Sintering of Niobium and Iron Phosphate Glasses for Uranium Immobilization - 9345

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ABSTRACT

Some of the drawbacks related to nuclear waste vitrification are the volatilization of radioactivity elements, corrosion of crucibles, contamination of the final wastform, the sedimentation and phase separation during the melting process, and also, there is the thermal stress that occurs when large glass blocks are cooled. Sintering might be a solution of all these problems. Sintered glasses have been previously investigated for the immobilization of HLW materials, however, some difficulties were found, such as the swelling of the wasteform. Sintered borosilicate glasses were evaluated (SG7 glasses) for the immobilization of HWR waste simulators. Hot press pellets were sintered in the temperature range of 725-825°C to obtain sintered glasses with 98.8% of the theoretical density (TD). For simulator loads above 10 volume % the chemical durability of the wastform declines. Other sintered glasses with chemical compositions similar to the SG8 and VG98/12 were also evaluated; densities around 97% of TD were reached. A similar amount of waste is expected to be immobilized when it is compared to the melting processes. In the present work sintering of niobium phosphate and iron phosphate glasses was investigated since these materials have been previously proposed for nuclear waste immobilization. Previously calcinated uranium silicide was added to the glass powder before sintering. Glass frits were prepared by melting and cooling suitable chemical compounds, ground, and sieved. The particle size distribution was determined by laser diffraction method. Pellets weighing 100 g and 7 to 50 mm in diameter were prepared by uniaxial press at 1 Ton/cm². Niobium glass powders were cold pressed and sintered in the temperature range of 720-795°C. The maximum density (99.41% TD) was reached for samples with the finest particle size distribution sintered at 750 °C. The variation of the shape of the pellets was also observed as a function of the sintering temperature by using a special digital camera attached to a furnace. The sintered glasses did not present any crystalline phase according to the X-rays diffraction (XRD). The maximum density of iron phosphate glasses was 86% TD when they were sintered at 558°C, however crystalline phases were detected by XRD. For niobium phosphate glasses mixed to uranium silicide, the sintering temperature was in the range of 752 - 835°C. The highest density (97.6% TD) was reached when they were sintered at 762 °C. For iron phosphate glasses that temperature is 591 °C, however the density was lower. We concluded that based on the densification obtained by the sintering process niobium phosphate glasses are more appropriate when uranium silicide is a component. A model is proposed to explain the differences observed among sintered and monolithic materials considering the opened porous as half spheres on the surface of the materials.

INTRODUCTION

Vitrification is usually performed to immobilize nuclear wastes. However, relatively high temperatures (~1500°C) are required to obtain the wasteform and to avoid the volatilization of radioactive elements, and heavy metals, such as Cs, Mo, Te and Ru; so sophisticated filtering systems are required. Besides that, the specific elements in the waste composition, even in small amounts might induce to phase separation of the glass matrix, as it is the case of $P(<1,5 \text{ mol}\% \text{ de } P_2O_5)$ in borosilicate glasses.

The sedimentation of the heavy components from the original waste in the melting is also a concern that favors the arising of macroscopic heterogeneities, besides the fact that cooling large glass blocks can cause thermal stresses due to the temperature gradient between the core and the surface of the block, and

increases the corrosion when in contact with water [1]. An alternative way to overcome these drawbacks is to use the sintering process which can be done at relatively lower temperatures when compared to the glass melting and it is capable to contain equivalent waste loads [2].

Sintering of glasses containing high level nuclear wastes (HLW) was previously performed in 1975 [1]. Waste and glass frits were mixed and heated to 500 K. However a reaction between the waste and the glass caused a swelling of the final wasteform [1].

