced to pass through a nozzle generating a jet, which is decomposed into droplets of uniform diameter. Their surfaces are hardened by chemical reaction with ammonia gas to prevent deformation or destruction when they colliding with the surface of an aqueous solution of ammonia, where they are collected and where the external gelation reaction is completed (Fig. 1). By this process, it is possible to produce microspheres of uranium dioxide, thorium dioxide, plutonium dioxide, or mixtures of these oxides, as well as carbides and oxi-carbides.

For UO₂ microspheres, the chemical reaction that takes place can be represented by:



uranyl nitrate + ammonium hydroxid → ammonium diuranate + ammonium nitrate + water

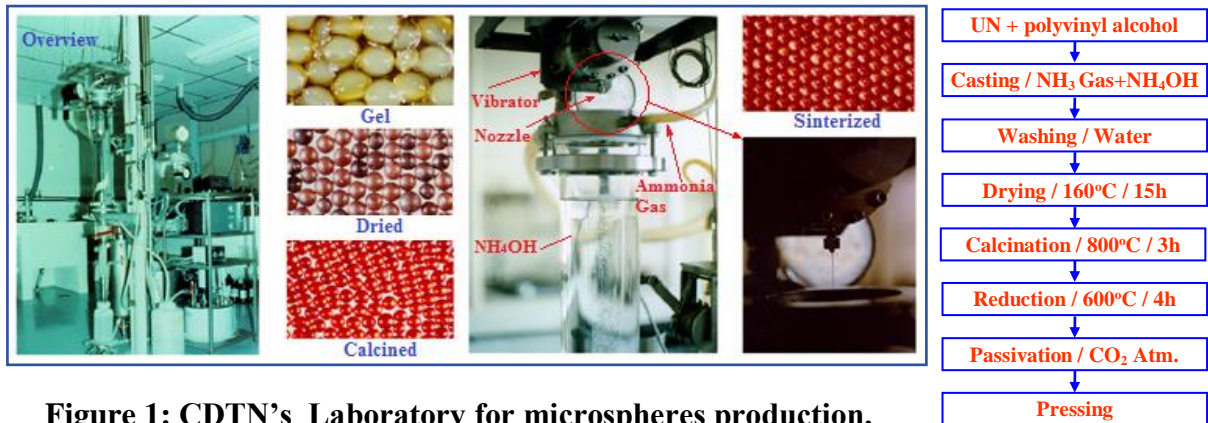


Figure 1: CDTN's Laboratory for microspheres production.

Subsequently, the gel microspheres are washed with water in order to eliminate the reaction by-product ammonium nitrate. Drying and calcining are performed in the air. Thus, the ammonium diuranate and the PVA are thermally decomposed and the carbon black is burnt, leaving pressing pores in the microstructure of the microspheres.

The drying was performed at 160°C for 16 hours and calcination at 900°C for 3 hours, followed by reduction to 600°C/1 hour in a hydrogen atmosphere, and passivation in atmosphere of CO₂, during the cooling of the furnace.

2.2. Pellets Fabrication

Beryllium oxide supplied by Sigma-Aldrich were mixed with the uranium dioxide microspheres with contents ranging from 1 wt% up to 14 wt%. The obtained mixtures were pressed in pellets using the special model of hydraulic press showed in Fig. 2, whose cycle is showed in Fig. 3 [12].

The utilized die has a diameter of 11.1mm, the system work with floating die to obtain the double effect, and it was used lubrication only in the surface of the die. It was employed the oil CL-OF-130 of Petrobrás. Were employed compaction pressures ranging from 300 MPa up to 700 MPa,



Figure 2: Hydraulic press for fuel pellet fabrication.

