

**PREPARATION AND CHARACTER IZATION OF SPENT NUCLEAR FUEL
SURROGATES TO MIMIC POROSITY.
(IONMAT PROJECT. SUBTASK 1.2)**

DIVISIÓN DE FISIÓN NUCLEAR

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TITULO: PREPARATION AND CHARACTERIZATION OF SPENT NUCLEAR FUEL SURROGATES TO MIMIC POROSITY. (IONMAT PROJECT. SUBTASK 1.2)

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ABSTRACT:

One of the most relevant microstructural changes occurring in irradiated UO_2 fuel at high burnup is the development of the rim region, characterized by significant porosity and the formation of sub-micrometric grains. Understanding the influence of porosity on fuel behavior is essential for modelling spent fuel performance during storage and disposal.

Within the framework of the IONMAT project, one of the goals was to fabricate UO_2 pellets with distinct porosities using U_3O_8 as a pore-forming precursor. Pellets containing 0, 5, 12 and 19 wt.% U_3O_8 were produced, sintered under reducing atmosphere and characterized by XRD, pycnometry, BET specific surface area method and SEM. The objective was to reproduce porosity levels comparable to those observed in spent nuclear fuel while maintaining a UO_2 matrix.

The results demonstrate that the addition of different U_3O_8 quantities slightly modifies the microstructure and density of the sintered pellets. The highest porosity levels, as well as the greatest lattice parameter and specific surface area values, were obtained for the pellets initially containing around 5 wt.% U_3O_8 , while the highest density corresponded to those where 19 wt.% U_3O_8 was added. XRD confirmed in all cases the preservation of the fluorite UO_2 structure after sintering. These materials constitute suitable surrogates for future studies focused on the role of porosity in spent nuclear fuel behavior.

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1. INTRODUCTION

The nuclear fuel microstructure changes during reactor operation due to irradiation damage, fission products (FPs) accumulation and strong thermal gradients. These microstructural modifications directly affect fuel thermal conductivity, fission gas behavior and long-term performance during storage and disposal [1].

At high burnup, the rim region of UO_2 fuel undergoes a significant microstructural reorganization, leading to the so-called high burnup structure (HBS). The HBS is characterized by extensive grain subdivision, fission gas redistribution and the development of a large quantity of micro-sized pores, resulting in porosity levels that can be around 20 % of the volume in the restructured region [2, 3].

The porosity produced during HBS formation differs from the as-fabricated porosity. Instead of being uniformly distributed, pores in the HBS are concentrated in the outer region of the pellet (rim) and are associated with the freshly formed “refined grain microstructure” [4]. The increase in porosity does not only involve changes in the local mechanical properties, but also considered as a feature that can play a significant role in the long-term evolution of the irradiated fuel.

Therefore, as part of the IONMAT project, Subtask 1.2 focuses on reproducing key characteristics of spent nuclear fuel using non-irradiated surrogate materials. Following the work reported in DFN/RA-05/SP-25 [5], where the effects of porosity and fission-product simulants were investigated using CeO_2 -based systems, the present study represents the next phase toward realistic UO_2 model materials.

The objective of this work was to fabricate UO_2 pellets with distinct porosities by incorporating different amounts of U_3O_8 , and to evaluate the influence of this pore-forming precursor on the final microstructure, density and specific surface area of the sintered pellets [6].



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2. MATERIALS AND METHODS

2.1. STARTING MATERIALS

Two uranium oxide powders were employed in this study: UO_2 and U_3O_8 (Figure 1). U_3O_8 was obtained by calcination of ammonium diuranate (ADU) precipitate ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ up to $800\text{ }^\circ\text{C}$ and 4 h at $800\text{ }^\circ\text{C}$, in air). UO_2 was attained by reduction of part of the U_3O_8 batch ($5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ up to $600\text{ }^\circ\text{C}$, $3\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ from $600\text{ }^\circ\text{C}$ to $1000\text{ }^\circ\text{C}$, and 8 h at $1000\text{ }^\circ\text{C}$, under 4.7% $\text{H}_2\text{-N}_2$).

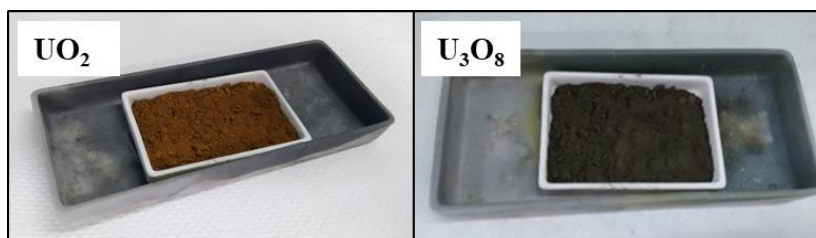


Figure 1. UO_2 and U_3O_8 powders used as starting materials.