In 1982 powder technology was used again in Kernforschungszentrum Karlsruhe, Germany, to immobilize HLW. $10^{\text{wt}/_0}$ of nuclear waste simulators typically produced in HWR type reactors, were added to glasses with composition 72SiO_2 -8.6 Al_2O_3 -8.3 B_2O_3 -7.4 Na_2O -2.7CaO-MgO, named SG7, and then sintered. Pellets were hot pressed and sintered in the temperature range of 725 - 825°C. The density was 98.8% of the density of the corresponding monolith. However the increase of the waste load was not possible without affecting the glass chemical durability.

Other glass compositions were also investigated such as the SG8 and VG98/12 [3] which were sintered with nuclear waste simulators by hot pressing. Temperatures were in the range of 600 - 800°C, and densities up to 97% were reached. However, devitrification of the glass matrix was noticed. Since the viscous flowing is the major mechanism of glass sintering, the density of the sintered glass depends on the sintering temperature, soaking time and the nonexistence of concurrent crystallization. When crystallization occurs simultaneously to the viscous flow, higher temperatures will be required for densification.

The nuclear fuel of some nuclear reactors, such as Research Nuclear Reactors, is U_3Si_2 . After calcination, this compound is decompounded to SiO_2 and U_3O_8 .

In the present work sintering of niobium phosphate and iron phosphate glasses was investigated since these materials have been previously proposed for nuclear waste immobilization. The sintering of mixtures of SiO_2 , U_3O_8 , and glass powders was also investigated. A model is proposed to explain the differences observed among sintered and monolithic materials considering the opened pores as half spheres on the surface of the materials.

EXPERIMENTAL PROCEDURE

Niobium phosphate $40Nb_2O_5.23K_2O.37P_2O_5$ (NPG) and iron phosphate $40Fe_2O_3.23K_2O.37P_2O_5$ (IPG) glass frits were produced by melting precursor compounds in air by using an alumina crucible into an electric furnace during 1h, cast in stainless steal molds at room temperature, ground and sieved. The melting temperatures were 1350°C and 1150°C for the NPG and IPG, respectively. The sintering of NPG and IPG powders were previously evaluated before adding U_3Si_2 .

Pellets weighting 0.5 to 100 g with 7, 10, and 50 mm in diameter were prepared by uniaxial press at 1 Ton/cm². Different NPG powders were used: powders with average particle sizes 6.86, 15.29, 26.30, 36.70 and 58.95 μ m were cold pressed and sintered in the temperature range of 720-795°C. Different amounts of U₃O₈ were added as a mixture of U₃O₈+SiO₂ (named in the present work as US). This component is the product of the oxidation reaction

 $U_{3}Si_{2} + 6O_{2} \rightarrow U_{3}O_{8} + 2SiO_{2}$ (Eq. 1)

which is previously performed before adding the material to the glass matrix.

The US mixture was grounded during 10 min to reduce the particle size in order to have an average particle size of 34.28 μ m. Further reduction of the particle size was not possible even by increasing the grinding time due to the hardness of U₃O₈. However, the particle size distribution is bimodal [4]. The finest particles were mainly SiO₂, which is less hard than U₃O₈ and can be grounded easily.

For niobium phosphate glasses mixed with uranium silicide, the sintering temperature was in the range of 752 - 835°C.

The chemical durability was determined by the MCC-1P [5] Static Leach Test Method, using aqueous solution and varying the pH in the range of 2 to 12. Samples were weighted after the immersion in water for 14 days. The dissolution rate (DR in $g.cm^{-2}.d^{-1}$) was determined according to Equation 2:

$$DR(t) = \frac{m_f - m_i}{S_0 t}$$
(Eq. 2)

where m_i is the initial weight, m_f is the final weight, S_0 is the surface area, and t is the time of immersion.

The particle size distribution was determined by using a Laser Granulometer MALVERN model Mastersizer Micro. Particles were previously dispersed in water containing sodium pyrophosphate by using ultrasound during 3 min.

Pellets were prepared by cold pressing mixtures of glass particles with different particle size distributions and different amounts of US and sintered at different temperatures and soaking time to determine the best processing conditions.

