

Immobilization of Preconditioned Spent Fuel From Nuclear Research Reactors in a Ceramic Matrix

Diego.O. Russo, Diego. S. Rodríguez, Arturo D. Heredia, Miguel Sanfilippo, Mario E. Sterba, Patricia Mateos.

Comisión Nacional de Energía Atómica - Centro Atómico Bariloche – Bariloche – RN – 8400 Argentina

SUMMARY

The fuel elements from nuclear research reactors consist in a laminated sandwich of aluminum with a core of some uranium compound. To process this material its necessary to previously eliminate the aluminum covering the fuel, before the conditioning of the rest of the fuel in a stable matrix, in order to obtain an acceptable waste form for a subsequent disposition in a geological repository. Normally, mechanical and chemical methods are proposed for that purpose.

One of the most developed techniques for immobilization of the radioactive elements above mentioned, is the vitrification. In this work we propose a method named **CERUS** (in Spanish *Ceramización de Elementos Radiactivos con Uranio Sinterizado* - Ceramization of radioactive elements with sintered uranium). This is a sinterization of the pre-treated fuel elements mixed with natural uranium oxide.

The properties of the blocks obtained are adequate for final disposal in a deep geological reservoir.

I. INTRODUCTION

We focused our research in uranium silicide based fuels (20% enriched in U-235).

The ceramization step consist in using a U_3O_8 (natural or depleted) powder to both, dilute and act as an immobilization matrix, for the pretreated spent fuel. In this way it is possible to reduce the U^{235} enrichment of the fuel and create an homogeneous material having structural integrity and good corrosion resistance provided by the sinterization of the U_3O_8 . This method (patent pending) has the advantage of avoiding the need of a vitrification process in which the volume involved increase substantially.

The ceramized material can be treated, regarding its final disposition, in the same way as the proposed alternatives for spent fuels of nuclear power plants.

We compared the leaching resistance in deionized water of the ceramized bodies with sintered U_3O_8 and UO_2 , with satisfactory results.

II. EXPERIMENTAL

II.1. Materials

For these experiences we used small plates of fuel material, which contain uranium silicide. These plates have the same structure as the plates used in function research reactors. They are composed of two cold laminated sheets of pure aluminum (AL 6066) with a uranium silicide core, called meat.

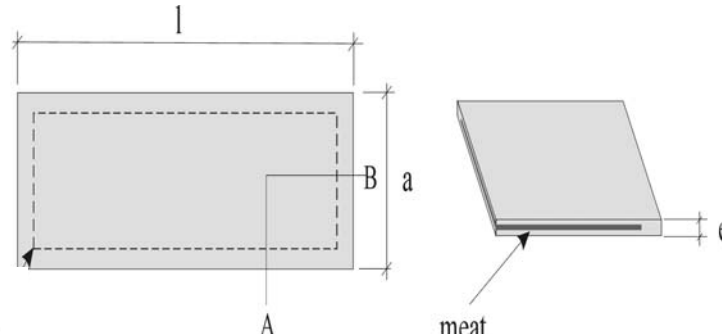


Figure 1. Front and cut view of a mini-plate (l = 130 mm, a = 35 mm and e = 1.4 mm).

Meat is a uranium silicide compound (U_3Si_2) – with an enrichment of 19,75% in U_{235} - plus 20% of aluminum powder. After the fuel material is used a 52,5% of total content of U_{235} has been burned.