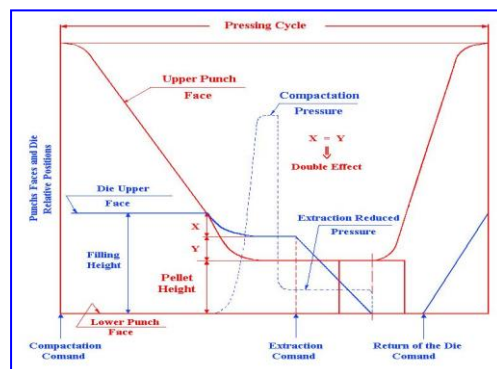


Figure 3: Pressing cycle.

The green density ρ_v of each tablet were geometrically determined using the usual method and equation ($\rho_v = m_v/\pi.d_v^2.h_v/4$, where: m_v is the mass of the green pellet, d_v its diameter and h_v its height). The pellet height and diameter were measured by a micrometer (resolution: 10^{-3} mm), and the mass were obtained with an analytical balance (resolution: 10^{-2} g). The sintering of the pellets were performed in atmosphere of hydrogen at temperatures of 1700°C/5hour for the first group of pellets with addition of 14wt%, 1750 °C/2 hour for the second group with additions of 1wt% and 3wt%, and 1750 °C/3 hour for the third group with addition of 2wt% of BeO. It was fabricated pellets with the same microspheres but without addition of beryllium oxide to compare the thermal diffusivity between the two arts of pellets.

To measure the density and open porosity of the sintered pellets, it were used the xylol penetration-immersion method developed by the Kraftwerk Union research center UO₂ Laboratory in Erlangen/Germany [13,14,15], that were absorbed, transferred and implemented in the CDTN's nuclear fuels laboratories [16,17]. It is used an analytical balance with resolution of 10^{-4} g.

2.3. Thermophysical Properties Measurements - Laser Flash Method

For the pellets thermal diffusivity measurement were utilized the laser flash method [18], and the in house made bench shown in the photographs of Fig. 4 [19].



Figure 4: In house made bench for the thermophysical properties measurements.
LMPT – Laboratório de Medição de Propriedades Termofísicas de Combustíveis Nucleares e Materiais.

In this method the front face of a small disk-shaped sample is subjected to a very short burst of radiant energy. The source of the radiant energy is usually a laser or a xenon flash lamp and irradiation times are of the order of milliseconds (Fig. 5).

The resulting temperature rise of the rear surface of the sample is registered and from the obtained thermogram, the thermal diffusivity is calculated by the following equation:

$$\alpha = \frac{1.37 \cdot L^2}{\pi^2 \cdot t_{1/2}} \quad (2)$$

where:

α is the sample thermal diffusivity [$m^2 \cdot s^{-1}$].

L is the sample thickness [m].

$t_{1/2}$ is the half time [s].

