Spent Fuel from Nuclear Research Reactors Immobilized in Sintered Glass

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Abstract

Different kinds of glasses, borosilicates, Iron borosilicates and Iron phosphates, were tested in order to determine its capability to immobilize calcined uranium silicide in a sintering process.
Iron phosphate glass developed in our laboratory showed the best results in SEM analysis. Also its gravimetric leaching rate is less than 0.45 $g.m^{-2}.day^{-1}$ for 7 and 10% loading which is lower than any previously studied for us.

1. INTRODUCTION

High activity nuclear waste by fusion vitrification is a well known technology which has industrial scale in France, England, Japan, EEUU. Borosilicates glasses are commonly used in this process.

Sintered glasses are an alternative to the immobilization task in which there is also a wide experience around the world.

The objective of this project is to develop the simplest process which allows immobilization of uranium silicide spent fuel in a solid sintered block of glass. This product must complies international rules.

This paper describes the first stage of the project in which different kind of powder glasses are mixed with calcined uranium silicide without irradiation and later sintered.

2. METHODS AND MATERIALS

Uranium silicide identified as 260301 ECRI was provided by Constituyentes Atomic Center through its Nuclear Fuels Group. Its composition is 91,4 wt% U and 7,45 wt% Si.

Uranium silicide was calcined at 1012°C prior to its use in the powder glass mixture.

Natural U_3O_8 powder was employed to simulate isotopic dilution.

Iron phosphate glass nominal composition is 64,9 wt% P_2O_5; 22,7 wt% Fe_2O_3; 8,1 wt% Al_2O_3 and 4,3 wt% Na_2O.

Borosilicate glass, SG8, nominal composition is 65,3 wt% SiO_2; 9,1 wt% B_2O_3; 6,6 wt % Al_2O_3; 0,9 wt % MgO;1,9 wt% CaO; 13,5 wt% Na_2O and 2,7 wt% TiO_2.

Iron borosilicate glass, VSR, nominal composition is 44.04 wt% SiO_2; 8.75 wt% B_2O_3; 14.23 wt% CaO; 11.63 wt% Na_2O and 21.35 wt% Fe_2O_3.

2.1. Vitrification analysis

Mass relationship between calcined Uranium Silicide and U_3O_8 was calculated in order to simulate 4% enrichment in the final waste mix. This dilution value was selected arbitrarily taking into account that the uranium silicide changes almost completely to U_3O_8 when it is calcined over 600 °C, so there is no meaningful difference between them in non radiated samples.

The glass samples were loaded with different percentages: 10%, 15%, 20% and 40% for SG8 borosilicates, 10% for VSR and 7, 10 y 15 % for Iron phosphates.

Pellets were pressed at 1,5 kg. cm^{-2} and sintered at temperatures between 660°C and 755°C for SG8, 510°C y 600°C for VSR and 580°C and 670°C for phosphates.

Geometric and immersion pellets density were determined.

Sinterability curves for each load were drawn in order to determine best conditions for the process.

2.2. Durability

Water dissolution resistance was tested from the best density pellets selected from the sinterability curves. The main objective was determining U_3O_8 retention capability.

The leach test adopted was based on the standard MCC-1 static leach test in which monolithic samples were exposed to deinoized water at 90°C for 7, 14 and 28 days. Sample surface vs. solution volume relationship equal to 0.1 cm^{-1}.

Glasses leaching rate were established through gravimetric leaching rate and dissolution rate normalized to the uranium element.

$$VRG = \frac{\Delta p\,(g)}{A\,(m^2) \times t\,(days)}$$

VRG: gravimetric dissolution rate

Δp: weight loss

A: Surface area

t: immersion time in water

Uranium content in SG8 glasses leaching water was determined by chromatography of inverted phase (Br-PADAP).

The leaching rate normalized to the Uranium element is

$$R_U = \frac{m_U\,(g)}{F_U A\,(m^2) \times t\,(days)}$$

R_U leaching rate normalized to uranium behavior

m_U total uranium mass in the leachates over leaching period of time

F_U uranium mass fraction in glass sample

A initial geometric surface area

T leaching period of time

Metallographic polished samples and fractured samples were also studied in SEM microscope and analyzed by Edax.

