Separation and Recovery of Uranium from Residues to Allow Disposal as VLLW – 15379

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ABSTRACT

During fabrication of uranium fuel, significant amounts of uranium contaminated wastes are generated. The uranium concentration in the waste is typically 1-10% in weight. With this uranium concentration, the residues constitute long lived Low Level Waste (LL-LLW) which need to be disposed of in a repository specifically for this type of waste.

Through recovery of uranium from the primary waste, the potential for reducing the concentration of uranium to such low levels that the remaining waste qualifies as Very Low Level Waste (VLLW) are significant. The remaining waste could then be disposed of in a less costly disposal than the primary waste. A method for recovery of uranium from waste has been developed and used in Sweden and includes leaching with sulphuric acid, solvent extraction and precipitation. The final result is ammonium di-uranate (ADU).

The remaining waste typically has residual uranium content in the range of 100 g uranium per tonne of waste. In several countries this would permit disposal at a hazardous waste landfill site after conditional clearance. During the development process, it has been shown that for certain types of waste it's possible to reduce the uranium concentration even further.

The paper gives an overview of the technology, its applications as well as advantages and limitations.

INTRODUCTION

When producing uranium nuclear fuel, there are generations of uranium contaminated waste which need to be managed properly. The uranium concentration in the waste is usually in the range 1-10 % weight, corresponding to 1-10 MBq/kg.

Waste with this concentration of uranium is normally considered as long lived LLW (LL-LLW). Legislation, would, in many countries, necessitate disposal of such residues in a repository licensed for long lived radioactive waste. This usually means costly handling and disposal of waste which basically holds only radioactive nuclides which occur naturally.

Recovery of uranium, in order to reduce the uranium concentration in the waste, to levels which makes it possible to re-classify the waste as VLLW or, if possible, make them subject to either general or conditional clearance will save money and space in the more expensive repository.

History

During the 1950s, a process was developed, by the state owned organisation AB Atomenergi, to leach uranium from alum shale found at several locations in Sweden. It began in 1949 with a decision to establish a process to make Sweden self-reliant of uranium for future nuclear usage [1]. A test facility was erected in 1949, in Kvarntorp, and the first trials were done. In 1950, a pilot plant was built for separation of uranium from “kolm”, small lens-shapes bituminous inclusion in alum shale containing 10 times the concentration of uranium than the shale itself, and during its operation (from1950-1954), a total of 1.5 tonnes of uranium were separated. In total 62 tonnes of uranium was produced at the leaching facility in Kvarntorp and the original process for leaching of uranium from alum shale was developed, the AE method. Commencing in 1960, the plant was no longer used on alum shale; instead uranium ore from Finland was used. The decision to close the Kvarntorp facility was made in 1961 and in 1964 the facility was decommissioned.

During 1951 to 1961, the uranium produced in Kvarntorp was transported to an old laboratory in Stockholm that was previously used by Alfred Nobel for production of explosives. Once refined, the uranium was transferred to yet another laboratory where it was used for experimental work for fabrication of oxide as well as metallic fuel. This laboratory produced fuel to support some experimental reactors or piles and the R1 reactor in Stockholm.

In the beginning of the 1960s a facility was built next to the uranium mine in order to produce uranium for Swedish reactors. The facility was named Ranstad after the village next to the plant and produced uranium from alum shale for fuel production for the Ågesta, R0 and R1 reactors. The Ranstad milling facility, see figure 1, was in operation until 1969 and produced 215 tonnes of uranium [2, 3].

