A Methodology for Post Operational Clean Out of a Highly Active Facility Including Solids Behaviour – 12386

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ABSTRACT

The Highly Active Liquor Evaporation and Storage (HALES) plant at Sellafield handles acidic fission product containing liquor with typical activities of the order of 18×10^9 Bq/ml. A strategy-experimental feedback approach has been used to establish a wash regime for the Post Operational Clean Out (POCO) of the oldest storage tanks for this liquor. Two different wash reagents have been identified as being potentially suitable for removal of acid insoluble fission product precipitates. Ammonium carbamate and sodium carbonate yield similar products during the proposed wash cycle.

The proposed wash reagents provide dissolution of caesium phosphomolybdate (CPM) and zirconium molybdate (ZM) solid phases but yields a fine, mobile precipitate of metal carbonates from the Highly Active Liquor (HAL) supernate. Addition of nitric acid to the wash effluent can cause CPM to precipitate where there is sufficient caesium and phosphorous available. Where they are not present (from ZM dissolution) the nitric acid addition initially produces a nitrate precipitate which then re-dissolves, along with the metal carbonates, to give a solid-free solution. The different behaviour of the two solids during the wash cycle has led to the proposal for an amended flowsheet.

Additional studies on the potential to change the morphology of crystallising ZM have presented opportunities for changing the rheology of ZM sediments through doping with tellurium or particular organic acids.

INTRODUCTION

The Highly Active Liquor Evaporation and Storage (HALES) facility at the Sellafield nuclear licensed site receives Highly Active (HA) raffinate from the THermal Oxide Reprocessing Plant (THORP) and Magnox reprocessing plant. The raffinate is concentrated by evaporation; the resulting Highly Active Liquor (HAL) is currently stored in some of 21 Highly Active Storage Tanks (HASTs) prior to immobilisation in a glass matrix in the Waste Vitrification Plant.

HAL typically contains an active inventory of fission products and actinides in 2 M nitric acid. This is concentrated to ~100 g(metals)/l giving typical activities of the order of 2×10^{10} Bq/ml and radioactive decay power output of up to ~5 kW/m^3. The HAL is maintained at 50 – 60°C through the use of water-cooled coils and jackets in the HAST.

HALES has operated since the 1950s and processed the highly active waste products from the equivalent of approximately 47,000 tonnes of irradiated fuel, the majority of this material has been encapsulated in glass at the sister Waste Vitrification Plant (WVP). Although the plant is currently still operating consideration has begun of Post Operational Clean Out (POCO).

POCO is a transition phase between normal operations and decommissioning. The key drivers are to:

- Reduce hazard at the earliest opportunity
- Facilitate decommissioning
- Simplify surveillance and maintenance
- Make the best use of existing facilities and resources.

POCO may only be a relatively short period in the lifecycle of an operational facility but poor planning, prior to this phase, may lead to an extended POCO phase and/or a significant detrimental impact on decommissioning timescales.
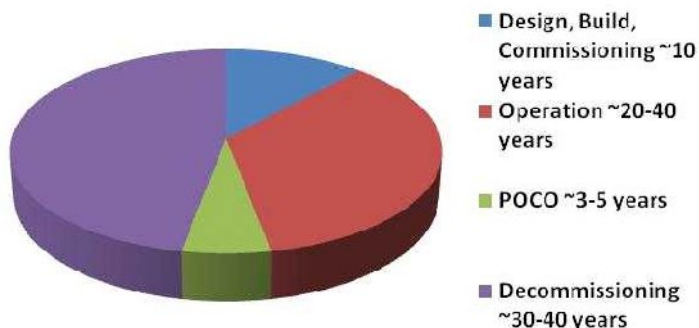

Fig. 1. Approximate timescales of the possible phases during the lifecycle of a nuclear facility.

DEVELOPMENT

The direct challenges during POCO can be summarised by the following:

1. Reduction of radiological hazards by:
   a. Removal of heels of liquor and/or solids.
   b. Removal of mobile activity associated with the vessel and in-tank equipment.
2. Engineering substantiation of facilities taken out of service and left in a quiescent state.
3. Unidentified and/or poorly labelled isolations.
4. Access (physical or chemical) to the facility.
5. Compatibility of POCO effluents with downstream processes.

