

## **Low Melting Temperature Glass for Immobilisation of Contaminated Zeolitic Ion Exchangers from Fukushima - 16494**

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### **ABSTRACT**

The clean-up of the Fukushima Daiichi site continues to generate large volumes of spent adsorbents which need to be disposed of permanently, one of the candidates is a low temperature immobilisation process to avoid volatilising radioactive Cs and Sr species. To this end an immobilisation process with a maximum temperature of 600°C was developed by sintering model waste with glass frit to form a dense Glass Composite Material (GCM) wasteform. A zeolitic model wasteform, chabazite, was sintered with two lead-based glass compositions, lead borosilicate (PBS) and a lead borate (PB) glass composition, at a maximum temperature of 600°C. Full encapsulation of the zeolitic wasteform was achieved for wasteloadings up to 40 wt.% in PBS and 30 wt.% in PB in all cases, with both GCM systems showing foaming. PBS GCM formation was successful at a maximum of 600°C, while the PB GCM formation was shown to be possible at a maximum temperature of 550°C.

### **INTRODUCTION**

Several water treatment systems are currently in place at Fukushima to remove radionuclides from the contaminated water used to cool the reactor cores, such as the HP-ALPS (High Performance Advanced Liquid Processing System), the high performance multi-nuclide removal equipment. However, the treatment of approximately 500 m<sup>3</sup>/day of contaminated water continues to generate large volumes of spent adsorbents, which can be highly radioactive (approximate level of activity concentration of the order of 1E11 Bq/kg to 1E12 Bq/kg). These spent adsorbents are currently stored on-site, but will require immobilisation in a suitable wasteform before being disposed of permanently. The most common radionuclide species present in the effluent cooling water are Cs and Sr species with short half-lives, the longest is Cs-137 with a 30.08 year half-life. The final ILW wasteform will have an estimated repository lifetime of 300 years and will likely be disposed of at a surface storage facility.

Another aspect to consider in any process used to immobilise the adsorbents is Cs and Sr volatilisation. Due to the use of seawater as an emergency coolant and the ingress of groundwater the system has a high chloride content. The high level of chloride could lead to CsCl and SrCl species. Both the chloride species of Sr and Cs are volatile at higher temperatures[1], so to ensure minimal volatilisation a low temperature immobilisation process is sought with a maximum temperature of 600°C. A fully homogeneous glass wasteform at this temperature is not achievable,

as a fully vitreous wastefrom incorporating these adsorbents is only achievable above 1100°C [2].

Radionuclide volatilisation is a problem that has been faced by the nuclear industry in many different clean-up scenarios, including volatilisation from Cs adsorbed onto zeolites. Gray[3] noted that the volatility is significant above 700°C, and this is echoed by Kamizano *et al.*[4] who notes that volatilisation can be significant above 1000°C. Furthermore, the presence of chloride species can greatly increase volatilisation, the presence of NaCl in a system can push the volatilisation of Cs to >99% above 1000°C. Due to the situation at Fukushima Daiichi, the waste has a significant chloride presence that would greatly increase both Cs and Sr volatilisation. For this reason alone classical industrial vitrification techniques are not suited to the immobilisation of this particular waste stream. The volatilisation concerns are too great and a viscous flow sintering process is opted for instead to create a GCM wastefrom.

Two lead-based glasses were chosen for their low temperature processing characteristics, specifically their ability to soften or sinter at low temperature. A lead borosilicate glass frit, with a softening temperature of 451°C was chosen to immobilise a simulant waste form in our experiments. A second glass composition a lead borate was chosen based on low temperature Cs and Sr vitrification work done by Erdogan *et al.*[5] In this work a more classical approach to nuclear waste vitrification is taken, with a fully homogeneous vitreous wastefrom produced at 950°C. The produced wastefrom exhibits good durability under MCC-1 Static Leach Test Method conditions. Lead-based glasses have previously been used in the nuclear industry, often for shielding purposes, however more recently also for waste immobilisation purposes. Lead borosilicate glass systems are currently used for the vitrification of Cs and Sr rich waste in India, such as WTR-62 [6, 7]. Temperature ranges for industrial vitrification processes are often reported between 1200°C and 1500°C, depending on the waste and glass composition [8]. While this temperature puts this process outside of our temperature range, the glass composition was used to encapsulate, i.e. fully seal within a glass matrix, the zeolitic model wastefrom at a lower temperature. The selected glass compositions were processed in direct sintering conditions to use viscous flow sintering to encapsulate the zeolitic model wastefrom below the chosen processing temperature. Glass encapsulation of nuclear wastefroms has been performed successfully on different wastefroms in the past [9]. Hence, in this paper, the different process optimisation steps that were carried out in order to obtain a bulk GCM wastefrom will be discussed.