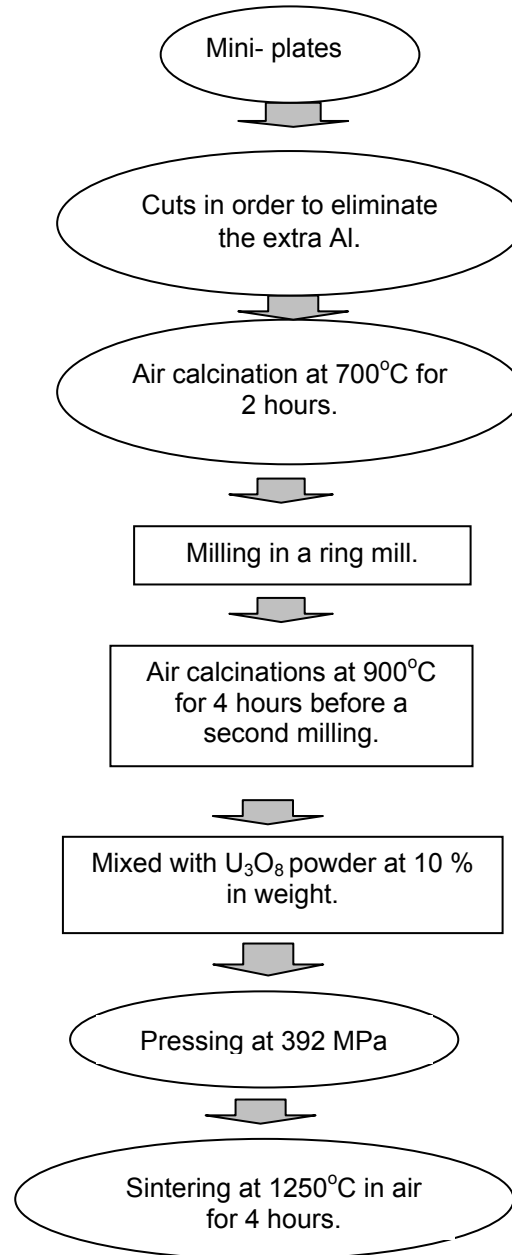
Because the meat finally remains with a 10 % enrichment in U_{235} , it must be diluted to achieve a final enrichment of 1 to 1,5%, for a final disposal this enrichment can be acceptable. To obtain the dilution of uranium, taking into account the initial enrichment and the fraction of burned fuel we can use the following equation:

$$(1) \quad z = \frac{x_0 (1 - Q) - r}{r - y}$$

Where:

- x_0 initial enrichment (%)
- Q burned fraction
- r final enrichment fraction desired
- z masic relation of material to add
- y enrichment of uranium to add (%)

For a dilution of 1,5% and a 52,5% of burned fraction, the natural uranium and spent fuel fraction is 10:1.

CERUS Process**Figure 2: Scheme of the CERUS process**

II.2. Process

The Figure 2 shows the work scheme of the CERUS process. This can be separated in the following stages:

Cutting: With cuts we take out all the aluminum from the frame of the mini-plates, this reducing the length (l) to 15 mm and the width (a) to 6 mm. After that, there remains approximately a 55% of uranium silicide and the other 45% corresponds to aluminum.

Calcination: After the cuts, the material was treated thermally in air at 700°C for 2 hours, in order to fragilize the aluminum layer before milling in a ring mill, or to be attacked by some chemical process. The weight gain due to oxidation after the heat treatment was around a 0,5%.

Milling: A second milling and a further calcination in air at 900°C followed the first calcination step. This stage was undertaken because we observed cracks in the sintered material: these defects were attributed to an incomplete oxidation of the meat and the aluminum. During sinterization, both materials complete their oxidation with a consequent volume increasing that causes the cracks to appear. With this second milling and calcination stage, we reach thermal stabilization of the powders and flawless sintered pellets were obtained.

Sinterization: The powders were mixed with U_3O_8 in a 10% by weight relation; after that, samples were pressed in cylindrical pellets of 2 grams, approximately, in a 10 mm diameter cylindrical stainless steel die. The pellets were sintered at 1250°C in air for 4 hours. To determine the adequate sintering temperatures, dilatometer tests were made using a Netzsch E402 high temperature dilatometer, where the length variations between U_3O_8 and Uranium silicide were compared as a function of temperature.

