The National Nuclear Laboratory's Approach to Processing Mixed Wastes and Residues - 13080

Howard Greenwood, Tahera Docrat, Sarah J. Allinson,
Duncan P. Coppersthwaite, Ruqayyah Sultan, and Sarah May
National Nuclear Laboratory, Springfields, Preston, UK, PR4 0XJ, howard.greenwood@nnl.co.uk

ABSTRACT

The National Nuclear Laboratory (NNL) treats 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. In the context of this paper, treatment is defined as recovery of uranium or other activity from residues, the recycle of uranium to the fuel cycle or preparation for long term storage and the final disposal or discharge to the environment of the remainder of the material. NNL's systematic but flexible approach to residue assessment and treatment is described in this paper. The approach typically comprises up to five main phases. The benefits of a systematic approach to waste and residue assessments and processing are described in this paper with examples used to illustrate each phase of work. Benefits include early identification of processing routes or processing issues and the avoidance of investment in inappropriate and costly plant or processes.

INTRODUCTION

The National Nuclear Laboratory (NNL) works with a variety of customers in the uranic waste and residue treatment area. Traditionally, treatment of materials has encompassed the recovery of uranium from relevant wastes or residues, its recycle to the fuel cycle or preparation for long term storage, and the final disposal or discharge to the environment of the remainder of the residue. The bulk of the wastes and residues assessed and/or treated to date have been produced as by-products of front end of nuclear fuel cycle operations and from decommissioning of associated plants. In the main they have arisen from the manufacture of nuclear fuels and intermediate products, uranium purification operations and enrichment operations.

In the context of this paper, a uranic waste is a material that cannot be disposed of without treatment, but which has no intrinsic value whereas a uranic residue is a material that has some intrinsic value owing to its uranium content.

Over the years, many similar residues from other parts of the nuclear fuel cycle and from other uses of uranium have been found to be treatable by similar methods to front end fuel cycle residues. This has allowed the experience gained by NNL to be applied over an ever widening range of materials. This paper describes the challenges that need to be addressed when dealing with uncharacterised and often unknown legacy materials and the future challenges posed by the wide range of materials which reside on the UK's nuclear sites.

HISTORICAL PERSPECTIVE

NNL has its roots in British Nuclear Fuels Limited (BNFL) and maintains close working relationships with the former BNFL companies, all of which are now separately managed under contract or under relatively new ownership. An extremely successful working partnership was initiated in the mid 1980's between the now NNL Preston Laboratory and SFL Waste Management; the aim of this partnership was to characterise and process the entire backlog of residues stored on the Springfields site.

At their peak, around 1998 to 1999, uranic residue stocks at Springfields totalled c. 40,000 drums (generally 205 dm^3 capacity plastic or metal drums), c. 150 ISO containers and a range of other items.

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 and by the end of 2011 drum numbers had been reduced to about one third of their peak. 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.

Many of the remaining and arising residues are being processed, or are expected to be processed, via existing SFL residue treatment plants. Some residues, however, currently have no proven treatment method or are unsuitable for treatment in such plants. A similar situation exists with respect to many off-site residues. For such residues, NNL has developed a systematic methodology which has facilitated the assessment of over 40,000 drums and similar items. The benefits of such an approach to waste and residue assessments have been shown to include the early identification of processing routes or processing issues and the avoidance of capital investment.

As experience has been gained during the SFL programme and as the issue of uranic residues in the UK has risen in prominence, it has become clear that many residues exist which could be processed via existing or planned NNL and SFL facilities. Accordingly, support work by NNL on behalf of SFL and other customers has expanded to cover such off-site residues, using similar methodologies to those developed for SFL residues.

A PHASED APPROACH

Investigations into residues deemed unsuitable, or at least not obviously suitable, for processing in existing or planned plant have been carried out using the methodology outlined in Fig 1 and described in detail in the following sections.