## **DESCRIPTION**

Two glass compositions were prepared for this study. A lead borosilicate glass (composition in wt. %: PbO 63, B<sub>2</sub>O<sub>3</sub> 25 and SiO<sub>2</sub> 12) was prepared by a melt quench from base oxides. This glass was melted for 2 h at 1200°C in a bottom loaded Lenton EHF 1800 furnace (Carbolite, Hope Valley, UK) using a platinum crucible. A lead borate glass composition (composition in wt. %: PbO 80 and B<sub>2</sub>O<sub>3</sub> 20) was prepared by a melt quench from base oxides. This glass was melted for 2 h at 950°C in a bottom loaded Lenton EHF 1800 furnace (Carbolite, Hope Valley, UK)

using a platinum crucible. Both melts were quenched in a large volume of deionised water kept at room temperature. The resulting glass frits were recovered, washed with acetone and dried for 12 h at 110°C. The dried frits were wet ball-milled with ethanol in a planetary ball mill. The ball milling was performed at low frequency (100 Hz) for 5 minutes, with recovered frit of a particle size  $\leq 38 \mu\text{m}$ .

The model waste without Cs and Sr loading was a commercially acquired chabazite. The chabazite used was acquired from Verdi Sp.A (Castelnovo di Sotto, Italy). The chabazite was ground and sieved with the 100  $\mu\text{m}$  - 125  $\mu\text{m}$  fraction retained. The chabazite is initially dried at 110°C to release any sorbed water. Calcination was performed at 600°C to remove any volatile species from the chabazite. Calcined (particle size: 100  $\mu\text{m}$  - 125  $\mu\text{m}$ ) and glass frit (particle size:  $\leq 38 \mu\text{m}$ ) were mixed in a turbula mixer for 12 h to homogenise at different wt.% waste loadings.

After mixing wasteforms were produced by mixing different chabazite (particle size: 100  $\mu\text{m}$  - 125  $\mu\text{m}$ ) waste loadings, in 10 wt% increments, with glass frit (particle size:  $\leq 38 \mu\text{m}$ ) for 12 h in a turbula mixer. The mixed powders were loaded into stainless steel ring-shaped (diameter 9.5 mm) moulds and sintered using the optimised sintering profiles. Sintering profile for the PBS system consisted of steps of 2 h at 350°C, 2 h at 600°C and 2 h at 550°C. Sintering profile for the PB system consisted of steps of 2 h at 350°C, 2 h at 550 °C and 2 h at 500°C (See Figures 1 and 2).

Produced wasteforms were analysed using SEM (JEOL JSM6400 and JEOL JSM6010) and Energy Dispersive Spectroscopy (EDS) (Oxford Instruments INCA). Surface and cross-sectional Secondary Electron Images (SEI) were taken to examine the microstructure.

