Novel Glass Formulations for Post Operational Clean Out of Highly Active Storage Tanks - 17596

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ABSTRACT

The UK has a successful history of reprocessing nuclear fuel from both UK nuclear reactors and for overseas customers. Highly Active Liquor (HAL), a waste product from reprocessing, is stored in stainless steel tanks before being incorporated into a stable glass matrix in one of three vitrification lines at Sellafield. Over the next 4 years Sellafield Ltd will cease reprocessing nuclear fuel, and the reprocessing plants and storage tanks will enter a Post Operational Clean Out (POCO) phase to remove the radioactive inventory and prepare for future decommissioning. POCO feeds are expected to differ greatly from current HAL, and will contain high levels of molybdenum solids.

This paper, and subsequent poster presentation, introduces the vitrification challenges expected with processing POCO wastestreams. The main challenge is the transfer and processing of high molybdenum containing solids. Details of the application of new glasses onto the active vitrification plant will also be included.

INTRODUCTION

Reprocessing operations generate a nitric acid based wastestream which contains the vast majority of fission products from spent fuel. HAL is sent to the High Active Liquor Evaporation and Storage plant (HALES) where it is concentrated and stored in 21 Highly Active Storage Tanks (HASTs). The waste in the HASTs is highly radioactive and heat generating, with dose rates upwards of 1 kGy/hr (gamma). Two types of HASTs exist to contain the HAL; Oldside and Newside HASTs as shown in Figure 1.

Eight old-side type HASTs with a working HAL volume of 50 m^3 were constructed in the 1950s. These were the first generation tanks, each containing an evaporator vessel and a series of cooling coils. These tanks have not been used to receive HAL for many decades. As reprocessing increased in scale, a second generation of tanks were constructed. These Newside type tanks have an increased working volume of 140 m^3, 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. Both types of tanks cool the HAL to below 60 ^{o}C to reduce corrosion rates in the HASTs.

a) b)

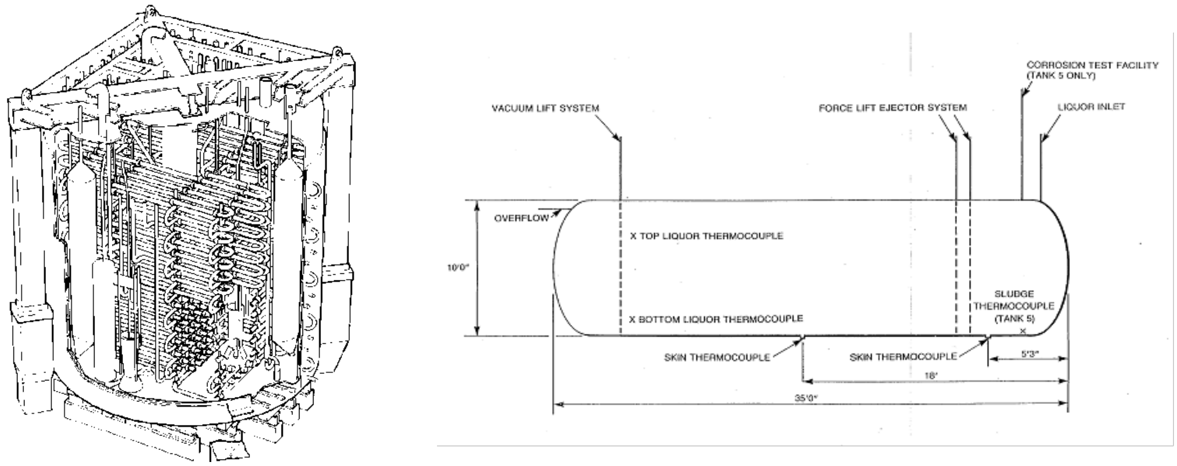

Figure 1: a) Newside and b) Oldside Highly Active Storage Tanks.

Sellafield Ltd's Waste Vitrification Plant (WVP) immobilises HAL from the HASTs into a stable borosilicate glass matrix through three vitrification lines. This glass form can be safely stored in the passively cooled Vitrification Product Store (VPS) before final disposal at a future Geological Disposal Facility or exportation to overseas customers.

In WVP, HAL is fed through a rotating furnace (calciner) with the addition of process additives; it is a two-step process of evaporation and denitration as shown in Figure 2. The calcine created from this process is fed into the melter with glass frit and once the desired properties are met, the glass is poured into a stainless steel product container. Once cooled, the container is sealed and the surface decontaminated and swabbed before the container is taken to the VPS for interim storage. Ultimately, the vitrified waste will be transferred to a future UK Geological Disposal Facility (GDF) for permanent disposal.