These starting materials were characterized by XRD and Raman spectroscopy (see Table II), in order to confirm their chemical composition and homogeneity. The X-ray diffractograms obtained on UO_2 and U_3O_8 powders are shown in Figure 2. Rietveld refinement analysis performed on the latter (data not shown) identified pure cubic UO_2 (Fm-3m, ICDD 03-065-0285) with lattice parameter $a = 5.4696\text{ \AA}$, and pure orthorhombic U_3O_8 (C2mm, ICDD 01-089-4906) with lattice parameters $a = 4.14596\text{ \AA}$, $b = 11.9556\text{ \AA}$ and $c = 6.7173\text{ \AA}$, respectively. Figure 3 gathers the acquired Raman spectra, which also correspond to the Raman fingerprints of UO_2 [7, 8] and U_3O_8 [9, 10] and corroborate the homogeneity of these samples. In particular, the contribution observed at around $500\text{-}700\text{ cm}^{-1}$ in the UO_2 Raman spectrum (see arrow in Figure 3) indicates that it corresponds to slightly hyperstoichiometric UO_2 [11, 12].



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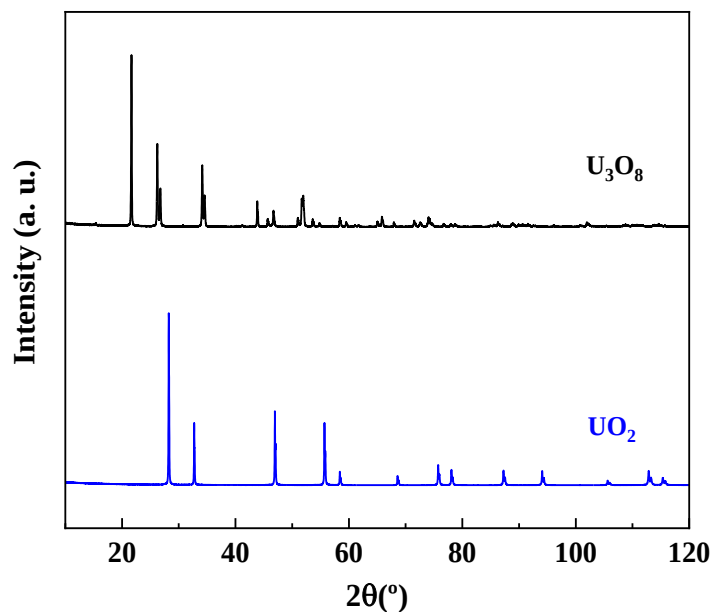


Figure 2. X-ray diffractograms of the starting UO_2 and U_3O_8 powders.

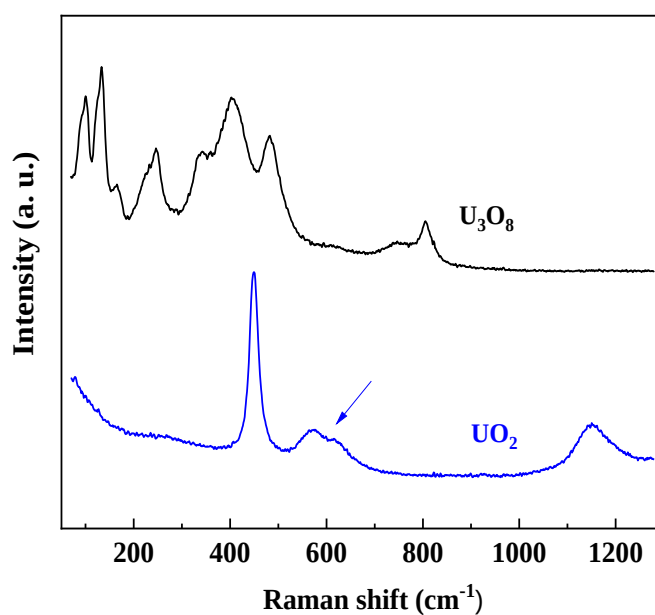


Figure 3. Raman spectra of the starting UO_2 and U_3O_8 powders.

