

Novel glass formulations for post-operational clean out of highly active storage tanks

Hannah Paterson and **Clive Brigden** describe the future high level waste vitrification challenges at Sellafield and results from R&D programmes to develop novel glass formulations

Sellafield Ltd has a long history of reprocessing nuclear fuel from both UK nuclear reactors and for overseas customers. During reprocessing uranium and plutonium are recovered from spent irradiated fuel to recycle into new fuel. The remaining fission products are immobilised into a stable glass matrix in the waste vitrification plant (WVP) at Sellafield for long term storage.

Over the next four years Sellafield Ltd will cease reprocessing nuclear fuel. This represents a major change in the mission of Sellafield, shifting the site focus from reprocessing operations to site remediation. Reprocessing and waste storage plants will enter a post operational clean out (POCO) phase to remove the radioactive inventory and prepare for future decommissioning.

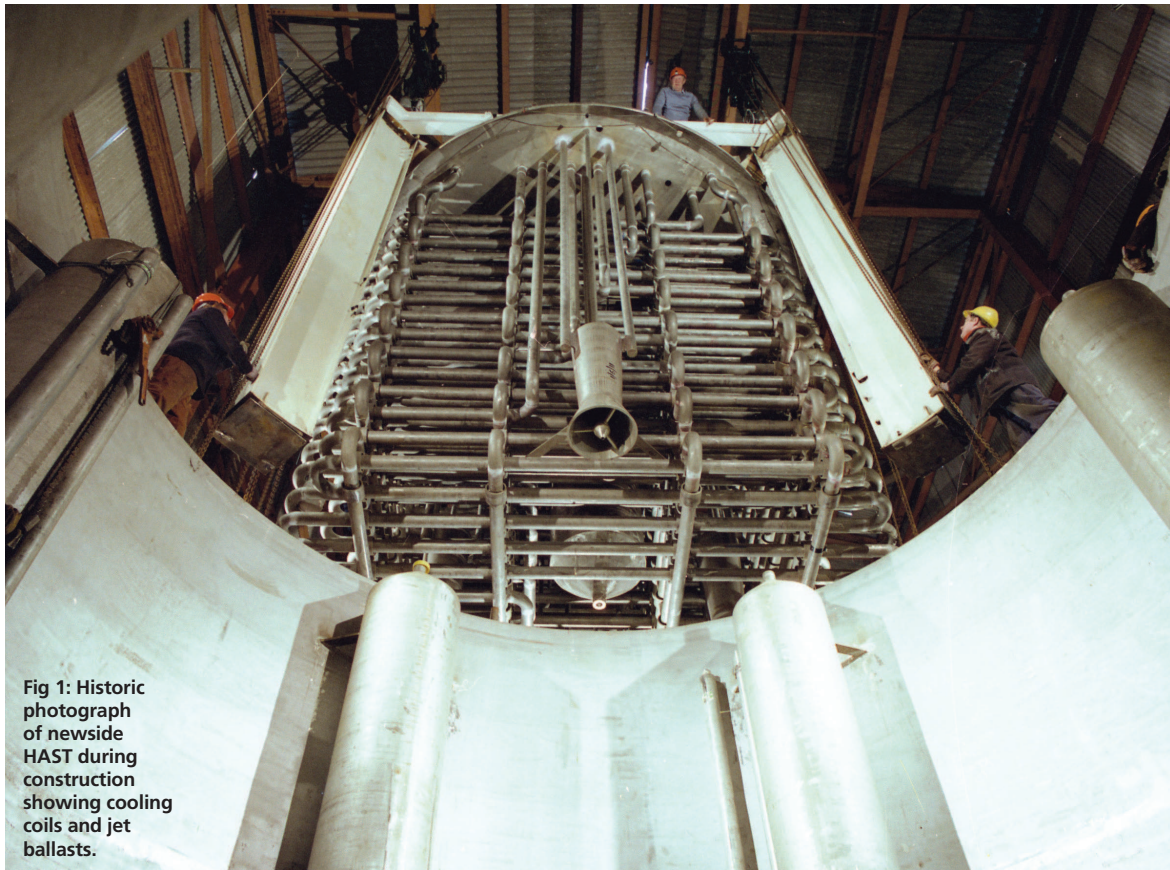


Fig 1: Historic photograph of newside HAST during construction showing cooling coils and jet ballasts.