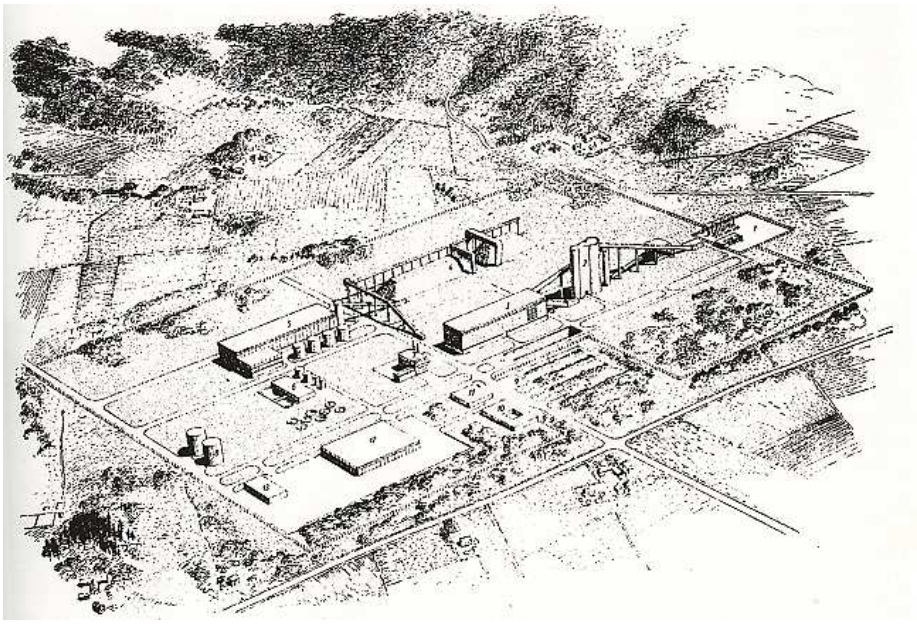

Fig. 1
The Ranstad facility

Based upon a need for treatment of the waste arising during operation and decommissioning of nuclear fuel facilities, a new business was developed and a new company, Ranstad Mineral AB was formed. The original process for the leaching of alum shale was developed after significant R&D efforts were modified for the optimal efficiency of the separation of uranium from several types of contaminated waste from nuclear fuel factories. Processing of contaminated waste started in 1980. Wastes from central Europe and Sweden was processed on a commercial basis up to the shutdown of the entire Ranstad plant a few years ago.

The method, which is known as the RMA Process, and its overall concept is presented below.

URANIUM CONTAMINATED WASTE FROM NUCLEAR FUEL FABRICATION

For some materials, there are indicative figures available of typical uranium concentrations and amounts that are generated annually.

Uranium contaminated waste, such as combustible waste or resins, that have been treated at RMA can come directly from the plant or from a treatment facility where the primary waste has been treated, for example arriving as an ash or a lime sludge.

Directly leachable wastes

Typical combustible materials are paper, fabrics, plastics, wood and other organic materials. The content of uranium is often around 1% by weight but from time to time can be up to 5%. A normal sized nuclear fuel factory generates 10 – 20 tonnes of combustible wastes per year.
Ion exchange resins normally consist of organic polymer materials (plastics) and concentrations in the order of 1% by weight. The annual consumption of resin is about one tonne in a typical size fuel factory.

The typical filters used are HEPA Filter (High Efficiency Particulate Air Filter) consisting of fabric plus a metallic or wooden frame. A standard filter has a weight of 10-20 kg including frame. The uranium content can be hundreds of grams of Uranium per filter with a concentration of 2-3% by weight. The annual consumption of filters is in the range of four tonnes for a typical facility.

Waste leachable after treatment

Some fuel factories treat their combustibles with thermal methods like incineration or pyrolysis to reduce the volume of the waste. These processes will reduce the mass of the waste by a factor of about 10 and the volume by a factor of 30. The specific uranium concentration increases proportionally with the mass reduction.

Typical uranium concentrations in ashes for leaching are 3-5% by weight but somewhat higher concentrations occur. The license conditions for the thermal treatment facilities used, for example maximum uranium content in a treatment batch, is a limiting factor.

Non-Leachable Wastes

Waste that is non-leachable may still be treatable in order to separate the uranium from the waste in order to avoid disposal for the whole waste batch.

Metal from scrapped equipment, molybdenum from scrapped sintering trays, Zircaloy from scrapped fuel rods are typical uranium contaminated metals which are generated in a fuel fabrication plant. The activity concentrations as well as the yearly volumes differ significantly based on the activities performed.

Non-metallic materials as replaced bricks from sintering furnaces as well as certain building materials will also generate uranium waste. The activity concentrations as well as the annual volumes differ significantly depending on the activities performed.

Also, uranium contaminated fluids (e.g., cutting fluids, etc.) from laboratories as well as production facilities may have a uranium content that requires treatment. Liquids are normally not accepted in a repository which means that they either have to be treated or absorbed.

DISPOSAL OF URANIUM CONTAMINATED WASTE

There are basically two ways to dispose of radioactive materials and waste

- clearance for reuse, recycling or disposal
- disposal in a repository licenced for radioactive waste

Clearance could either be for un-conditional use or conditional clearance, i.e. for example disposal in a landfill for hazardous waste. For material for un-conditional use, no requirements apply after the clearance measurements have been reviewed and approved. The clearance levels for conditional clearance are significantly higher than for un-conditional clearance, typically one order of magnitude or more.