The starting UO_2 and U_3O_8 powders were also characterized by N_2 -BET specific surface area measurements and laser diffraction particle size analysis (see Table II). UO_2



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powder exhibited a BET specific surface area (SSA) of $2.772 \pm 0.003 \text{ m}^2 \cdot \text{g}^{-1}$ (correlation coefficient = 0.9999), while U_3O_8 showed a slightly higher value of $3.040 \pm 0.004 \text{ m}^2 \cdot \text{g}^{-1}$ (correlation coefficient = 0.9999). The particle size distributions (PSD, measured with alcohol, Figure 4) revealed fine powders with broad size distributions in both cases. UO_2 presented $D[3;2] = 1.68 \text{ }\mu\text{m}$, $D[4;3] = 12.6 \text{ }\mu\text{m}$, $D_x(10) = 0.69 \text{ }\mu\text{m}$, $D_x(50) = 2.20 \text{ }\mu\text{m}$, $D_x(90) = 42.60 \text{ }\mu\text{m}$ and $\text{SPAN} = 19.045$, whereas U_3O_8 exhibited $D[3;2] = 1.02 \text{ }\mu\text{m}$, $D[4;3] = 8.04 \text{ }\mu\text{m}$, $D_x(10) = 0.45 \text{ }\mu\text{m}$, $D_x(50) = 1.25 \text{ }\mu\text{m}$, $D_x(90) = 24.30 \text{ }\mu\text{m}$ and $\text{SPAN} = 19.128$. PSDs of both UO_2 and U_3O_8 powders displayed a broad bimodal character, consisting of a dominant fine fraction centered around $1 \text{ }\mu\text{m}$ and a second coarser population extending to several tens of micrometers. Such bimodal distributions are typically associated with the presence of agglomerates and may enhance powder packing by allowing fine particles to occupy the interstitial spaces between larger particles. The U_3O_8 powder showed a finer overall distribution than UO_2 , as reflected by its lower $D_x(50)$ ($1.25 \text{ }\mu\text{m}$ vs. $2.20 \text{ }\mu\text{m}$) and $D_x(90)$ ($24.3 \text{ }\mu\text{m}$ vs. $42.6 \text{ }\mu\text{m}$), together with a slightly higher SSA value.

These results indicate that the U_3O_8 powder consisted of finer particles and possessed a slightly larger specific surface area than UO_2 , which may influence powder packing, mixing homogeneity and the subsequent sintering behavior.

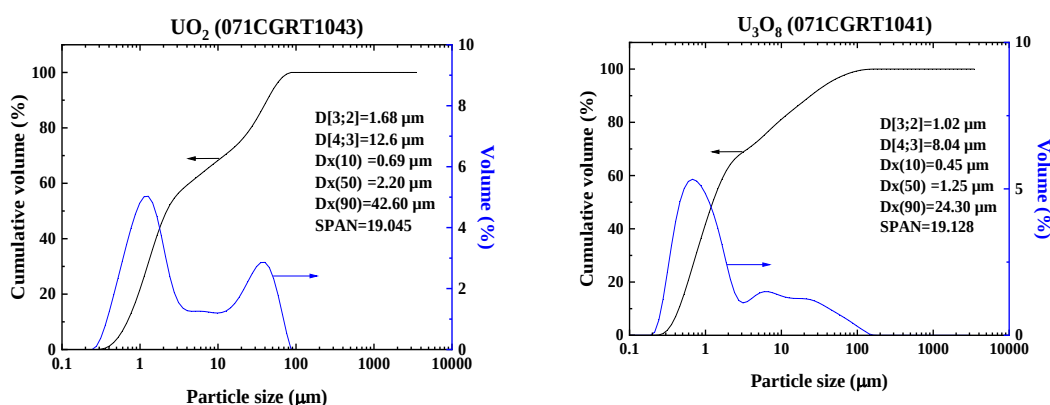


Figure 4. PSD of the starting UO_2 and U_3O_8 powders.



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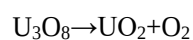
2.2. PELLETS FABRICATION

The desired proportions of UO_2 and U_3O_8 (Table I) were manually mixed and homogenized. Firstly, a pre-compaction at 100 MPa for 15 s was applied. Then, samples were granulated and finally pressed at 400 MPa for 30 s. Ethylene-bis-stearamide (EBS) was used as lubricant before pressing each batch of samples.

Table I. Prepared samples, with different proportions of UO_2 and U_3O_8 .

Reference	UO_2 (wt.%)	U_3O_8 (wt.%)
UO_2 -0% U_3O_8	100	0
UO_2 -5% U_3O_8	95	5
UO_2 -12% U_3O_8	88	12
UO_2 -19% U_3O_8	81	19

Sintering was performed under 4.7% H_2 -Ar atmosphere using a heating rate of 200 $^\circ\text{C h}^{-1}$ up to 1675 $^\circ\text{C}$, followed by a 6 h isothermal dwell. For that, the reduction reaction is:



The obtained pellets are shown in Figure 5.



Figure 5. Picture of the UO_2 pellets sintered with increasing content of U_3O_8 .



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2.3.CHARACTERIZATION TECHNIQUES

After sintering, the samples were characterized using a variety of techniques: X-ray diffraction (XRD), pycnometry, BET specific surface area method and scanning electron microscopy (SEM). The corresponding properties extracted from these techniques and the equipment used are included in Table II.

Table II. Characterization techniques used in this study.