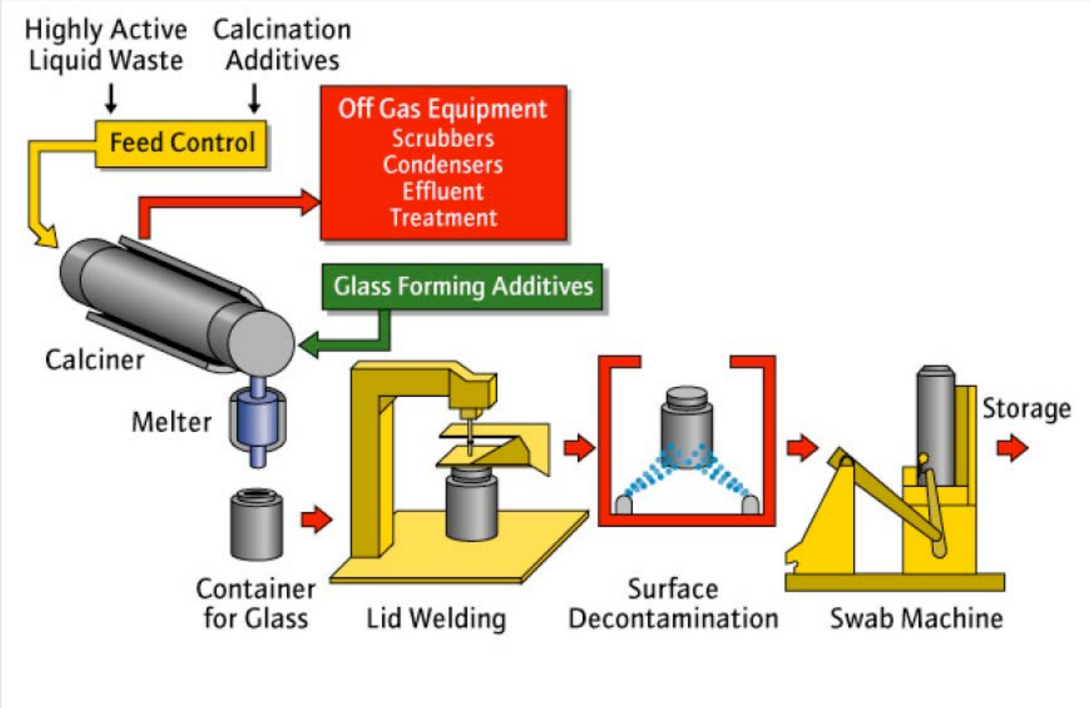

Figure 2: WVP Process Overview.

The Post Operational Clean Out Challenge

Over the next 4 years Sellafield Ltd will cease reprocessing nuclear fuel and the reprocessing plants and the HALES plant will enter a Post Operational Clean Out phase (POCO) to prepare for decommissioning [1]. POCO is an important part of the transition from operations to decommissioning, involving hazard reduction activities (e.g. removal of operational material and waste) that are undertaken immediately after cessation of operations.

The end of reprocessing and onset of POCO brings unique chemistry challenges to the vitrification plant. Most notably, the HASTs in HALES, which have stored the highly active acidic waste liquors since the 1950's, will require emptying.

The HASTs are expected to contain large volumes of formed and settled solids which will be predominantly barium/strontium/aluminium/magnesium nitrates, caesium phosphomolybdate ($Cs_3PMo_{12}O_{40}.14H_2O$) and zirconium molybdate ($ZrMo2O7(OH)_2.2H_2O$). Oldside HASTs have no agitation systems; therefore a larger build-up of solids is expected in these tanks. Future POCO feeds containing high levels of solids will need to be incorporated into the vitrified product. The total mass of all solids is estimated to be around 28,000 kg.

There is currently limited direct sampling in the HASTs. In the oldside HAST there is no way to directly sample the liquor. Current understanding is based upon historic knowledge of tank inventory and the use of modelling combined with an understanding of the tank chemistry. A large programme of work is underway to characterize and model the inventory in the HAST tanks.