II.3. Characterization of the samples

II.3.1. Powders

Using SEM (scanning electron microscopy), we made morphological observations of the powders. The particle size was measured with a Malvern Mastersizer particle analyzer. With X-ray spectroscopy we analyzed the calcination of the samples. Figure 3 show the X-ray spectra from the miniplate material in comparison with U_3O_8 , its possible to see that most Uranium was transformed to the more stable U_3O_8 compound.

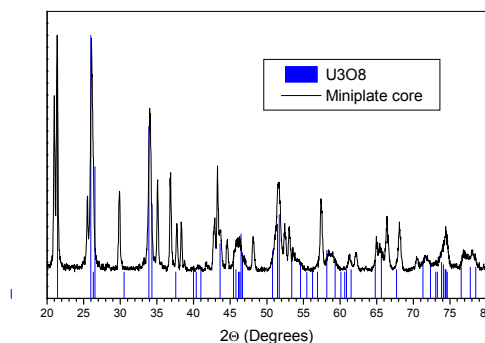


Figure 3 Miniplate core material compared with U_3O_8

II.3.2. Sintered blocks

We determine the geometric and immersion density of the sintered blocks and the surface morphology by using SEM microscopy.

Using the MCC-1P [1] protocol we performed leaching experiments in aqueous solutions. The times of lixiviation were from 20, 40, 60 and 140 days in deionized water at 90°C. We made other tests using hydrogen peroxide (to see if it was any effect of increasing the oxygen content in the water, as we can expect in some geological media) for 60 and 120 days.

We also prepared sintered blocks of UO_2 with a density of 10,4 g/cm³, and U_3O_8 (density 7,7 g/cm³), in order to compare them with the obtained blocks.

The gravimetric dissolution rate (GDR) of the blocks was calculated from the mass lost (Δp), the surface area (A) and the immersion time in water (t), using the following formula:

$$GDR = \frac{\Delta p (g)}{A (cm^2) \times t (days)} \quad (2)$$

III. RESULTS

In the figures 4, 5 there is a photograph sequence of the treatment employed. Figure 4 corresponds to the as received material; figure 6 is the calcined sample at 700°C..



Figure 4. Mini- plates as received.



Figure 5. Mini-plates calcined at 700°C in air

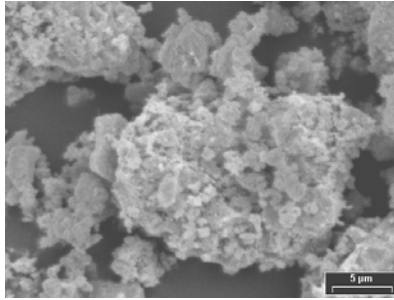


Figure 6. SEM image of the powders.

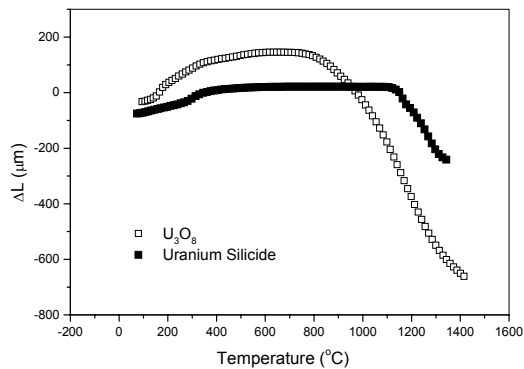
III.1. Powders

A typical morphology of the grains, after milling, is shown in figure 6, where we can observe that big particles are agglomerates of finer ones. Mean particle diameter was 100 microns after first milling operation and 75 microns after the second.

III.2. Sintered samples

Pressing and sintering

After mixing with U_3O_8 the material was pressed at 400 Mpa and the sintering temperature was obtained by dilatometric measurements. As can be seen in figure 7, the densification started at temperatures over $1200^{\circ}C$. In this way we could establish that good densification was achieved at $1250^{\circ}C$.