Technique	Obtained properties	Equipment
XRD	Microstructure/crystalline identification and phase quantification	D8 ADVANCE Eco (Bruker) <i>Cu Kα radiation ($\lambda=1.54056 \text{ \AA}$), 40 kV and 25 mA. Bragg-Brentano configuration geometry</i> DIFFRAC.TOPAS software (Bruker Analytical X-Ray Systems) Alpha-alumina ($\alpha\text{-Al}_2\text{O}_3$, corundum) was used as an external XRD standard for correction of 2 θ peak shifts caused by instrumental zero-point errors and specimen displacement.
Raman spectroscopy	Microstructure and chemical composition identification	LabRam HR Evolution (HORIBA) <i>He-Ne laser with a wavelength of 632.8 nm</i>
Pycnometry	Density	AccuPyc II 1350 (Micromeritics)
BET	N ₂ -BET specific surface area	ASAP 2020 (Micromeritics)
PSD	Laser diffraction particle size analysis	Mastersizer Series 3000 Hydro EV (Malvern Panalytical)
SEM	Surface morphology and grain size	TM4000 Plus 15 kV (HITACHI)



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3. RESULTS: EFFECT OF U_3O_8 LOADING ON UO_2 PELLETS. CHARACTERIZATION

In the following section, the main results obtained in this study are reported.

3.1. PHASE ANALYSIS (XRD)

XRD measurements carried out on the pellets sintered with 0, 5, 12 and 19 wt.% U_3O_8 identified pure cubic UO_2 in all cases (Figure 6). The absence of residual U_3O_8 confirmed the correct reduction and stabilization of the fluorite UO_2 structure after sintering.

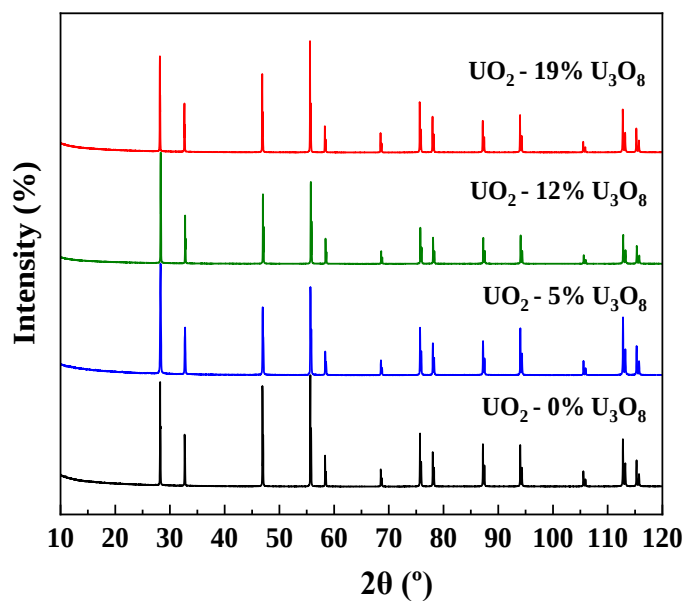


Figure 6. Diffractograms of the UO_2 pellets sintered with increasing content of U_3O_8 .

Rietveld refinement analysis (not shown) was performed on the diffraction patterns to evaluate possible microstructural variations as a function of the initial U_3O_8 content. The obtained UO_2 lattice parameters are reflected in Table III and their evolution with increasing U_3O_8 content in Figure 7. The quality of the refinements was assessed through the weighted profile residual (Rwp), also included in Table III.



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Table III. Lattice parameters of the UO_2 pellets sintered with increasing content of U_3O_8 , together with the obtained Rietveld refinement Rwp parameters.

Reference	Phase identification	Lattice parameter, a (Å)	Rwp (Weighted profile residual)
UO_2-0% U_3O_8	UO_2 (Fm-3m)	5.47113(2)	9.88
UO_2-5% U_3O_8	UO_2 (Fm-3m)	5.47143(4)	15.34
UO_2-12% U_3O_8	UO_2 (Fm-3m)	5.47128(2)	11.08
UO_2-19% U_3O_8	UO_2 (Fm-3m)	5.47085(2)	13.92