Current alkali borosilicate glass can only incorporate limited quantities of molybdenum and sodium (from the solids dissolution reagent). Sellafield Ltd has been investigating alternative glass formulations for high molybdate bearing POCO wastes. This will reduce the number of vitrified product canisters produced, and provide a significant saving to the UK taxpayer. The remainder of this paper will discuss the programmes of work being undertaken to create new glass frit compositions which can incorporate expected POCO feeds.

DISCUSSION

Calcium / Zinc Glass for POCO of Newside Tanks

Newside HASTs are expected to contain a high concentration of molybdenum. As Newside solids contain mixing systems, precipitate build up is not expected to be as prominent as in the Oldside tanks. Therefore, to remove the HAST inventory the current strategy is to wash the tanks with concentrated nitric acid and water to remove the HAST contents.

The current glass used in WVP, 'MW glass', has a limited molybdenum solubility of approximately 3%w/w MoO_3. In excess, molybdenum forms an undesirable secondary phase in the glass product called 'yellow phase'. Yellow phase is composed of a variety of metal nitrates including lithium, caesium and strontium nitrates as well as mixtures of chromates and sulphates. These components are water soluble affecting the chemical durability of the glass and corrosive affecting the remnant life of WVP.

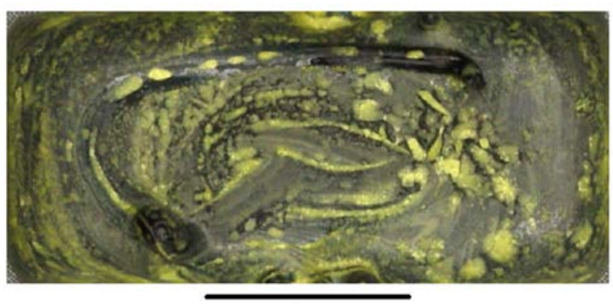

Figure 3: Yellow phase formation in a glass sample.

To enable increased molybdenum incorporation, a new glass formulation has been developed, resulting from many years of research and development at Sellafield Ltd. The glass, titled 'Ca/Zn glass' is based upon the current MW glass with the addition of calcium, aluminium and zinc as shown in Table I.

TABLE I. Composition of MW glass and Ca/Zn Glass.

	'MW' Glass		'Ca/Zn' Glass	
Oxide	Weight %	Mole %	Weight %	Mole %
B_2O_3	22.4	19.0	23.4	20.6
Li_2O	5.3	10.5	4.2	8.6
Na_2O	11.1	10.5	8.6	8.5
SiO_2	61.2	60.0	47.6	48.7
Al_2O_3	-	-	4.2	2.5
CaO	-	-	6.0	6.6
ZnO	-	-	6.0	4.5
Total	100.0	100.0	100.0	100.0

The addition of Caesium in the new Ca/Zn glass formulation enables stable calcium molybdate crystals to form in the glass matrix, in preference to yellow phase. The new Ca/Zn glass has enabled the incorporation of molybdenum to increase to at least 6.5%w/w.

The POCO strategy is still under development and it is anticipated that POCO feeds could range from high molybdenum and zirconium feeds through to feeds that are very similar to feeds currently being processed [2]. Therefore the new Ca/Zn glass needs to be qualified for use on WVP using typical feeds currently being processed, as well as feeds containing significant quantities of POCO material.

Following successful laboratory trials, in 2013 the new Ca/Zn glass formulation was manufactured at large scale. In 2014-2015 a full scale inactive trial was performed on the Vitrification Test Rig (VTR) on the Sellafield site to assess the new glass composition with anticipated POCO feeds and current feeds.

The VTR is a full scale rig which operates using an inactive feed simulant representative of the active HAL processed in WVP. It has operated since 2004 with the research aim of underpinning improvements to the vitrification process and to widen the process envelope. The rig consists of a full scale calciner, melter and off-gas system. Figure 4 shows a photograph of the Vitrification Test Rig.

The full scale experiments on the Vitrification Test Rig defined the operating conditions required to utilise the Ca/Zn glass with current HAL feeds and predicted feeds which will arise from POCO operations. A number of product containers were produced on the rig, as well as at laboratory scale, and the vitrified product was consequently tested to determine its durability and long term stability.

Figure 4: Photograph of the Vitrification Test Rig.

High Sodium Glass for POCO of Oldside Tanks

The historic Oldside tanks have no agitation systems and as such will contain high levels of settled molybdenum solids. Detailed programs of work have identified that the most feasible option is to remove the solids via chemical dissolution. Two wash reagents have been selected as suitable for dissolving these solids; sodium carbonate and ammonium carbamate.

