

EARLY GAS EVOLUTION AND CALCINE DISSOLUTION ON MELTING BOROSILICATE GLASS WITH SIMULANT HIGH LEVEL, RADIOACTIVE WASTE (HLW)

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Summary

The processes occurring in a simulant high level waste calcine during the early stages of vitrification have been studied. Gas chromatography- mass spectrometry has been used to analyse simulant waste samples and their offgas under various atmospheres during melting. Results indicate decomposition of nitrates contained within the simulant waste give some gaseous products which are difficult to extract from the offgas system using conventional solvents such as water.

(Key words: vitrification, borosilicate glass, nitrates, offgas)

Introduction

Nuclear fuel reprocessing is undertaken in few countries, notably France, Japan and the UK. Spent Nuclear fuel (SF) is taken from nuclear reactors and stored in cooling ponds allowing time for the majority of the heat to dissipate. These SF rods are then sheared, the cladding removed, and dissolved in 6M HNO₃ in order that the remaining Pu and U can be separated from the fission products for re-use. High level radioactive waste in the form of nitrates is then calcined using a rotary calciner, consisting of 4 heating zones. The waste undergoes both dehydration and partial denitration processes within the calciner, before being fed into the Inconel 601 melter in a granular form. After the calcine addition, a mixed alkali, borosilicate glass frit is added to the melter to form a glass melt.^{1,2} The melter is charged at a rate of 25 kg/hr and agitated by sparging to achieve homogeneity. The feeding of the melter generally takes around 8 hours and is followed by, on average, a one hour soaking time. This allows full incorporation of the waste with in the glass and a homogeneous end product. This molten glass is then poured into a stainless steel canister and allowed to cool.³ The glass does not undergo annealing at this stage of the process. This high level waste (HLW) is classified as a heat generating, highly radioactive material, mostly generated from the reprocessing of spent fuel. Radiogenic heat is produced by the decay of radioactive isotopes such as Cs- 137 and Sr- 90, and safe handling involves using remotely operated machines and shielding consisting of several meters of concrete and lead (DEFRA 2001).⁴

This paper outlines a study which is part of larger programme, aimed at more fully understand the properties of solid HLW generated within the UK. Part of the reprocessing of HLW by BNFL(UK) involves using a "blend" waste, which is an incorporation of Magnox and Oxide wastes, in a 25/75 ratio. During the melting of a simulant (non-radioactive) blend waste, thermal analysis in conjunction with Gas Chromatography- Mass spectrometry (GC-MS) has been used to analyse the offgas of a small batch (~50mg) under inert and oxidising atmospheres.

Experimental

The preparation of all samples was undertaken using a BNFL supplied borosilicate glass frit and blended simulant waste, (Tables I and II). The simulant waste was prepared from a solution of nitrates mixed in appropriate stoichiometric ratios, and passed through a full scale rotary calciner as part of the commissioning phase of a new vitrification line at the BNFL Sellafield Waste Vitrification Plant (WVP). Interactions between the calcine and glass melt during the early stages of vitrification was examined by heating a batch of glass frit and simulant calcine in a pre-heated Inconel 601 crucible (75ml capacity) at 1050°C. The glass frit used had the composition given in Table I. The batch composition was calculated to yield a calcine waste loading of ~25wt%, taking into account Loss- on-

Ignition figures determined by thermal analysis. A waste loading of 25wt% is equivalent to that employed on the full scale vitrification lines at the Sellafield Waste Vitrification Plant (WVP). Thermal analysis was carried out on the simulant waste and frit using a TA Instruments SDT 2960 Simultaneous DTA-TGA. Samples were heated in air at 3 different rates of 1°C, 4°C and 8°C/min, to allow for the shift in the reaction times due to the small sample size. A rate of 4°C/min was selected and four 25wt% waste loaded samples were analysed under air, reducing, oxidizing and inert conditions. Samples weighing approximately 50mg were batched separately in a Pt crucible to produce a 25wt% waste loaded glass and heated at a rate of 4°C/min to 1050°C where they were held for 1 hour. This analysis was carried out in several atmospheres, including air, 2.84% H₂ balanced with Ar, O₂ and He, all flowing at a rate of 50ml/min through the furnace chamber.

