

Proven Uranium Recovery Solutions for the Nuclear Fuel Manufacturing Market – 16060

Kevin Askew, Westinghouse

ABSTRACT

During the Nuclear Fuel Manufacturing process a number of by-products and residues are generated from various sources. In recent years, Westinghouse has characterised and processed around 50,000 drums of residue comprising of numerous different types generated over 60 years from the manufacture of numerous types of fuel for greater than 50 reactors. These include, AGR, Magnox (uranium metal fuel), PWR, fast reactors and various test reactors.

Different organisations have different definitions and names for each of these categories but essentially they fall into one of the following categories:

- Clean Scrap (U3O8, UO2, UO3, UF4, powders, pellets)
- Dirty Scrap (U3O8, UO2, UO3, UF4, powders, pellets)
- Gd Contaminated Scrap (U3O8, UO2, powders, pellets)
- Ash
- Sludge
- Combustible / soft residues (e.g. ventilation filters, gloves, plastic bags)
- Contaminated metals (including contaminated scrap zirconium tubes)
- Materials arising from decommissioning

Routes have been developed across the industry for a number of the categories listed above, however in numerous examples, routes have not been established and materials have been stored creating a significant legacy.

Westinghouse understands the issues regarding legacy uranic material and the financial and regulatory impact of storage. Interim storage of materials may seem like a low cost option in the short term; however ongoing costs for facilities, manpower and equipment, without a permanent and final solution can result in significant lifetime material management costs.

Recovery of uranium and sending materials for safe disposal of enriched uranium residues is not easy because of the criticality risk both during processing and at a disposal site. Therefore quantities of materials than can be sent via permitted disposal routes are very limited

The development of regulations often means that finding solutions is becoming more difficult. It is believed that timely resolution is ultimately the most cost effective solution. In addition, the intrinsic value of recycling this material is also high and in some cases can mitigate the cost of processing.

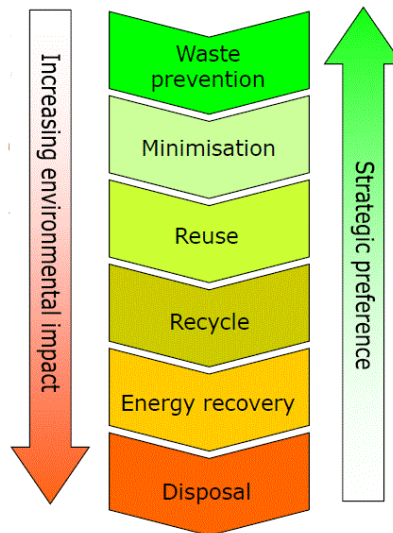
INTRODUCTION

Springfields Fuel Ltd (SFL) is part of the Westinghouse group and has its roots in British Nuclear Fuels Limited (BNFL). SFL have characterised and processed around 50,000 drums and hundreds of ISO containers of residues of numerous types.

The stocks comprised many diverse materials which were grouped together in a number of different categories; these were dependent on the nature (or suspected nature) of the materials, potential or defined processing routes, and the enrichment (i.e. isotopic abundance, or IA) of the uranic component of the residue. Much of this residue backlog has been or is currently being processed. As historic residues are processed, process residues continue to arise and, as decommissioning and demolition of old plant accelerates, new types of residue are arising both at the Springfields site and from elsewhere in the UK.

In addition to the residues at Springfields the global nuclear industry generates a wide variety of materials produced as by-products of the nuclear fuel cycle, mostly from uranium purification and fuel manufacture but also including materials from uranium enrichment and from the decommissioning of obsolete plants.

The recovery of uranium from scrap and waste materials is also in line with the waste hierarchy. In addition to the decision to recover uranium, the use of existing routes and existing technologies is also a positive contribution to the waste hierarchy. Preservation of capacity at waste repositories is also a consideration therefore the more materials that can be processed to remove the uranium and allow for disposal at very low level waste sites is a preference.



Over the years many routes have been developed for the processing of this wide variety of materials. This has been achieved through working in collaboration with The National Nuclear Laboratory (NNL) in the UK.

NNL also have their roots in BNFL and have laboratories based at the Springfields site.

The collaboration of using the research and development capabilities of NNL alongside the experience and capabilities of Springfields has delivered the success

of processing the vast residues from the Springfields site, residues from other UK nuclear sites and in recent years, developing routes for customers from overseas.

The method taken by both Springfields and NNL is through a phased approach. In summary this is the process developed to take any residue type from any background and work through a series of steps to identify its ultimate processing route.