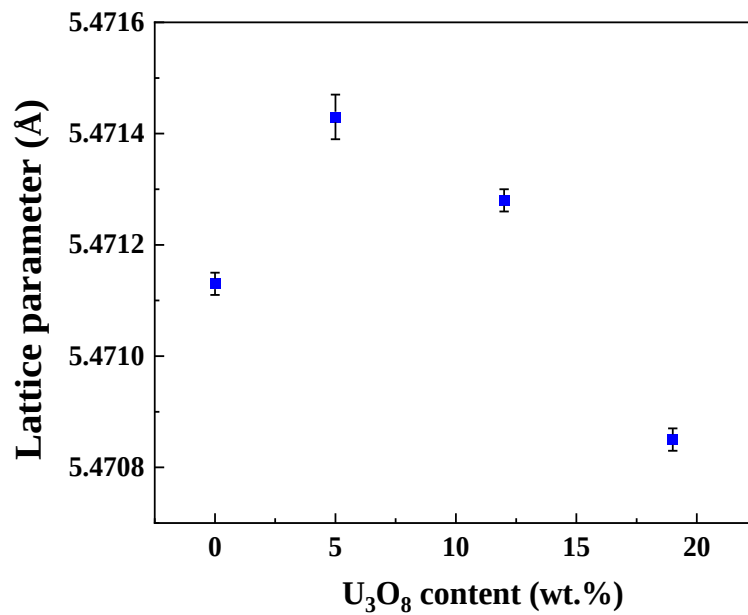


Figure 7. Evolution of the lattice parameter of the UO_2 pellets sintered with increasing content of U_3O_8 .

The a lattice parameter of the cubic UO_2 structure suffers a slight growth when adding 5 wt.% U_3O_8 before sintering, but then it seems to steadily decrease when increasing the amount of added U_3O_8 (even reaching at 19 wt.% U_3O_8 a value lower than that corresponding to the sample with no initial U_3O_8 content). This behavior indicates that the theoretical density of the UO_2 pellet decreases with 5 wt.% U_3O_8 , but from that point it gets denser, achieving the highest theoretical densification with the incorporation of 19 wt.% U_3O_8 to the initial UO_2 powders.



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3.2.DENSITY EVOLUTION

Density was determined by helium pycnometry. Then, ten successive pellet volume were measured, and their average value was estimated. The density values obtained by this technique ranged between 9.402 and 9.511 g·cm⁻³ for all compositions, corresponding to relative densities of around 86-87% of the theoretical density (see Table IV). The relative density was calculated using the theoretical density proposed by Physical Measurement Laboratory of National Institute of Standards and Technology (NIST-PML), 10.96 g·cm⁻³. Although these values are lower than those typically reported for conventional nuclear fuel pellets (usually ~95–96 % of theoretical density), this level of densification was intentionally targeted in the present work in order to preserve a significant porosity fraction and evaluate the influence of U₃O₈ additions under these processing conditions. As shown in Figure 8, the density initially decreases with the addition of 5 wt.% U₃O₈, reaching its minimum value for this composition. Further increases in U₃O₈ content result in progressively higher densities, with the sample prepared with 19 wt.% U₃O₈ exhibiting the highest densification among all the compositions investigated. It is worth noting that this evolution follows the same qualitative tendency as the one deduced by XRD analysis (Figure 8).

Table IV. Density values of the UO₂ pellets sintered with increasing content of U₃O₈.

Reference	Density (g·cm ⁻³)	Relative Density (%)
UO ₂ + 0% U ₃ O ₈	9.474 ± 0.006	86.44
UO ₂ + 5% U ₃ O ₈	9.402 ± 0.007	85.78
UO ₂ + 12% U ₃ O ₈	9.43 ± 0.01	86.04
UO ₂ + 19% U ₃ O ₈	9.511 ± 0.01	86.78



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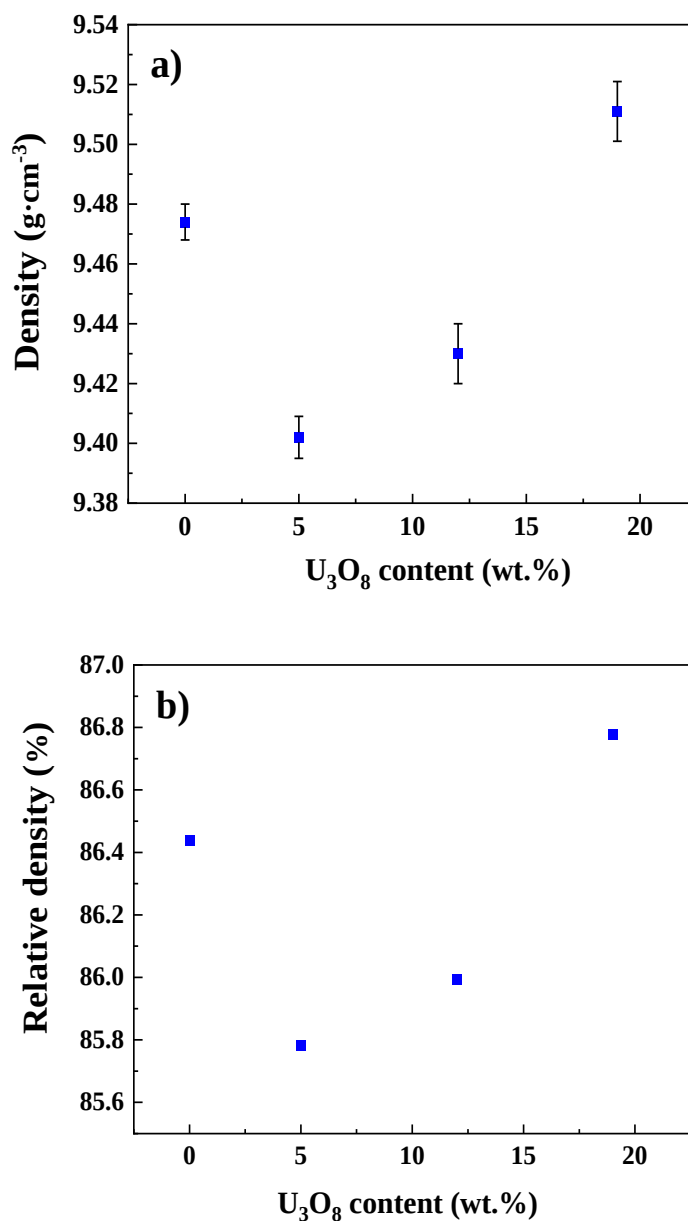