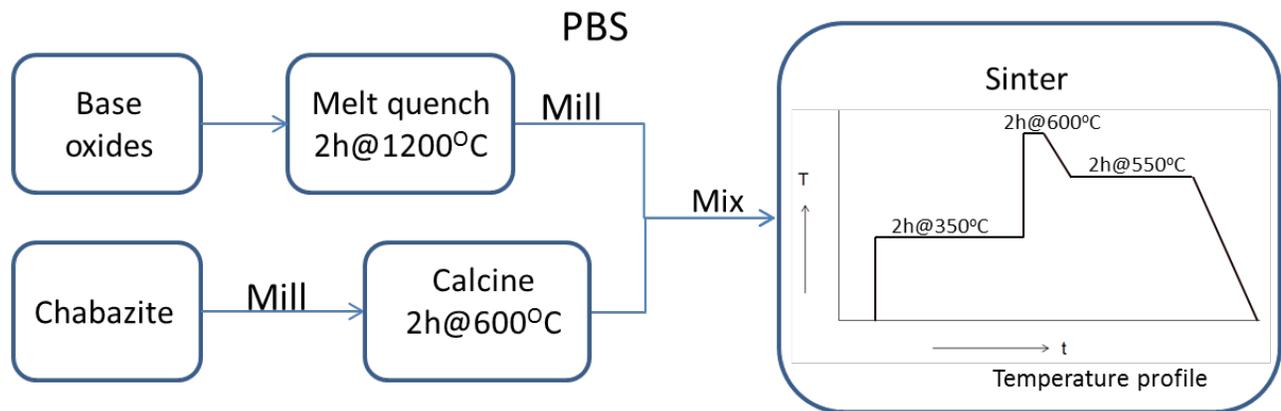
## **DISCUSSION**

Aqueous species in a radioactive wasteform may undergo radiolysis and produce various unwanted and dangerous species such as hydrogen, radicals and peroxides [10] which can be corrosive or explosive. Hence, both aqueous and organic volatile species sorbed to the zeolites should be removed before encapsulating them into a matrix. For this a calcination step of the zeolitic model waste followed by direct sintering of the mixed glass frit and calcined model waste was adopted. In direct sintering the powder compact is transferred into a furnace pre-heated to sintering temperature. Applying fast heating rates was found to improve viscous flow sintering at lower sintering temperatures by Chinnam *et al.* [10] Therefore, a similar method was tested on lead borate GCM composites and lead borosilicate GCM composites.

### **Sintering Conditions**

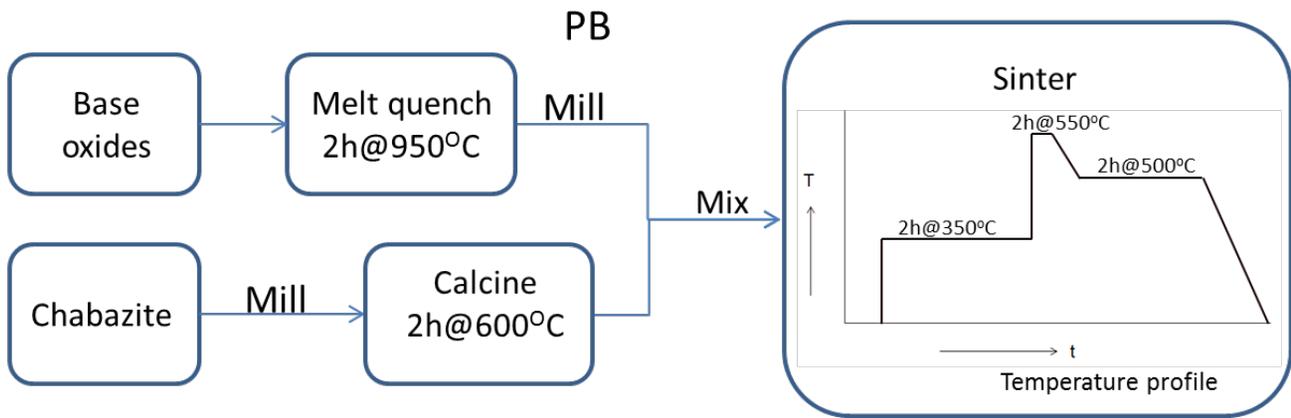
Initial attempts were done with cold-pressed lead borosilicate samples subjected to a two-step sintering profile, where the first step is to direct sinter the sample at 600°C for 10 min followed by cooling the sample to 550°C and annealing for 6 h. The sintering step at 600°C is chosen to activate viscous flow sintering and the

subsequent 550°C annealing is chosen to homogeneously densify the material. The resulting wasteform was found to have a glazed surface, but was bloated [11]. This bloating could be due to volatilisation of sorbed species from the zeolitic model wasteform. During direct sintering, as soon as the powder compact was introduced into the furnace, the surface lead borosilicate glass particles soften and block all open surface pores. Temperature homogenisation of the bulk would have softened the compact resulting in viscous flow. During this process the release of any volatile material would be blocked by the lack of open porosity. Hence, the gases get trapped and lead to foaming [12]. The chabazite is hygroscopic and a possible source of foaming in the direct sintered compacts is water sorbed on to chabazite. To obtain a denser material, an initial calcination step at 350°C for 2 h was added to volatilise any material or water vapour before the viscous flow of glass occurs. GCM foaming was greatly diminished by evaporating volatile species from the chabazite in an additional sintering step. To further eliminate adsorbed species from the model wasteform an extra calcination step was added to the process. The chabazite was calcined at 600°C for 2 h to remove any possible volatile species that may have adsorbed to the chabazite during processing (Figures 1 and 2).



