



Hydrogen in Uranium Dioxide Pellets

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ABSTRACT. Four BWR fuel assemblies were fabricated. The average hydrogen content of the accepted lots was 0.34 $\mu\text{g/g}$ UO_2 and five lots were rejected for high hydrogen content, in some cases over the specification limit. The pellets have controlled porosity and does not change the hydrogen content even after immersion in water. The drying in dry hydrogen at 1050 °C reduces the hydrogen content of the high hydrogen pellets, but it is still over 0.5 $\mu\text{g/g}$ UO_2 . Higher temperatures and wet hydrogen or cracked ammonia atmospheres could bring the strongly bonded hydrogen content to the normal values found elsewhere.

1. INTRODUCTION.

Four prototype fuel assemblies for the Laguna Verde reactors (BWR type, 2 units of 654 Mwe each) were fabricated at the Instituto Nacional de Investigaciones Nucleares^[1,2] (National Institute of Nuclear Research). They have been under irradiation since December 12, 1996. The uranium dioxide was imported already homogenized and granulated. Four types of powder were used: ADU (ammonium diuranate), recycled ADU, a blend of the two first ones and a blend of two ADU powders with different enrichments. The UO_2 was prepared for pressing, adding an internal lubricant (Micronized Acrawax-C) and a pore former (milled ammonium oxalate) to the granules. A double effect mechanical press with a floating die was used for pressing. After sintering for five hours in a molybdenum batch furnace at 1780 °C, a density of 96.5 ± 0.5 TD (theoretical density) was obtained. The pellets were then wet ground, pre-dried in vacuum and dried at 1050°C in dry hydrogen atmosphere. The structure consists of a matrix 98-99% dense and controlled porosity. During the ceramic fabrication of this fuel, 99 lots of approximately 10 kg were accepted. The main cause for lot rejects was inhomogeneous density due to powder problems. The second cause was the high hydrogen content, in some cases over the specification limit. Five lots were rejected for this reason, with hydrogen content ranging from 0.86 to 1.7 $\mu\text{g/g}$ UO_2 , at the time of fabrication and after exposure to the normal atmosphere. Repeated high temperature drying operations reduced the hydrogen content somewhat, but still kept it on the high side. The average hydrogen content of the accepted pellets was 0.34 $\mu\text{g/g}$, higher than the normal hydrogen content of 0.10 to 0.15 $\mu\text{g/g}$ UO_2 , obtained elsewhere with sintering in continuous furnaces in wet cracked ammonia or wet hydrogen, followed by dry grinding. This higher hydrogen content produced by the sintering in dry hydrogen has been reported by Wheeler^[5] in UO_2 single crystals at 1000 °C, and has also been found in ZrO_2 ^[6]. The reason for the hydrogen solubility variation is due to small, undetectable variations of the O/U ratio arising from the

sintering conditions^[5]. However, these small differences in composition produce detectable changes in the thermodynamic properties. If the O/U ratio is > 2.00, as can occur if wet hydrogen is used for sintering, the oxygen potential of wet hydrogen is slightly higher than the oxygen potential for dry hydrogen, and the interstitial oxygen ion concentration is slightly higher. The sites available for the hydrogen in the structure are few, so the hydrogen content will be reduced. If the O/U ratio is < 2.00, uranium metal will probably be precipitated and uranium hydride will be eventually formed.

2. HYDROGEN IN UO₂.

Hydrogen (or water) can be introduced in the pellet during fabrication from several sources: the sintering; the wet grinding; and the atmosphere when the pellet is stored, waiting for the rod loading. All the sintering atmospheres contain hydrogen. The sintering gas could be trapped in the closed porosity at the sintering temperature. It is released^[3,4] at temperatures over 1000 °C. in the form of water accompanied by smaller amounts of elemental hydrogen in a process that, according to Olander et al^[3] is not diffusion controlled. Another possibility is to have the hydrogen dissolved in the fluorite type structure of the UO₂. According to Wheeler^[5], this solubility of hydrogen in UO₂ varies between 0.03 and 0.4 µg/g UO₂, depending on the defect structure of the UO₂ with no simple correlation with the temperature and pressure. This author indicates that the excess hydrogen present could be trapped at the closed pores or at the grain boundaries. Different authors indicate different possibilities for storing the hydrogen in the pellet, but all agree that high temperature is needed to release it. Our pellets, as was mentioned before, were dried at 1050 °C for two hours. It is clear that better results could have been obtained drying at higher temperatures in wet hydrogen or cracked ammonia. The problem of higher drying temperatures is the possible densification of the pellet, which is already at the final density and dimensions.

