

Recent Progress in the Understanding of UK Highly Active Liquor Chemistry and Properties – 17144

Steven Thomson*, Tracy Ward*, Barbara Dunnett*, Rachel Roberts*
Jonathan Cheesewright**

* UK National Nuclear Laboratory

** Sellafield Ltd

ABSTRACT

In the UK Highly Active Liquor (HAL) waste is stored in stainless steel tanks prior to encapsulation in glass in one of three lines in the Waste Vitrification Plant (WVP). The chemistry and physical properties of HAL from the historic and ongoing UK reprocessing operations is well understood, following years of operations and associated research and development programmes using primarily non-active simulants. However the imminent progression to POCO of the Highly Active Storage Tanks (HASTs), where the HAL is stored, requires a more in-depth understanding of the properties of the HAL, in particular the solid phases that are known to exist. Changes in operations are expected (Ref. 1), including the addition of new chemical wash reagents, which will result in some fundamental changes to the chemistry in the HASTs. This paper will highlight some of the key findings from recent studies into areas such as solids formation and morphology, chemical dissolution and associated re-precipitation of solids, rheology modification and chemical conversion mechanisms.

INTRODUCTION

In the UK re-processing of used nuclear fuel has long been the favored strategy for fuel from the various civil Magnox, AGR and PWR reactors providing electricity to the national grid. As the existing reactor fleet reduces in size due to the retirement of ageing reactors the associated reprocessing plants are approaching the end of their operating lifetimes and no new reprocessing facilities are planned to process future used fuel arisings. As a result new HAL arisings, which result from concentrated aqueous raffinate fission product waste from the re-processing plants, are limited and the strategy for operating the facilities that currently process this waste is changing (Ref. 1).

The aforementioned HAL arisings are both generated and then processed into their final long-term waste forms at the Sellafield nuclear site, which is one of the most complicated nuclear sites in Europe and indeed the world. It was home to the first ever commercial nuclear reactor, Calder Hall, and has housed the UK used fuel reprocessing operations and associated waste treatment facilities over the last 50+ years. This has included early experimental technologies and more latterly established plants such as Magnox Reprocessing, Thermal Oxide Reprocessing (Thorp), Highly Active Liquor Evaporation and Storage (HALES) and (WVP). A variety of associated effluent and grout encapsulation plants are also located at Sellafield, alongside a number of fuel storage ponds, waste silos and miscellaneous support

facilities. In recent years the focus on the Sellafield site has changed from primarily reprocessing operations to a combination of reprocessing and decommissioning missions as focus increased on cleaning up some of the legacy facilities on the site. A number of the current operational plants are also approaching the end of their operational lifetime.

The HALES plant fulfils a central role at Sellafield as it processes the nitric acid based aqueous waste raffinates from both the Magnox and Thorp reprocessing plants, which contain the vast majority of the fission products from the spent fuel. The raffinates are concentrated in Highly Active (HA) evaporators to a pre-defined end point, producing HAL which is heat generating due to radioactive decay of many of its components. The HAL is stored in Highly Active Storage Tanks (HASTs), which are actively cooled, prior to onward processing in WVP where the waste is vitrified for long term storage. Early HALES operations were carried out in “old-side” HASTs, each equipped with their own small scale evaporator vessel. When scaled up operations were later required a new approach was adopted. Larger volume/throughput HA evaporators were built as were “new-side” HASTs with increased volume, cooling capacity and agitation capability which the old-side vessels did not contain. The HA evaporators and HASTs were built over a number of decades; including the present day as a new HA evaporator (Evaporator D) is currently nearing completion. A high level illustration of the HALES plant process was previously presented in Ref 1.

As is often the case when considering challenges within the nuclear industry the POCO and subsequent decommissioning of the HASTs presents a complex scenario. Used fuel reprocessing will continue in the medium term with the aspiration to simultaneously make progress in reducing the decommissioning challenge by optimising POCO operations within the same HA facility. Working alongside Sellafield Ltd plant operators NNL has provided multi-disciplinary research and development support in areas such as HA chemistry, nuclear physics, plant inspection (Ref. 2), waste characterisation, plant lifetime assessment (Ref. 3), process modelling, statistics and corrosion, to name but a few.

In recent years increased research into the chemistry and physical properties of HAL has been carried out into areas such as solids morphology, chemical dissolution and rheology modification. Re-precipitation of solids (following chemical dissolution) has also been investigated, as has further assessment of chemical conversion mechanisms and crystallization of solids from concentrated liquors, building on knowledge from previous studies. This paper will now provide an overview of the key aspects of new findings from recent studies, alongside the POCO strategy context (Ref. 1).

DESCRIPTION

HAL Chemistry – Historic Knowledge

The chemistry of HA liquors from the historical and ongoing UK reprocessing operations is well understood, following years of operations and associated research

and development programs. However reducing HAL stock volumes due to ongoing WVP operations consequently require the imminent progression to POCO of the HASTs, where the HA liquor is stored. This will result in some fundamental changes to the chemistry in these vessels. HA liquors are known to contain solids which, alongside the heat generating nature of the liquors, present the most significant challenges in handling and processing these wastes. The characteristics of these solids will change as a result of the POCO operations, and thus the way in which the HA wastes are treated will also change.