Base oxides: PbO 63wt.%, B<sub>2</sub>O<sub>3</sub> 25wt.%, SiO<sub>2</sub> 12wt.%

Figure 1. Process flow diagram of PBS wasteform production



Base oxides: PbO 80wt.%, B<sub>2</sub>O<sub>3</sub> 20wt.%

Figure 2. Process flow diagram of PB wasteform production

### Lead Borosilicate Sintered Wasteforms

To closely mimic the final industrial application the mixed powders were loaded into stainless steel rings before sintering. While optimisation was performed with a 10 wt.% chabazite waste loading, further waste forms were produced in 10 wt.% increments, up to a 40 wt.% waste loading. Due to increasing waste loading of chabazite more adsorbed species need to be eliminated from the wasteform during thermal treatment. This requires a longer treatment step at 350°C before full viscous flow sintering at 600°C.

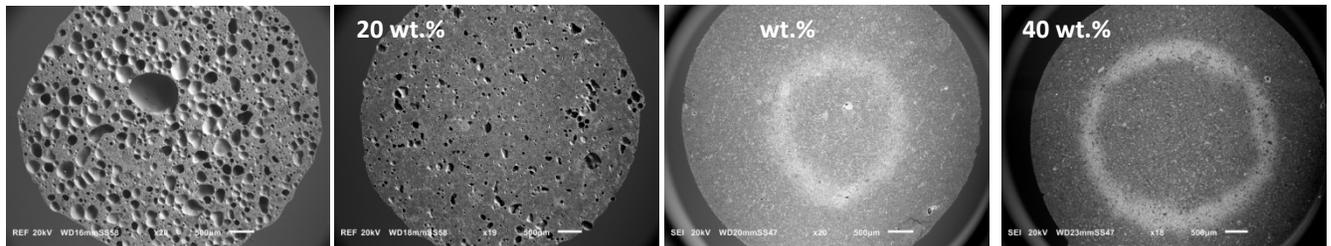


Figure 3. Cross-sectional SEI micrographs of PBS samples.

Cross-sectional SEI in Figure 3 of the different waste loadings in PBS show different microstructures, with especially 10 wt.% exhibiting foaming, however this is decreased at increasing waste loading. The observed halo effect in the 30 wt.% and 40 wt.% is an artefact of the sample preparation for SEM and is due to the resin used for the cold mounting. Work is currently in progress to ensure full densification at all waste loadings.

Cross-sectional SEI micrographs and EDS maps from 10 wt.% (Figure 4) and 30 wt.% (Figure 5) waste loadings reveal homogeneous waste distribution in the vitreous matrix. Each sample shows similar GCM microstructures, with EDS spectra showing different phases in the microstructures. The Al, Si, and K-rich chabazite phases and Pb-rich glass phase became mixed in the final microstructure.

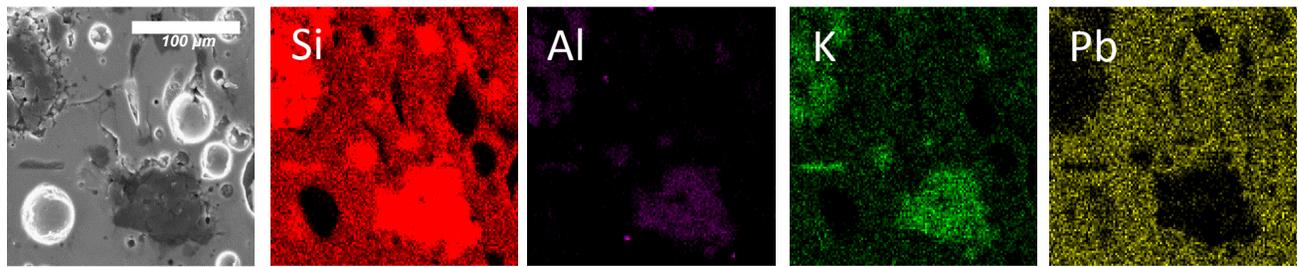


Figure 4. 10 wt.% PBS SEI and EDS micrographs.