3. RESULTS

3.1. Uranium silicide Differential Thermal Analysis (DTA) and Thermogravimetry (TG)

Uranium silicide in powder was calcined at different temperatures in air. Changes in DTA and TG curves are shown meanly in the temperature range between 300°C and 750°C,. when heated at 10°C/min to 1020°C, Fig. 1

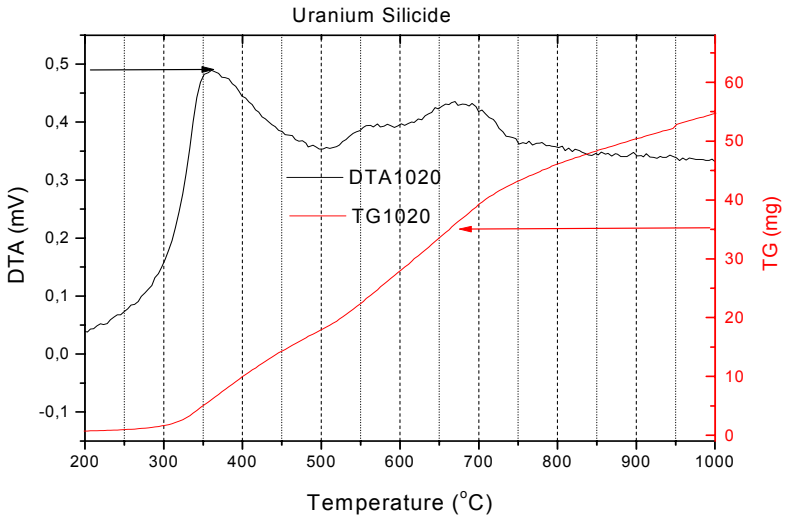

Fig I. DTA and TG curves from Uranium Silicide

DTA curve show a maximum at 356°C followed by other irregularities up to 750°C where it smoothes.

TG shows continued weight growth from 300°C.

Samples were calcined during 20 minutes at different temperatures. Changes in weight taken from balance and from TG showed weight growth followed by volume growth up to 22,3% at 1012°C, Fig 2.

If initial Uranium silicide was only U_3Si_2 and the only reaction with heating was

$$U_3Si_2 + 6\ O_2 \longrightarrow U_3O_8 + SiO_2$$

Thus, performed weight growth could be explained by this reaction which accounts for 24,93% increment. Other reactions could explain the difference.

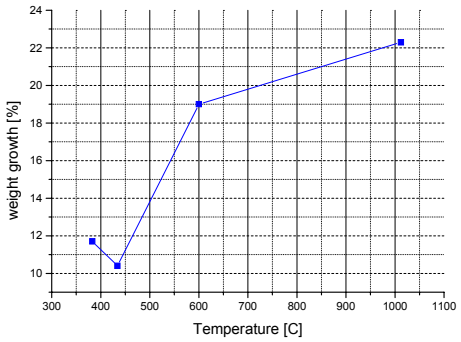

Fig II. Uranium silicide weight growth at different calcined temperatures

3.2. X-Ray uranium silicide spectrum from samples calcined at different temperatures

Uranium silicide powder was heated at different temperatures and the resulting spectrums were compared with U, Si, O and Al compounds spectrums.

Al was present in Edax analysis, it comes out from grinding process. However it could not be identified in X-Ray analysis because of its low percentage in weight.

Edax analysis gave:

Element	weight %
Al	between 1,6 and 5,6
Si	between 4,9 and 11,5
U	between 84,2 and 92,7

Uranium silicide as made has a spectrum very close to $Si_2\ U_3$.

When heated at temperatures between 350°C and 450°C it fits closely U_3O_7 spectrum. Further heating at 600°C shows a transformation from U_3O_7 to U_3O_8.

At 1012°C uranium silicide is transformed to U_3O_8, Fig. 3.