THE PHASED APPROACH

Before a processing route can be confirmed for a residue type it is necessary to understand the residue and its characteristics. In some cases this is a quick and simple process however in others, the process requires multiple steps.

Where no obvious route is available for processing in existing or planned plant have been carried out using the methodology outlined in Fig 1 and described in the following sections.

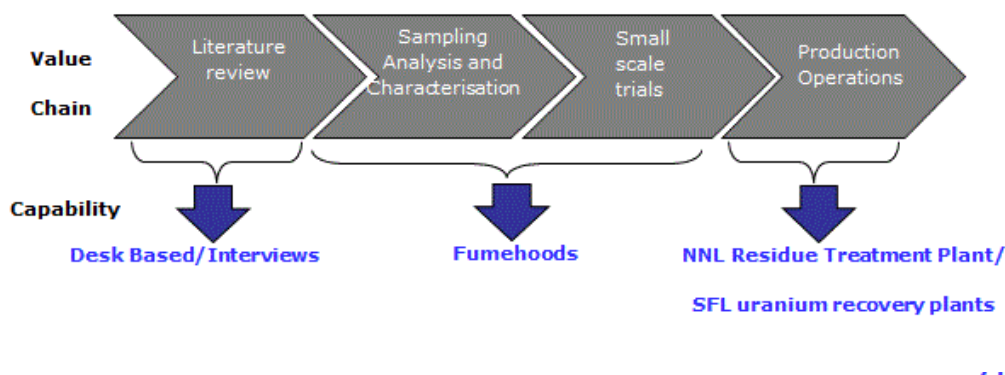


Fig 1. Residues Phased Methodology

Phase 1

The initial stage in an investigation comprises the gathering of historic information in an attempt to discern the chemical and physical characteristics of any given residue, how it arose, what problems might be associated with its processing and whether any fraction of the material has previously been processed by any currently viable method.

Although the questions posed at this stage of an assessment can seem somewhat mundane, their importance cannot be overstated since the outcome of a detailed Phase 1 investigation could negate the need for further development work and may result in the direct processing of the material through existing routes. Historically, lines of investigation have targeted uranic wastes and residues but many of the questions are equally applicable to other materials containing a wider variety of radioisotopes. The questions are grouped into a number of categories as described below.

General description

It is important to understand the material in terms of its general composition, its history, its level of characterisation and its uranium content.

Storage

How a material is stored, particularly in terms of its storage container(s), is much more important than it might seem. This can be for two reasons. The first being how easy is it to remove the contents from their storage containers. The second is the materials of the storage containers. This is important to consider how long materials have been stored and consider if the materials have degraded in any way. The down stream process can be impacted by chemical compatibility if the materials from the container are also present in the processing materials.

Physical Properties

The physical nature of the material impacts on how it might be processed, in particular how the material is handled in terms dust hazards, flammability, the tipping of drums, the removal of organics or pre-processing requirements such as sorting and crushing.

Chemical Properties

The chemical properties of the material are paramount in determining its processibility. They affect the process by which the residue may be treated, the processing rate and how effluent liquors and solid residues may be disposed of.

Radioisotope content

The radioisotope content of the material is very important in terms of the specification of any final product. Uranium isotopes such as ²³²U, ²³⁴U and ²³⁶U are of particular interest since they cannot be removed during residue processing, though blending opportunities can often be considered.

Radiological Properties

This section refers to dose rates associated with the material. Owing to the nature of many of the materials historically treated on the Springfields Site, many of the processes tend to involve a reasonable amount of manual intervention which can increase an operators dose if not managed.

Other factors

While the preceding lines of investigation have been found to be reasonably comprehensive in terms of initial material assessments, the nature of many wastes and residues dictates that something unexpected is likely to be found. As such, it is important that any additional information relating to the material is shared.

Phase 2

Springfields operates a number of uranium recovery plants. Laboratory investigations and detailed analysis of materials aimed at determining if materials are processible via existing routes are termed "Phase 2" investigations. These

generally involve leaching in nitric acid under typical plant conditions and analysis of leachates and residual undissolved solids.

The development of the facilities at Springfields has resulted in the significant volume of residues being processed with the uranium being returned to the fuel cycle and the liability being removed.

In some cases, generally in lower volumes, it is not possible to process the residues through mainline uranium recovery routes. In this case a further phase of characterisation is required and outlined below.

Phase 3

Where the outcome of phase 2 investigations has been to recommend the development of a residue specific process, this work has generally been termed "Phase 3". Much current waste and residue treatment work is managed through the NNL Preston Laboratory and is concentrated on those residues, identified in prior investigations or experimental work, as unsuitable for treatment through the existing mainline Springfields uranium recovery plants. These targeted development programmes involve detailed technical investigations designed to produce viable processing methods allowing particular residues to be sentenced with confidence.