POCO feeds to WVP are expected to differ greatly from the current feed due to the chemical species that have formed in the storage tanks over time.

A large collaborative programme of work has been undertaken at Sellafield to understand the challenges POCO waste streams will bring to WVP and to create new novel glass frit compositions which can incorporate expected POCO feeds.

Highly active liquor generation and storage

During reprocessing, the fuel is dissolved in nitric acid and the uranium and plutonium are extracted for re-use. The remaining nitric acid based liquor, known as highly active liquor (HAL) is sent to the highly active liquor evaporation and storage (HALES) plant where it is concentrated and stored in 21 stainless steel highly active storage tanks (HASTs).

This concentrated waste contains the majority of the spent fuel fission products and is highly radioactive and heat generating, with typical activities of the order of 2×10^{10} Bq/ml.

Eight oldside type HASTs were constructed in the 1950s. These were the first generation tanks each containing cooling coils. These tanks have not been used to receive HAL for many decades and, as they do not contain agitation systems, HAL solids have accumulated at the base of the tanks. As reprocessing increased in scale, a second generation of tanks were constructed (see Fig 1).

These newside type tanks are almost three times the volume of the oldside tanks with improved cooling capacity and in-built agitation. Each newside tank contains seven jet ballasts and four airlifts to mix the HAL and reduce build-up of precipitates. The airlifts and jet ballasts also mix the tanks' contents before liquor transfers to produce a homogenous feed for WVP. Both types of tank cool the HAL to below 60°C to reduce corrosion rates in the HASTs.

High level waste vitrification

The HAL from HALES is transferred to the WVP where the liquors undergo evaporation followed by denitration in a rotating furnace called a calciner to produce a granulated product.

The granules are mixed with a borosilicate glass frit, heated in a melter and poured into stainless steel containers and left to cool before being sealed and decontaminated (see Fig. 2). The process ensures the radioactive isotopes are chemically bonded into the glass matrix forming a stable and durable wasteform suitable for future disposal. The three production lines began operation in 1990, 1991 and 2002, respectively, and have produced over 6500 vitrified product containers to date.

The vitrified product containers are stored in the passively cooled vitrified product store at Sellafield awaiting final disposal at a future UK geological disposal facility. Over 700 vitrified product containers have been sent to overseas customers as part of an agreement to return the radioactive wastes generated from Sellafield reprocessing to the originators of the spent nuclear fuel.

The post operational clean out challenge

Sellafield's thermal oxide reprocessing plant (THORP) is scheduled to close by the end of 2018 and Magnox reprocessing is due to finish by

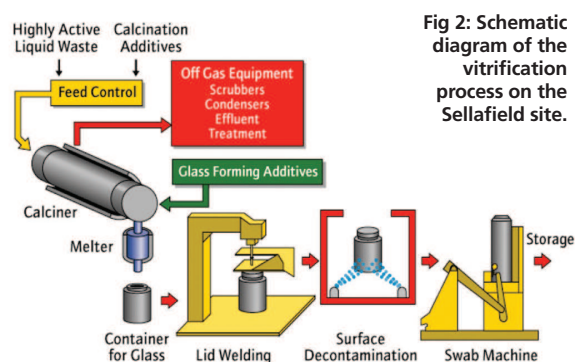


Fig 2: Schematic diagram of the vitrification process on the Sellafield site.

the end of 2020 [1]. The reprocessing plants will enter a POCO phase to remove the radioactive inventory and will generate a dilute feed as reprocessing ceases and the process vessels are washed out.