**Figure 7. Sintering curves for U_3O_8 and U_3Si_2 .
Note that above $1250^{\circ}C$ the material achieves
a good densification**

To determine the adequate pressure for the preparation of the compacts, we sintered samples at $1250^{\circ}C$ compacted at three different pressures: 343 MPa, 392 MPa and 427 MPa. Table 1 shows the density of the samples. It can be noted that the highest density was obtained at 392 MPa. Thus this is the pressure used finally for all samples.

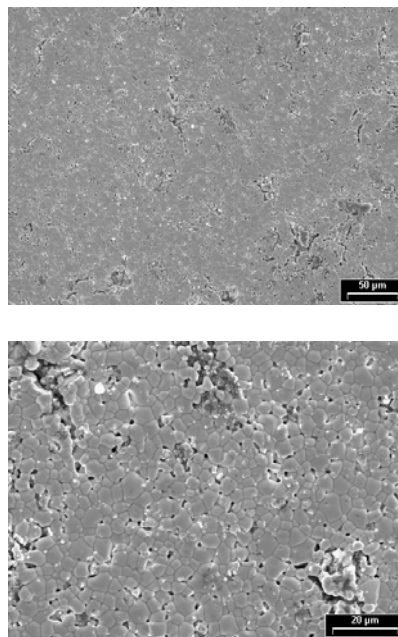
Table 1. Pressure as function of the density for samples sintered at 1250°C.

Pressure (MPa)	Immersion density (g/cm ³)	Geometric density (g/cm ³)
343	7.54	7.29
392	7.78	7.46
427	7.75	7.39

Morphology

Figure 8 shows SEM microphotographs of a sintered sample the smaller size of the particles can be due to the two milling stages before the sintering This leads to a better sintering.

We produced samples at 1450°C. The higher temperature improves the nucleation and growth of the grains with a closer structure, but the density values obtained were very similar. We opted to work with a lower temperature in order to reduce costs in a further application.

**Figure 8. SEM images of a sintered sample .***Durability*

The results of the dissolution rates for the different samples are resumed in the Table 2.

The U₃O₈ sample showed an increase instead of a mass loss it can be attributed to the hydration of the material and for this reason the dissolution velocity was negative.

The values for borosilicate glasses were taken from the literature.

Table 2. Dissolution rates of different samples.

Sample	GDR in deionized water [g.cm ⁻² .d ⁻¹]	GDR in oxygenated water [g.cm ⁻² .d ⁻¹]
This work	6,29x10 ⁻⁶	5.58x10 ⁻⁵
U ₃ O ₈	-3.38x10 ⁻⁵	
UO ₂	2,4x10 ⁻⁶	1.02x10 ⁻⁴
Typical Borosilicate Glasses	~ 10 ⁻⁵ – 10 ⁻⁶	

IV CONCLUSIONS

We can see that the CERUS process is dry (no need of a chemical attack) and we observed from figure 8 that the densification is better because we start with a smaller particle size. The problem is that we are working with larger volumes than the other method (50% more in volume and 22% more in mass with respect to variant 1)

We conclude that the durability is:

- One order of magnitude greater than the borosilicate glass.
- Same order of magnitude as UO₂ sintered at 1750°C (which has a higher density than the other samples), when the test is done in deionized water.
- Better if the test is performed in hydrogen peroxide.

A temperature of 1250 °C was enough to get satisfactory results, so it is no need to go beyond that value.

We conclude finally that the CERUS process is a good method to be used in the conditioning of spent fuel from nuclear research reactors with the advantage of managing smaller amounts of materials than other methods.

These blocks can be stored in a deep geological repository by using the same techniques developed for spent nuclear fuel from power reactors.

V REFERENCES

[1] Materials Characterization Center, *Materials Characterization Center Test Methods*, PNL-3990, Battelle Pacific Northwest Laboratories (1981).