The second source of hydrogen retention is the water absorbed by the pores. If the pellet open porosity is high it could absorb moisture very rapidly when exposed to the atmosphere^[1]. This moisture could be released from the open pores at temperatures of 100 – 150 °C^[3]. However, “hard to dry” pellets in the density range 95-96 % TD and open porosity close to 1% were reported. It is necessary to dry these pellets at 400 °C in order to evaporate the water. This could be due to bottleneck (or tea kettle) shaped pores^[3]. Liquid water from the wet grinding could enter these pores due to capillarity, but the vapor release when the pellets are heated would be performed at a rate controlled by the conductance of the constriction. These pores may be connected to the outside surface of the pellet or to the main pore system.

The pellets fabricated for the Laguna Verde reactors have a controlled microstructure. They have, as was mentioned earlier, a 98 - 99 % TD dense matrix, and pores coming from the pore former and lubricant. The open porosity was determined by vacuum outgassing for two hours, immersion in water for two hours, rolling in a lint free paper towel and weighing. The open porosity is slightly higher for the high hydrogen pellets. For the low hydrogen pellets, it ranges from 0 to 0.02 % and for the high hydrogen pellets it ranges from 0.02 to 0.08 %. The difference is small and the method sensibility not very high. In order to test if the high hydrogen content comes from differences in porosity, we have to study the porosity shape and distribution looking for bottleneck pores.

Our pellets were wet ground. After this operation, they were dried a 1050 °C in dry hydrogen atmosphere for two hours as mentioned above. According to the literature, it is possible to still have some water or hydrogen retained in the pores or interstitially dissolved in the UO₂ lattice.

Due to the fact that dry hydrogen atmospheres produce pellets with more hydrogen, we need to change them. Our molibdenum batch furnaces permit one to dry the pellets switching the dry hydrogen atmosphere to dry nitrogen at 800 °C, during cooling. Thus, there could be an additional release of hydrogen. Higher temperature without hydrogen could produce damage in the furnace molibdenum.

Even if we reduced the hydrogen coming from sintering or wet grinding, the pellets could pick up moisture during storage. We have to dry the pellets again and follow the hydrogen content evolution with time.

3. EXPERIMENTAL PROCEDURES

The aim of the experiments is to investigate the existence of a relationship between the porosity shape and distribution and the high hydrogen content. Furthermore we want to determine if the high hydrogen could be eliminated by heat treatments without important changes in the pellet dimensions and density. In this way we could rework the pellets keeping them within specifications.

3.1. Pellet hydrogen content.

The hydrogen content was determined in a LECO RH-404 analyzer. The extraction temperature used for the analysis was over 1600 °C. There were wide variations in the hydrogen content in pellets of the same lot. We are reporting, as was in fact done during production, the average of hydrogen in five pellets. The hydrogen content of the pellets used in this study can be seen in table 1. The high hydrogen content occurred in two batches of ADU powder blended to obtain the required enrichment, and one unblended ADU powder. Some lots have more than one drying operation at 1050 °C in dry hydrogen. The last two lots

Table 1. Hydrogen content of lots used in the study

Lot Identification	Type of powder	µg/g one drying	µg/g Present content
340011	blended ADU	1.71	1.36
340014	blended ADU	1.25	0.79
260010	blended ADU	1.4	0.54
260012	blended ADU	0.86	0.57
320023	ADU	0.81	0.67
071012	ADU	0.22	0.153
240001	ADU	0.07	-----

are low hydrogen control lots. We used different control lots because at the time we had a few pellets of each.

3.2. Pore characterization.

The pellets were cut longitudinally. The pieces were mounted in lucite for the optical microscope and in diallyl phthalate filled with copper for the SEM. Rough polishing was conventional. Final polishing was performed with 30 % of 0.05 μm aluminum oxide suspension and 70 % of hydrogen peroxide. The samples for the SEM were vacuum evaporated with gold. The most convenient film was about 65 Angstrom. There is not a great difference in observing the samples without the evaporated film, but the film protects the microscope from loose small UO_2 pieces. The structure of a low hydrogen pellet, lot 240001, is shown in fig. 1. The pores are more or less round and have a random distribution. In fig. 2 lot 260010, one of the lots of high hydrogen pellets, can be seen. There is a bimodal pore distribution. It has a pressing defect due to high slugging pressure. The original UO_2 grains were not broken. The other high hydrogen lots have a structure similar to those in fig. 1, but the pores are smaller. Aggregated laminar porosity generally associated with high open porosity, is not present.