Once the dilute feeds have been processed through HALES and WVP, HALES will enter a POCO phase.

This will bring a unique chemistry challenge to the vitrification plant. Most notably, all the HASTs in HALES, which have stored the highly active acidic waste liquors since the 1950s, will require emptying. The HASTs are expected to contain large volumes of formed and settled solids, particularly at the base of the tanks which have built up over many decades. Solids are expected to be predominantly barium/strontium/aluminium/magnesium nitrates, caesium phosphomolybdate ($\text{Cs}_3\text{PMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$) and zirconium molybdate ($\text{ZrMo}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$).

The POCO feeds containing high levels of solids will need to be re-suspended and transferred from HALES to WVP to be incorporated into the vitrified product.

This poses a unique challenge as the alkali borosilicate base glass 'mixture windscale' which is currently used in WVP can only incorporate limited quantities of molybdenum of approximately 3 wt% MoO_3 in the final product glass.

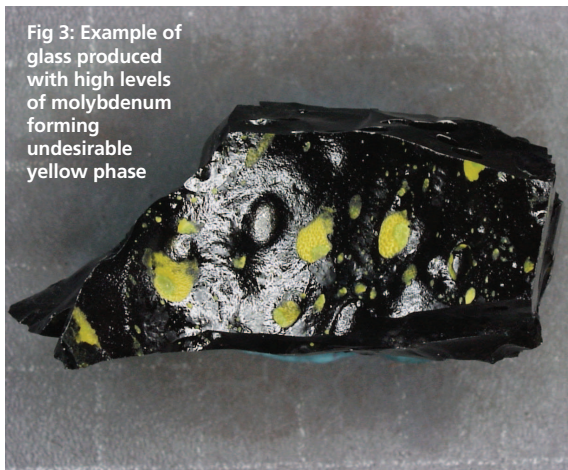
In excess, molybdenum forms an undesirable secondary phase in the glass product called 'yellow phase', shown in Fig. 3. Yellow phase is composed of a mixture of alkali metal, alkaline earth and rare earth molybdates as well as small quantities of chromates and sulphates. Several of these components are water soluble, which reduces the chemical durability of the glass, and are corrosive to the melter, thereby affecting the remnant life of WVP.

Calcium/Zinc Glass for POCO of new side tanks

As newside HASTs contain agitation and mixing systems, molybdenum precipitate settling is not expected to be as prominent as in the oldside tanks. Therefore, to remove the new side inventory the current strategy is to wash the tanks with either concentrated nitric acid or water to remove the HAST contents.

To enable increased molybdenum incorporation, Sellafield Ltd has developed an alternative base glass formulation for vitrifying high molybdenum bearing POCO wastes. This new glass will mean that over 300 less vitrified product containers will be produced providing

Fig 3: Example of glass produced with high levels of molybdenum forming undesirable yellow phase



an estimated saving of over £55 million.

Resulting from many years of research and development, this new base glass formulation called 'Ca/Zn' is based upon the currently used mixture windscale base glass with increased levels of CaO, ZnO and Al_2O_3 and a corresponding reduction in SiO_2 . The addition of calcium in the new Ca/Zn glass formulation enables a stable durable calcium molybdate phase to form in the glass matrix, in preference to yellow phase.

Following successful laboratory trials, in 2013 the new Ca/Zn base glass formulation was developed and manufactured at large scale. In 2014-2015 a full scale trial was performed on the vitrification test rig on the Sellafield site. The vitrification test rig is a full scale replica of one of the WVP process lines consisting of a full scale calciner, melter and off-gas system as shown in Fig 4. The rig has operated since 2004 using an inactive feed simulant representative of the active HAL processed in WVP.

The full scale experiments on the vitrification test rig defined the WVP operating parameters required to process the Ca/Zn glass with current HAL feeds and predicted feeds which will arise from HALES POCO operations. A number of product containers were produced on the rig, and the vitrified product was consequently tested which confirmed that the glass product durability and long term stability were within acceptable limits. The new Ca/Zn glass has enabled the incorporation of molybdenum to increase to over 6.5 wt%.