Current and historic HAL is a complex mixture of dissolved metal nitrates and a variety of solids such as cesium phosphomolybdate (CPM), zirconium molybdate (ZM), barium/strontium nitrate, zirconium hydrogen phosphate (ZHP) and magnesium lanthanide nitrates (MLN). The majority of these solids are dense and fast settling, with the exception of ZHP which is flocculent and slow settling in nature. The exact chemistry of HAL is dependent on a number of things, most importantly the source fuel from which it has been produced, and the burn-up and cooling of the fuel prior to reprocessing. For example, Magnox reprocessing results in high MLN concentrations, whereas THORP reprocessing results in HAL with low MLN concentrations but higher concentrations of barium/strontium nitrate and CPM. HAL is a nitric acid based waste and is maintained at a controlled acidity to help control the chemistry of the liquor and the solids it contains, and to mitigate against hydrogen formation. HAL is significantly heat generating and is actively cooled to reduce the corrosion rates in the HASTs and to prevent the potential release of volatile radioactive species.

The nature of the solids present in HAL is somewhat dynamic. Solids such as barium/strontium nitrate and MLN can dissolve or precipitate depending on the overall nitrate content of the liquor, thus they are not expected to present a significant issue during POCO as they can be dissolved and removed via simple water and dilute nitric acid washes. CPM, ZM and ZHP are not sufficiently soluble in water or nitric acid and hence they present a far more difficult problem to deal with. Importantly CPM is known to convert to ZM under normal HAST conditions. The kinetics of this conversion are controlled by a number of factors including acidity, concentration, temperature and agitation, however long HAL storage times result in complete conversion to ZM (Ref. 4). The formation of ZM is considered beneficial because, unlike CPM, it does not produce radiogenic heat from decay of its constituents and hence does not present the same hotspot risk when settled on the tank base. Hotspots can form at the bottom of HASTs and unless mitigated and removed can potentially present a corrosion risk if allowed to remain established for any period of time.

HAST Design Variations

The Sellafield HASTs are of two fundamentally different designs, incorporating vastly different operating capacities, vessel shapes, cooling capability and agitation systems. There are small number of old-side HASTs which each have a relatively small working volume of HAL, cooling coils and no installed agitation systems. The

new-side HASTs have a larger working HAL volume, a number of cooling coils and various configurations of cooling jackets. Each new-side tank also contains significant agitation capability via 7 installed jet ballasts and four airlifts. The jet ballasts are used to keep solids moving on the base of the HASTs, thus helping prevent hotspot formation, while the airlifts are used to thoroughly mix the tank contents prior to liquor transfers. Figure 1 shows photos of the old-side and new-side HASTs, respectively, during construction. If only new-side HASTs were present then the POCO challenge would be more straightforward as the installed agitation system could be used to transfer the bulk of the liquor from the tanks, including the more difficult solids such as CPM, ZM and ZHP that cannot be removed by simple water/acid dissolution. However a significant amount of HAL solids require to be removed from old-side tanks which have no agitation system installed. Following consideration of all possible options the favored approach for removing these solids is currently chemical dissolution and significant development work has been carried out to identify and test appropriate reagents.

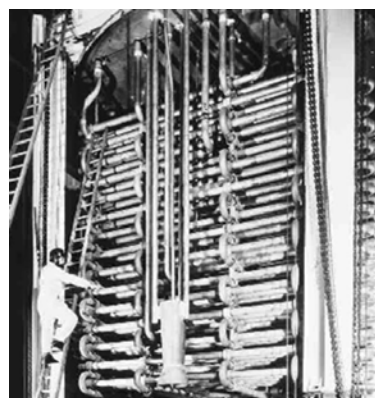
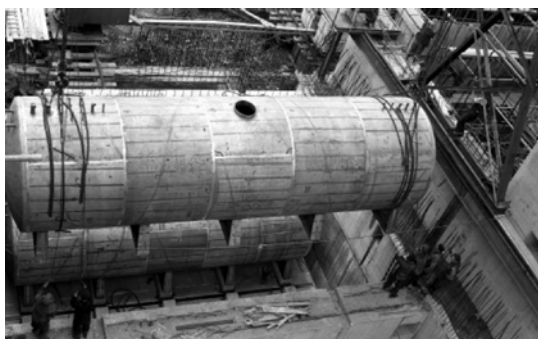


Fig. 1. Old-side (left) and New-side (right) HAST during construction

Chemical Dissolution Reagent Development

Reagent assessments began a number of years ago where a variety of options were initially considered and down-selected depending on operational constraints and overall effectiveness. A small number of viable options were quickly identified with two reagents emerging as front runners, which will be termed “reagent 1” and “reagent 2” hereafter. In recent years detailed programs of work have been carried out to evaluate the advantages and disadvantages of both reagents. The reagents are both alkaline in nature and this presents an issue as old-side HAST wash liquors will require re-acidification following transfer to the new-side tanks, prior to final processing through WVP to form a vitrified waste for final disposal. Key aspects such as solids properties and characterization, solid dissolution rates and solubility limits have been studied, as has the formation of secondary solids and the re-precipitation of solids on re-acidification in the new-side tanks. Work is still ongoing to answer some of the questions that remain, but significant advances in the understanding of both current HAL chemistry and the future impacts of POCO operations have been made.