A huge variety of materials have been assessed for treatment via Phase 3 process development, and subsequently successfully processed.

WESTINGHOUSE MAINLINE URANIUM RECOVERY ROUTES

Westinghouse has several highly specialised facilities with skilled and experienced operators for uranium recovery. These are spread over the various Westinghouse sites. The facilities can handle varying volumes of material and can offer pre-processing services such as sampling, material sorting and segregation, size reduction, fuel de-fabrication and re-drumming.

The larger mainline uranium recovery facilities are located at Springfields and can be summarised into broad business areas as outlined below.

Enriched Uranium Residue Recovery Plant (EURRP)

The EURRP is a plant capable of processing uranium bearing materials of varying types, including liquids and powders. This mainline facility is limited to enrichments up to 5% however through a number of pre-processing routes, enrichments higher than this can be accepted at Springfields for the purposes of uranium recovery. Nitric acid dissolution is the backbone of the EURRP facility followed by solvent extraction. The unique design of the Westinghouse dissolver enables a wide range of materials to be processed.

The eventual output of the facility is U₃O₈ or UO₂ powder that meets the ASTM specification and is returned back into the fuel cycle.

Nitric Acid Wash Facility (NAWF)

In many nuclear facilities around the world significant volumes of 'soft residues' are generated. Soft Residues are items that are ancillary to the product lines and include materials such as cloth, paper, plastics, rubber, ventilation filters. These items are generally contaminated which prevents direct disposal. Items as described above are generally bulky and take a reasonable amount of space. To manage these residue streams many facilities have employed the use of incineration to reduce the volume of these residues. The output from the incinerator is uranium bearing ash. This is a secondary product that requires further processing to remove sufficient uranium to enable disposal. This secondary treatment can be difficult and can be at a high cost.

Westinghouse have developed an alternative to incineration. The process is called the 'Nitric Acid Wash Facility'. The NAWF provides a unique, innovative process which removes uranium from the contaminated soft residues directly thus allowing the materials to be sentenced and disposed of to a very low level waste disposal facility.

The resultant uranium is recovered through a contaminated liquid recovery route and ultimately recovers the uranium through to U₃O₈ or UO₂ powder which can be returned back into the fuel cycle.

Natural and Depleted Uranium Recovery Plant

During the nuclear fuel manufacturing process residues are generated at all stages. At earlier stages of the fuel cycle these materials are natural and in some cases depleted uranium. Although the uranium has a lower value than enriched uranium they still require processing to recover the uranium and enable the waste to be disposed of.

The chemistry of processing natural and depleted materials is virtually identical to that of enriched materials however due to the criticality restrictions required for enriched materials, processing rates are generally lower and hence the operational costs are higher. There are a number of reasons for this including the requirements for Criticality monitoring, control and emergency arrangements, and constraints such as plant geometry ie. Safe by shape vessels.

Employing a different processing facility enables high volumes of natural and depleted uranium residues for immediate return to the fuel cycle or conversion to UO₃ for storage.

In the natural and depleted facilities, several thousand drums per year can be processed depending on the residue form. The plant is capable of processing uranic liquids, powders, metal, slurry, sludge or bulk feed material. The plant normally processes materials up to 1% enrichment however materials up to 1.4% enrichment can be considered on a case by case basis.

Natural and depleted materials contaminated with heavy metals.

It is common for uranic bearing residues to also have other chemical contaminants present. One such residue that comprised of sodium diuranate, copper hydroxide/fluoride/sulphates, sodium fluoride/sulphate, plus carbonates, chlorides in addition to others.

Through the collaboration between Westinghouse and NNL the phased approach was employed and a bespoke process developed to process this large volume of materials.

The process utilizes a batch dissolver to produce a liquor which is a compromise between rapid and massive crystallisation and the processing of huge volumes of very dilute liquor.

A solvent extraction process is used to remove the uranium which is recovered and returned to the fuel cycle.

A cyclic PH precipitation process is used to separate out the copper, which is a highly insoluble brochantite.

The phased approach developed the route and the plant was designed and constructed to process the large volumes of material.

Decontamination of materials

In all nuclear applications numerous materials become contaminated resulting in the materials needing decontamination before they can be disposed of. In addition to materials arising from operations, during the decommissioning process numerous items are generated which require decontamination.