Ca/Zn glass frit was successfully implemented on the plant in March 2017 and Sellafield Ltd is producing Ca/Zn glass product. This has prepared WVP for POCO feeds well in advance of the POCO programme and represents a significant cross-discipline collaborative effort between the National Nuclear Laboratory and Sellafield Ltd.

Low sodium glass for POCO of oldside tanks

The historic oldside tanks have no agitation systems and as such will contain higher levels of settled molybdenum solids. The current POCO plan involves the removal of these oldside solids after the newside tanks have been emptied.

Detailed programmes of work have identified that the most

feasible option to remove the bank of solids in the oldside tanks is via chemical dissolution. A selection of wash reagents have been selected as suitable for dissolving these solids, including sodium carbonate.

All reagents have different solubility limits and solid dissolution rates, in addition to both forming secondary solids. Large volumes of wash reagent will be required to dissolve the substantial quantities of solids in the oldside tanks, and this will invariably have an impact on the chemistry of the resulting POCO wastestream.

In the event that sodium carbonate is used as a wash reagent, a much higher level of sodium will be present in the waste stream than is currently processed. In the current mixture windscale glass, the practical sodium loading limit is around 5 wt% Na_2O arising from the waste. Above these levels, phase separation tends to occur. A new base glass will be required which will allow for both increased incorporation of sodium as well as increased molybdenum.

A three year Innovate-UK funded project entitled 'Immobilisation challenges with POCO residues' was initiated in May 2015 to enable a collaborative approach to the issue of processing high sodium and molybdenum containing feeds. Alongside Sellafield Ltd, the project partners are NNL, University of Sheffield and Cera Dynamics Ltd.

The aim of this collaborative programme is to develop a new glass formulation that can be used to immobilise feeds containing high sodium and molybdenum. Removing all alkali metals (sodium and lithium) from the current mixture windscale or Ca/Zn glasses is not a viable option due to challenges manufacturing the glass frit and processing the resulting higher melting point glass. Therefore, in order to maximise the amount of waste sodium that can be incorporated in the product glass, the concentration of sodium in the base glass has to be minimised.

There are a handful of glass compositions around the world which can incorporate high levels of sodium.

High-level waste glasses currently used in Europe all have similar sodium loadings of ~10-15 wt% Na_2O however, the 'American Hanford' low activity waste glass [2] and the 'Defence Waste Processing Facility' high-level waste glass [3] are reported to incorporate up to 24 wt% total sodium.

Titanium containing glasses, such as the high-level waste advanced vitrification system glass used in India [4-5] have shown similarly high incorporations [6]. Although not a primary glass former, titanium can be combined with other network formers in substantial quantities [7]. The lower metal-oxygen bond strength of TiO_2 can lower the fusion temperature and viscosity of the system [8].

Due to the promising sodium loadings of titanium containing glasses, these were chosen as a target for the Innovate UK project. Two main base glass compositions have been explored (in mol%):

Series 1 – $33.3\text{Na}_2\text{O}-(33.3-x)\text{TiO}_2-x\text{M}_2\text{O}_3-33.3\text{SiO}_2^*$
Series 2 – $40.0\text{Na}_2\text{O}-(30.0-x)\text{TiO}_2-x\text{M}_2\text{O}_3-30.0\text{SiO}_2^*$
(M = aluminium (Al) or boron (B) x = 2.5, 10 or 15)
*Glass composition prior to zirconium and molybdenum loading

Partial substitution of titania (TiO_2) by alumina (Al_2O_3) was investigated to try to improve durability; substitution by boron oxide



Fig 4:
Photograph
of the
vitrification
test rig
showing the
full scale
calciner

(B_2O_3) was investigated to reduce formation of undesirable phases.