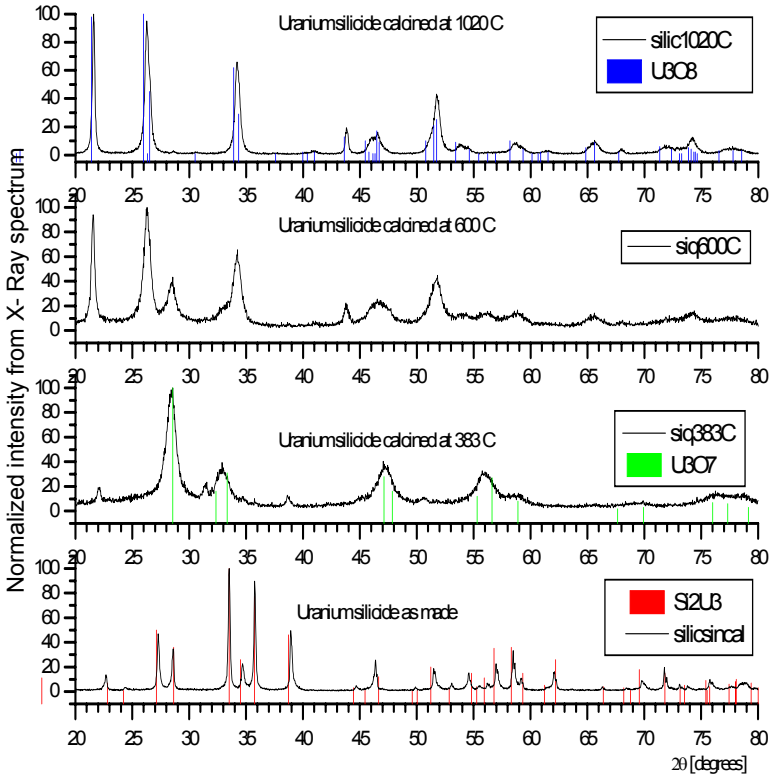

Fig. III. Uranium silicide X-Ray spectrums at different temperatures

3.3. Vitrification Essays

Glass samples were loaded with different waste percentages, pressed and heated at different temperatures. Immersion and geometric density was taken in order to determine the best sintering conditions for each mixture.

SG8 borosilicate glass curves show better behavior at lower loads, 10 and 15%, with a wide range for good sintering conditions, from 700 to 715°C, Fig. IV.

Higher loads show different curves: 20% load has a sintering range from 730 to 750°C but sample with 40% load was discarded, Fig. V.

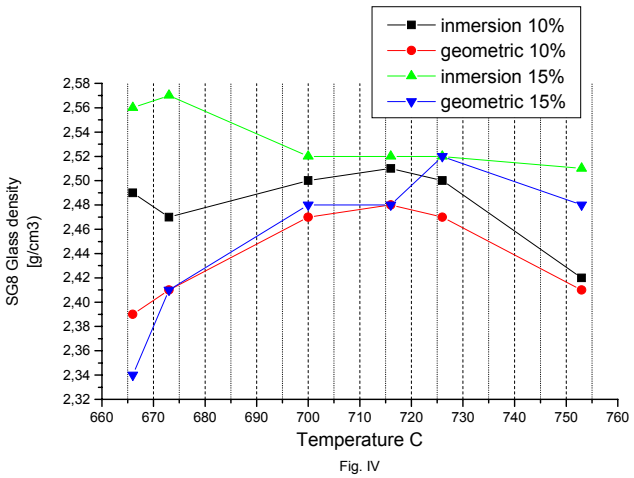

Fig. IV

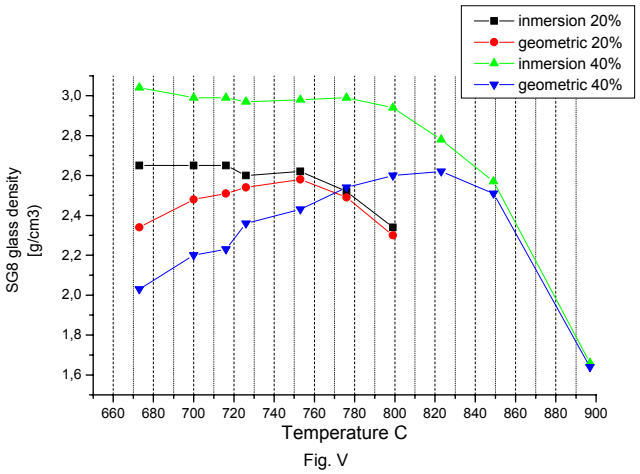

Fig. V

Only 10% loading was tested for VSR glass, giving optimal density conditions in the 535-560°C temperature range, Fig VI.

Iron phosphate glass was loaded in 7, 10 and 15 % giving the best densities in the range 600 and 640°C, Fig. VII.