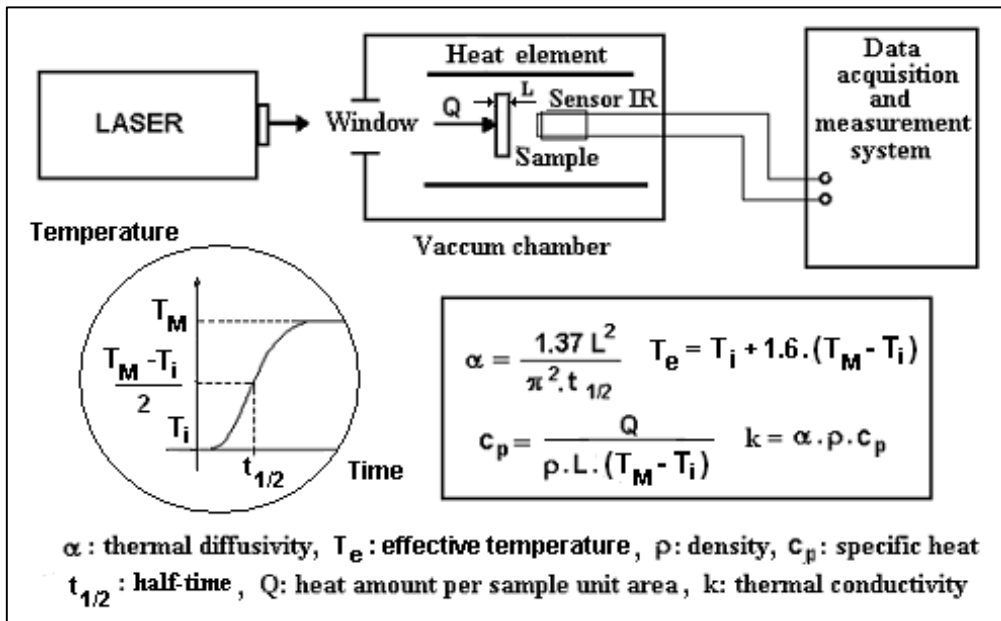


Figure 5: Principle of the Laser Flash Method.

The used CO₂ laser has a maximal power output of 100 Watts and an infrared thermometer measures the temperature of the sample rear face. The sample oven has a heat element of platinum / 30%Rodium that can be heated up to 1700°C, but the measurements were made at room temperature. The thermal conductivity k [W·m⁻¹·K⁻¹] of each pellet was calculated by the following equation:

$$k = \alpha \cdot \rho \cdot C_p \quad (3)$$

where C_p is the specific heat of the material [J·kg⁻¹·K⁻¹], and ρ its density [kg·m⁻³].

3. RESULTS

The Fig. 6 shows a photograph of the produced microspheres and Figures 6,7,8,9,10 and 11, microstructures of some obtained pellets.

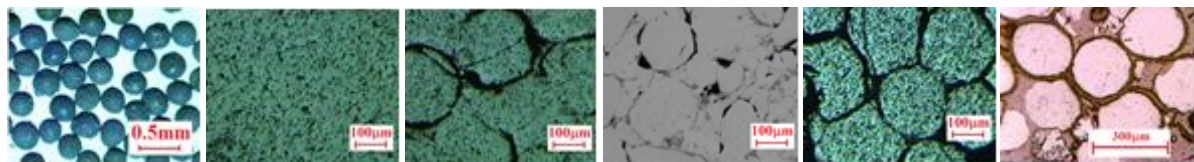


Figure 6:
Microspheres
of UO₂

Figure 7:
UO₂ Pellet

Figure 8:
Pellet of UO₂
+ 1wt%BeO

Figure 9:
Pellet of UO₂
+ 2wt%BeO

Figure 10:
Pellet of UO₂
+ 3 wt%BeO

Figure 11:
Pellet of UO₂
+ 14wt%BeO

Table 1 presented the pelletizing data and results of the characterizations of the green obtained pellets, Table 2 the sintered pellets data, and Table 3, the thermophysical properties

measurements results. The sintered pellets densities of the Group 2 were geometrically obtained.

Table 1. Pelletizing data and results of the characterizations of the green pellets.

Group	Pellet Number	Material	Compaction Pressure [MPa]	Height h_v [cm]	Diameter d_v [cm]	Mass m_v [g]	Green Density ρ_v [g·cm ⁻³]
1	BE 011	UO ₂	300	-	-	-	-
	BE 012	UO ₂	300	-	-	-	-
	BE 001	UO ₂ +14%BeO	300	1,0576	1,1230	4.56	4,356
2	BE 032	UO ₂	300	0,324	1,114	1,69	5,352
	BE 033	UO ₂ +1%BeO	300	0,370	1,130	1,95	5,255
	BE 034	UO ₂ +3%BeO	300	0,364	1,124	1,86	5,150
	BE 036	UO ₂	500	0,284	1,120	1,60	5,718
	BE 037	UO ₂ +1%BeO	500	0,330	1,126	1,86	5,660
	BE 038	UO ₂ +3%BeO	500	0,340	1,124	1,80	5,335
	BE 040	UO ₂	700	0,272	1,124	1,58	5,854
	BE041	UO ₂ +1%BeO	700	0,314	1,124	1,81	5,809
	BE 042	UO ₂ +3%BeO	700	0,320	1,124	1,78	5,606
	3	BE 044	UO ₂	300	0.310	1.120	1.59
BE 045		UO ₂ +2%BeO	300	0.294	1.120	1.57	5.420

Table 2. Sintered pellets dimensions, density and open porosity.