Springfield's has 2 large uranium decontamination facilities. The first is the enriched decontamination facility which can process material with uranium enrichments up to 5%. The capabilities include sorting and size reducing as well as dismantling and cutting up of larger items. This facility uses a range of techniques including acid washing/pickling and is capable of processing materials such as metal, wood, rubber, plastics etc. The criteria is to remove sufficient uranium for disposal however the process is continuously being refined and a reasonable proportion of materials are now able to be decontaminated to allow them to be released for recycle.

The natural decontamination facility follows the same principles and has the same wide range of capabilities as the enriched facility however is limited to natural or depleted uranic's.

Hex Cylinder Services

Hex cylinders have been used widely in the nuclear industry worldwide for many years. There are numerous types of hex cylinder, some have current transport licenses however there are many that are obsolete.

WM2016 Conference, March 6 – 10, 2016, Phoenix, Arizona, USA

Westinghouse has the capability to manage the complete life cycle of hex cylinders. The services include cylinder washing of current enriched hex cylinders (eg type 30B) and natural hex cylinders (eg type 48Y) in addition to the washing of virtually any obsolete hex cylinder.

The wash facilities use a chemical process to clean the internals and externals of the hex cylinders and dry them ready for inspection and returning to service.

Westinghouse has technical experts that can cover all aspects of cylinder licensing and engineering.

The liquid residues that arise from the washing of the cylinders are processed in the various facilities, outlined above, and the uranium is recovered for use back in the fuel cycle.

In some cases hex cylinders have been stored for many years and the residues that remain inside are unknown. The obsolete hex cylinder wash facility is segregated from the main washing facilities to enable cylinders to be washed and the contents be treated through a bespoke route if the materials do not meet the ASTM specification.

Any cylinders that reach the end of their life or are deemed to be obsolete can be washed then transferred to our dismantling rig where they are cut up. From here the metal is transferred to the decontamination facilities outlined above where the metal is decontaminated and in many cases the metal can be sent for recycle. Worst case the metal is sent for very low level waste disposal. The methods that have been developed including the chemical washing and aggressive decontamination result in the complete liability removal of hex cylinders. There are alternative methods employed around the world across various organizations but many of these result in a secondary waste that is returned.

NNL BESPOKE PROCESSING ROUTES

Where the result of the phased approach is that the residue type cannot be processed through an existing Westinghouse mainline process, NNL have developed a number of bespoke capabilities for smaller volumes of complicated residues.

The NNL Preston Laboratory Residue Treatment Plant contains a wide variety of modular plant items which can be quickly configured to differing roles. The plant area was constructed with a view to being used both for development work in chemical engineering and for specialist processing tasks requiring unusual equipment and/or close technical control by professional staff.

The plant area comprises 10 large "Bays", each Bay having a series of "risers" supplying services such as power, process and cooling water, off gas extraction, compressed gases, steam etc. Modular plant available currently includes a variety of stirred vessels, some lined for corrosion resistance. These can be used for a wide variety of tasks such as dissolution, leaching, precipitation, settling, decantation and oil and solvent clean up; a variety of solid-liquid separation equipment; a

flammable solvent treatment rig; oil/water centrifuge; nitric acid capable industrial washing machine and; solvent extraction equipment.

Although constrained in terms of processing capacity, there are many advantages of Preston Laboratory equipment for low to medium volume materials requiring particularly complex multistage processes. Specifically designed stirrers and vessels have been incorporated for improved solids suspension, resulting in improved dissolution/leaching. In addition, corrosion resistant plant allows processing of high fluoride/sulphate/chloride residues to be undertaken and materials other than nitric acid to be used.

The manual nature of many of the Preston Laboratory operations means that wet, sticky and/or reactive materials can be fed safely and with relative ease. Ongoing processing is supported by integral laboratory facilities and professional staff who are available for immediate trouble shooting.

Thousands of drums of residues, intractable to processing in conventional recovery plants, have been processed to date and processing programmes extend out for some years into the future. Processing of residues has ranged from single drums of material to many tens of similar drums; some future work is likely to involve thousands of drums of essentially similar materials using processes not applicable to normal processing plant operations.

In order to address the issue of contaminated organics, the National Nuclear Laboratory (NNL) has developed a suite of treatments designed to recover uranium and to render the organic waste suitable for disposal. The developed processes are operated at considerable scale via the NNL Preston Laboratory Residues Treatment Plant.

'OWL' (Oil Waste Leaching)

OWL is a fully industrialised process used for the treatment of contaminated oils. Approximately 200 te of uranium contaminated oil has been treated via various installations within the NNL Preston Laboratory Residue Treatment Plant. Processed oils include "water emulsifiable" cutting oils, lubricating oils, hydraulic oils/fluids and "Fomblin" (fully fluorinated) oils.