Subsequently, the DTA/TGA was connected to a Hewlett Packard 5890 GC-MS which analysed the offgas of the system. 25wt% waste loaded samples, again weighing approximately 50mg, were melted using a heating rate of 4°C/min. Further GC-MS analysis was conducted using a pure silica crucible, containing 10g of 25wt% waste loaded batch, was placed in a furnace equipped with a quartz- viewing window and melted. The crucible was sealed and melts were conducted under inert and oxidising conditions. The atmospheres used were 2.84%H₂ balanced with Ar for the reducing conditions, 21%O₂ balanced with He for oxidizing, and He for inert atmospheres. Compressed air was not used in this series due to the ‘flooding’ effect on the MS detector yielding unsuitable data. For quantitative evaluation and analysis of the sample offgas, a series of calibration gases were analysed containing all the gases expected to be evolved during the experiment.

Fourier-Transform Infra-red spectroscopy (FT-IR) was used to analyse samples of the simulant calcine heat treated at a series of temperatures. Sample pellets were pressed from a heat treated, ground calcine material (2mg) and KBr (200mg), using a Perkin Elmer Spectrum 2000 FT-IR in transmission mode (range 4000– 600cm⁻¹).

The calcine samples were also examined using X-ray powder diffraction. Specimens (ground and sieved to <100µm) were front loaded into aluminium sample holders and analysed with a Philips PW1410 X-ray Powder Diffractometer employing Cu-Kα radiation and operating in reflection mode.

Table I: Borosilicate glass frit

Component	Wt%
SiO ₂	62.9 ± 1.0
B ₂ O ₃	23.0 ± 0.8
Na ₂ O	11.4 ± 0.5
Li ₂ O	2.7 ± 0.4

Table II: Simulant (non- radioactive) HLW composition

Oxide	Weight % in simulant calcine	Oxide	Weight % in simulant calcine	Oxide	Weight % in simulant calcine
Gd ₂ O ₃	8.15	Pr ₆ O ₁₁	2.35	Na ₂ O	<0.10
Nd ₂ O ₃	7.60	La ₂ O ₃	2.35	SiO ₂	0.06
ZrO ₂	7.48	SrO	1.60	B ₂ O ₃	<0.05
MoO ₃	6.00	Sm ₂ O ₃	1.26	TiO ₂	0.01
Li ₂ O	5.53	TeO ₂	0.86	CaO	<0.01
CeO ₂	4.97	BaO	0.71	K ₂ O	<0.01
Cs ₂ O	4.86	Cr ₂ O ₃	0.61	RuO ₂	<0.01
MgO	4.02	NiO	0.40		
Al ₂ O ₃	3.74	P ₂ O ₅	0.27		
Fe ₂ O ₃	2.81	HfO ₂	0.10		

Results

Thermal analysis (Figure I) of fully waste loaded samples revealed, as expected, around a 15% weight loss for all samples, with some variation depending on sample size. However, TGA demonstrated that weight loss under reducing, oxidising and inert conditions differed, depending upon the atmosphere in which the sample was immersed at the time. Under reducing conditions the weight loss appears to occur more rapidly than under oxidising conditions.