Group	Pellet Number	Material	Height [cm]	Diameter [cm]	Mass [g]	Density [g·cm ⁻³]	Open Porosity % V
1	BE 011	UO ₂	0,2753	0,9093	1,7619	9,903	6,80
	BE 012	UO ₂	0.1226	0,9093	0,7859	9,917	6,78
	BE 001	UO ₂ +14w%BeO	0,9038	0,9591	4,3774	7,062	12,02
2	BE 032	UO ₂	0.2572	0.9093	1.5972	9.914	7.14
	BE 033	UO ₂ +1w%BeO	0.3000	0.9137	1.8529	9.743	7.07
	BE 034	UO ₂ +3w%BeO	0.2997	0.9144	1.7574	9.280	9.34
	BE 036	UO ₂	0.2305	0.9292	1.5129	10.059	6.20
	BE 037	UO ₂ +1w%BeO	0.2789	0.9329	1.7779	9.719	7.41
	BE 038	UO ₂ +3w%BeO	0.2731	0.9335	1.7250	9.587	6.58
	BE 040	UO ₂	0.2263	0.9389	1.5021	10.008	6.51
	BE041	UO ₂ +1w%BeO	0.2656	0.9421	1.7264	9.642	6.92
	BE 042	UO ₂ +3w%BeO	0.2700	0.9441	1.6974	9.290	5.02
	3	BE 044	UO ₂	0,2444	0,8847	1,5590	10,377
BE 045		UO ₂ +2w%BeO	0,2351	0,9080	1,4960	9,827	-

Table 3. Thermophysical properties measurements results.

Group	Material	BeO	Sintering	Thermal	Sintered	Specific	Thermal	Thermal
		Content						
		wt%	°C/hour	$\times 10^6 \text{ m}^2 \cdot \text{s}^{-1}$	$\text{g} \cdot \text{cm}^{-3}$	$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	$\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	%
1	UO ₂	-	1700/5	0.94	9.903	259	2.40	-
	UO ₂	-		0.94	9.917	259	2.40	-
	UO ₂ +BeO	14		1.81	7.062	424	5.41	125
2	UO ₂	-	1750/2	2.21	9.994	310	6.85	-
	UO ₂ +BeO	1		2.23	9.701	356	7.71	12.6
	UO ₂ +BeO	3		2.73	9.386	401	10.28	50.1
3	UO ₂	-	1750/3	3.40	10.377	286	10.11	-
	UO ₂ +BeO	2		3.91	9.827	284	10.92	8.1

Fig.12 shows a graph of the pellets sintered density decrease, Fig. 13, a graph of the thermal conductivity, and Fig. 14, a graph of the thermal conductivity increase, as a function of the beryllium oxide content. Group 1 was sintered at lower temperature (1700°C) resulting in lower densities, in comparison with the other two groups, which was sintered at the higher temperature (1750°C), in order to achieve higher densities. Therefore, group 1 showed relatively low thermal conductivity.