The process can be operated using various equipment within the NNL Preston Laboratory; a large industrial scale centrifuge is available together with tanks capable of treating varying volumes of oils. Approximately 1000 drums of oil have been treated via OWL and tens of tonnes of uranium contaminated TBP/OK solvent (including badly degraded solvent) have also been treated via a process and equipment more or less identical to OWL.

Oil samples are tested via the laboratory to determine the optimum processing conditions for the bulk residue. As such, representative sampling is crucial, especially regarding any settled sludge. Laboratory testing is used to investigate whether bulk solids removal is required and at what stage this is most advantageous. In addition, the agitation/mixing conditions, the contact time, the number of contacts, the operating temperature, the sulphuric acid concentration and the oil/sulphuric acid volumetric ratio are optimised at this stage. The

requirement for additives which can aid uranium extraction is also assessed. The OWL process has also been tested in conjunction with non-uranic alpha contaminated oils, yielding a very high decontamination factor even in the presence of a considerable amount of active solids. It would be expected that OWL could easily be applied to many other contaminated oils, though some alteration to the chemistry might be required or be advantageous.

'STAR' (Solvent Treatment Advanced Rig)

STAR is a small treatment plant which allows volatile and flammable solvents to be treated in aqueous sulphuric acid. The rig is ATEX rated and operates under an inert atmosphere during solvent processing. STAR has treated a few hundred litres of uranium contaminated solvents in recent years.

Part of the STAR rig can also be utilised in the treatment of water miscible solvents. This process involves the addition of caustic soda solution to precipitate uranium for recovery.

'SWORD' (Springfields Waste Organic Residue Digester)

SWORD was developed to treat a specific residue comprising a resinous floor polish/PVC matrix contaminated with gross levels of uranium dioxide (UO_2). Incineration of the residue proved very problematic, with the production of large volumes of flammable gas and "vitrification" of the inorganic component. This latter issue resulted in the encapsulation of uranium, rendering the furnace treated material unleachable in anything other than hydrofluoric acid.

Direct treatment with aqueous mineral acid, caustic soda and solvents was completely ineffectual and/or produced large volumes of intractable by-products. NNL have developed the "wet oxidation" SWORD process to treat the target residues.

Hot concentrated sulphuric acid acts as a powerful oxidising agent. When heated, sulphuric acid decomposes and produces nascent oxygen, which helps in the oxidation process.

The process has also been tested in conjunction with a tritiated oil; in this process (TOAST, or "Tritiated Oil Advanced Sulphuric Treatment"), the oil was initially treated in concentrated sulphuric acid at a temperature selected to prevent oil boiling/evaporation, followed by the normal carbon digestion step. Tritium recovery to the acid was effectively quantitative with no measurable tritium escaping as off gas.

It is clear that the SWORD process will be applicable to a wide variety of organic wastes, most of which will be far less intractable than the residues for which it was developed.

'SCIMITAR' (Springfields Complex Intractable Material, Total Actinide Removal)

SCIMITAR has been developed for the treatment of uranium solvent extraction (SX) plant cruds. The cruds comprise a mixture of TBP/OK, aqueous liquor (impure uranyl nitrate/nitric acid), inorganic solids such as zirconium hydrogen phosphate

and similar, magnesium fluoride and silica plus c. 20 % w/w organic solids; the residues are contaminated with uranium, and with very high levels of thorium and protactinium (as ^{231}Pa).

CONCLUSIONS

Over a number of years Westinghouse has developed bespoke and novel processing systems with exceptional capabilities focused purely on Uranium Recovery and have put these to the test for their own materials and for customer owned materials.

In collaboration with NNL, Westinghouse has developed routes for virtually all residue types and have proven these routes through the processing of over 50,000 drums and over 150 ISO containers worth of combustible soft residues.

Westinghouse has extensive experience in Uranium Recovery and Uranium Hexafluoride Cylinder Management and can provide unique, effective and practical solutions.

Westinghouse is currently working globally providing Uranium Recovery and Legacy Management services.

In many examples customers have a legacy but have little capability and understanding of the materials and what options are available. Through a phased approach and in collaboration with partners Westinghouse provides technical assessment and route development services to help customers understand the problem and options available.

Westinghouse believes that the extensive development work and significant knowledge accumulated could be of benefit to any other organisation with similar materials.

REFERENCES

- NNL Preston Laboratory Technologies/Processes for the Treatment of Organic Wastes
H. Greenwood, T.I. Docrat, S.J. Allinson, D.P. Coppersthwaite
- The National Nuclear Laboratory's Approach to Waste and Residue Processing
H. Greenwood, T.I. Docrat, S.J. Allinson, D.P. Coppersthwaite