Samples were characterized by X-rays diffraction (XRD), Differential Thermal Analysis (DTA) Thermogravimetry (TG), Dilatometry, and Scanning Electron Microscopy (SEM).

The variation of the shape of the pellets was also observed as a function of the sintering temperature by using a special digital camera attached to a furnace.

RESULTS AND DISCUSSION

NPG sintering

The density of a monolithic NPG was previously determined by helium pycnometry and it is 3.42g/cm³. The relative density of NPG sintered pellets was determined comparing to the monolithic density value.



Fig 1 – Density of NPG sintered pellets as a function of sintering temperature for pellets produced from powders with different average particle sizes: (\diamond) 6,86 µm, (\Box) 15,29 µm, (\diamond) 26,30 µm, (Δ) 36,80 µm, (+) 58,95 µm.

The maximum densification was reached at 750°C for all particle size distribution. The highest densification (99.4%) was reached for powders with average particle size equals to 6.86 μ m when sintered at 750°C. The lowest densification (96%) was for powders with average particle size equals to 58.95 μ m.

Fig. 2 shows the micrographs of pellets sintered at 750, 774 and 795°C, for 1 h, produced from powders with average particle size equals to 15.29 μ m.





(c) 795°C/1h Fig 2 – Micrographs of NPG sintered at (a) 750°C/1h, (b) 774°C/1h, (c), and (d)795°C/1h.

As the sintering temperature increases the number and size of pores also increase. It is assumed that gas phases originally trapped in the glass are released during the sintering process causing the pore formation. It is also possible that the pore size increases due to the trapped gas expansion and the coalescence of small pores. In Fig. 2(d) it is noticed four small pores attaching to a large one. This result is in agreement to the density decrease of pellets sintered above 750°C. When pellets produced from powders with average particle size equals to 6.86 μ m are sintered at 795°C, the relative density reaches 92.2%, and at 750°C the relative density reaches 99.3%. Hence as the sintering temperature increases 45°C the densification is reduced 7.1%.

The particle size distribution of NPG powder with average particle size equals to 15.29 μ m is shown in Fig. 3. Although powders have different average particle sizes, the particle size distribution is bimodal or trimodal, and always a fraction of particles smaller than 1 μ m is noticed. For all particle size distribution the maximum densification was reached at the same sintering temperature.



Fig.3: Particle size distribution of NPG powders with average particle size equals to 15.29µm.

Fig. 4 shows the shape variation of $7x8 \text{ mm}^2 \text{ NPG}$ pellets as a function of temperature. The variation of the surface area was also determined (Fig. 5).



Fig. 4- Shape variation of NPG pellets at different temperatures.

The surface area decreases for temperatures above 747°C, reaching the minimum at 796°C. Then, as the temperature increases a slight increase of surface area is again noticed. This effect is caused by gas expansion, pore size increase, and swelling of the pellet. This effect is more predominate when sintering is performed for 1 h, when the time is enough to release the trapped gas.



Fig. 5: Surface area variation as a function of temperature for NPG pellets.

No crystallization evidence was found by analyzing the XRD patterns of NPG pellets sintered at 795°C during 12h. This is an outstanding result because there is no concurrent crystallization and the relative density is 99.3%. The softening point determined by dilatometric measurements is 782°C.

IPG Sintering

IPG powders with average particle size 7.31 and 31.82 μ m were sintered at different temperatures. Fig. 6 shows the particle size distribution of a powder with average particle size equals to 31.82 μ m.



FIG.6 – Particle size distribution of IPG powder with average particle size equals to 31.82 µm.

The IPG monolithic density is 4.21g/cm³ (determined by helium pycnometry). The relative density of IPG pellets sintered at different temperatures is shown in Fig. 7.

The shape variation of $7x8 \text{ mm}^2$ IPG pellets is shown in Fig. 8 as a function of temperature. The surface area was determined and shown in Fig. 9.