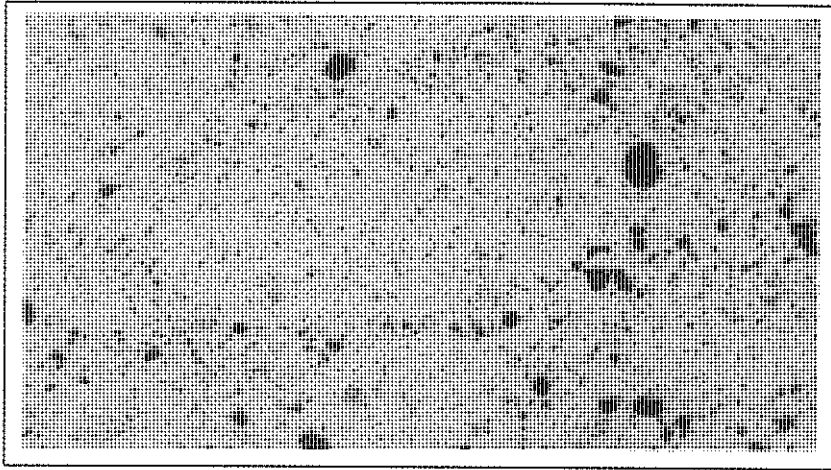


Fig.1.- Lot number 240001 – 0.07 $\mu\text{g/g}$ UO_2 Pore structure, 70x

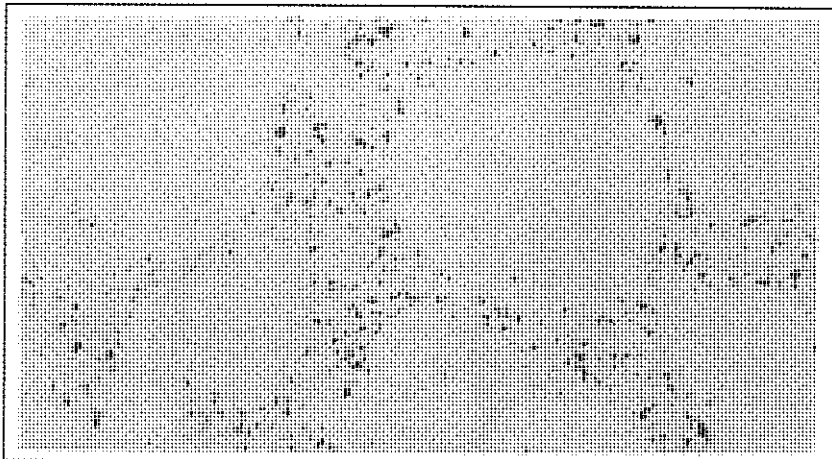


Fig.2.- Lot number 260010 – 1.4 $\mu\text{g/g}$ UO_2 Pore structure, 70x

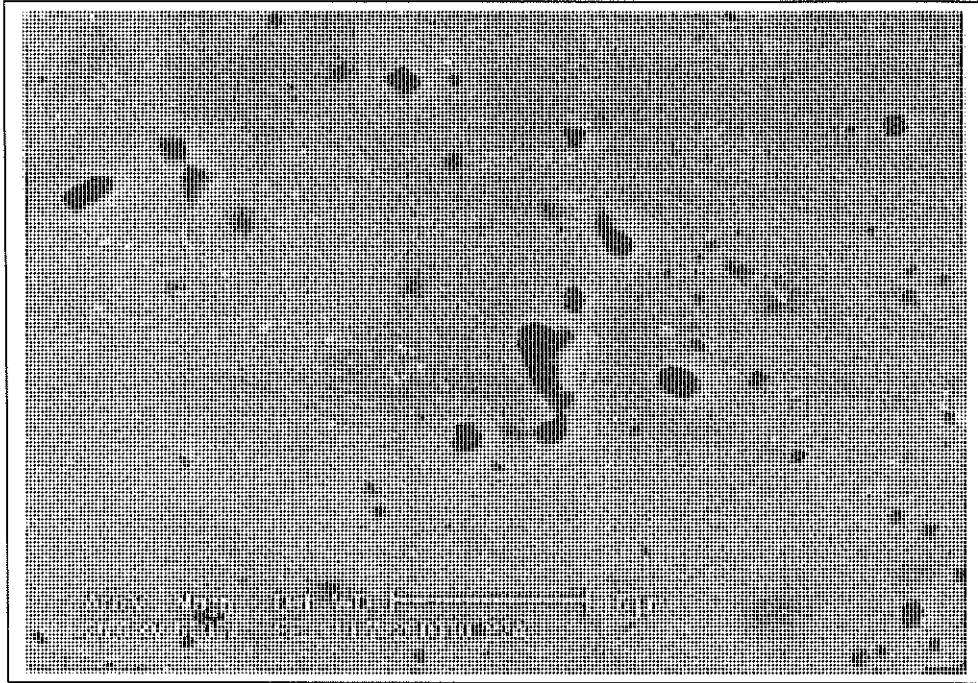


Fig. 3.- Lot number 260010 – 1.4 µg/g UO₂ Pore structure, 5000x

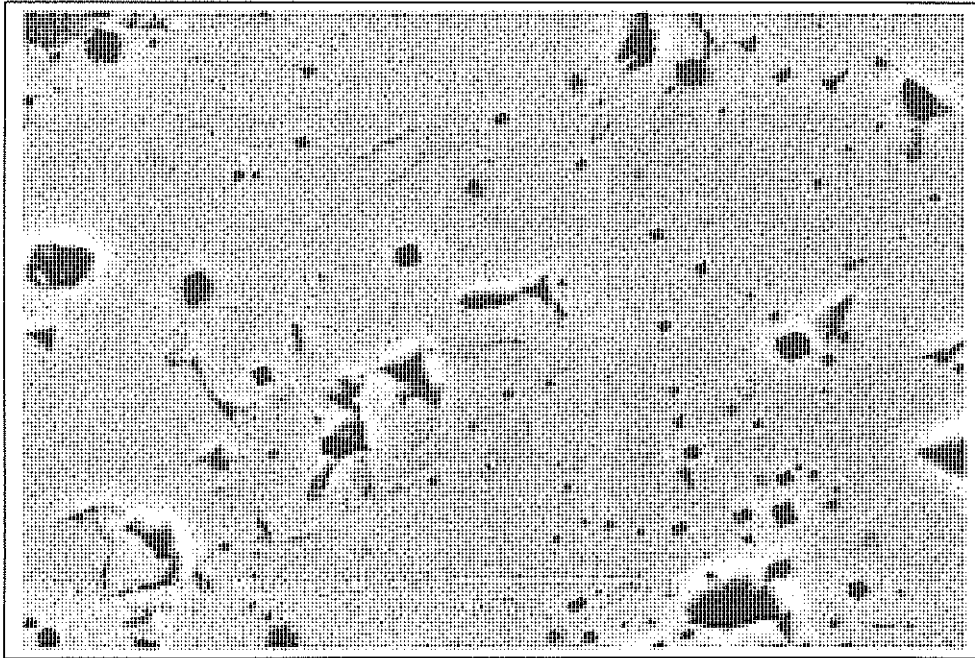


Fig.4.- Lot number 240001 – 0.07 µg/g UO₂ Pore structure, 5000x

In the observation of the same samples at 5000 x in the SEM (fig. 3 and 4) the high hydrogen pellets with a bimodal structure have bigger pores forming chains. This is the powder grain structure. At this magnification there are no interconnections between the pores. The polyhedral pores come from the ammonium oxalate. The lubricant pores can not be seen at this magnification. The other high hydrogen samples do not have either pore interconnections or bottleneck shaped pores. It is difficult to obtain a good resolution with magnifications over 10 000 x. The best combination was 70 % of secondary electrons and 30 % of back scattering electrons.

