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Comparison of the corrosion resistance of sintered and monolithic iron phosphate and niobium phosphate glasses containing U_3O_8

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Vitrification is currently the main process for the immobilisation of high level nuclear wastes. However, radioisotopes can be volatilised during the melting process; sintering is advantageous in this case. In the present work, a comparison is made between the properties of niobium phosphate and iron phosphate glasses. Sintered glasses were prepared and characterised. Mixtures of U_3O_8 and glass particles were pressed and sintered, or melted to produce simulant wasteforms. The thermal stability of the glasses was evaluated by differential thermal analysis. The dissolution rates in aqueous solutions with pH in the range of 2–12 were determined. As the pH increased, the dissolution rate also increased. The chemical durability of the niobium phosphate glasses was not significantly changed when uranium oxide was added. Based on the thermal stability, densification, and chemical durability, sintered niobium phosphate glasses are considered to be potential candidates for nuclear wasteforms.

1. Introduction

Spent nuclear fuels are highly radioactive materials. Uranium is the largest fraction of the spent fuel composition being about 66 wt% of the fuel assembly mass or 95 wt% of the spent fuel itself.(1) The remaining 5 wt% consists of minor actinides and fission products. Therefore if compared to regular high level nuclear wastes (HLW), spent nuclear fuels contain a large amount of uranium. In Brazil, the reprocessing of spent nuclear fuels is prohibited. While spent fuels are not generally immobilised, but usually stored and reprocessed, if no further use is predicted immobilisation should be considered to avoid dangerous misuse. Glasses are ideal for the immobilisation of HLW, and vitrification is today the main process for this purpose. Unfortunately there is no single glass composition that can be used to safely immobilise all types of nuclear wastes, particularly ones that contain relatively large fractions of uranium. So, alternative compositions and processing techniques have been evaluated for this purpose. Sintering processes have the advantage of reducing the processing temperature, and have previously been investigated to immobilise HLW.(2) However, swelling of the material was observed. When concurrent crystallisation occurs, densification is jeopardised leading to higher temperatures and longer times being required for sintering.(3) Sintered lead iron phosphate glasses (LIP) have previously been evaluated for the immobilisation of Cs(4) and lead iron phosphate glasses have been developed for nuclear waste immobilisation.(5) Lead free phosphate glasses have also been investigated for the immobilisation of nuclear spent fuels.(6) Other iron phosphate glass compositions have also been investigated for the immobilisation of HLW using conventional melting processes.(7) However the dissolution rate in water of these glasses depends strongly on the Fe^{2+}/Fe^{3+} ratio. The addition of niobium oxide in the composition of phosphate glasses with the aim of producing glasses with improved chemical durability and optical transparency in the visible region has previously been reported.(8,9) Although niobium with different valences can be present in the glass structure, the dissolution rate in water does not depend on the Nb^{5+}/Nb^{4+} ratio.

The Nuclear and Energy Research Institute located in Sao Paulo, Brazil, has an operational research reactor that uses an U_3Si_2–Al fuel. The structural cladding and aluminium matrix is removed from the spent fuel to reduce the waste volume. The remaining U_3Si_2 is then oxidised. In the present work niobium phosphate and iron phosphate glasses were evaluated as alternative materials to be used in the immobilisation of spent nuclear fuels containing U_3O_8 by two different processes: glass sintering and melting.

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2. Experimental procedure

Reagent grade niobium oxide (supplied by CBMM) and iron oxide (supplied by CAAL) were mixed with $(NH_4)_2HPO_4$ (supplied by VETEC) and potassium hydroxide (supplied by CAAL), and melted in an alumina crucible to produce phosphate glasses with nominal compositions $40Nb_2O_5.23K_2O.37P_2O_5$ (named NPG) and $40Fe_2O_3.23K_2O.37P_2O_5$ (named IPG) with improved corrosion resistance. Potassium hydroxide was added to act as a glass flux. The melts were cast into stainless steel molds and annealed at 740 and 550°C for NPG and IPG, respectively. The melting temperatures were 1350 and 1150°C for NPG and IPG, respectively. Glass powders were produced by grinding the glass in an agate mill to obtain a particle size distribution with average diameter of 6·4 μm. Uranium disilicide had previously been heat treated in air to decompose it to U_3O_8 and SiO_2. This treatment was necessary to avoid the swelling of the material during the sintering process due to the reaction $U_3Si_2+6O_2 \rightarrow U_3O_8+2SiO_2$. Different amounts of the mixture $U_3O_8.2SiO_2$ (hereafter referred to as US for simplicity) were either mixed with glass particles, cold pressed and sintered, or mixed with glass particles and melted to obtain monolithic wasteforms. The uranium disilicide had previously been milled in a stainless steel jar for 10 min to reduce the particle size (D_{50}=50 μm). Glass sintering was performed in the temperature ranges 750–850°C for NPG and 540–730°C for IPG, in air for 1 h, to determine the best processing conditions. Figure 1 shows a schematic diagram of the experimental procedure. Chemical durability was determined by the MCC-1P Static Leach Test Method, using an aqueous solution and varying the pH in the range of 2–12. Samples were weighed after immersion in water for seven, 14, and 28 days. The particle size distribution was determined by using laser diffraction (Malvern). Samples were characterised using x-ray diffraction (XRD) over the 2θ range 20–80° with an angular step of 0·02°, a time step of 3 s and Cu K_α radiation. Differential thermal analysis (DTA) was performed over the temperature range 20–1200°C with a heating rate of 10°C/min to determine the glass transition temperature, and maximum crystallisation temperature. Scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) were also undertaken.