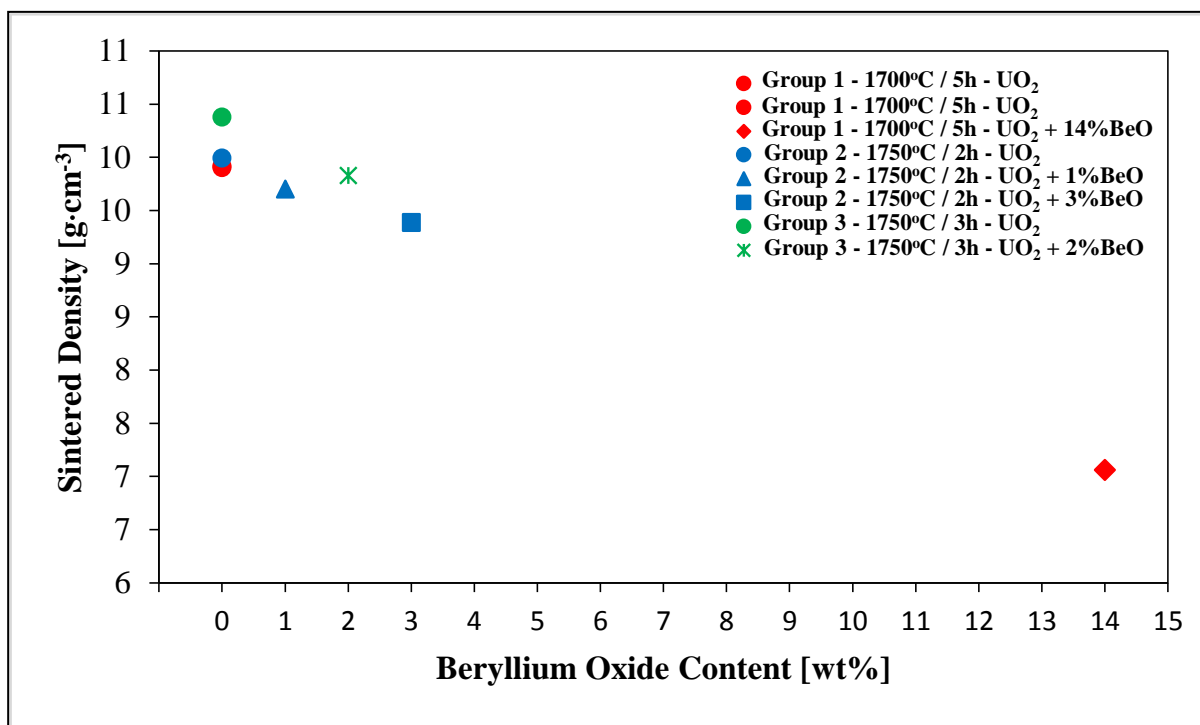


Figure 12: Pellets sintered density decrease with the increase of the beryllium oxide content.