Due to the HA nature of the facilities in HALES physical access is not desirable, reducing containment, and any process involving intrusion will rank poorly against less invasive options.

POCO is likely to be conducted in a number of phases with POCO of redundant facilities conducted prior to curtailing routine operations. Within HALES, the HASTs are likely to present the greatest challenge; the eight oldest HASTs are no longer required for storage and present an opportunity for early POCO.

As with many older plants worldwide, much of the earliest parts of the plant were not designed with cognisance of end-of-life operations. The challenge therefore requires an understanding of the facility to be cleaned out, including its potential contents and limitations with respect to installed equipment (off-takes, cooling coils, etc.).

The eight 'Oldside' HASTs in HALES were commissioned between 1955 and 1968 and the last transfer of HAL to these tanks was in 1970 [1]. They are large horizontal cylindrical tanks with four HASTs containing one cooling coil and the remaining tanks having three. They have redundancy with respect to off-take ejectors although the transfer rate is slow. There is no in-built agitation system.

The lack of agitation has resulted in the accumulation of solids that have crystallised from the stored HAL, either during concentration via evaporation or in the HAST itself, and deposited on

the base of the tank[1]. Studies of the possible composition of these solids have shown them to be a mixture of caesium phosphomolybdate ($Cs_3PMo_{12}O_{40}.14H_2O$, CPM), zirconium molybdate ($ZrMo_2O_7(OH)_2.2H_2O$, ZM), zirconium phosphate (known to be of variable composition, e.g. $Zr(HPO_4)(OH)_2.H_2O$) and a variety of metal nitrates. The approach to POCO of these tanks will involve a water washout cycle that will dissolve the metal nitrates and, since it is expected to be mobile, remove any zirconium phosphate. The remaining challenge is therefore to remove the sparingly soluble CPM and ZM. As discussed the ability to retro-fit equipment is limited thus the options for removal of the CPM and ZM are restricted.

Above 1.8 g(Mo)/l CPM is formed in the evaporator, the mass precipitated being limited only by the availability of molybdenum or phosphorous, caesium being in excess in the HAL. However, it has been found that under conditions similar to those during storage in a HAST – relatively high temperature (~60°C) and low acidity (2 M nitric acid) – that the CPM will convert into ZM [2]. The degree of conversion in the Oldside HASTs is not known due to an inability to sample these tanks but it is likely that the majority of the CPM has converted to ZM. CPM is inherently radioactive due to the presence of Cs-134 and Cs-137. Since conversion will release the caesium into solution and the majority of the active molybdenum and zirconium isotopes will have decayed before reaching HALES formation of ZM may be beneficial. However, there is expected to be some activity related to the ZM through association – surface adherence or trapped within the crystal.

The lead remaining option for the removal of the CPM and ZM is dissolution in a suitable wash reagent. A wide variety of wash reagents have been trialled with varying success, many of those that are good solvents for the solids are unsuitable due to their low stability in the HA environment or incompatibility with process liquors downstream. The most suitable wash reagents identified are carbonate-type reagents, these provide two benefits. The first benefit is that they are good solvents for CPM and ZM whilst showing good compatibility with existing plant and equipment when liquor mixing is controlled; the second is the concomitant evolution of gases. The reaction of the carbonate group with residual acid permeating the solids causes the release of CO_2, resulting in localised disruption and partial suspension of the solid. The re-suspension of the solid permits increased dissolution rate compared to a packed sediment bed.

Previous studies have examined the solubility and rate of dissolution of the CPM and ZM phases in AC with the influence of condition variables. The kinetics of gas forming reactions on mixing with acid solution and by-products on addition to HAL have also been studied. Process routes and the ability of installed equipment in plant have also been assessed as part of the POCO feasibility and flowsheet development exercise.

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[1] The remaining 13 'Newside' HASTs are vertical cylinders capable of holding twice the volume of HAL compared with the Oldside HASTs. They contain 7 cooling coils and an external sectional jacket; they also have in-built agitation systems. These HASTs may also have an inventory of solids, however, optimised performance with agitation and sufficient water and acid washes is expected to be sufficient to achieve POCO of these tanks.