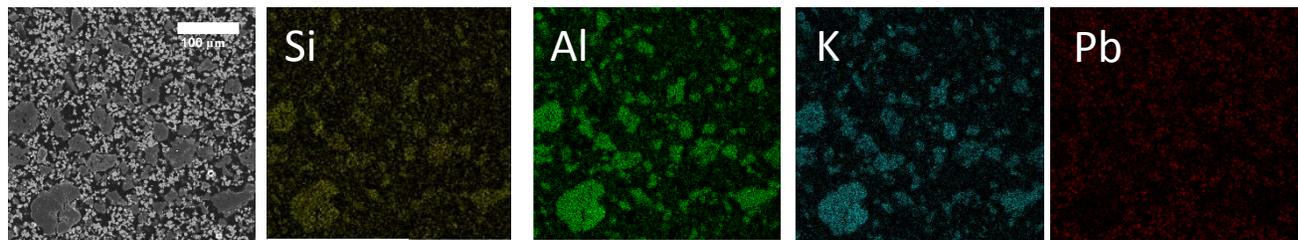


Figure 5. 30 wt.% PBS SEI and EDS micrographs.

The SEI in Figure 3 show a dense microstructure in the 30wt.%, but 10 wt.% still shows bubble formation. At higher waste loadings foaming is greatly diminished. Due to the higher waste loading initial sintering and pore occlusion is presumed to take longer, giving adsorbed volatiles longer to diffuse out of the wastefrom, and leaving dense microstructures.

## Lead Borate Sintered Wasteforms

The PB glass composition lacks the silica phase as a glass former, with the lead phase acting as the glass former. The lack of silica in the glass lowers the melting temperatures and the flow point, leading to lower processing temperatures during processing [5]. The PB frit was mixed with the pre-calcined chabazite and loaded into stainless steel rings before sintering. Waste loading was done in 10 wt.% increments, up to 40 wt.%. However 40 wt.% waste loading were not robust enough, so only up to 30 wt.% samples were analysed. The 350 °C pre-treatment step was retained, to ensure removal of any sorbed volatile species from the chabazite. After this the composites were sintered at 550°C for 2 h and then treated at 500°C for a further 2 h. Afterwards samples were left to cool in equilibrium in the furnace.

Cross-sectional SEI of the samples (Figure 6) show foamed microstructures.

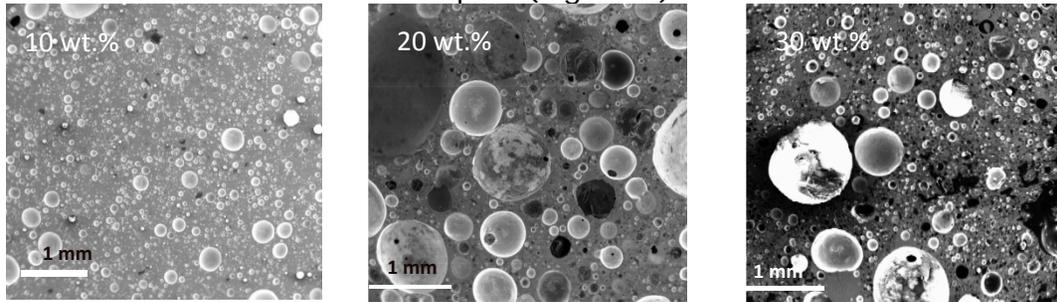


Figure 6. Cross-sectional SE micrographs of PB samples.

PB GCM wasteforms are similar to PBS GCM wasteforms in their foaming behaviour, as seen in the un-optimised PBS samples in Pletser *et al.* [11], and the SEI of the PB in Figure 6. While the microstructures exhibit strong foaming characteristics, encapsulation of the chabazite model waste is achieved for all waste loadings.

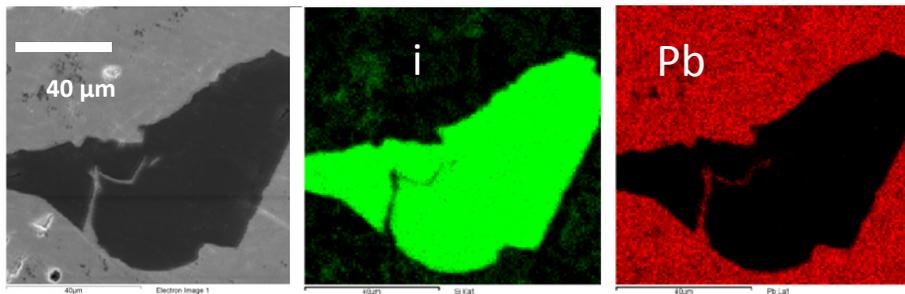


Figure 7. 10 wt.% waste loading PB EDS maps.