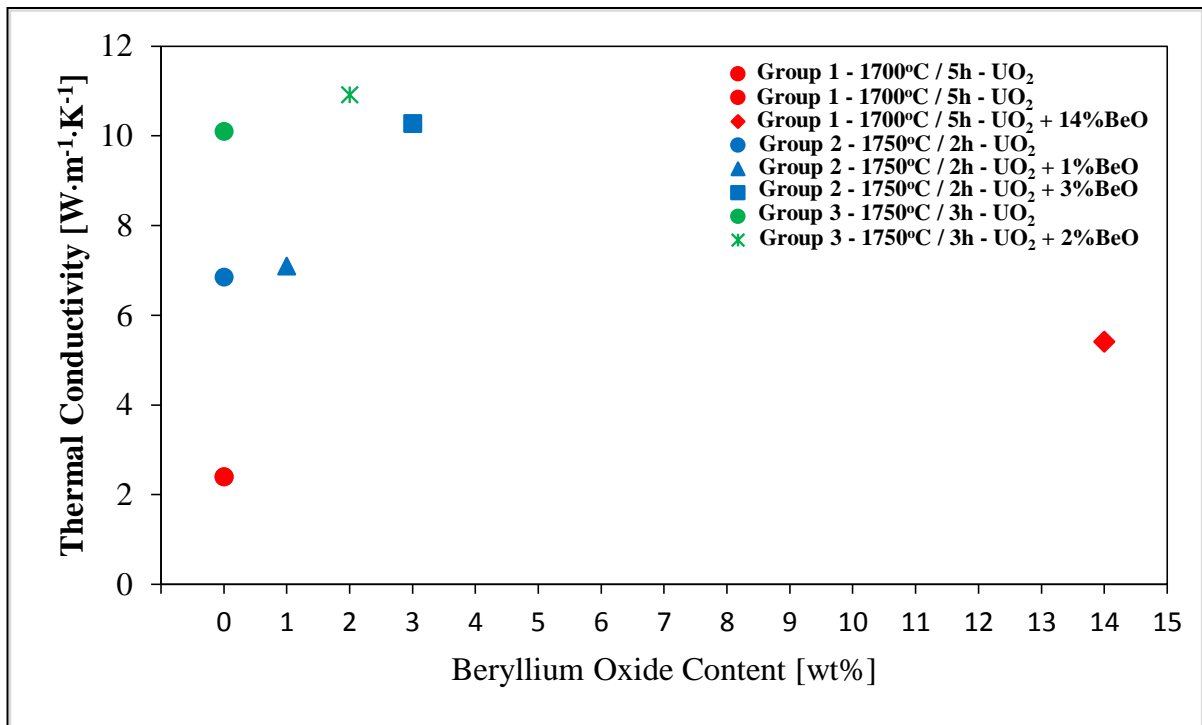


Figure 13: Pellets thermal conductivity as a function of the beryllium oxide content.

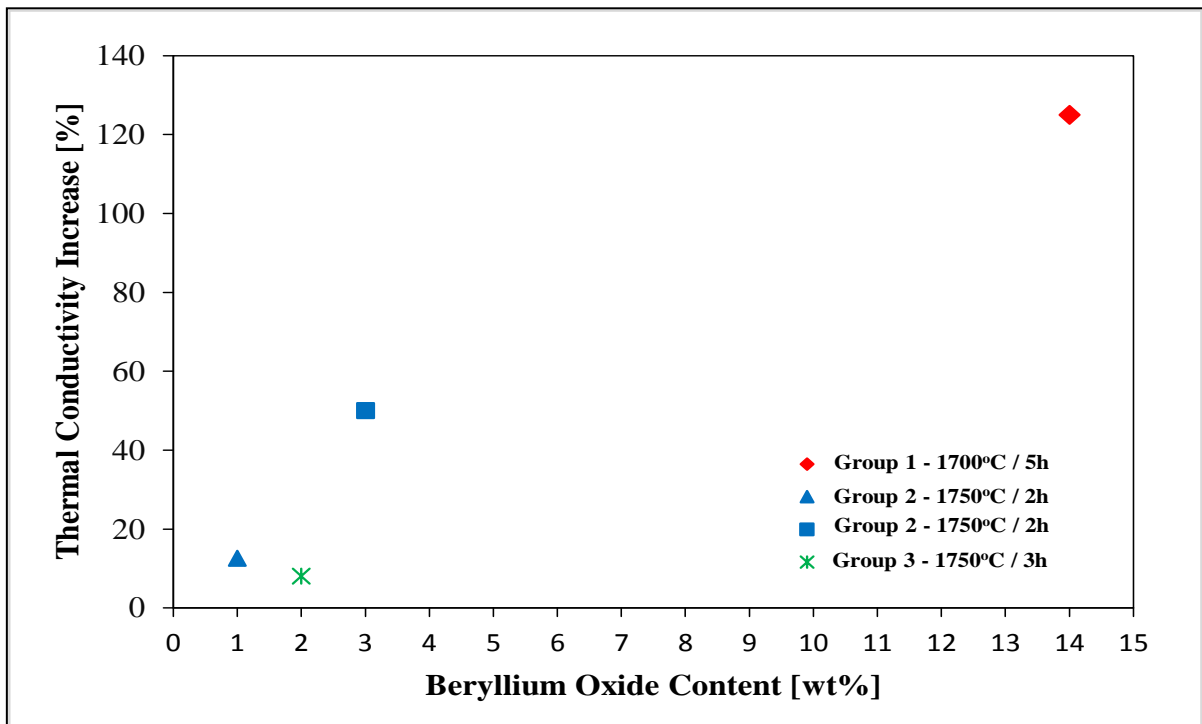


Figure 14: Pellets thermal conductivity increase as a function of the beryllium oxide content increase.