Figure 8. a) Absolute and b) relative densities of the UO₂ pellets sintered with increasing content of U₃O₈.



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3.3. BET SURFACE AREA EVOLUTION

As expected for sintered pellets, the measured SSA values determined by BET method and following the ISO 12800 standard [13], were substantially lower than those of the starting powders. The UO_2 and U_3O_8 precursor powders exhibited SSA values of 2.77 and $3.04 \text{ m}^2\cdot\text{g}^{-1}$, respectively (see section 2.1), whereas the sintered pellets showed values between 0.17 and $0.35 \text{ m}^2\cdot\text{g}^{-1}$ (see Table V). The higher surface area and finer particle size of the U_3O_8 precursor (see section 2.1) indicate that the pore-forming additive was initially more finely dispersed within the powder mixture. During sintering, reduction of U_3O_8 to UO_2 and simultaneous oxygen release may influence pore generation and densification processes, ultimately affecting the residual porosity and accessible surface area of the pellets.

The evolution of the obtained SSA values with increasing U_3O_8 content is reflected in Figure 9. The trend observed is consistent with the density measurements obtained by helium pycnometry and follow the same qualitative evolution as the lattice parameter determined by XRD. In particular, the incorporation of 5 wt.% U_3O_8 produced the highest SSA value ($0.352 \text{ m}^2\cdot\text{g}^{-1}$) and the lowest density. Despite U_3O_8 presenting a somewhat larger surface area than the UO_2 starting powder, the evolution of the pellet SSA after sintering was not proportional to the initial powder surface area, indicating that microstructural development during reduction and sintering dominates the final porosity state. Above 5 wt.% U_3O_8 , a progressive decrease in SSA was observed, consistent with increased densification and reduced accessible porosity.

Table V. Specific surface area of the UO_2 pellets sintered with increasing content of U_3O_8 .

Reference	SSA ($\text{m}^2\cdot\text{g}^{-1}$)
$\text{UO}_2 + 0\% \text{ U}_3\text{O}_8$	0.27 ± 0.02
$\text{UO}_2 + 5\% \text{ U}_3\text{O}_8$	0.352 ± 0.008
$\text{UO}_2 + 12\% \text{ U}_3\text{O}_8$	0.20 ± 0.01
$\text{UO}_2 + 19\% \text{ U}_3\text{O}_8$	0.170 ± 0.008



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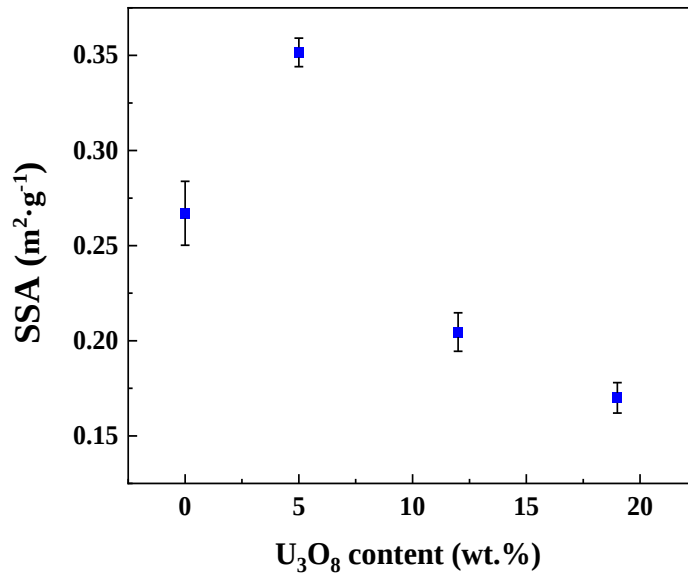


Figure 9. Evolution of the specific surface area of the UO₂ pellets sintered with increasing content of U₃O₈.