METHOD

A preliminary flowsheet for the POCO of the Oldside HASTs has been prepared that includes a series of water, acid and wash reagent washes followed by discharge of the resulting effluent to the 'Newside' HASTs. Whilst unlikely to represent the final POCO flowsheet this exercise identified the following principle chemistry steps during POCO:

1. Delivery of the wash reagent to a HAST heel containing solids with residual HAL supernate (*interaction of alkaline wash reagent with acid*).
2. Transfer of the resulting liquor from the Oldside to Newside HASTs (*introduction of alkaline reagent containing dissolved solids into acid with the potential for crystallisation of solids*).
3. Concentration of the liquor volume (*potential for further solids precipitation*).

In turn this process identified questions and opportunities that require further study before a final POCO scheme can be implemented:

a. The carbonate-type wash reagents through previous studies have been reduced to a short-list of ammonium carbamate (AC, $NH_2CO_2NH_4$), sodium carbonate (SC, Na_2CO_3) and caesium carbonate (CC, Cs_2CO_3) – ammonium carbonate and lithium carbonate previously dismissed due to the superior performance of AC and the relatively poor solubility of lithium carbonate.

b. Any of the steps pinpointed above may result in the precipitation of solids. It is necessary to identify and characterise these solids in order to establish any impact downstream.

c. The possibility of re-precipitating solids provides an opportunity to affect a crystallisation in a preferred morphology such that the resulting solid phase properties are beneficial to the process.

In order to address these issues and refine the flowsheet further a programme of work has been undertaken.

Quantities of ZM and CPM were prepared as described in reference [3] and nitric acid slurries of each solid subjected to pre-determined volumes of 2 M wash reagent; AC, SC and CC were all investigated. The acid slurry was made by addition of either 2 M nitric acid or a HAL simulant of a similar acid strength, containing non-active equivalents of the fission products resulting from a 25 GWd/teU, 5-year cooled PWR fuel. Following wash reagent addition a quantity of 6 M nitric acid was added to re-acidify the wash effluent before the resulting solution was concentrated by evaporation. Each experiment was completed in duplicate, any solids formed at each process stage were sampled, dried and analysed using powder x-ray diffraction (Equinox 1000) and scanning electron microscopy (JEOL 5600) fitted with energy-dispersive x-rays spectroscopy capability.

Studies have also been conducted into the influence of dopants on the morphology of crystallising ZM. The ability to tailor the morphology of the crystallising phase gives the opportunity to control the settling and rheological properties of the precipitated solid thereby enabling more efficient suspension by operation of the available engineered systems. A wide variety of dopants were individually introduced into the mother liquor during formation of ZM. The choice of dopant was based on prevalence in HAL solution, previously identified structure-directing organic materials [4] and elements that were considered to have a non-detrimental

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affect on plant, processes or final product quality. The morphology study was conducted at the University of Bristol and a full description of the methods and results can be found elsewhere [5].

RESULTS

Wash sequence

As might be expected a general pattern has formed in the process sequence, although it differs for CPM and ZM. In each case the initial addition of the wash reagent leads to a reaction with the acid, generating froth and neutralising the acid. Once the acid has been consumed additional wash reagent dissolves the solids. For the acid only solutions this gave a clear solution, however the presence of other cations in the HAL simulant leads to formation of a mobile brown phase – see figure 2.
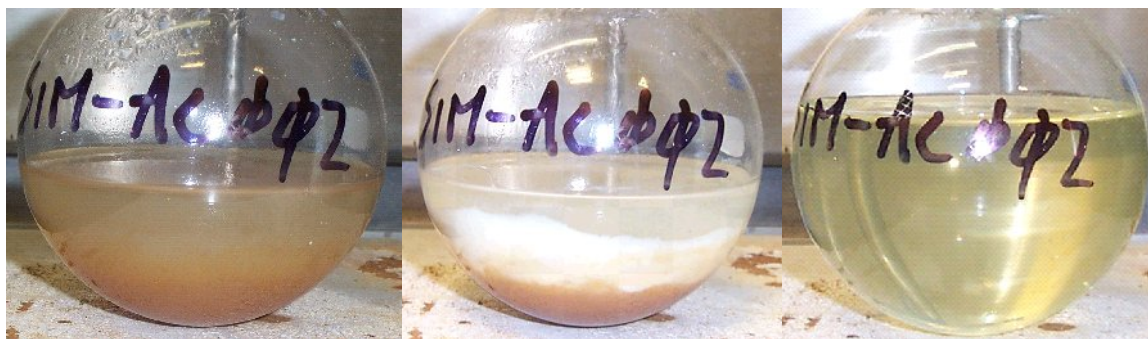