Updated Knowledge – CPM to ZM Conversion

Targeted non-active laboratory studies and anecdotal observations on long stored HAL simulant solids have previously indicated that CPM [$\text{Cs}_3((\text{MoO}_3)_{12}\text{PO}_4) \cdot 14\text{H}_2\text{O}$] is capable of converting to ZM [$\text{Zr}(\text{Mo}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$] in the latter stages of HA evaporation and more significantly during storage in the Highly Active Storage Tanks (HASTs). Molybdenum heterocomplexes such as $[(\text{MoO}_3)_{12}\text{PO}_4]^{3-}$ will not form ZM without degradation. The conditions of molybdenum complex degradation are complicated and controlled by four factors: heat, acidity, radiation and time.

As acidity is reduced in the Water Acid Reduction (WAR) stage of the HA evaporation cycle, CPM will exist increasingly in equilibrium with simpler ions in solution. The combination of these simpler molybdate ions with zirconium species leads to zirconium molybdate precipitation. Evaporation trials indicate that CPM dominates initial precipitates but conversion to ZM will occur when favorable conditions (high temperature, low acidity and some agitation) prevail. Such conditions are not present until the latter stages of WAR (a brief period of time) or subsequent longer term HAST storage. Gradual conversion of CPM to ZM during HAST storage is hence anticipated. Conversion times differ significantly with conditions – when optimized, conversion can be achieved in only a few days.

For the Oldside HASTs, it is expected that all CPM which was once present will have converted into ZM, given the timescales and conditions of storage. However, this expectation was previously based on observations made on non-active simulants, and required confirmation in the presence of radiation and isotope decay. It is possible, during CPM to ZM conversion, that active medium to long-lived isotopes are incorporated into the ZM or subsequently absorbed into ZM or absorbed onto the surface. The presence of such species has the potential to significantly impact the heat inventory of the solids. Hence, the previous assumption that ZM is not active (active isotopes of Zr and Mo having short half-lives) may have been unrealistic. In order to alleviate such uncertainties an active study was carried out to determine if CPM to ZM conversion occurs in the presence of radiation, and whether any radioactive species are associated with the ZM.

Using real HAL samples taken from feed prepared for WVP, analysis was carried out to determine whether the conversion of CPM to ZM observed in non-active laboratory experiments had occurred in HAL. Investigation of whether any elements associate with the solid and whether they can be removed by simple washing, or are chemically/physically bound to the solids, was also carried out.

Examination of the analytical results for the solid phase in the HASTs indicated:

1. ZM was the dominant solid phase.
2. A small quantity of CPM was present, with ~83% of the CPM originally present converting to ZM. The remaining CPM was attributed to fresh HAL liquor arisings which had not had sufficient time to undergo conversion.
3. An additional zirconium phase considered to be Zr hydrogen phosphate (ZHP) was also present, which had been expected from previous non-active studies.

4. The possible presence of nitrate crystals *e.g.* $\text{Ba}(\text{NO}_3)_2$, either due to being present in the HAL or having formed during evaporation of liquor on storage of the HAL sample prior to analysis. Again the presence of $\text{Ba}(\text{NO}_3)_2$ is no surprise as it is known to form in previous non-active studies.
5. Tellurium may be associated with the ZM phase with only a small quantity (if any) being removed during washing with nitric acid. A very small quantity of antimony also appeared to be associated with ZM. No other elements were identified as being chemically or physically associated with ZM.

In summary the results showed that there was strong evidence to suggest that CPM does convert to ZM in the HAL during storage in the HASTs and tellurium is incorporated into the ZM. This is considered to be a significant step forward in knowledge as previously there has always been some uncertainty that the results of the detailed non-active studies may not be applicable to active liquors. This recent work has gone some way to eliminating this uncertainty and hence allowing more informed assessment and planning towards POCO operations to be carried out.

Updated Understanding of the Morphology of ZM in HAL

ZM is known to have widely varying morphology, with crystal growth being susceptible to interference by a range of elements in HAL and possible process additives, giving defects in the crystal structure. Examples of various morphologies are shown in Figure 2. Formation of ZM, via chemical conversion, from a simple mixture of CPM and Zr in nitric acid is found to yield cubic crystals. In the presence of other fission product elements in HAL solution (in particular tellurium), a slow settling “wheat-sheaf” morphology has been observed. With citric acid (not present normally in HAL), the product is a square section rod.