The experimental strategy has involved the development of base glass (the formulation to which the waste is added) and full product glasses (the final formulation once the base glass has incorporated the waste) in tandem. The total sodium fraction in the series 1 and 2 glass formulations was reduced by between 25-75 % which allowed this fraction of the sodium to be added via the waste.

The effect of substituting the sodium fraction in the base glass for lithium or potassium and introducing calcium was also investigated however, did not appear to improve the glass product. This was to attempt to reduce the formation of sodium molybdate (Na_2MoO_4), which is highly water soluble.

Full product version glasses were either prepared in a single step using batched precursor reagents of all the final components or by the introduction of a simple simulated waste stream comprising molybdenum trioxide (MoO_3), sodium carbonate (Na_2CO_3) and zirconium dioxide (ZrO_2) to the base glass using an effective Na_2O :

MoO_3 molar ratio of 5: 1 and 10: 1, and a MoO_3 : ZrO_2 molar ratio of 2: 1. All initial fabrication temperatures were 1050 °C and samples were annealed at 470 °C for 6 hours.

Results show a definite effect of both aluminium and boron in the samples. In the aluminium-containing full product samples, the corresponding alkali molybdates were detected in virtually all cases and the temperature at which the glasses readily poured also increased. Significant phase separation of sodium molybdate was observed even at lower molybdenum contents (see Table 1). This phenomenon, known as liquid-liquid phase separation involves liquid sodium molybdate separating and solidifying separately from the main glass.

The phase separation is very significantly suppressed by boron. This is thought to arise due to the reduced availability of sodium, which is charge balancing the $[BO_4]^-$ units [9-10] in the glass structure. The addition of boron was also shown to lower the processing and pour temperatures.

Series 1					Series 2	
Target MoO ₃ content/wt%	Al ₂ O ₃		B ₂ O ₃		Target MoO ₃ content/wt%	B ₂ O ₃
	x=2.5	x=10	x=10	x=15		
3.4	19	6	Nil	Nil	3.8	Nil
6.4	62	-	Nil	Nil	7.4	Nil
7.4	-	-	5	Nil	8.8	<1
9	85	100	31	3	10.7	16

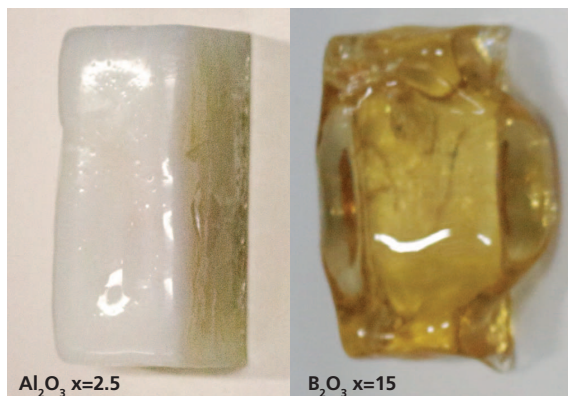
Table 1: % separation of sodium molybdate on pouring in series 1 and 2 glasses

The colour and opacity of the aluminium and boron containing glasses are remarkably different as shown by comparing samples with similar molybdenum contents of ~3.4 wt% in Fig. 5. Aluminium containing glasses appear opaque due to the finely dispersed micro-crystallites of separated sodium molybdate in the sample, as confirmed by microscopy analysis. At larger concentrations this phase is detectable by X-ray diffraction.

To assess chemical durability, ASTM product consistency tests method B [11] were carried out using deionised water at 90 °C with a surface area to volume ratio of ~2,000 m⁻¹.

Fig. 6 shows the results from seven day product consistency tests results for a group of series 1 product glasses. Negligible or no phase separation was found in these samples. Results show that at ≥ 10 mol% B₂O₃ the boron leachability increases and at 15 mol% durability is dramatically lowered. Leaching results for below 10 mol% B₂O₃ content all look fairly constant and formulations 1a-1c are of the same order as leaching levels from mixture windscale and Ca/Zn glass (see Fig.6) [12]. The apparent good durability is encouraging, particularly as high pH levels were recorded in the leachates of between 12.4 and 12.8. Titania in the glass network could be acting

Fig 5: Photos of series 1 glasses.



to increase the durability as it is highly insoluble at high pH.