The type of repository uranium contaminated waste varies between countries as each country has their specific conditions. There are some countries where all un-irradiated uranium contaminated wastes can be disposed of as NORM (natural occurring radioactive material) in specified landfills; other countries classify uranium contaminated waste depending on where the waste has been generated while yet other countries consider all uranium contaminated wastes as alpha contaminated wastes to be disposed of in a repository for radioactive waste. So as a conclusion, there is no general rules when it comes to disposal of uranium contaminated wastes. However, in all cases it is better to recover/recycle the uranium than to dispose of it, as it is for most natural resources.

HANDLING OF URANIUM CONTAMINATED WASTE

Direct disposal in a landfill of uranium contaminated organic waste without any pre-treatment is in most cases neither allowed nor recommended. Whether the waste should be disposed as is, in a repository licenced for radioactive waste or be reduced in volume by thermal treatment or super compaction prior to disposal, or be treated for recovery of most of the uranium from the waste prior to clearance or disposed as VLLW depends on several factors.

A number of treatment alternatives are available such as recovery of uranium, decontamination and volume reduction.

Recovery of uranium
Leaching and separation is a well proven technology for recovery of uranium. Several methods have been used within the industry. Among the most common is leaching with nitric acid. Recovery of uranium has a number of driving forces such as recycling of the uranium back into fuel production, open up for clearance or reclassification of waste to VLLW.

Decontamination
Decontamination applies mainly to materials like metals where all of the uranium contamination is on the surface and removable with standard decontamination methods. For uranium contaminated steel, melt decontamination is an alternative. Stainless steel can, in addition to decontamination by blasting or chemical solutions, be decontaminated during melting by adding of certain salts. The uranium is transferred to the slag and removed from the molten metal. The process is repetitive even after casting and remelting. Decontamination is widely used but has limitations for example decontamination of bricks and other materials with large surface areas are difficult and sometimes nature prevents decontamination, for example melt decontamination of uranium contaminated aluminium is almost impossible.

Treatment for volume reduction.
This can be divided into two groups, volume reduction with intact mass and volume reduction combined with mass reduction. Volume reduction without mass reduction, like high force compaction, will not increase the mass specific activity with could be beneficial if the specific activity has an impact on the disposal route or cost for the actual waste.

Volume reduction with mass reduction like in the case of a thermal treatment like incineration or pyrolysis will give a larger volume reduction. It may also be combined with high force compaction to reduce the volume even further. Thermal treatment can also be a pre-treatment step for leaching, depending on which material and uranium concentration the primary waste have.

The value of volume reduction depends on what limiting factors are used for disposal, if it is specific activity, total activity per customer, volume per customer or some other criteria.

THE RMA PROCESS

The well proven uranium recovery process, the RMA Process, as mentioned in the section History section above, was developed by the Swedish company Ranstad Mineral AB and is based on the technologies used in the uranium extraction industry in Sweden.

The Ranstad Mineral AB operations also benefitted from the existing Ranstad facilities as well as some of the equipment when the RMA process was materialized. The process facility consisted of two leaching alternatives, percolation leaching or agitation leaching.

The process includes the following steps, also illustrated in figure 2:

- Pre-treatment: Crushing, grinding and shredding

- Leaching in sulphuric acid: Percolation leaching or agitation leaching
- Solvent extraction
- Precipitation (with ammonia)
- Pressing in filter press