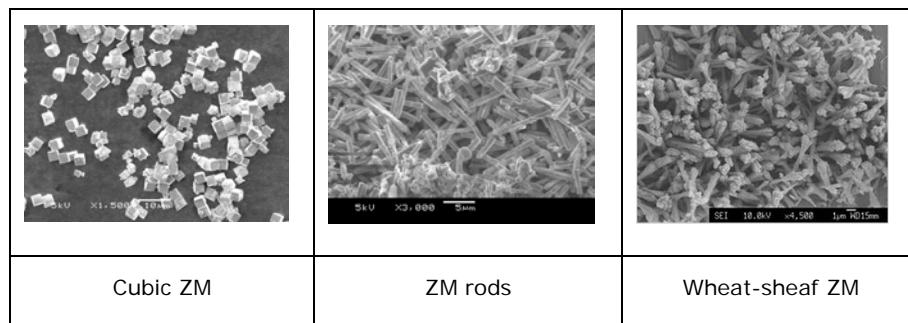


Fig. 2: SEM images showing examples of possible morphologies of ZM

In this context recent work has shown that rod and cuboidal morphologies have been observed when carrying out controlled CPM to ZM conversion in non-active HAL simulants, as shown in Figure 3.

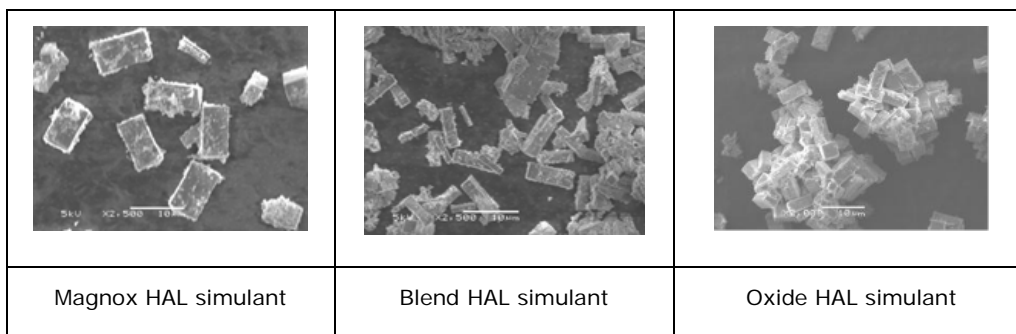


Fig. 3: ZM morphology observed for CPM to ZM conversion with HAL simulants

Following completion of historic HAL simulant chemical and physical property assessments various HAL simulants were stored in incubators at $\sim 50\text{ }^{\circ}\text{C}$ for extended periods of time. For one particular sample, originally containing predominantly CPM, the initial yellow solid (symbolic of the CPM) converted to a white/cream solid throughout its sediment layer, as shown in Figure 4. Whilst conversion of settled CPM solids in the compacted layer at the bottom of the bottle occurred slowly due to the overlying solids, these observations indicate that CPM will convert to ZM in un-agitated storage tanks. X-ray Diffraction (XRD) analysis confirmed the presence of ZM. Scanning Electron Microscopy (SEM) analysis, shown in Figure 4, indicated that the ZM did not exhibit a consistent morphology with a variety of morphological variations seen. This is likely to be due to the many elements present in the simulant influencing different crystal growth. All the particles were $<5\text{ }\mu\text{m}$ with the majority exhibiting an elongated morphology. Since this was observed with a chemically accurate HAL simulant it shows that consideration of the morphology of ZM is a complicated area and hence requires careful attention in the context of reagent dissolution during HALES POCO. This topic will be discussed further later in this paper.

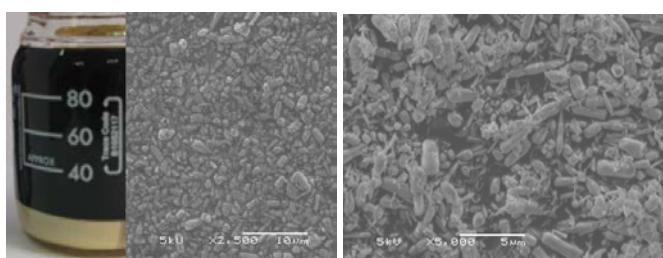


Fig. 4: HA simulant after storage at $\sim 50\text{ }^{\circ}\text{C}$ and SEM images of the solids present

CPM and ZM Dissolution Overview

Results have shown that both reagents 1 and 2 have different advantages and disadvantages such as in relation to varying solids dissolution rates, re-precipitation, by-products formed and the effect on the glass matrix used in the final vitrified waste form.

Significant research has been carried out into the mechanism of dissolution of CPM and ZM. Raman and NMR studies have indicated that CPM can be dissolved in alkaline solution through the hydrolysis of the large Keggin anion, $(\text{PMo}_{12}\text{O}_{40})^{3-}$ to give smaller, more soluble, phosphomolybdate, phosphate and molybdate anions. Provided enough base is present then the cluster anion will be broken up completely to form $[\text{MoO}_4]^{2-}$ and PO_4^{3-} . The rate of dissolution of ZM appears to depend on the formation of specific Zr^{IV} complexes in relation to the chemical nature of reagent 1 and reagent 2, resulting in reagent 2 being more effective. However, the overall solubility of the reagent in solution is also important and in turn this favors reagent 1, thus compensating somewhat for the chemical affect mentioned above.