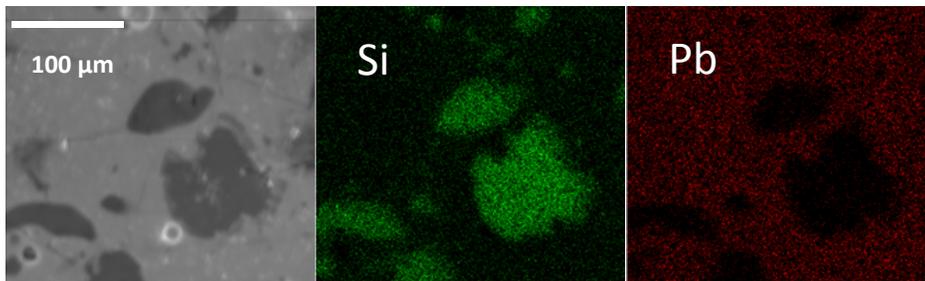


Figure 8. 20 wt.% waste loading PB EDS maps.

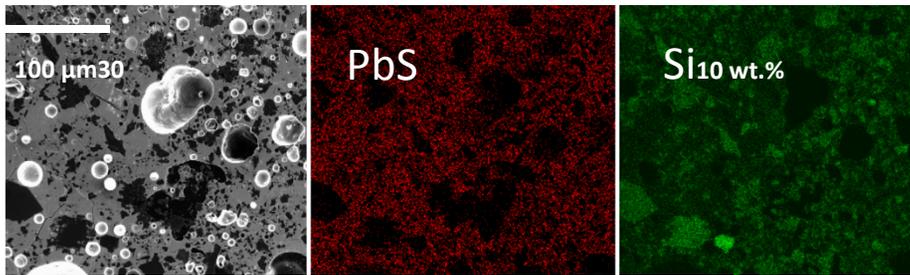


Figure 9. 30 wt.% waste loading PB EDS maps.

EDS maps of all samples show, despite foaming, good encapsulation of the chabazite, revealed by the presence of Si surrounded by lead borate glass, as shown by the Si and Pb maps (Figures 7-9). The successful encapsulation of the model wastefrom with the lead borate glass shows that even at temperatures as low as 550 °C a viable GCM wastefrom can be produced.

The microstructural foaming is manageable with the right thermal treatment, as shown in this work and by Chinnam *et al.*[12]. Foaming is exhibited consistently in both the PBS and the PB GCM wastefroms. The successful optimisation of sintering profiles to improve densification in the lead borosilicate GCM will be applied to the lead borate GCM. Work is currently in progress to determine the exact nature of the volatile species and its implications for the densification.

The PB and PBS glass compositions chosen to produce GCM wastefroms were chosen based on their low temperature processing characteristics. Work performed with PBS GCM wastefroms proved that accurate tuning of microstructural characteristics by strict control of sintering conditions was possible [11]. Work done with the PB GCM exhibits strongly similar low temperature processing characteristics, with a tendency towards pore occlusion due to glass softening and subsequent bloating, albeit it at a lower temperature than with the PBS system. Microstructural control of the PB GCM wastefrom would be exerted with the tuning of the sintering profiles. Notable differences between the two systems are the lower sintering temperature of the PB system and different maximum waste loading currently achieved in the PB system.

## CONCLUSION

Glass composite wastefroms were successfully produced to immobilise volatile Cs and Sr containing waste generated in the clean-up of the Fukushima Daiichi site. The challenge of overcoming a low processing temperature to design a viable model nuclear wastefrom was successfully achieved by producing a GCM loaded with chabazite and subjected to direct sintering to form a bulk material with a maximum operating temperature of 600°C. Two different glass compositions, PBS and a PB composition, were used to produce the wastefroms. These two compositions were studied for their low temperature processing capabilities and their results compared. The release of adsorbed volatile species was enabled by modifying the sintering profile, as during viscous flow sintering a glaze can form on the surface of the wastefrom, impeding the diffusion of volatile species, leading to bloating and a foamed microstructure. These initial results open up a promising route of processing

for these spent adsorbents and the possibility of low temperature immobilisation of volatile nuclear waste in general.

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