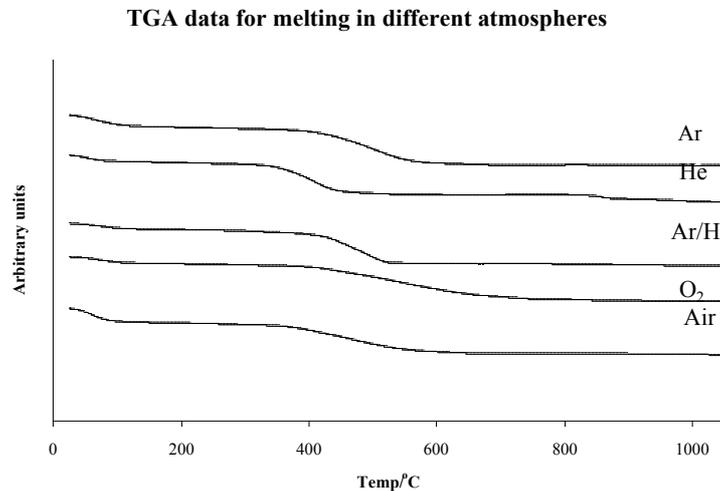


Figure I: TGA data from 25wt% waste batches heated at 4°C/min to 1050°C

Initial analysis of a fully waste loaded sample using GC-MS in conjunction with DT-TGA showed that gas evolved from the system was almost completely composed of NO in both inert and oxidising atmospheres. This is as expected due to the residual nitrates present in the calcine. Some small amounts of O₂ were detected during all experiments conducted using the simultaneous DT/TGA technique, but since this was constant throughout all experiments, it was thought that this was due to a small air leak in the furnace chamber. The total amount of NO evolved whilst in He- O₂ atmosphere was 2.60×10^{-3} g from a 50mg batch, and in He a total NO evolution was 2.42×10^{-3} g. This gas evolution corresponded with the main weight loss peak of the TGA curve (Fig. II).

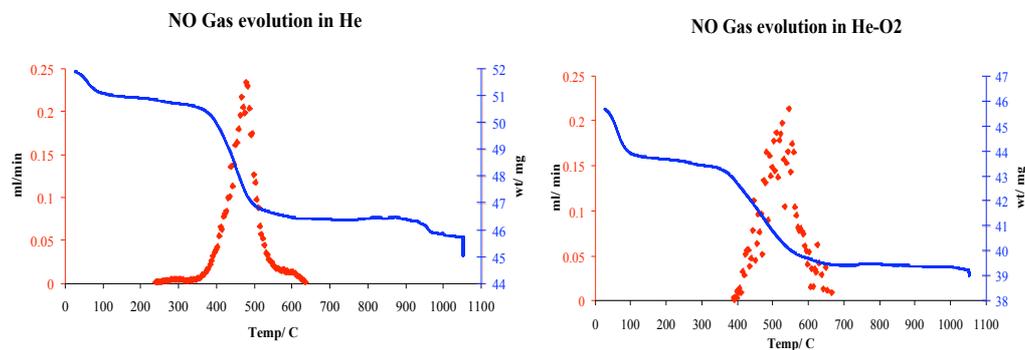


Figure II: NO Evolution in inert and oxidising atmospheres

During larger scale melting of a 10g batch in, NO was again evolved, but N₂O and CO₂ were also detected. It was decided the CO₂ was a product of corrosion of the stainless steel tube used as the crucible inlet, due to the fact that the calcine material used was produced using nitrates, not carbonates, and the visual appearance of the inlet tube blackened as the experiment continued. The evolution of the two NO_x gases took place at different times during the melting process with most of the N₂O evolved in the early stages of the melt, from around 135°C to 335°C. The NO detected by the GC-MS began to evolve at 280°C, and finished around 695°C. In total, 6.87g of NO were evolved, 1.71g of O₂ and 0.464g of N₂O when the melt was conducted under inert conditions (Fig. III).

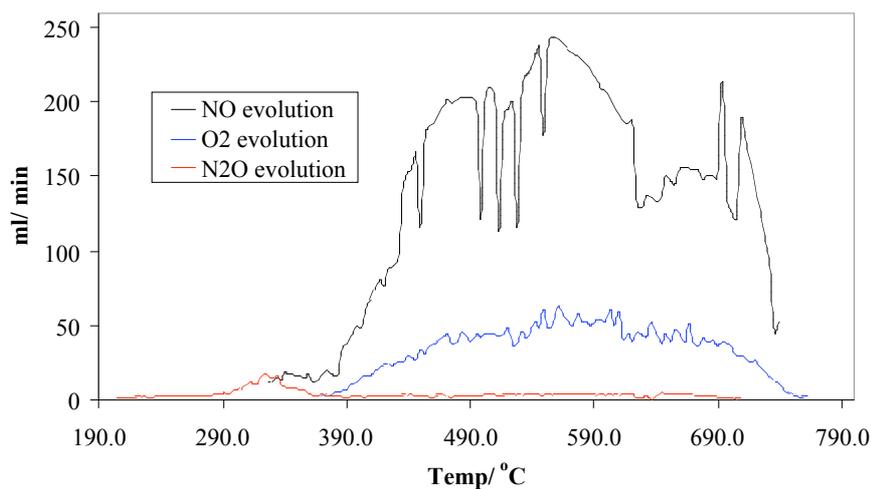


Figure III: NO, N₂O and O₂ evolution from a fully loaded glass in He atmosphere.