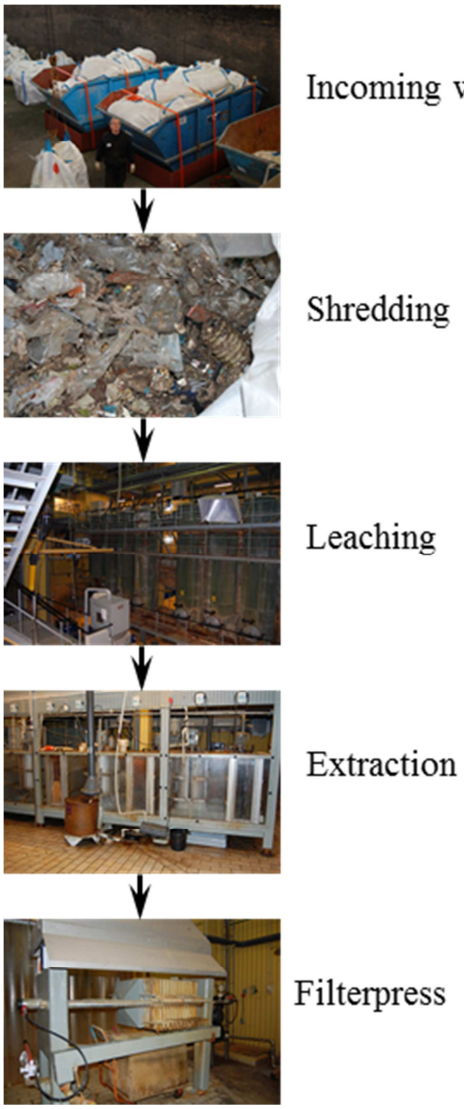

Fig. 2
Principle of the RMA process

The final product in the process is AmmoniumDiUranate (ADU); an alternative final product can, if so preferred, be Sodiumdiuranate (NaDU) by a slight modification of the process.

The uranium is returned to the owner of the incoming waste for recycling in nuclear fuel production while the remaining waste contains such low concentration of uranium that a permit can be obtained from the authorities regarding clearance for disposal to landfill.

The process, as such, is very similar to other leaching processes, as leaching processes tends to be and the feature which makes the RMA process unique is the possibility to reach low uranium concentration levels in the residues after treatment, its robustness and its versatility when applied to uranium contaminated waste. There are few waste matrices that can withstand the chemistry and, if the leaching is not totally successful, there are many possibilities to tweak the chemistry to achieve the wanted results.

Pre-Treatment

Combustible wastes usually arrive in plastic bags. To prevent dusting all wastes are steam wetted before shredding to optimal size. Ashes and similar materials are crushed and ground instead of shredded. HEPA filters are disassembled and leached without shredding.

Leaching

The leaching step is the key part of the process, as this is the step that lowers the uranium concentration in the waste to permit clearance or reclassification to VLLW.

There are two methods for leaching used in the process. Percolation leaching for combustible wastes and HEPA filters. Agitation leaching is used for ashes, sludge and leaching residues.

Percolation Leaching
Large tanks are used for the leaching. Hot diluted sulphuric acid plus some additives are circulated in the tanks.

A counter flow process with three steps is used:

- First step, acid from second step
- Second step, acid from first step
- Third step, new acid

Normally four days are used for leaching. Further steps or repetition of the process can be applied if needed, which means if the secondary waste still has high amounts of uranium left that can be leached.

Agitation Leaching
Agitation leaching is used for slurries. Hot sulphuric acid plus additives are used but temperatures and concentrations are different from the percolation leaching process. The slurry is stirred and a counter flow process with three steps is used for agitation leaching as well.

Solvent Extraction

The mixer-settler technology is used for the extraction over a number of steps and after the extraction there is an intermediate scrubbing of the organic phase. Ammonium based additives are used for the stripping of uranium from the liquid.

The process follows these steps:

- Mixer-settlers
- Multi stage extraction
- Intermediate scrubbing (water)
- Three stripping steps

Precipitation

Hot acid is added to destruct residues from the earlier additives and after this ammonia is added to precipitate ADU which will be captured in a press filter for dewatering. If NaDU is preferred, an alkaline sodium additive is used instead of ammonia for precipitation. The precipitate, i.e. uranium as ADU, is returned to the waste owner.

General Processing Experience and Results

As mentioned above processing of contaminated waste using the RMA Process started in 1980. Since then up to the shutdown of the Ranstad plant wastes from central Europe and Sweden has been processed on a commercial basis.

A total of 900 tonnes of waste has been processed and 10 000 kg of uranium recovered. The treated waste has consisted of 300 tonnes of combustible waste, 100 tonnes of HEPA filters, 400 tonnes of sludge and 100 tonnes of ashes.

The uranium concentration in the leaching residues has generally been below 200 grams per tonne. Until 2004 leaching residues were, after conditional clearance, disposed of at municipal landfill sites and at landfill sites for hazardous waste. From 2004 and forward all residues have been returned to the customers for further management and disposal.

EXPERIENCE FROM LEACHING OF DIFFERENT ASHES

Combustible waste have often a large volume and due to the content of organics repositories may have restrictions on the amount allowed due to their degradation which may result in gas production or release of chealates. Incineration or pyrolysis of combustible wastes, including ion exchange resins, will produce an inert waste form for disposal as the organics are destroyed in the thermal process. An inert waste form is beneficial independently of repository type, radioactive waste repository or hazardous waste landfill.