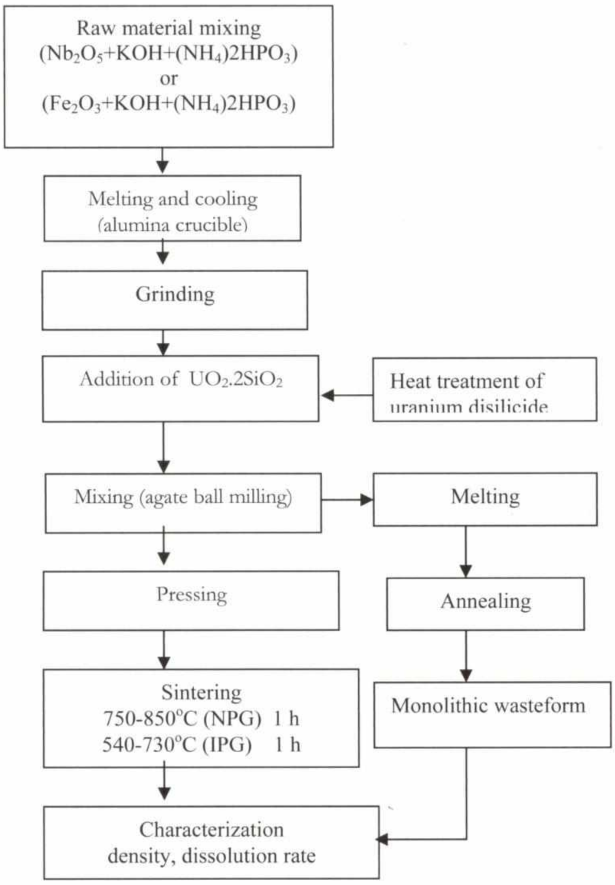

Figure 1. Schematic diagram of the experimental procedure

3. Results and discussion

The XRD patterns for monolithic pieces of NPG, IPG, NPG-US, and IPG-US are typical of amorphous materials. Table 1 shows the final composition of the niobium phosphate glasses determined by EDS of five samples. Contamination of the glass composition with 2·31 mol% of aluminium is due to the alumina crucible used for the melting. No major differences were observed when comparing the nominal and the final compositions. The glass transition temperature (T_g) determined by DTA for the NPG glass is 719±3°C. The maximum of crystallisation occurs at 936±3°C. The T_g for the IPG is 561±3°C and the maximum crystallisation is at 656±2ºC. Based on the Hübry parameter (K_H) NPG has good thermal stability (K_H=0·82). K_H is equal to 0·42 for the IPG. The reason for this is that Nb is always a glass former while Fe is a glass modifier in some situations.(10) The maximum density of sintered NPG (99% of the theoretical density) was achieved after sintering at 750°C. For sintering temperatures above 746°C the amount of open porosity is very small and the final density depends mainly on the presence of closed pores. During the heating process, the glass viscosity is reduced and dissolved gases are evolved resulting in the expansion of the closed pore volume; the density is then reduced. The maximum density for sintered IPG (86%) was reached

Table 1. Nominal and final composition of the niobium phosphate glass determined by EDS of five samples

	Elements (mol %)			
	Al	*P*	*Nb*	*K*
Nominal	-	37	40	23
Sample 1	2·08	38·47	40·93	18·52
Sample 2	2·19	38·65	40·61	18·55
Sample 3	2·41	38·29	40·72	18·58
Sample 4	2·16	38·60	40·34	18·90
Sample 5	2·69	38·46	40·2	18·65
Average	2·3±0·2	38·5±0·1	40·6±0·2	18·6±0·2