FIG. 7– Relative density of IPG pellets as a function of sintering temperature. Powders with average particle size: (\Box) 7.31 µm and (\Diamond) 31.82µm.



Fig. 8- Shape variation of IPG pellets during heating at different temperatures.

For temperatures above 579°C the surface area decreases reaching the minimum value at 612°C. For temperatures above 612 °C, the surface area increases until 681°C. This behavior is assumed to be caused by gas release.



Fig. 9: Surface area variation as a function of temperature for IPG pellets.

The surface area variation of NPG is larger than the one observed for IPG; a larger densification of NPG is also noticed. The major difference between the shape variations of both materials is related to the wetability. It seems that NPG wets the substrate at lower temperatures while IPG will wet the substrate only at temperatures higher than 860°C.

The XRD for the IPG pellet sintered at 676° C/1h shows diffraction peaks corresponding to KFe₄(PO₄)₃ (JCPDS: 35-0391) (Fig.10).



Fig.10 – XRD for IPG pellet sintered at 676 $^{\circ}C/1$ h.

The relative density of IPG pellets made from powder with average particle size of 7 μ m, and sintered at 558°C/1 h is 86%. As in the NPG, the particle size distribution was bimodal or trimodal and a fraction of particles smaller than 1 μ m was noticed. Fig. 11 shows the micrograph of IPG pellets sintered at 676°C/1h. The dark regions are pores.



Fig. 11. Micrograph of IPG pellets sintered at 676°C/1h

Crystallization is undesired because it can change the dissolution rate and thermal expansion coefficient. Densification can also be constrained since the sintering mechanism of glasses and crystals are different. In the glass, viscous flow is the predominant mechanism, and in polycrystalline materials sintering occurs through diffusion or liquid phase formation, which require higher temperatures and longer times. Since crystallization occurs concurrently with the viscous flow sintering of IPG glasses, that is the reason of the lower densification of these materials when compared to NPG;

Sintering of NPG and IPG containing U₃O₈ and SiO₂

From the DTA/ TG curve of U_3Si_2 in the temperature range of room temperature to $1200^{\circ}C$ an exothermic reaction was observed beginning at 300°C, and extending up to 800°C. In the same temperature range a weight gain was also observed. It is therefore assumed that this reaction is related to the oxidation of U_3Si_2 [6].

The particle size distribution of U_3Si_2 before and after calcination is shown in Fig. 12. The average particle sizes are 63 and 61 μ m, respectively. However the variation is considered small. Cracks in the particles caused by the volume expansion related to the oxidation of U_3Si_2 are noticed in the micrograph of Fig. 12 b. The particle size distribution is monomodal in both situations.

After the calcination of U_3Si_2 the material was milled during 10 min to obtain a particle size distribution with average particle size equals to 34 μ m [Fig. 13]. The use of longer milling times did not reduce the particle size substantially because U_3O_8 is relatively hard however the particle size distribution became bimodal [6]. The fine particles are most SiO₂ particles because this material is less hard than U_3O_8 , and it is easily milled.



Fig. 12 – Particle size distribution and micrograph of uranium disilicide: (a) before calcination, and (b) after calcination at 1020 °C/2 h.

The calcined U_3Si_2 powder (named US) was mixed to NPG or IPG frits, uniaxilly cold pressed, and sintered (pellets were named NPG, IPG + xUS, where x is the amount of US in ^{wt}/_o. The nominal density of each pellet was calculated to the rule-of-mixture.

NPG+xUS pellets were sintered in the temperature range of 752 - 835° C for 1 h. The NPG powders used for this purpose had an average particle size of 7 and 37 μ m. Density was determined by the Archimedes' method using water.



Fig.13 – Particle size distribution and micrograph of U₃O₈+SiO₂ after milling.