Incineration would, in most cases, be considered to be the most straightforward alternative as incinerators are more common, at least in Europe, than pyrolysis plants or facilities for direct leaching. All uranium remains in the ashes as they are not volatile in the form they are used in a fuel factory, i.e. UO_2.

Incineration gives a significant volume and mass reduction for organic waste. Based on a typical annual generation of combustible waste in the range of 50 m^3 with the 10 tonne mass and a content of about 100 kg of uranium, it is estimated that the incineration will generate approximately 1 tonne of ashes. Without further treatment, the ashes have to be disposed as long lived LLW. In some cases, VLLW becomes LLW due to the mass reduction, but the waste is

inert from a disposal point of view, and is considered non-leachable under normal repository conditions, i.e. pH > 8.

If incineration is combined with leaching in the RMA process, there is a possibility to recover uranium. However, it is difficult to leach ashes from incineration as the uranium aggregates with the silica in the waste during incineration and forms hard to leach chemical substances. As the RMA process is based on processes developed for the mineral industry, it is very well suited to be applied directly or as in the case of incineration ashes after some modification. For leaching of incineration ashes the process has been modified by adding hydrofluoric acid to the hot concentrated sulphuric acid in order to increase the efficiency of the process. With the modifications to the RMA method, there is a potential for recovery of about 60% of the uranium from incineration ashes. It is, however, unlikely that the leaching will result in a reclassification of the ashes to VLLW, but recovery of valuable enriched uranium can still make the process worthwhile.

An alternative process to incineration is pyrolysis. Pyrolysis is a process where organics are decomposed in a low oxygen environment and therefore not fully oxidised to carbon dioxide, water and other chemical substances. A pyrolysis facility can therefore be built with a higher control of the incoming oxygen/air and other gases than an incineration facility where excess oxygen must always be provided. The pyrolysis process can be constructed so that temperatures which can cause the uranium to react with the silica in the waste are not allowed. Ashes from pyrolysis are therefore much more easily leached than ashes from incineration. The mass and volume reduction will usually be somewhat lower than for incineration.

Using pyrolysis for volume and mass reduction rather than incineration provides an option for future uranium recovery. Lab-scale testing has shown very promising results of the leachability of pyrolysis ashes.

Direct treatment of untreated organic waste is the preferred method if the ambition is to recover as much as possible of the uranium as the uranium has not been through a thermal process and is therefore present as uranium oxide. The actual treatment results shows that 99% of the uranium can be recovered.

An example:
Waste with a volume of about 50 m^3, a mass of 10 tonnes and a uranium content of 100 kg is treated with the RMA Process.

The treatment results in two waste streams;

- A small volume of ADU containing 99 kg of uranium and
- leaching residues with a volume of about 25 m^3 holding not more than one kg of uranium

There is also a possibility to incinerate the leaching residues in instances where the disposal of organic waste is not allowed. The final volume of waste to be disposed would then be reduced to one cubic meter and the increase in specific activity must then be observed in the final product.

This can, in many cases, open make the residual waste subject to conditional clearance which then can make it possible to dispose of the ash at a conventional landfill site instead of in a repository for radioactive waste.

When it comes to the recovery of uranium from organic wastes, it is most beneficial to either leach directly or after pyrolysis. Incineration gives a much harder ash to leach, but the ash can be leached to some degree.

The residues from direct leaching and pyrolysis/leaching may be possible to dispose of as VLLW, depending on each countries regulations and definitions while the residues from incineration/leaching is less likely to be able to dispose of as VLLW.

DEVELOPMENT POTENTIAL

There is a potential for further development of the RMA process on its own or combined with other pre- or post-treatment steps. The development of the process to be able to treat other kinds of incoming wastes is, as always, based on the type of wastes the customer needs the uranium to be extracted from. The process efficiency can, do some degree, be adopted so that the residual waste will meet disposal criteria, for example in a landfill. Based upon the R&D work performed [4] a final concentration below 10 g of uranium per tonne (i.e. 10 ppm) in the residual waste appears to be achievable, however this needs to be verified for different primary waste fractions.

CONCLUSION

There are several technologies available for separation of uranium from different types of residues which could allow a re-classification from LLW to VLLW. With advanced techniques like the RMA, process it is in many cases possible to meet the conditions for conditional and general clearance of the waste after leaching. The operational records also show that it is possible to recover most of the uranium for recycling back into the nuclear fuel fabrication. The RMA process is robust and has several parameters that can be tweaked so that the process works for many different waste matrices, such as ashes from incineration and pyrolysis, as well as untreated organic waste in the form of trash, heap filters and ion exchange resins.

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