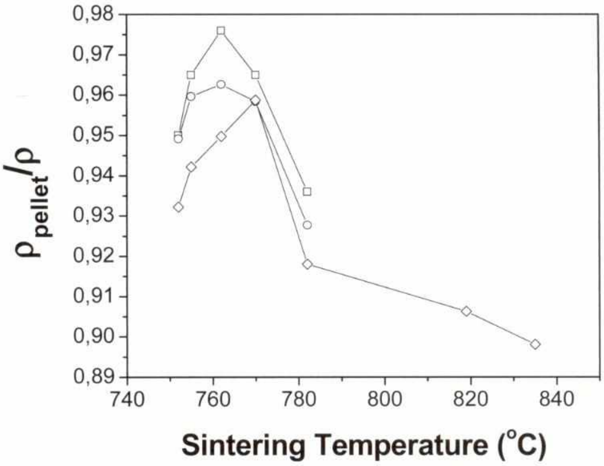

Figure 2. Relative density as a function of sintering temperature: (□) NPG+10US, (o) NPG+15US, and (◊) NPG+20US. The average particle size is 6·86 μm

at 558°C. Figure 2 shows the relative densities of NPG containing 10, 15, and 20% by weight of US.

For glasses containing US the maximum density was reached at around 760°C for NPG, and 590°C for IPG. No crystallisation is observed in sintered NPG, however XRD peaks related to the presence of crystalline $KFe_4(PO_4)_3$ are observed in sintered IPG. The relative density for sintered NPG+US is lower when compared to sintered glasses without US. A possible explanation is the low wettability of the US particle surfaces by the glass. Figure 3 shows the interface of the glass matrix and a US particle surface where a lack of adhesion is observed. The presence of pores is possibly the reason for the lower density. This effect has been previously observed for VSG8 and VSR glasses.(10)

The dissolution rate at 90°C for 14 days for NPG increases from $1{\cdot}6\times10^{-6}$ g cm^{-2} d^{-1} to $1{\cdot}3\times10^{-3}$ g cm^{-2} d^{-1} as the pH increases from 2 to 12. Similar results have been obtained for sintered samples. The dissolution rate for IPG increases from $6{\cdot}6\times10^{-6}$ g cm^{-2} d^{-1} to $6{\cdot}4\times10^{-3}$ g cm^{-2} d^{-1} for monolithic materials, and from $5{\cdot}8\times10^{-5}$ g cm^{-2} d^{-1} to $1{\cdot}1\times10^{-2}$ g cm^{-2} d^{-1} for sintered materials as the pH increases from 2 to 12.

Since the US-DOE limit is 0·3 g m^{-2} d^{-1} for a pH of 7 at 90°C, some of the glasses reported in the present work meet this requirement. Another encouraging aspect is that NPG does not crystallise when sintered, which could cause cracks and jeopardise the immobilisation of nuclear wastes. The dissolution rates for NPG+US glasses are presented in Table 2. The dissolution rates for the IPG+US glasses are presented in Table 3.

As the amount of US increases in the sintered materials, the dissolution rate also increases in all tested solutions. This result differs from the one observed in melted materials containing US. A possible explanation is that by increasing the amount of US the densification of sintered materials decreases, by increasing the amount of open porosity, and consequently the material dissolution. Comparing sintered glasses containing 20%US, NPG shows the lowest dissolution rate.