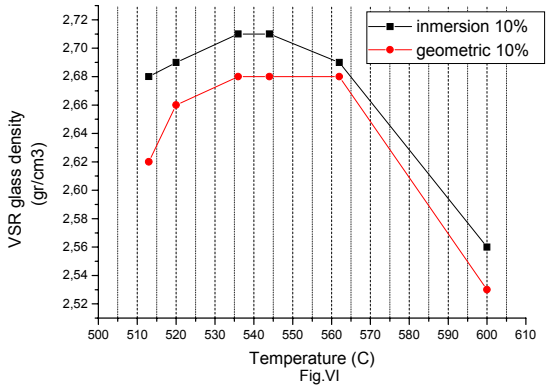

Fig.VI

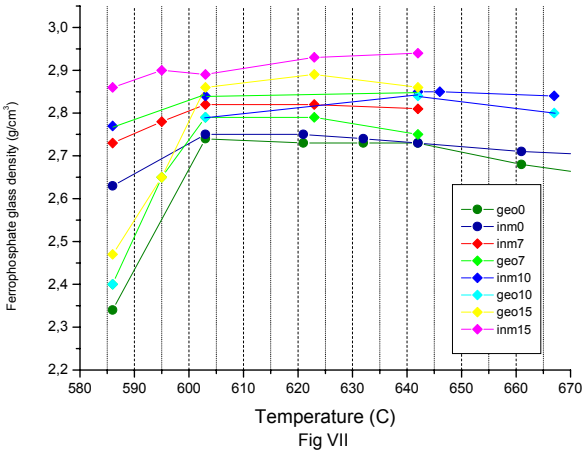

Fig VII

3.4. Durability

Pellets were cut in pieces 1mm width, geometrically measured and put in Teflon leach containers with deinoized water.

3.4.1. SG8 Borosilicate glass

Gravimetric leaching rate for SG8 borosilicate glass for 10 and 20% loading was less than 0.6 g. $m^{-2}.day^{-1}$. Dissolution rate normalized for uranium behavior for the same loadings was less than 0.1 $g.m^{-2}.day^{-1}$.

These values are the same magnitude order than those previously observed in our laboratory for other loadings.

3.4.2. VSR Iron borosilicate glass

Teflon leach containers showed completely stained.

3.4.3. Iron phosphate glass

Gravimetric leaching rate for 7 and 10% loading show even lower values than SG8 glass: less than 0,45 $g.m^{-2}.day^{-1}$, Fig. VIII

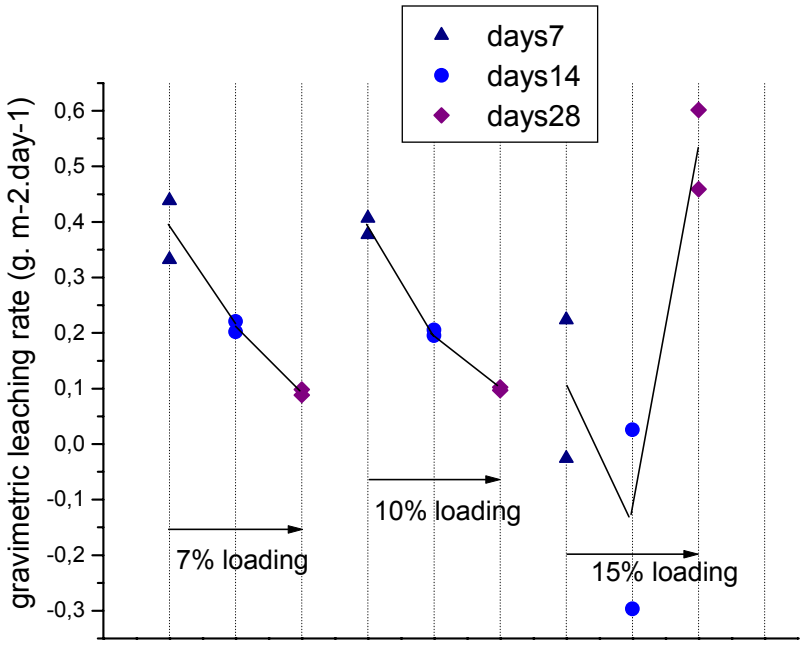

Fig VIII

3.5. SEM and EDAX analysis

SEM photographs show how "sticked" are the uranium particles in the different glasses.