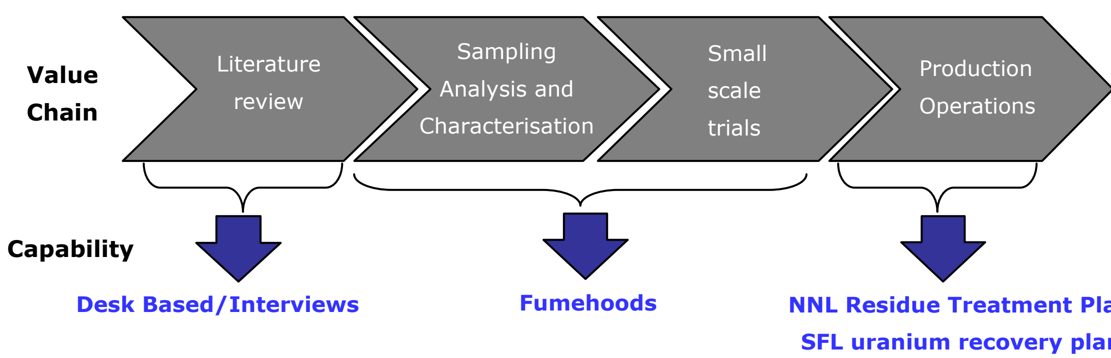

Fig 1. NNL Residues Phased Methodology

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 in existing or planned NNL or SFL plants. 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 (if relevant). It is essential to understand whether more than one type of material is present since minor fractions can prove to be the most problematic when it comes to processing. For example, materials such as tissues, gloves, wipes, filter media, tape, vacuum bags, etc. can be processed but segregation from the bulk material is typically required (Fig 2).

Fig 2. A fairly typical decommissioning residue

The presence of reprocessed uranium or isotopes not normally associated with uranium processing and fuels manufacture can be problematic for certain processing routes and effluent/solids discharges. As such, characterisation data is an extremely important factor in understanding what is known about the material and what still needs to be discovered.

While assessing any available characterisation data, it often useful to concurrently assess the softer or more anecdotal data relating to the waste or residue. Such data may include when, where, how the material arose and how long it has been in its current form.

Experience has shown that the older the material, the less well characterised it is likely to be. It is similarly useful to know whether the material has always been in the possession of the customer, whether they actually produced it themselves and has any processing been attempted by any method, be it at laboratory or full scale. If processing had been attempted, what was the outcome and why was such processing nor pursued?

Storage

How a material is stored, particularly in terms of its storage container(s), is much more important than it might seem. Many plant processes require feedstocks to be fed from a specific container and

modifications to feed from different containers is expensive in terms of plant modification and impact on ongoing operations. Re-drumming of materials can also be considered at this stage.
The presence of secondary containers such as bags or bottles will have a major impact on material processing as these will probably need to be removed and would rule out direct processing in some plants.

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.

Key factors which affect pre-processing requirements include whether the material is physically homogeneous i.e. are there distinct differences between drums of ostensibly the same material or within individual drums; whether the bulk material comprises fine powder, coarse powder, lumps or a mixture of all three; whether the material is mixed with tramp objects such as hard agglomerates of the main constituent material or extraneous materials such as wire, plastic, metal, paper, etc; whether the material is dry, damp or contains free standing liquor; whether the material contains macroscopic quantities of organic materials such as oils, solvents or solid organics and; whether the material is free flowing, sticky or adhesive.

Chemical Properties

The chemical properties of the material are paramount in determining its processiblitiy. 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. As with physical properties, homogeneity both within drums and across the stock is important since much reported data on chemical composition is based on sampling and analysis. It is vital that any chemical analysis is based on representative sampling of the material to avoid processing issues down the line. In many cases, fully representative sampling is impossible and a degree of judgement is required.

Many factors will affect the process selection but the main considerations usually include; how the material would behave on contact with acid e.g. gas evolution, foaming, heat evolution and the generation of flammable gases; the properties of the leach slurry e.g. corrosivity (particular in relation to 304L stainless steel) and; the presence of any species which would impact on discharge authorisations or could adversely affect uranium purification. For uranium targeted for reintroduction into the fuel cycle, a range of additional factors which might affect product specifications would also need to be considered.

Radioisotope content

The radioisotope content of the material is very important in terms of the specification of any final product. Uranium isotopes such as ^{232}U, ^{234}U and ^{236}U are of particular interest since they cannot be removed during residue processing, though blending opportunities can often be considered. For material which has undergone enrichment blending involving highly enriched uranium (HEU), unusual ^{234}U concentrations are often encountered whereas ^{232}U and ^{236}U are often encountered when reprocessed uranium has been processed in the same plant as non-irradiated uranium. All minor uranium isotopes are tightly controlled in fuel and intermediate product specifications.

Isotopes not normally encountered in nuclear fuel processing are of increasing interest as the range of wastes and residues amenable to treatment expands. NNL works closely with SFL, the Springfields Site License holder, and the Environment Agency (EA) to develop pragmatic strategies for dealing with any discharge issues arising from such isotopes. Early identification of potential discharge issues is paramount in developing appropriate processing and effluent treatment options.