3.4. POROSITY ESTIMATION

For evaluating the porosity levels induced in the sintered pellets by different U₃O₈ loadings, the two followed approaches consisted in estimating the total porosity from the relation between the density values obtained by pycnometry (Table IV) and the theoretical densities. The difference between these approaches lay in the theoretical densities considered. In the first case, the tabulated theoretical density (NIST-PML, 10.96 g·cm⁻³) was used for all the samples; in the second one, the theoretical crystallographic density of each sample was calculated from the XRD lattice parameters (Table III).

All the estimated porosity values are reflected in Table VI. Figure 10 shows the evolution of the two sets of values as a function of initial U₃O₈ loading. As can be seen, the tendency followed in both cases was very similar to the one observed for BET (specific surface area) results. The maximum values of porosity were achieved for the 5 wt.% U₃O₈ sample and it steadily decreased towards the 19 wt.% U₃O₈ sample.



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Table VI. Porosity values estimated for the UO_2 pellets sintered with increasing content of U_3O_8 .

Reference	Porosity estimated from tabulated theoretical density (%)	Porosity estimated from theoretical crystallographic densities (%) ± 0.02 (%)
$\text{UO}_2 + 0\% \text{U}_3\text{O}_8$	13.56	13.50
$\text{UO}_2 + 5\% \text{U}_3\text{O}_8$	14.22	14.14
$\text{UO}_2 + 12\% \text{U}_3\text{O}_8$	13.96	13.94
$\text{UO}_2 + 19\% \text{U}_3\text{O}_8$	13.22	13.17

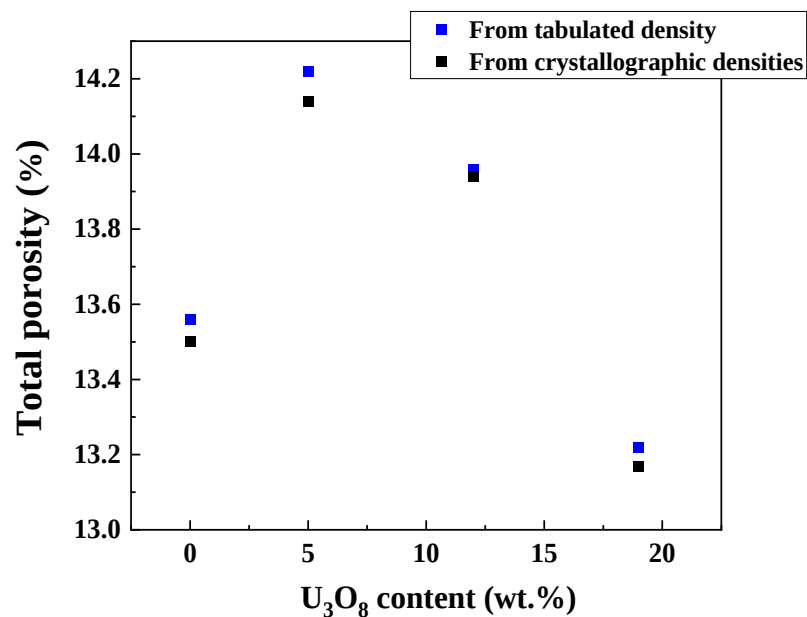


Figure 10. Evolution of porosity (estimated by the two different considered approaches) for the UO_2 pellets sintered with increasing content of U_3O_8 .

The porosity values estimated from the tabulated density and those calculated using the crystallographic densities exhibited excellent agreement, with differences below 0.1% for all compositions. Both methods identified the 5 wt.% U_3O_8 sample as the most porous specimen and the 19 wt.% U_3O_8 sample as the least porous one, supporting the consistency of the observed densification trend.



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3.5.SEM

Morphological characterization of the pellets was also performed by SEM, using backscattered electrons configuration. Several images were recorded on the surface of the samples, at different magnifications. Figure 11 shows selected images taken at 3000X magnification on each of the studied UO_2 pellets (containing 0, 5, 12 and 19 wt. % U_3O_8 before sintering).

SEM micrographs revealed negligible differences among the samples. Regarding porosity, the presence of a slightly greater amount of intragranular pores can be deduced from the image corresponding to the addition of 5 wt.% U_3O_8 , what is in accordance with the rest of previously mentioned outcomes. Nonetheless, it must be taken into consideration that the variation in porosity values reported in the previous section is so small, that only a subtle distinction would be expected in the SEM images.