Fig. 2. Development of the wash sequence. Left image shows solution 65 hours after ammonium carbamate addition – ZM has dissolved and brown carbonate solids have precipitated from reaction with other metals in the simulant. In the centre after a small addition of acid a white solid appears which fully dissolves, together with the brown phase, on further acid addition (right hand image).

Addition of 6M nitric acid to solutions previously containing CPM led to the immediate re-precipitation of CPM. However, for ZM Initial addition of the 6M acid leads to precipitation of white, gel-like nitrate species corresponding to the wash reagent used: ammonium nitrate for AC, sodium nitrate for SC and a caesium salt for CC. Further addition of acid lead to dissolution of this phase where AC and SC had been used, this can be seen in figure 2; however the caesium salt did not re-dissolve on further acid addition. In fact the CC gel expands to take up the entire liquor volume (under laboratory scale experiments).

Evaporative concentration of the liquor, at the atmospheric pressure boiling temperature, results in the re-precipitation of zirconium molybdate. The re-formed material had a similar particle size and morphology to the experimental feed (similar to figure 3 top left). Where the experimental feed had been a mixture of CPM and ZM a mixture of the two solids was formed at the end of the experiment due to the limited quantities of caesium and phosphorus available for reaction; however, where the additional caesium and phosphorus was available the entire contents precipitated as CPM before concentration.

Zirconium molybdate morphology

Zirconium molybdate may be formed through direct synthesis (e.g. [6]) or through conversion from CPM as described earlier. A cube-like morphology (e.g. figure 3, top left) is typically observed in HAL simulant studies, giving a rapidly settling densely packing sediment. Over 25 different dopants have been trialled to test their affect on ZM crystallisation via both syntheses, in particular the morphology of the resulting crystals. Of these, significant changes in the crystal morphology were noted when the conversion of CPM to ZM was carried out in the presence of tellurium or one of several organic acids.

Crystal bundles described as 'wheatsheaves' have been seen in previous HAL simulants in small quantities. It has been found that it is the presence of tellurium (present in the HAL simulant) that leads to the precipitation of this morphology, and increased doping, above that normally seen during operations can lead to a sample composed entirely of crystals in the wheatsheaf morphology (see figure 3, top right). Quantitative rheology studies of this phase are currently still in progress but qualitative analysis has show that the wheatsheaf morphology leads to solids that are slower settling, do not adhere to surfaces with the same strength and are more easily re-suspended from compacted beds.