VSR glass show borders with holes and the Metallographic polishing have taken out part of uranium, Fig IX. This agrees with the glass leaching behavior.

SG8 glass show better bonds with uranium, Fig. X.

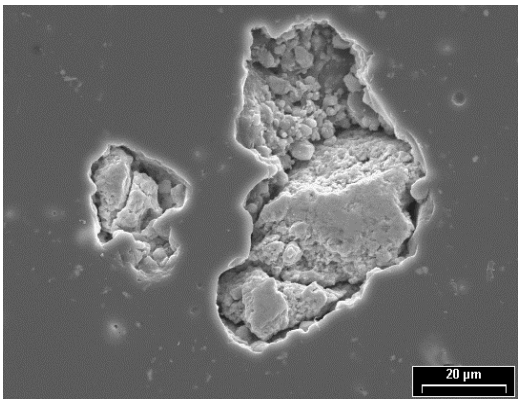

Fig. IX. VSR glass with uranium mix

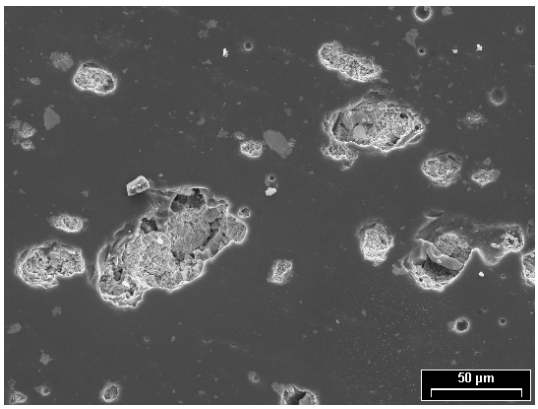

Fig. X. SG8 glass with uranium mix

The behavior of Iron phosphate glass show the best bonding as shown in Fig XI and XII.

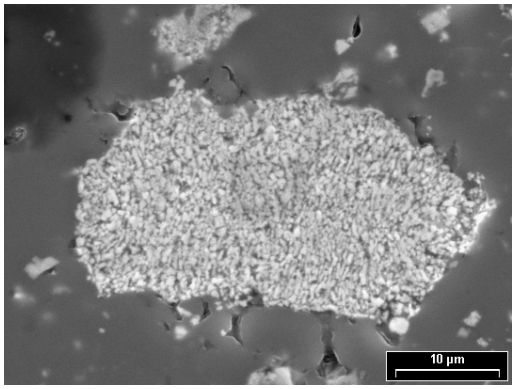

Fig. XI. Iron phosphate glass with uranium in a polished sample

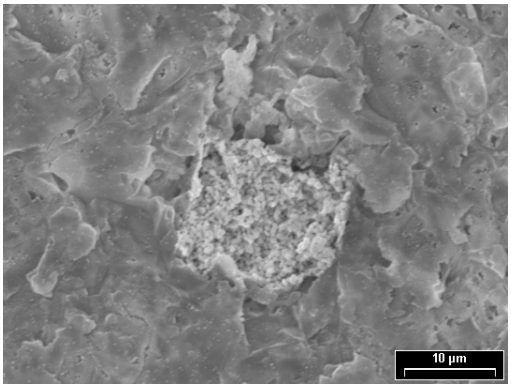

Fig. XII Iron phosphate glass with uranium after 28 days leaching, sample not polished

4. SUMMARY AND CONCLUSIONS

As seen in X-Ray spectrum and confirmed by DTA, Uranium Silicide transforms almost completely into U_3O_8 when heated over 750 °C. Taking into account this result, glass mixtures were prepared with calcined uranium silicide to avoid volume changes during sintering.

SG8 borosilicate glass showed better behavior than VSR Ironsilicate glass as it is showed from leaching and SEM analysis. SG8 leaching rates are the same order of magnitude as other previously studied borosilicate glasses with different loading. Nevertheless the mechanic polishing have shown some uranium loss from them.

The best results have been found with 7 and 10% loading in Iron phosphate glass developed in our laboratory. They show the lower leaching rates and SEM examination proved the uranium is tightly bonded in the glass. Furthermore samples after leaching tests have shown the particles still firmly bonded in the glass.

We continue working with chemical analysis from leaching tests water.

The project will continue with simulated waste in Iron phosphate glass.

Acknowledgements

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5. REFERENCES

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