The relative density (% of density calculated by the rule-of-mixture) of NPG+xUS sintered pellets are shown in Fig. 14. The best densification is reached at temperatures higher than the ones for NPG glasses without the addition of US. For NPG+10US and NPG+15US sintered at 762°C the maximum relative densities are 97.6% and 96.3%, respectively , and for NPG+20US sintered at 770°C the maximum relative density is 95.9%.



Fig. 14 – Relative density (□) NPG+10US, (○) NPG+15US and (◊) NPG+20US; powders with average particle size equals to 6.86 µm.

NPG powders with average particle size equals to 38 µm were mixed with US and sintered. The best densification was reached at 762°C for NPG+10US and NPG+15US, and at 770°C for NPG+20U. The relative densities were 96.8, 91.7 and 86.9% respectively (Fig. 15).



Fig. 15 – Relative density of (□) NPG40+10US, (○) NPG+15US and (◊) NPG+20US; the average particle size of the starting NPG glass powder was 36.70 µm.

The relative densities of NPG+xUS sintered pellets are smaller than the ones for pellets without US. A possible reason for this fact is related to the lower wetability of the glass on the US particle surface, as shown in Fig. 16. The existence of pores is probably the reason for the lower densification. This phenomenon has been previously reported for the VSG8 and VSR [5] glasses.



Fig. 16-SEM micrographs of Nb40+20US sintered at 770 °C/1 h.

Agglomerates of US particles are also noticed due to the lack of dispersion during the mixing process. These agglomerates interfere in the sintering process, and consequently in the final densification. Fig. 17 shows the relative density of IPG+US pellets sintered at different temperatures.



Fig. 17 – the relative density of IPG+US pellets sintered at different temperatures: (\Box) IPG+10US, (\circ) IPG+15US, and (\diamond) IPG+20US.

The maximum densification is reached at 591°C for all pellets. The relative densities are 68.4, 68.2, and 62.0 % for the IPG+10US, IPG+15US, and IPG+20US, respectively. These values are relatively small to assure that the material can be considered as a trustable wasteform. Approximately 30 % in volume are just pores. Therefore the IPG composition was discarded to function as waste immobilization considering the sintering process.

The NPG is the matrix with the largest densification when sintered with US.

Table 1 shows the dissolution rates at 90°C after 14 days of monolithic and sintered glasses as a function of the pH of the leaching solution.

pН	Dissolution rate $(g.cm^{-2}.d^{-1})$			
	NPG (monolithic)	NPG (sintered)	IPG (monolithic)	IFG (sintered)
2	1.6 x 10 ⁻⁶	1.7 x 10 ⁻⁶	6.6 x 10 ⁻⁶	5.8 x 10 ⁻⁵
7	1.0 x 10 ⁻⁶	1.4 x 10 ⁻⁶	1.2 x 10 ⁻⁶	4.2 x 10 ⁻⁵
10	8.3 x 10 ⁻⁵	1.1 x 10 ⁻⁴	2.6 x 10 ⁻⁴	8.0 x 10 ⁻⁴
12	1.3 x 10 ⁻³	2.4 x 10 ⁻³	6.4 x 10 ⁻³	1.1 x 10 ⁻²

Table 1 – Dissolution rate of monolithic and sintered glasses as a function of pH's.

The dissolution rates for the monolithic NPG were the lowest for all pH's. The dissolution rates for sintered glasses were close to the ones for monolithic species for NPG immersed in solutions at pH's 2 and 7, but for pH's 10 and 12 the monolithic species presented better corrosion resistance. To explain these differences some assumptions can be considered: sintered glasses can have a larger surface area compared to monolithic species even after the standard grinding used before the leaching test. The grinding process could cause the opening of originally closed pores, and consequently increase the surface area of sintered pellets. However considering that the porosity of sintered NPG is relatively small (0.06%) this assumption was discarded. The second assumption concerns the differences between the surface of monolithic species, which were annealed after casting, and the surface of sintered species. As the sintering temperatures are higher than the annealing temperatures, sintered particles are completely free of thermal stress. At least the thermal stress of monolithic species would be the same of the sintered pellets. The sintering process is by viscous flow and therefore new surfaces will be created at the expense

of glass particles. After the sintering process, the glass is cooled down to room temperature without any annealing treatment. The difference of dissolution rates is then attributed to differences in the surface of both kinds of materials.