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 be somewhat “hands-on” when compared with other nuclear sites. This is highly advantageous in terms of ease of implementation but means particular cognisance of operator doses must be taken into account. Dose rates in excess of those normally encountered during processing of low enriched uranium (typically up to 5 g ^{235}U/100 g U) are of interest. Additionally, those materials for which working times exist would require further consideration.

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.

A further consideration relating to processed materials is whether the customer is expecting to take back process wastes or separated uranium and what constraints this might impose on processing routes. If there is a requirement to return materials, it is important to understand whether there is a specification for the materials generated.

PHASE 1A

Many materials cannot be sentenced as a result of Phase 1 assessment due to a lack of prior characterisation or a low level of confidence in the precise nature of the material, its origin or its storage conditions. In these cases, inspection and sampling of the residue stocks is required. This phase is routinely supplemented by instrumental analysis of feedstocks, particularly where poorly understood materials are involved. The instrumental analysis of materials was introduced as an additional phase of work to allow some characterisation prior to specifying the next phase of work. Samples of the dried material are typically subjected to X-ray diffraction (XRD) analysis and scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analysis and the results used to assess the composition of the residue. Other techniques, such as thermogravimetric analysis (TGA) and infra-red spectroscopy (IR) are utilised as required.

A typical inspection programme will involve opening drums or other containers and visually examining the contents. The selection of drums is guided by the findings of Phase 1, particularly where groupings of items was apparent. The grouping of drums or other items is normally based on the apparent source of the material and sequences of batch numbers or other identifying marks but experience has shown that mislabelling or misidentification of drums can occur. As such, it is crucially important that the proportion of drums inspected and sampled is sufficient to provide reliable data on the entire stock. For certain poorly characterised and highly variable materials, 100 % sampling can be required. These types of materials normally require the development of specific processing routes and are discussed in more detail under Phase 3. Inspection and sampling can be undertaken in the field by NNL or Customers’ staff or within purpose built facilities within the Preston Laboratory.

Characterisation work typically involves the identification of major phases within the residue, often with identification of the main acid soluble species and the quantification of any organic content. This initial characterisation work, coupled with the inspection programme, allows those materials which are obviously unsuitable for processing in SFL uranium recovery plants to be identified at an early stage in the programme, avoiding unnecessary process testing. Those materials identified as potentially suitable for SFL plants, either directly or following pre-treatment, are subjected to Phase 2 process testing. Targeting processing via SFL plants is often the most cost effective route where large volumes of residues requiring reasonably standardised processing conditions exist.

Many materials have been sentenced directly to established residue processing routes following Phase 1A characterisation. This tends to occur when only confirmation of a material type is required.

PHASE 2

SFL operates a uranium recovery plant for the treatment of depleted to c. natural enrichment residues and a separate plant for enriched residues. Laboratory investigations and detailed analysis of materials aimed at determining if materials are processible via these SFL plants are termed “Phase 2” investigations. These generally involve leaching in nitric acid under typical plant conditions and analysis of leachates and residual undissolved solids.

A “standard” leach apparatus (Fig 3), with a typical capacity of 2 dm^3, is used in the majority of this work, though smaller equipment sizes can be utilised as considered necessary. The reaction vessel is fitted with a multi-necked and flanged lid, and located on a halogen hotplate. The central lid neck is fitted with a stirrer which is connected to an overhead stirrer motor. One neck of the lid is fitted with a condenser, and a second with a temperature probe (typically a PTFE coated thermocouple connected to a digital thermometer). Spare necks are fitted with stoppers.

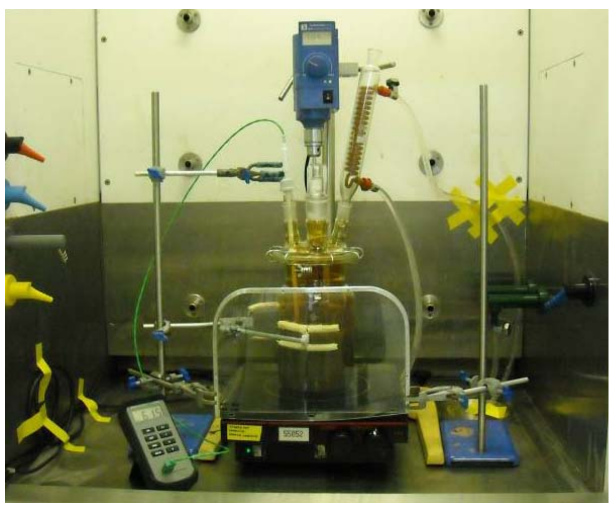

Fig 3. The “standard” Phase 2 leach apparatus.