Sample compositions 1.b and 1.c were selected as the most promising glasses as they contain both low levels of aluminium (which improves durability) and also exhibit low leaching results as shown in Fig.6. These new glasses have been successfully manufactured on the tonne scale at Cera Dynamics Ltd.

Further base glass plus simulated waste combination trials are currently underway using these two formulations to produce full product glasses. The effect of increased molybdenum loadings and the tolerance to high levels of the other solids expected to be seen in the tanks such as caesium phosphomolybdate and metal nitrates is also under investigation.

Durability tests will be conducted on the resulting product glasses. These glasses will allow increased sodium incorporation from the waste from 5 to 15 wt% giving a threefold increase in the incorporation of sodium compared to the Ca/Zn or mixture windscale glasses.

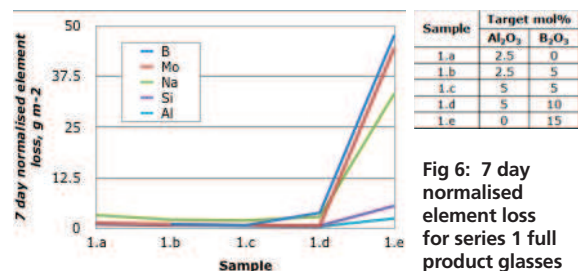


Fig 6: 7 day normalised element loss for series 1 full product glasses

Figure notes

1. target mol% Al₂O₃ and B₂O₃ is before waste substitution.
2. The seven day normalised release is calculated based on measured glass oxide concentrations.

Conclusion

Over the next four years reprocessing will cease at Sellafield.

Once the remaining reprocessing HAL stocks have been processed, the HALES plant will enter a POCO phase that will produce a washout feed containing high levels of molybdenum solids. A new glass formulation 'Ca/Zn' has been successfully developed, manufactured and implemented on the active vitrification plant in preparation for HALES POCO activities.

Ca/Zn glass allows for increased molybdenum loadings of >6.5 wt% compared to the 3 wt% achievable in the current mixture windscale glass. This will substantially reduce the number of vitrified containers produced from POCO wastes offering significant savings to the UK tax payer and acceleration of the HAL remediation programme.

In addition, a novel glass is under development for use with oldside liquors that could enable a threefold increase in the concentration of sodium that can be incorporated from a potential chemical washout waste feed, while also incorporating high molybdenum.

Acknowledgements

We would like to acknowledge and thank NNL, Cera Dynamics Ltd and Russell Hand and Lisa Hollands at The University of Sheffield for their contribution to the Innovate UK project and/or Ca/Zn experimental work. We would also like to acknowledge the use of the MIDAS facility and give special thanks to Katy Spencer and Michael Ingrams in Operations Technical at Sellafield Ltd and Mike Harrison Technology Manager at NNL, for their contributions to this paper. Copyright © by WM Symposia. All Rights Reserved. Reprinted with permission

Abbreviations

Highly active liquor (HAL)

Highly active liquor and storage plant (HALES)

Highly active storage tank (HAST)

National Nuclear Laboratory (NNL)

Post operational clean out (POCO)

Waste vitrification plant (WVP)

About the authors



Hannah Paterson

Hannah Paterson is a technical advisor for the High Level Waste Plants at Sellafield. She previously worked at the US Department of Energy, Office of Environmental Management and in the Scottish Government as a Decommissioning and Radioactive Waste Policy Advisor.



Clive Brigden

Clive Brigden is an inorganic and materials chemist with research experience in glass and ceramics. He is currently a postdoctoral research associate at the University of Sheffield working on the Innovate UK project 'Immobilisation challenges with POCO residues'.

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