For IPG the dissolution rate of sintered pellets is larger than the ones for monolithic blocks. The reason for that behavior is that sintered IPG have a relatively high porosity which can be assigned to opened pores, leading to larger surface areas and consequently to higher dissolution rates. The fraction of surface area due to opened pores was not considered when the dissolution rate was previously determined. The weight loss per surface area was determined considering only the external surface of the pellets measured geometrically. Even considering that the real dissolution rate of sintered IPG is lower than the ones determined experimentally, the low densification is still a drawback to consider this material as a potential matrix for nuclear waste immobilization. Low densification means larger empty volumes, and larger surface area which could participate in the corrosion process.

Dissolution rate of sintered classes.

To determine the dissolution rate of sintered glasses the contribution of the surface area related to opened pores must be taken into account. A simple model then is proposed where opened pores are considered half spheres located on the surface (Fig. 18); hence an additional term is added to Eq. 2 related to the total surface area of the half spheres.



Fig. 18– Model of opened pores on the surface of sintered pellets (r_p is the pore radius).

To estimate the open pore surface area, it was considered that the penetration of water in the opened pores and the total volume corresponded to the water volume, which was determined by weighting. The difference between the dried sample weight and the wet sample weight was attributed to the amount of water that penetrated the pores and the volume was estimated considering the water density. The average pore radius (r_p) was determined by SEM, and the surface area of each pore S_p is half of the surface area of a sphere according to Eq. 3.

$$S_p = 2\pi r_p^2 \qquad (Eq. 3)$$

The number of pores (n_p) is given by:

$$n_p = \frac{V_w}{V_p} \tag{Eq. 4}$$

Where V_w and V_p are the volume of water and pores, respectively. The total surface area of pores can now be estimated considering n_p and S_p . The dissolution rate can now be determined from Eq. 5:

$$DR = \frac{mf - mi}{t(S + S_p, n_p)}$$
(Eq. 5)

Fig. 19 shows the dissolution rate of IPG pellets as a function of the sintering temperature. The dissolution rate was determined by using the Eq. 2 (without correction) and Eq. 5 (with correction).



Fig 19 – Dissolution rates determined for IPG sintered at different temperatures. Values were determined: (\Box)with correction, and (\Diamond)without correction.

By increasing the sintering temperature the number of opened pores decreases and consequently the exposed surface area decreases. As expected the dissolution rate for the sintered IPG is around 2.7×10^{-6} g.cm⁻².d⁻¹ after corrections.

Although this value is approximately twice the dissolution rate of monolithic IPG, it is in the same order of magnitude, and the model proposed for the pore surface area is validated. Therefore the weight loss associated to the exposure of opened pores to the leaching solution must be included in the determination o the dissolution rate of sintered materials. A possible explanation is that the ionic exchange inside the pores is more effective and the corrosion rate will be higher due to the localized increase of the pH.

CONCLUSIONS

The sintering process is suitable to immobilize nuclear wastes based on uranium and silicon when niobium phosphate glasses are used as matrix. Sintered glasses with relative density of 99% were obtained with dissolution rates in the order of 10^{-6} g.cm⁻¹.d⁻¹. No crystalline phases were detected on niobium phosphate sintered glasses. Sintered niobium phosphate glasses containing up to $20^{\text{wt}}/_{0}$ of U_3O_8 and SiO₂ reach relative densities around 97 %. A model based on the surface area of spherical pores was proposed and validated to determine the correct dissolution rate of sintered materials.

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