Several studies have been undertaken to determine the solubility limits for CPM and ZM in reagent 1 and reagent 2 at laboratory ambient temperature, in order to provide comparable data for both wash reagents over a range of solution concentrations. The solubility of CPM and ZM in reagents 1 and 2 has recently been re-investigated, due to the variability of previous results, and this work has given a significantly improved understanding of the appropriate solubility limits. Experiments were undertaken where CPM and/or ZM were incrementally added to the reagent solutions, until the presence of solid in the solution was persistently observed. At this point the test was ended. It was anticipated that the concentration of CPM/ZM added to the solution prior to the final addition of CPM/ZM would be equivalent to the solubility limit.

However, the results were compared with the concentration of dissolved CPM/ZM determined by analysis of molybdenum content using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) as part of a parallel dissolution study. In the dissolution study, the molybdate solid was present in excess. The comparison indicated that the concentration of dissolved CPM/ZM based on analysis of the solution in the dissolution study was greater, sometimes significantly greater, than that determined by the observation of solids from incremental addition of CPM/ZM in the solubility study.

It was concluded that the undissolved solids observed in the solubility study were secondary solids. That is, the dissolution of a sufficient quantity of CPM/ZM results in a solution which is able to dissolve more CPM/ZM, but in doing so generates an additional, so called "secondary", solid. Hence the tests carried out using incremental addition of solids actually determined the concentration of CPM/ZM above which secondary solids will be present. The true solubility limit is greater than the concentration at which secondary solids form. This distinction was not recognized in earlier work with the variable results obtained being representative of the concentration at which secondary solids were observed. The solubility limits and concentration above which secondary solids form determined by the more recent work are therefore more accurate and useful in the ongoing development of HAST wash-out strategies.

The dissolution of ZM and CPM in reagents 1 and 2 has been investigated in a number of studies. Initial results were not reliable as the supernate sampling method did not take into account concentration gradients within the static (un-stirred) systems, comprising a solid bed with overlying wash reagent. It was found that the height at which the supernate sample was taken had a significant effect on the results

obtained. The experimental method was improved such that all of the supernate was removed from the samples following a pre-determined dissolution period, then homogenized prior to determination of the dissolved molybdenum concentration by ICP-OES resulting in reliable dissolution rates.

Experimental tests were also carried out under static conditions where the dissolution was monitored from measurement of the height of a settled bed of ZM. An apparent induction period was observed where no reduction in the solid bed was initially seen. It has been postulated that this was most likely due to the build-up of secondary solid species on the surface of the solid bed, as a result of the presence of a layer of high concentration of dissolved molybdate solid next to the bed surface. Thereafter, the height of the settled solid bed was observed to decrease with time.

Despite the variability in quantitative data obtained, there is evidence from these studies that the rate of dissolution increases with temperature, reagent concentration, and agitation. Further dissolution tests have recently been undertaken which examined the effect on the rate of dissolution for various parameters such as degree of agitation, particle morphology, reagent concentration, temperature, CPM:ZM ratio and the effect of removal and replacement of wash reagent. Results from these tests are discussed below.

Effect of Agitation

Results from some ZM dissolution/agitation experiments are shown in Figure 5.

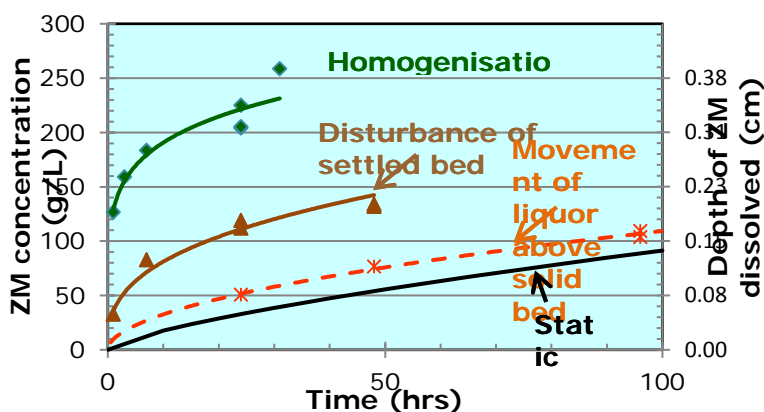


Fig. 5: Increase in dissolution with solids agitation

As would most likely be expected the dissolution rate of solids increases with increasing agitation, as illustrated by four distinct agitation regimes which can be related to the dissolution rate of a settled bed of ZM solids in either wash reagent. The four distinct wash regimes were accounted for within the experimental study by changing the method and/or speed of stirring, as described in Figure 6.