For each experiment, the apparatus is assembled and the acid heated to the target temperature. Any required materials such as alumina are then added (alumina is normally added where fluoride is present at notable levels, to ensure complexation for the purposes of dissolution and minimisation of corrosion), followed by the feedstock residue.

Residue additions are initially made in small aliquots to determine if any vigorous reaction occurs, and then in bulk if this is indicated as safe by the initial additions. The slurry is then heated (if necessary) to a desired temperature and held there for the desired time.

Following leaching and cooling, the apparatus is inspected and the appearance of the contents noted; the apparatus is then dismantled and the slurry subjected to solid-liquid separation. Recovered solids are washed with deionised water with the bulk of the wash water being collected separately from the leachate. Recovered solids are weighed, dried and reweighed before being crushed and mixed prior to sampling and subjected to quantitative uranium analysis. In addition, samples of dried residual undissolved solids are (where considered necessary) subjected to analysis by XRD and SEM-EDX techniques.

Leachates are analysed for uranium, uranium enrichment, heavy metals, and a range of chemical species and radioisotopes of importance to onward uranium processing and site discharges.

Using the Phase 2 experimental data, the processibility of the materials via SFL plants has generally been assessed in terms of the chemical and physical form of the residues, likely ease of feeding to dissolution equipment, reactivity on contact with nitric acid, solid-liquid separation of leach slurries, residual solids uranium concentrations, and onward processing of recovered liquors in terms of chemical compatibility with the residue plants, environmental discharges and the presence of materials which might cause out of specification pure uranic product post purification.

The outcome of Phase 2 investigations has historically been to recommend processing in SFL plant, sometimes with a specific non-standard process regime stipulated, or to recommend the development of a residue specific process (this latter generally being termed “Phase 3” – see later)

Often, parts of existing plants can be adapted to permit the implementation of a non-standard process. The processing of Casting Shop Graphite which historically made up a large fraction of the Springfields residue stock is an example of such an adaptation. The graphite residue from the vacuum casting of uranium metal into rods had been accumulating since 1966 when the previous method of treating the material ceased. The residue comprised relatively large pieces of graphite, occasionally with pieces of uranium adhering to the surface, and free uranium metal (Fig 4).

Fig 4. Casting Shop graphite.

The requirements for the graphite treatment process were that it should utilise existing Springfields facilities as far as practically achievable in order to recover the uranium for recycle and render the graphite suitable for disposal. While direct leaching could clearly recover the bulk of the uranium, the leached graphite contained too much residual uranium to allow direct disposal to landfill. Disposal of leached graphite to LLWR was not considered feasible due to the high volume of material (> 10,000 drums) that would need to be disposed of and the substantial residual alpha activity associated with the leached graphite. The unsuccessful leaching of bulk graphite was believed to be due to be presence of uranium metal in the pours of the graphite and size reduction prior to leaching was considered necessary.

NNL undertook Phase 2 leaching trials using, as a basis, leach conditions that could be realistically achieved in the Springfields magnesium fluoride treatment line. This line involved a wet milling process followed by leaching in dilute nitric acid at ambient temperature. It was demonstrated that near quantitative removal of uranium from graphite could be achieved if graphite was milled to the size likely to be achieved in the magnesium fluoride treatment line.

Following demonstration of the process feasibility, SFL undertook to segregate the bulk of the uranium from the graphite by hand sorting and worked with NNL and equipment suppliers to identify a suitable pre-crusher for use in reducing the size of the graphite pieces prior to milling. Selection of crushing equipment was complicated by the presence of residual uranium metal (post sorting) which could present a pyrophoricity hazard or might damage the crushing equipment. Owing to these concerns, high speed crushers were considered to be unsuitable.

Following the identification and successful testing (using new graphite components) of suitable low speed crushing equipment, a unit was installed at Springfields in 2006. Extended plant trials were undertaken in order to optimise the residue feed rate to the milling stage of magnesium fluoride treatment line and the acid and water feeds to the process. The resulting process was successfully implemented in 2007 with the bulk of the residue stock being processed over a period of c. 4 years. About 40 te of extracted uranium has been returned to the fuel cycle (Fig 5) via this process.