Further studies have been conducted in the presence of several organic acids that have been used in previous studies to control morphology, e.g. [4]. Those organic reagents that did affect the morphology lead to crystals with a larger aspect ratio and in the case of citric acid twinning of the crystals – see figure 3, lower right.
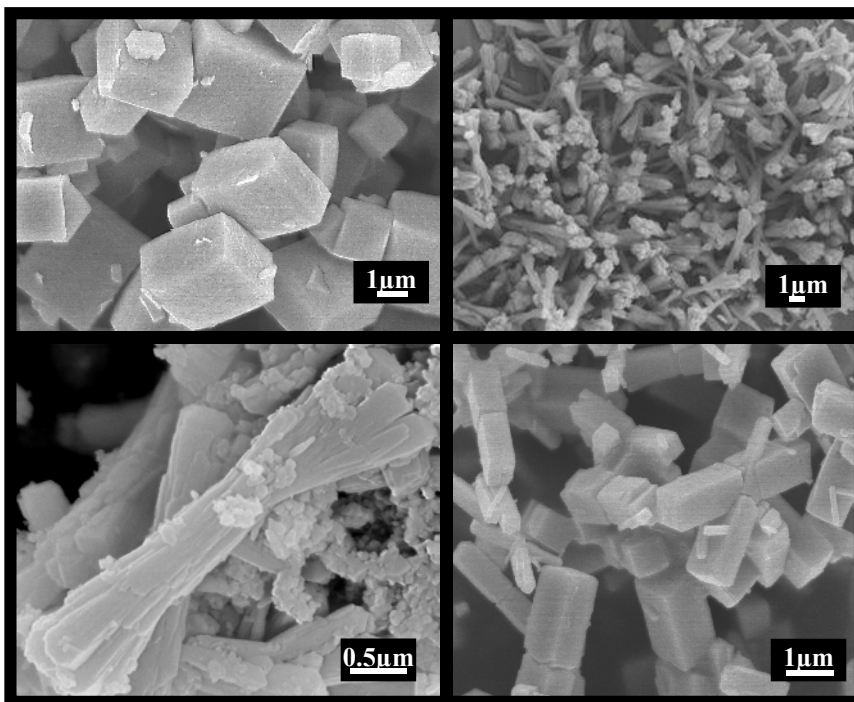

Fig. 3. Scanning electron microscope images of zirconium molybdate products. The image top left is formed from CPM conversion in the absence of any dopant. The image top right shows the wheatsheaves produced in the presence of 6 mol% telluric acid. At the bottom left is a higher magnification of a 'wheatsheaf'. The image bottom left shows twinning of ZM grown in the presence of citric acid.

DISCUSSION

The early generation of a preliminary flowsheet has allowed identification of potential challenges during POCO. In particular gaps in our chemical knowledge have been identified[2]. This allowed an experimental programme to be developed to directly target those areas of uncertainty. The experimental results have allowed the number of wash reagents to be reduced whilst refining the available options for a potential wash scheme.

The use of ammonium carbamate or sodium carbonate in the dissolution of ZM leads to the production of clear, solids-free liquor when the nitric acid is added in excess (permitting dissolution of an intermediate phase) that will be suitable for transfer from the Oldside to the Newside HASTs. The solid formed on introduction of nitric acid to a caesium carbonate however are not re-dissolved by addition of excess acid and for this reason the use of CC has been discounted.

The remaining wash reagents, AC and SC, are both effective for the dissolution of the solids. There is precedence for the use of both reagents in the clean out of similar liquors, AC has been used for unblocking process lines and vessel clean out in Sellafield reprocessing plants but not on the HAST scale and SC has been used to clean out tanks in the vitrification test rig at Sellafield, although this is a non-active test facility using inactive HAL simulant. Consideration of their impact downstream show that there are pros and cons to each; the use of AC will require no additional volume of vitrified product glass as its decomposition produces gaseous products during calcination, however it will generate large quantities of ammonium nitrate that may lead to problems in the off-gas systems. SC will result in additional sodium that must be incorporated into the vitrified glass, although this could be accommodated by a change in the glass formulation.

The use of a wash reagent and nitric acid for the wash out of the Oldside HASTs produces different results depending on the solid to be dissolved. Following dissolution of CPM, with either AC or SC, the introduction of nitric acid results in its re-precipitation; whereas for ZM, excess acid results in a solid free solution until concentrated. Although the majority of the solids are expected to be ZM (through conversion) the presence of CPM cannot be ruled out. The implications of this for the flowsheet are that the wash out might be required in two phases; a first phase, for the removal of ZM, involving wash reagent use and re-acidification followed by transfer of the liquor to the Newside. The second phase would be a 'wash reagent only' clean out to remove the CPM. This would leave an alkaline heel in the HAST and the wash liquor transferred would be re-acidified on introduction to the Newside HASTs. A schematic of this is illustrated in figure 4.