Static conditions	Movement of liquor above settled solid bed	Disturbance of settled solid bed	Homogenization of solution
-------------------	--	----------------------------------	----------------------------

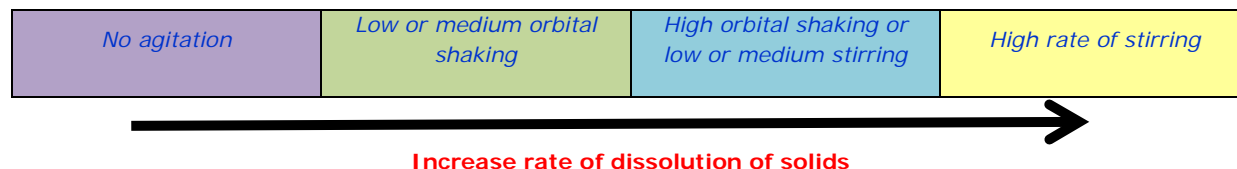


Fig. 6: Increase in dissolution with solids agitation

As mentioned previously the old-side HASTs do not currently contain an installed agitation system so careful consideration of the wash strategy and methodology are required. Installation of a new agitation system would be both challenging and expensive, hence other options such as improvised use of installed instrumentation (e.g. pneumatic bubblers) and/or regular replacement of the wash reagent (to disturb the surface of the solids bed and prevent the formation of a concentrated molybdate layer) will be fully investigated before such an undertaking is made.

Effect of ZM Morphology

As discussed earlier the morphology of the ZM can vary, with crystal growth susceptible to interference by a range of elements present in HAL, giving defects in the crystal structure. The majority of the ZM dissolution experiments carried out recently have predominantly used ZM with a cubic morphology. A selection of the dissolution tests were also carried out under various agitated conditions using ZM with the different rod and wheat-sheaf morphologies. An SEM image of the morphology of these ZM feeds, along with the cubic morphology which was used for the majority of the experiments, is shown in Figure 2. The results, demonstrated that the rate of dissolution of the ZM is independent of its morphology.

Under static conditions, observation of the dissolution of a settled bed of ZM with morphologies described as "cubic" and "brick" (i.e. cubes elongated along one axis) in a 2M solution of reagent 2 indicated that the morphology of the ZM had a significant effect on the initial dissolution. An induction period of ~100 hours was seen for the cubic form, which was found to be much shorter than for the brick morphology. Once dissolution was underway (i.e. after the induction period) the dissolution rate was found to be similar for each morphology.

Effect of Reagent Concentration

Dissolution of ZM and CPM in different reagent concentrations (reagent 1, 0.5 – 5M and reagent 2, 0.2 – 2M) was investigated under a range of agitated conditions. In all cases, the dissolution rate of the molybdate solid increased with increasing concentration of the alkali reagent. With reagent 1, the increase in dissolution rate going from 3 M to 5 M was not significant, with similar dissolution rates observed.

Effect of Temperature

A selection of the dissolution experiments were undertaken at both ambient conditions (~20 °C) and an elevated temperature of 40 °C. The effect of increasing temperature on the dissolution of ZM, CPM or a mixture of both in varying concentrations of reagents 1 and 2 were investigated. In general, increasing the temperature increased the dissolution rate. However, no direct correlation between the increased temperature and increased dissolution rate has been made as it varies depending on the target solid, reagent used and degree of agitation. It is noted, however, that for ZM in reagent 2, increasing the temperature from ambient (~20 °C) to 40 °C had a minimal effect on the dissolution rate.

Mixed Settled Bed of CPM and ZM

Dissolution of a settled bed was examined where the settled solid bed contained a mixture of CPM and ZM. Ratios, by weight, of 25:75, 50:50 and 75:25 CPM: ZM were investigated. For both reagents 1 and 2 it was found that the CPM rapidly dissolves, within the first hour in reagent 1 and within the first day in reagent 2. It also appears that any overlying ZM did not hinder the dissolution of CPM in the 4mm bed depth investigated. Various dissolution rate equations have been derived for different single and mixed solids experiments, but they are not included here.

With regards to ZM, which dissolves more slowly than CPM, the presence of CPM dissolved in the reagent appears to markedly hinder the dissolution of ZM as it was significantly slower than in the absence of CPM. In addition, as the concentration of dissolved CPM in the solution increased, due to a higher ratio of CPM to ZM in the mixed solids, the dissolution rate of ZM decreases in both reagents. Therefore, if full conversion of CPM to ZM has not occurred in the HASTs, the presence of CPM may hinder the dissolution of ZM. In order to mitigate this, since the CPM dissolves rapidly, it has been postulated that during the initial wash-out of the HAST the wash reagent should be removed and replaced with fresh reagent in order to help dissolve the ZM at a faster rate.

Effect of Replacing Wash Reagent

Experiments were carried out, under static conditions, to investigate the effect on ZM dissolution of removing and then replacing the dissolution reagent with either the same reagent sample that was removed or a fresh sample of the same reagent. In each experiment the same mass of ZM and volume of reagent were used.