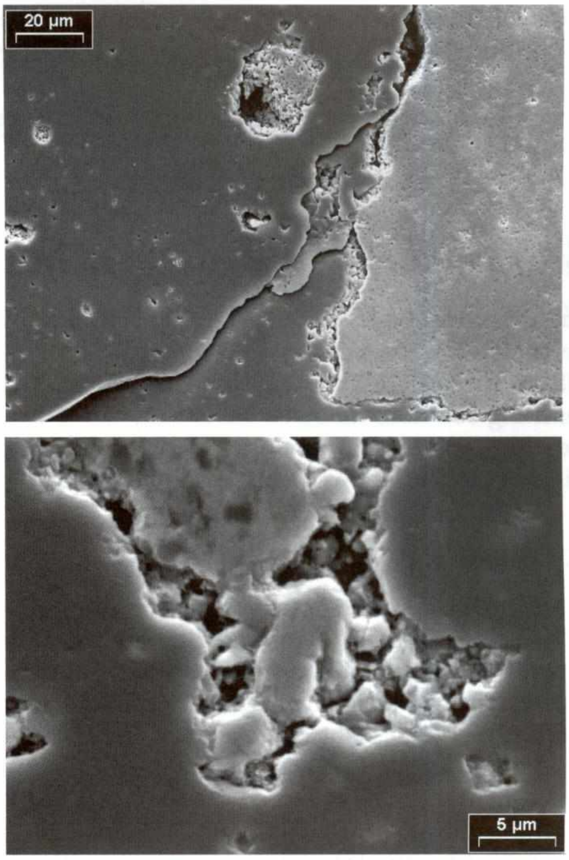

Figure 3. Scanning electron micrographs of Nb40+20US sintered at 770°C for 1 h

The dissolution rates for IPG+US are higher than the ones for NPG+US. The dissolution rates of IPG+US increases from $9{\cdot}1\times10^{-6}$ g cm^{-2} d^{-1} to $1{\cdot}5\times10^{-2}$ g cm^{-2} d^{-1} as the pH increases from 2 to 12 and as the amount of US increases from 10 to 20 mol%.

The advantage of using NPG over IPG for the immobilisation of US is that the chemical durability of NPG is not significantly changed when US is added. Samples of the leaching solution were also analysed by ICP to determine the elements that were leached out. For monolithic pieces of NPG, IPG, NPG+US, IPG+US, and sintered NPG+20US and IPG+20US, only K and P were detected. The amounts of Nb, Fe, and U in the leaching solution were lower than

Table 2. Dissolution rate for NPG+US glasses after 14 days at 90°C versus pH

pH	Dissolution rate (g cm^{-2} d^{-1})			
	NPG +20 mol%US (melted)	NPG +10 mol%US (sintered)	NPG +15 mol%US (sintered)	NPG +20 mol%US (sintered)
2	$5{\cdot}1\times10^{-7}$	$9{\cdot}3\times10^{-7}$	$9{\cdot}8\times10^{-7}$	$3{\cdot}2\times10^{-6}$
7	$1{\cdot}6\times10^{-6}$	$6{\cdot}2\times10^{-6}$	$9{\cdot}4\times10^{-6}$	$8{\cdot}9\times10^{-6}$
10	$1{\cdot}3\times10^{-5}$	$8{\cdot}1\times10^{-5}$	$8{\cdot}7\times10^{-5}$	$6{\cdot}5\times10^{-4}$
12	$8{\cdot}4\times10^{-4}$	$6{\cdot}7\times10^{-4}$	$4{\cdot}2\times10^{-4}$	$1{\cdot}6\times10^{-4}$

Table 3. Dissolution rate for IPG+US glasses after 14 days at 90°C versus pH

pH	*Dissolution rate* $(g\ cm^{-2}\ d^{-1})$			
	IPG +20 mol%US (monolithic)	*IPG +10 mol%US (sintered)*	*IPG +15 mol%US (sintered)*	*IPG +20 mol%US (sintered)*
2	$9{\cdot}1\times10^{-6}$	$3{\cdot}7\times10^{-5}$	$5{\cdot}7\times10^{-5}$	$6{\cdot}5\times10^{-5}$
7	$6{\cdot}2\times10^{-6}$	$4{\cdot}4\times10^{-5}$	$8{\cdot}5\times10^{-5}$	$1{\cdot}2\times10^{-4}$
10	$1{\cdot}3\times10^{-4}$	$2{\cdot}4\times10^{-3}$	$6{\cdot}5\times10^{-3}$	$7{\cdot}4\times10^{-3}$
12	$7{\cdot}8\times10^{-3}$	$8{\cdot}1\times10^{-3}$	$1{\cdot}5\times10^{-2}$	$8{\cdot}4\times10^{-2}$

the detection limits (0·010, 0·015, and 0·20 µg/mL respectively). Melted glasses containing 20 wt% of US show the lowest concentration of P and K in the leaching solution, followed by glasses without US. Leaching solutions from sintered glasses show the highest concentration of leached elements.

4. Conclusions

Niobium phosphate glasses with composition $37P_2O_5$–$23K_2O$–$40Nb_2O_5$ have the lowest dissolution rates in water when compared to iron phosphate glasses with composition $37P_2O_5$–$23K_2O$–$40Fe_2O_3$, and they are thermally stable which makes them potential candidates for nuclear wasteforms. Niobium phosphate glasses can be sintered without crystallisation reaching densities up to 99%. Iron phosphate glasses crystallise when sintered. Since the densification of niobium phosphate glasses is better than iron phosphate glasses, niobium phosphate glass can be considered more suitable for wasteforms than iron phosphate glass with a similar composition. Simulants of spent fuels were immobilised by melting or sintering $37P_2O_5$–$23K_2O$–$40Nb_2O_5$ glasses.

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