The dissolution and re-precipitation of solids offers the opportunity to tailor the morphology of the crystallising species. Introduction of a dopant with the wash reagent would permit this addition. The use of organic materials would normally be considered folly as they will break down in the HA environment. However, during POCO the activity levels are expected to be much lower giving the reagents much greater lifetime. The dopant also only needs to be present for the short period of crystal formation. Preliminary results suggest that the elongation of the crystals reduces settling rate and yield stress leading to more effective re-suspension and transfer to vitrification. Furthermore the presence of the organic material will not contribute to the final vitrified product as its decomposition during calcinations gives only gaseous products.

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[2] In fact a wide range of other challenges were identified at this stage but are not reported here.
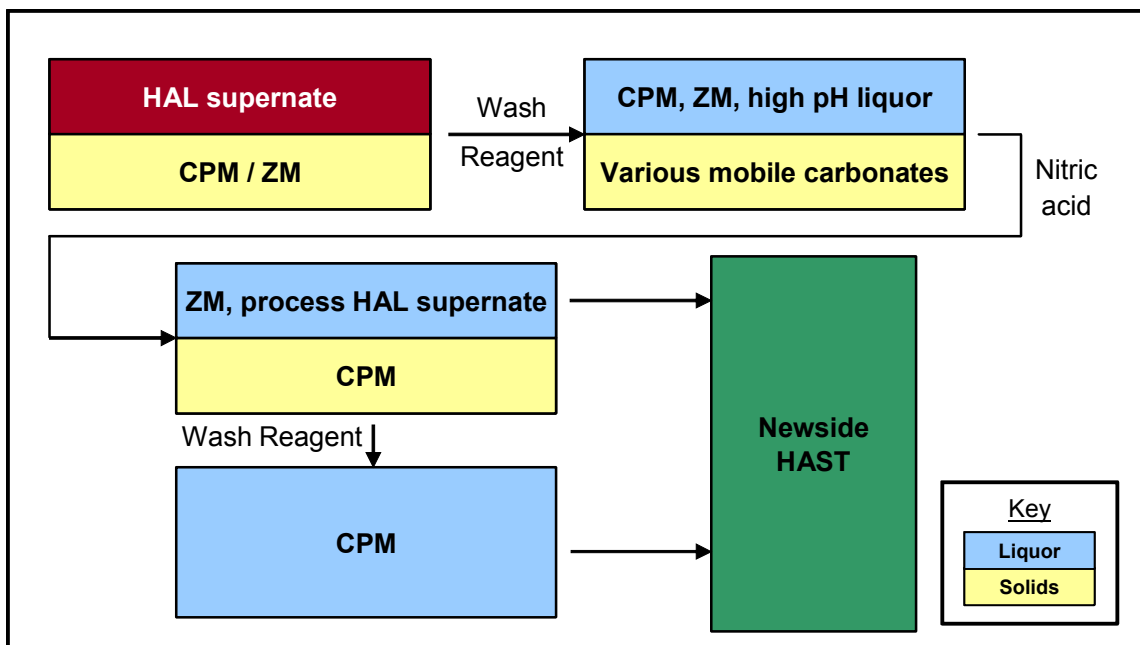
Fig. 4. Schematic of proposed Oldside HAST wash sequence wash sequence.

The use of tellurium gives a more unusual morphology that shows even greater reduction in settling rate and yield stress. Since there is already tellurium present an assessment is required of the additional quantity required and the potential impact on vitrified products.

CONCLUSIONS

Two different wash reagents have been identified as being potentially suitable for the POCO of HALES Oldside HASTs. AC and SC both yield similar products during the proposed wash cycle. However, the different behaviour of the two principle HAL solids, CPM and ZM, during the wash cycle has led to the proposal for an amended flowsheet.

Additional studies on the potential to change the morphology of crystallising ZM have presented opportunities for changing its rheology through doping with tellurium or certain organic acids.

A strategy-experimental feedback approach has been used to establish a wash regime for the POCO of the HALES facility at Sellafield. The close working of the strategy and experimental teams has permitted a wash sequence to be developed which is considered to be robust by both sides. The technical underpinning of the strategy is expected to make stakeholder buy-in more readily achievable.

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