The image analyses were done in LECO 2001 version 2.02 image analyzer at 1000 x counting pores over 0.5 μm , but without any upper limit. Pigmentation discrimination with a grey color similar to the pores was used. Sixteen readings equally spaced in the longitudinal section were counted. The porosity was calculated in percentage assuming round pores. Two results of high and low hydrogen pellets are compared in tables 2 and 3. The point to point variation is wide, as could be expected at the magnification selected. No special pattern in the pore distribution was found.

Table 2. Lot 340010; 0.21 $\mu\text{g/g}$ UO_2 Pore percentage

6.34 %	10.67 %	8.38 %	10.78 %
5.92 %	10.68 %	6.66 %	4.34 %
3.20 %	3.40 %	5.10 %	2.90 %
2.72 %	4.73 %	2.50 %	1.26 %

Table 3. Lot 320023; 0.76 $\mu\text{g/g}$ UO_2 Pore percentage

2.80 %	3.63 %	0.31 %	1.40 %
3.85 %	6.82 %	2.60 %	1.72 %
4.30 %	2.13 %	1.84 %	0.31 %
7.72 %	9.40 %	8.70 %	2.40 %

3.3. Heat treatment.

In order to see if the high hydrogen pellets absorb hydrogen from the atmosphere, we dried them again with the normal cycle: temperature 1050 $^{\circ}\text{C}$; time 2 hours; Atmosphere dry H_2 (changed for dry N_2 at 200 $^{\circ}\text{C}$). The pellets were unloaded at approximately 80 $^{\circ}\text{C}$. The storing conditions are the following.

- A. Immediate analysis (stored in vials for 1 to 2 hours)
- B. Analyzed after three days in the laboratory
- C. Analyzed after four days in humid atmosphere
- D. Analyzed after six days in the laboratory
- E. Analyzed after six days in humid atmosphere
- F. Analyzed after 18 days immersed in water, dried in the laboratory four days

Table 4. H₂ content after storage

Lot Identification	H ₂ content µg/g						
	Initial	A	B	C	D	E	F
260010	0.54	0.57	0.51	0.49	0.59	0.51	0.47
340011	1.36	0.94	0.88	0.79	0.68	0.72	0.89
071012	0.22	0.13	0.10	0.07	0.11	0.08	0.23

The hydrogen content after drying was reduced only in lot 340011. However, the hydrogen did not change after storing the pellets in different atmospheres, even after 18 days in water.

Since hydrogen could be retained in the pellet pores or interstitially in the UO₂ lattice, we then tried to change the cooling atmosphere of the drying operation for N₂, at 800 °C. This is the highest temperature we can use with pure N₂ without damaging our furnaces. The storing conditons are:

- A. Immediate analysis (stored in vials for 1 to 2 hours)
- D. Analyzed after six days in the labortory
- E. Analyzed after six days in humid atmosphere

The results are included in table 5.

Table 5. Hydrogen content after cooling in N₂ at 800 °C

Lot Identification	H ₂ content µg/g			
	Initial	A	D	E
260010	0.54	0.59	0.62	0.60
340011	1.36	0.87	1.02	0.85
071012	0.22	0.18	0.27	0.21

As was the case before, only lot 340011 reduced the hydrogen content. There was no difference after changing the cooling atmosphere at a higher temperature. The pellet controlled microsture produced, almost exclusively, closed pores. The immersion in water did not produce changes in the hydrogen content in the pellets. Room temperature drying brought the hydrogen content to the values obtained before immersion. At least part of the hydrogen is strongly bonded to the pellets. As suggested in ref. 3 and 4, drying temperatures above 1000 °C are probably needed to reduce the hydrogen content. However higher temperatures could modify the diameter of the ground pellets, which is not convenient.

4. RESULTS AND CONCLUSIONS

The pellets with controlled porosity (matrix 98-99 % TD and added pores) produced a stable hydrogen content. They can even be immersed in water and the hydrogen content does not change.

In the pellets with a hydrogen content over $0.5 \mu\text{g/g UO}_2$, the drying at 1000°C is not effective for reducing the hydrogen content. Only higher drying temperatures and atmospheres different from dry hydrogen could reduce the hydrogen content. These higher temperatures are not practical for ground pellets with the final dimensions.

Clearly, it is not convenient to sinter in dry hydrogen since it always produce hydrogen contents higher than other atmospheres used industrially.

It is necessary to continue the research in order to determine the hydrogen accumulation place: the pores and grain boundaries, the interstitial solution in the lattice or a hydride formation.

5. REFERENCES.

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