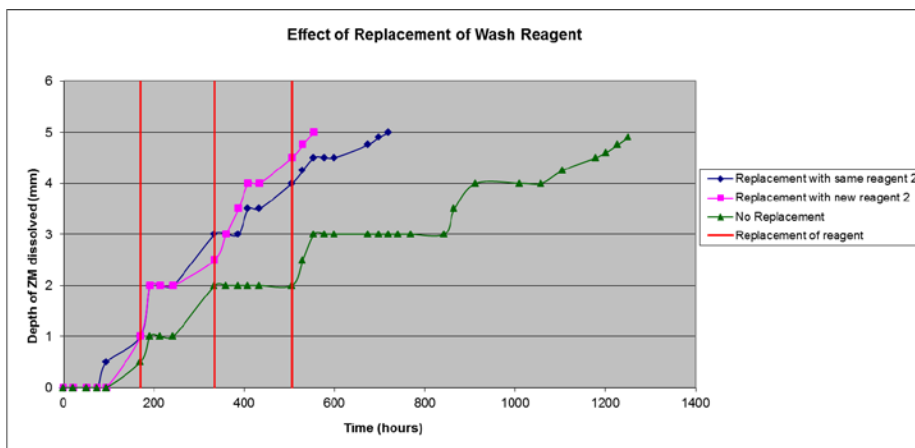


Fig. 7: Effect of Replacement of Wash Reagent on the Dissolution of ZM

Figure 7 shows that replacing the wash reagent weekly, with either the same or fresh reagent, has a significant effect on the dissolution rate over no replacement, with the solids being dissolved at approximately twice the rate. There does not appear to be any difference between replacement with the same or fresh reagent. As there is presumed to be a saturation layer at the solid-reagent interface, removing the “old” reagent would also remove this saturation layer and therefore when “fresh” reagent is added, dissolution is unhindered, returning the dissolution rate back to the initial rate (after the observed induction period). When the same reagent is removed and then replaced it is thought that the saturation layer is mixed into the entire volume of reagent and therefore when it is replaced dissolution also starts unhindered by a saturation layer. The dissolved ZM, present in the solution when the same liquor is replaced, does not appear to have any effect on the dissolution rate compared to fresh reagent.

Re-precipitation of Dissolved Solids

Following dissolution of the HAL solids by either reagent 1 or 2 it is expected that the resulting solution will require acidification in order to ensure that the liquor is compatible with evaporation and WVP processes. Current expectations suggest the following 4 process stages to represent POCO (Figure 8):

The impact of both reagent options on stages 3 and 4 of this process has been investigated and experimental work was carried out using CPM and/or ZM solids, with wash reagents of various concentrations. Solids were wetted with either nitric acid or HAL supernate, and subsequently treated with the alkaline wash reagent to allow dissolution to occur. The samples were then acidified to ~2M acidity by addition of the appropriate volume of nitric acid or HAL simulant and then concentrated either by boiling under atmospheric or reduced pressure, or by passing air over the samples at an elevated temperature of 80 °C.

1	2	3	4
Start	Wash reagent addition	Acid addition (neutralization)	Concentration of wash effluent
Old-side HAST	Old-side HAST	New-side	Evaporator D
Acid supernate and solids (following a flush of the HAST heel)	Effervescence and dissolution	Effervescence (possible intermediate solid)	Solids re-precipitation

Fig. 8: Proposed POCO stages

Initial addition of the nitric acid to dissolved molybdate solutions led to precipitation of white, gel-like nitrate species which was different for each wash reagent used depending on the cation present. Further addition of acid led to dissolution of this phase. Acidification of alkali liquors, resulting from both wash reagents, containing dissolved ZM did not precipitate any solids when acidified with 2M HNO₃ or HAL simulant. When the acidified liquor was subsequently concentrated ZM was seen to precipitate, predominantly with rod or cubic morphology.

When alkali wash reagents containing dissolved CPM were acidified with nitric acid or HAL simulant, CPM was precipitated. The precipitated CPM generally had a spherical morphology, similar to the starting material, however occasionally clumps or cubes of similar particle size formed. The quantity decreased with increasing HAL simulant concentration, such that at 250 L/teU no or extremely little CPM precipitated. This suggested that the HAL simulant or a species within the simulant was inhibiting CPM formation. When concentrated, ZM precipitated from the reagents acidified with HAL simulant, the quantity increasing with the HAL simulant concentration used for the acidification. The ZM exhibited generally rod morphology, with cubic morphology being observed at the lower HAL simulant concentrations. It has been found that, when Zr is present in the HAL simulant the re-precipitation of CPM is hindered with ZM forming preferentially when the acidified solution is concentrated. At lower simulant concentrations CPM forms due to there not being enough Zr present to entirely complex with the Mo, thus allowing CPM to form. Therefore, when alkali solutions containing dissolved CPM are acidified, any Zr present will preferentially complex with Mo to precipitate ZM.