Both 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. Work is continuing to identify advantages and disadvantages of each reagent before a washout strategy is formed.

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 borosilicate glass, sodium arising in the waste has a limited loading of around 5%w/w Na_2O. Above these levels, due to the necessary presence of alkali in the base glass, phase separation occurs. A new base glass will be required which will allow for both increased incorporation of sodium as well as increased molybdenum.

A three year project titled 'Immobilisation challenges with POCO residues' was set up in May 2015 with funding from Innovate UK to enable a collaborative approach to the problem of processing high sodium and molybdenum containing feeds. Alongside Sellafield Ltd, project partners are NNL, University of Sheffield and Cera Dynamics Ltd.

The aim of this collaborative research programme is to develop and underpin a glass formulation that can be used to immobilise feeds containing high sodium and molybdenum. Removing all alkali metals (sodium and lithium) from the current MW glass is not a viable option as the glass melting point and viscosity become unmanageable within current plant operating equipment.

The initial stage of work involved reviewing candidate glass compositions which can incorporate higher waste loadings, such as Hanford Low Activity Waste glass, sodium titanosilicate and sodium aluminium phosphate glasses. The most promising glass family identified for WVP was the sodium titanosilicates.

A variety of glass samples have been created through alternating the weight percent of Al_2O_3, CaO, Li_2O, K_2O and B_2O_3. Glass frit has been melted with ZrO_2 and MoO_3 to simulate a waste feed containing zirconium molybdate (ZM) solids. Over 150 individual samples have been created to date. Samples were inspected visually to determine if undesirable qualities existed, such as phase separation and unincorporated material, voids or cracks. If any of these were present glass compositions were determine unsuitable.

An example of the glass compositions created in early trials is shown in Table II. RP75SB_ZM1 had a 2.37%w/w ZM simulant added as a waste and RP75SB_ZM2 had 4.74 %w/w ZM simulant added.

TABLE II. Glass Compositions for Low Soda Glass

	Glass Trial	
	RP75SB_ZM1	**RP75SB_ZM2**
	Weight %	**Weight %**
Na_2O	29.32	28.61
TiO_2	34.92	34.07
Al_2O_3	3.68	3.59
SiO_2	28.42	27.73
CaO	1.29	1.26
MoO_3	1.66	3.32
ZrO_2	0.71	1.42
Total	100.00	100.00

Figure 5 shows photographs of the glass ingots. At the higher waste loading of ZM the glass appears opaque. This is thought to arise due to finely dispersed microcrystalline Na_2MoO_4 in the glass matrix and develops upon pouring and cooling of the glass.

a) b) c)

Figure 5: a) Photograph of 50g sample of glass RP75SB_ZM1 with 2.37%w/w ZM simulant, b) Photograph of 50g sample of RP75SB_ZM2 with 4.74 %w/w ZM added, c) Large scale (500g) batch of RP75SB_ZM2

Initial trials of small scale glass samples have shown that reduced (e.g. 50%) soda versions of these sodium titanosilicate glasses can incorporate large quantities of a high sodium ZM-based waste stream. This programme is currently ongoing to investigate further the microstructure of the acceptable sodium titanosilicate glasses and determine incorporation limits of Oldside wash out liquors.

CONCLUSION

Within 4 years the reprocessing plants and the Highly Active Liquor Evaporation and Storage (HALES) plant at Sellafield will enter a Post Operational Clean Out (POCO) phase which will produce a washout feed containing high levels of molybdenum solids. A new glass formulation ‘Ca/Zn glass’ has shown increased molybdenum loadings of >6.5%w/w compared to the 3%w/w currently achievable with base glass. This glass is currently being implemented for use on the Waste Vitrification Plant (WVP) at Sellafield. In addition, a novel glass is under development for use with Oldside liquors which will enable a larger concentration of sodium to be incorporated from the feed. Implementation of these novel glass formulations will represent a large reduction in the number of vitrified product containers to be produced from POCO wastes offering significant savings to the UK tax payer and acceleration of the Highly Active Liquor (HAL) remediation programme.

REFERENCES

1. *“Nuclear Decommissioning Authority Strategy”*, Nuclear Decommissioning Authority, March 2016

2. Thomson, S. “*Progress in defining the UK Highly Active Storage Tanks POCO Strategy*”, Waste Management 2016 Conference, March 6 – 10 March 2016, Phoenix, Arizona, USA.

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