Fig. 15 shows the increase of the thermal conductivity of the UO_2 pellets with the increase of the sintered density, caused by the increase of the sintering temperature.

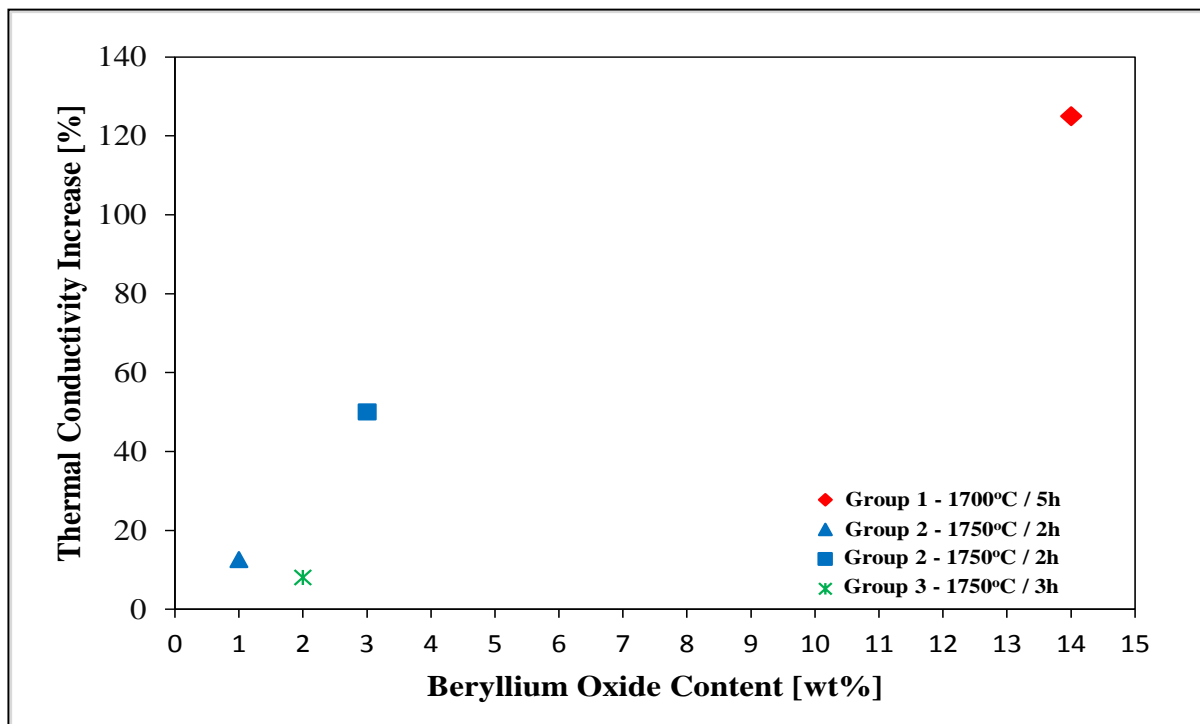


Figure 15: Increase of the UO_2 pellets thermal conductivity with the increase of its densities.

These results are compatible with data of the literature [20].

4. CONCLUSIONS

It was possible to produce a new type of fuel with enhanced thermal conductivity in comparison with the conventional fuel, using a mixture of beryllium oxide and microspheres of UO_2 produced by the sol-gel process. There was obtained thermal conductivity increases between 8.1% and 125% depending on the content of beryllium oxide between 2wt% and 14wt%. This type of fuel promises to be safer than current fuels, improving the performance of the reactor, in addition to last longer, resulting in great savings.

It is expected that in the future this new type of nuclear fuel come to be produced in the Brazilian fuel elements plant. With some simple adaptations in the standard UO_2 production line, such as a system of self-milling to obtain spherical particles and a sieving system to separate the resulting fines, it is possible to produce this type of fuel from UO_2 powder, instead of using microspheres produced by the sol-gel process.

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