Discussion

When incorporating HLW into a glass, there are several factors to be considered, one of which is the amount of waste to be immobilised in the glass and the offgas products and thermal events which this entails. Basic analysis of a 25wt% waste loaded batch showed that the weight loss of a fully loaded batch occurred much more rapidly under reducing conditions than the same batch under oxidising conditions. This weight loss is due to nitrate decomposition, as identified in some part by X-ray powder diffraction. Two major crystalline phases present within the calcine are LiNO₃ and Sr(NO₃)₂. These two phases identified using powder X-ray diffraction are the only crystalline nitrate phases, and as thermal analysis highlights the fact that the calcine material is made up of around 25-30wt% nitrates, then the majority of the nitrates present are there as amorphous material. The presence of nitrates in an amorphous and crystalline form within the calcine is confirmed by absorption bands seen in the infra- red spectrum of this material at ~3430cm⁻¹ and 1387cm⁻¹. These bands are attributed to the O-H and N-O stretches of H₂O molecules and the NO₃²⁻ anion (see Figure IV). The implications for this are that the more rapid the denitration within the calciner, the less energy expenditure in both the calcining and melting processes.

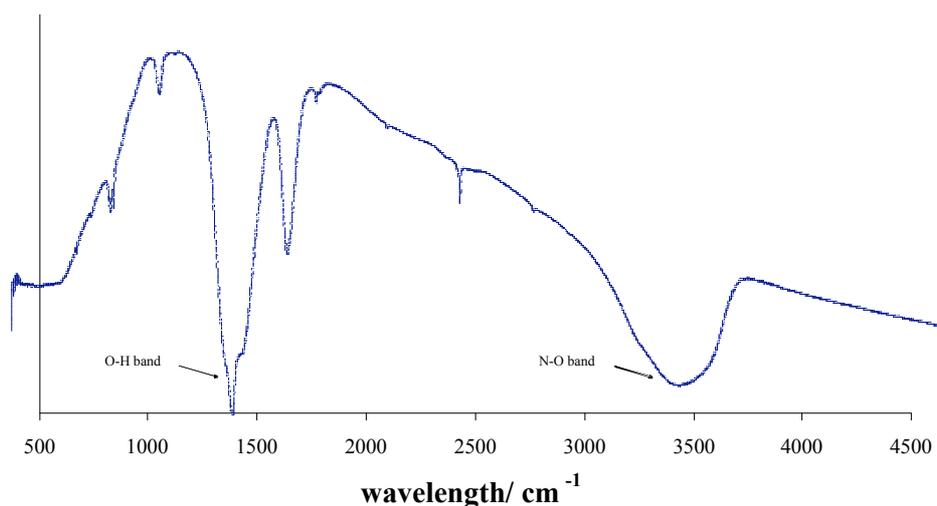


Figure IV: FT-IR showing the O-H and N-O absorption bands of the as-received calcine material

Combined thermal analysis and GC-MS highlighted the fact that the major decomposition product of the full batch was NO. This is due to the decomposition of the two major crystalline phases and other amorphous nitrates. The gas evolution begins at around 240°C and continues to 600°C. This corresponds with the melting point of LiNO₃ at 253°C, and Sr(NO₃)₂ at 640°C.⁵ In total, 6.87g of NO were evolved, 1.71g of O₂ and 0.464g of N₂O when the melt was conducted under inert conditions. Nitrates, when incorporated into a glass, not only decompose to evolve NO_x, but also form nitrites, at the same time releasing 0.5M O₂ for every mole of nitrate decomposed to nitrite. This is consistent with the amount of O₂ released during the melting of the larger batch of waste loaded glass, suggesting that before full decomposition of the nitrates, some nitrite compounds were formed within the calcine which then went on to decompose or incorporate within the glass melt at a later stage. As an offgas product, NO is also a problem due to the difficulty of scrubbing the offgas and the insolubility of NO in water which is commonly used to remove the NO_x products from the system.

In conclusion, FT-IR and thermal analysis have highlighted the extent of the presence of nitrates within the calcined waste. More complete denitration of the calcine would be beneficial since this would avoid the evolution of problematic nitrous oxides in the melter, and also the extraction of heat from the glass melt to effect denitration *in situ* which is accompanied by a drop in the melt temperature.

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