Hence the results indicate that if (as expected) only ZM is present in the old-side HAST, re-precipitation of the dissolved solids present in the wash reagent will not occur until the acidified liquor is concentrated. If CPM is also present in the old-side HASTs, it is likely that the precipitation of CPM will be prevented on acidification, with ZM being precipitated when the solution is concentrated in the evaporator.

Settling of Solids and Potential Rheology Modification

Concern has been raised over settling of the solids present in HAL during POCO of the HASTs. It is expected that, during washout of the HASTs with water or weak nitric acid, dilution will alter the HAL composition, potentially allowing rapidly settling solids like CPM, ZM and barium/strontium nitrate to settle and remain in the HASTs,

or to settle during slow flow rate transfers through the associated pipework. It has been postulated that, by introducing a compatible viscosity thickener to the HAL, it may be possible to keep these dense solids in suspension.

Recent lab studies were carried out to identify possible viscosity modifying additives. Organic additives were quickly discounted due to their poor performance and concerns over degradation under irradiation. It was concluded that three of the additives investigated are appropriate for full experimental tests, ZHP, Laponite EP™ (layered silicate synthetic clay), and pyrogenic silicon (IV) oxide (SiO₂).

The current HAST POCO strategy is to operate the plant in such a way as to avoid the requirement to add a viscosity modifier to HAL and work is currently ongoing to support this strategy. However, should the addition of a viscosity modifier later become necessary sufficient work has been carried out to show that one or more of the above additives could be added to effect the desired viscosity modification.

Possible Tank Wash Strategies

Further to the reagent selection challenge different wash strategies have been assessed to investigate the most efficient way of transferring solids from the new-side HASTs to WVP for encapsulation in glass. Minimisation of the number of WVP containers produced is a key consideration and co-processing of POCO wash liquors alongside ongoing re-processing arisings (Ref. 1) is one possible way of achieving this minimization. A number of different new-side wash strategies have been assessed and the potential generation of varying volumes of additional wash liquors (e.g. acid/water), depending on which wash strategy is chosen, has also been considered as these liquors will need to be processed alongside the solids removed.

Related Work

The work discussed above is a key part of the overall POCO strategy. However, a significant amount of related work is also ongoing, which also forms a key part of the overall requirements. Tank emptying trials have been carried out on a 4/10th scale HAST rig (Ref. 1) and HA Evaporator D is currently undergoing commissioning. The development of new tools and techniques to characterize the POCO challenge and monitor its progress is ongoing and research and development work is underway on the slurry transfer rig, (full scale) vitrification test rig (Ref. 5) and corrosion rigs to support the POCO program, as reported at WM2016 (Ref. 1).

CONCLUSIONS

A complex program of work is underway, which has involved close working between Sellafield Ltd staff, NNL and some key supply chain providers. Significant progress has been made in determining the POCO operating strategy (Ref 1.) and this has included significant advances in the knowledge of HAL chemistry.

Specific recent progress has been made in the confirmation that CPM to ZM conversion occurs in radioactive HAL, confirming the findings of previous non-active research. Progress has also been made in understanding the morphology of ZM solids and how this then affects the properties of the solids towards dissolution.

The most significant advance has been in the identification and development of two potential wash reagents to be used in the dissolution of difficult to manage solids such as CPM and ZM. As a result the development of a detailed POCO wash strategy is now well underway. Many gaps in knowledge applicable to HALES POCO have now been filled, but a small number of questions still remain.

A wider program of HALES POCO support work is ongoing but significant steps forward have been achieved, not in the least the ongoing commissioning of HA Evaporator D, which is programmed to come online in the near future and is key to ensuring the success of POCO operations in HALES and across the Sellafield site.

REFERENCES

1. S. THOMSON, *"Progress in Defining the UK Highly Active Storage Tanks POCO Strategy"*, Waste Management 2016 Conference, March 6 – 10, 2016, Phoenix, Arizona, USA.
2. S. THOMSON, *"Black Cell Operations – UK National Nuclear Laboratory Experience"*, Waste Management 2014 Conference, March 2 – 6, 2014, Phoenix, Arizona, USA.
3. S. THOMSON, *"Operational Plant Lifetime Assessment – UK National Nuclear Laboratory Experience"*, Waste Management 2015 Conference, March 15 – 19, 2015, Phoenix, Arizona, USA.
4. D.F. BRADLEY, M.J. QUAYLE, E. ROSS, T.R. WARD, N. WATSON, *"Promoting the conversion of caesium phosphomolybdate to zirconium molybdate"*, Proceedings of Atalante 2004.
5. JI. ROE, *"Vitrification Test Rig: Supporting Vitrification at Sellafield"*, Waste Management 2014 Conference, March 2 – 6, 2014, Phoenix, Arizona, USA.

ACKNOWLEDGEMENTS

The authors would like to thank Sellafield Ltd for their agreement in allowing this paper to be published. The authors would also like to thank NNL and Sellafield Ltd colleagues, too numerous to mention, who have worked tirelessly in recent years in the development of the HAST POCO wash reagents and wider POCO strategy.