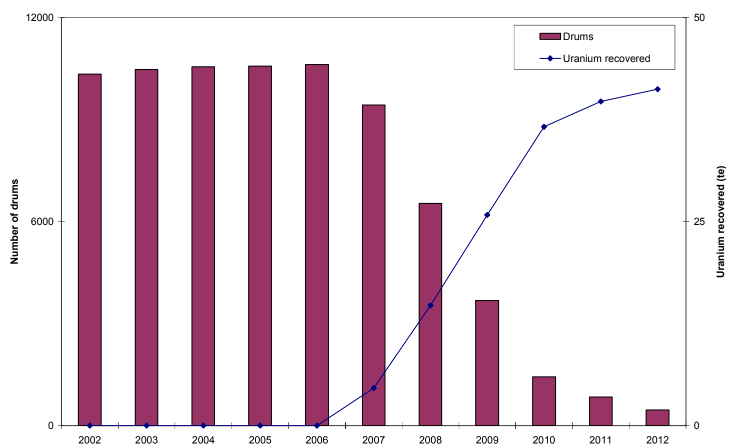

Fig 5. Casting Shop graphite processing.

The graphite slurry was filtered using standard plant filtration equipment with a modified wash procedure to ensure adequate removal of dissolved uranium and nitric acid from the free draining graphitic filter cake.

The success of the adapted graphite process has allowed the plant and process to be further flexed to allow the processing of several other previously intractable resides such as building rubble and incinerator ashes.

PHASE 3

As previously mentioned, 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 within the NNL Preston Laboratory is concentrated on those residues, identified in prior investigations or experimental work, as unsuitable for treatment in SFL residue 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 has been assessed for treatment via Phase 3 process development, a few examples are presented as part of this paper.

- Filter cakes containing high concentrations of uranium from previous chemical leaching operations (typically containing uranium encapsulated within nitric acid insoluble materials).
- "Oily residues"; typically cutting or lubricating oils containing pyrophoric uranium swarf or degraded uranium fines.
- Contaminated oils and solvents containing dissolved uranium (including oils and solvents absorbed on filter aid, sawdust or similar.
- "Copper based" residues (copper hydroxides, fluoride-sulphates, bicarbonates) containing uranium.
- Sludges from solvent extraction operations (some are > 50 years old; high in ^{231}Pa).
- Resinous floor polish containing high concentrations of enriched uranium.
- Highly pyrophoric "uranium-zirconium" metal residues stored under kerosene.
- Various uranium metal and alloy items.
- Ventilation filters of many kinds.
- Contaminated paper, plastic, clothing, gloves etc.
- Decommissioning residues (concrete, bricks, blocks, timber, metals, etc).

Phase 3 experiments are carried out in similar fashion to the Phase 2 leaches, with ad hoc modifications as necessary, such modifications being specifically tailored to the individual residue. Typically, experimental work is carried out at a scale of several hundred grams but pilot scale processes of several tens of kilograms can also be employed.

The outcome of the Phase 3 experiments is generally a fully defined process, specified for particular residue type or group of residues. The developed methods are generally, but not exclusively, targeted for full scale implementation via the NNL Preston Laboratory Residue Treatment Plant which is far more flexible than the conventional uranium plants.

PHASE 4 PROCESSING

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 (Fig 6) 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 and with capacities from 100 dm^3 to 10 m^3, 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.

Fig 6. The NNL Preston Laboratory Residue Treatment Plant

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. A typical material loading operation by a member of the NNL production team is shown in Fig 7. Ongoing processing is supported by integral laboratory facilities and professional staff who are available for immediate trouble shooting.

Fig 7. Loading a corrosive residue into a leach vessel.

Hundreds 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 hundreds of drums of essentially similar materials using processes not applicable to normal processing plant operations.

CONCLUSIONS

Historically, at Springfields, waste and residue treatment work for "no route" or "orphan" residues tended to concentrate on one particular residue at a time. It was recognised in the mid 1990s that the broader picture needed to be assessed. In 1997, BNFL Springfields (now Springfields Fuels Ltd) embarked on a major programme of residue characterisation and method testing/development; most of the technical aspects of this work are being carried out by NNL. This programme, known within NNL as the Uranium Residues Management Support (URMS) Programme, has now been running for 15 years and has some years at least to run. Similar programmes have been carried out at other NDA sites over the same time period and more recently NNL has started to forge partnerships with a range of new customers.

These ongoing waste and residue characterisation and treatment programs developed between NNL and its partner organisations demonstrate that wide ranging legacy uranic materials can be successfully treated with recovered uranium being returned to the fuel cycle or rendered stable for long term storage. Success in discharging historic liabilities has been achieved through the maintenance of a long term and co-ordinated approach to residues and a clear and structured technical strategy.