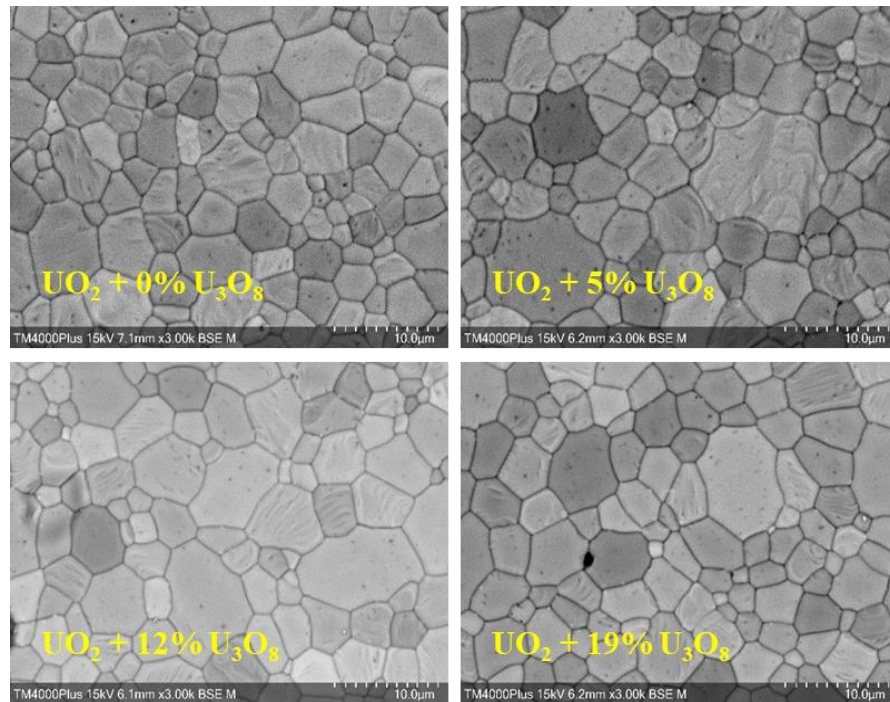


Figure 11. SEM images the UO_2 pellets sintered with increased content of U_3O_8 .



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4. SUMMARY OF RESULTS

UO₂ pellets containing 0, 5, 12 and 19 wt.% U₃O₈ were produced and sintered under reducing atmosphere. The objective was to use U₃O₈ as pore-former, in order to reproduce porosity levels comparable to those observed in spent nuclear fuel while maintaining a UO₂ matrix. Pure UO₂ and U₃O₈ starting powders were firstly characterized by XRD and Raman spectroscopy, confirming both their adequate chemical composition and homogeneity. The starting U₃O₈ powder showed a slightly higher BET specific surface area (3.04 m²·g⁻¹) and smaller characteristic particle size (D_x(50) = 1.25 μm) than the UO₂ powder (2.77 m²·g⁻¹ and D_x(50) = 2.20 μm), favoring its homogeneous distribution within the powder mixtures prior to pellet fabrication.

The sintered pellets were characterized by XRD, pycnometry, BET specific surface area method and SEM, aiming to assess the influence of the induced porosity on their final microstructure, density and specific surface area. XRD confirmed the preservation of the fluorite UO₂ structure in all cases after sintering. The highest porosity levels (or lowest density), obtained for the pellets initially containing around 5 wt.% U₃O₈, and the tendency of steady decrease in porosity from that point went up to 19 wt.% U₃O₈ (which revealed the highest density), were in good agreement with the results obtained by XRD, BET and SEM. In fact, an analogous trend to that of porosity behavior was observed for the evolution of the lattice parameter and the specific surface area values as a function of pre-sintering U₃O₈ loading. SEM observations revealed only slight microstructural differences between compositions, which is consistent with the relatively small variation in total porosity observed among the pellets.

These materials constitute suitable experimental samples for future studies related to the investigation of the influence of porosity on the behavior and degradation of spent nuclear fuel analogs. However, in order to achieve higher porosity levels, further investigation is recommended using higher U₃O₈ contents than those used here (to see if over 19 wt.% U₃O₈ content the tendency changes) or by incorporating other pore-forming additives, such as PMMA (polymethyl methacrylate), that decompose during heat treatment.



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<u>FIRMANTE</u>	<u>NOMBRE</u>	<u>FECHA</u>	<u>NOTAS</u>
FIRMANTE[1]	JONE MIREN ELORRIETA BAIGORRI	23/09/2026 11:10 Sin acción específica	
FIRMANTE[2]	MARIA NIEVES RODRIGUEZ VILLAGRA	23/09/2026 11:41 Sin acción específica	
FIRMANTE[3]	M.SOLEDAD FERNANDEZ FERNANDEZ	23/09/2026 11:44	
FIRMANTE[4]	ENRIQUE MIGUEL GONZALEZ ROMERO	23/09/2026 13:35 Sin acción específica	

