PARTITIONING AND TRANSMUTATION OF ACTINIDES AND FISSION PRODUCTS CONSIDERATION OF MEDIUM AND LOW LEVEL WASTE STREAMS

R K WEBSTER
FOR AEA TECHNOLOGY, HARWELL UK

ABSTRACT

The partition-transmutation process has been proposed for the treatment of radioactive waste. A complete scheme requires:

- inclusion of all radionuclides which might have radiological impact after disposal;
- consideration of all significant waste streams.

The first point requires extension of the range of nuclides, for example to cover chlorine-36 and radium-226. This point has been covered in a previous paper and will not be discussed further.

On the second point, most schemes concentrate on the treatment of highly active waste liquor only. However, a complete scheme requires consideration of all subsidiary waste streams: solid, aqueous, organic, and gaseous. For example, up to 2% of plutonium could be present in these streams.

It is necessary to consider all waste streams from the fuel cycle, covering fuel fabrication, enrichment and reprocessing. The components of a conceptual process will be outlined, including:

- conversion of organic waste to inorganic aqueous waste by catalysed electrochemical treatment in nitric acid;
- dissolution of insoluble plutonium oxide by a similar electrochemical process;
- separation of the required radionuclides from aqueous streams by selective electrochemical ion exchange.

1. INTRODUCTION

This paper will concentrate on the removal of minor actinides (Np, Am, Cm) and on the improved recovery of U and Pu, in both cases from secondary waste streams. The proposed processes can be regarded as either (i) a potential input into schemes to increase the recovery of actinides from waste streams for destruction by transmutation, or (ii) as a step in the longer term for increasing the quantity of energy which could be obtained from a given inventory of uranium by recovery and recycle of the actinides.

A few comments will be made on long-lived fission products, as appropriate.

2. INVENTORY

Table 1 shows the volumes and activities of conditioned wastes expected to arise in the UK up to the year 2030, in order to illustrate the problem. The total volume of about one million cubic metres is divided between:

HLW: High Level Waste; in Japan this will consist of the high level liquid waste from reprocessing, or the vitrified waste product.

ILW: Intermediate Level Waste; in the UK this includes other wastes where the alpha activity exceeds 4 GBq/te, or the beta-gamma activity exceeds 12 GBq/te.

LLW: Low Level Waste; wastes below these limits, but in the UK with a cut-off of 0.4 Bq/g.

Table 1

Volumes and Activities of Conditioned Wastes from
All Sources to 2030

Waste type	Volume m^3	Activity	
		TBq alpha	TBq beta/gamma
HLW	3,800	7,900,000	660,000,000
ILW	260,000	67,000	43,000,000
LLW	730,000	100	590

Table 2 provides the corresponding percentage comparison. It highlights the need for attention to ILW which represents about 26% of the total waste volume, and contains nearly 1% of the alpha activity.

As with the fission products, the alpha radioactivity of the total inventory is dominated by short-lived species. In the current UK inventory to 2030, nearly 80% of the alpha activity is accounted for by curium-244 which decays with a half-life of 18 years to its long-lived daughter plutonium-240. Americium-241 is another major contributor, with a half-life of about 460 years. However, from a processing viewpoint, the actinide mass is also important and most of this is associated with the longer-lived components.

Table 2

Percentage Comparison of Volumes and Activities of UK Conditioned Wastes from All Sources to 2030

Waste type	Volume %	Activity	
		% alpha	% beta/gamma
HLW	0.38	99.2	93.9
ILW	26.20	0.8	6.1
LLW	73.40	0.001	0.0001

3. SOURCES OF ALPHA CONTAMINATED ILW

The following comments identify potential sources of waste. Not all will occur, depending on the flow-sheet and the plant design.

(a) Reactors, fuel transport, fuel storage

The inventory from routine operations will be primarily beta-gamma activity from activated corrosion products. The issues raised by damaged fuel and accidents, as at Chernobyl, are not covered by this note.

(b) Fuel reprocessing: head-end section

In the head-end section of the plant, irradiated fuel assemblies or pins are sheared, and the fuel dissolved in nitric acid.
Wastes will include:

- fuel hulls;
- centrifuge cake (PuO_2 fuel residues; insoluble fission product alloys);
- HEPA filters;
- off-gas scrubber liquors;
- shear pack decontamination liquor.

(c) Separation plant: Cycle-1

The main outputs are:

- U and Pu product steams;
- HA waste stream;

- solvent scrub liquors;
- solvent for recycle.

The solvent is normally washed with sodium carbonate and dilute nitric acid to remove degradation products; this generates:

- solvent wash raffinate (SWR), a sodium nitrate steam,

and if the SWR is concentrated by evaporation:

- off-gas scrubber liquors;
- HEPA filters.

Eventually solvent will need to be replaced, leaving

- waste solvent.

(d) HA waste stream

HA waste will normally pass to buffer storage, evaporation, storage, and vitrification.

Wastes will arise as:

- off-gas scrubber liquors;
- HEPA filters;
- plant washings.

The recovery of actinides from the HA waste stream itself is the subject of other papers, and is not discussed in this note.

(e) Separation plant: cycles 2 and 3

These are the medium and low active stages, and will vary with the flowsheet. The terms medium and low active refer to fission product activity: the uranium, and plutonium throughputs will be as in Cycle-1. Similar alpha contaminated wastes will arise as in sections 3(c) and 3(d) above. The medium and low active aqueous waste streams are noted as secondary wastes, but in practice they might be concentrated by evaporation and recycled to the HA waste stream.

Plutonium and uranium product streams may be washed by the solvent diluent to remove traces of tributyl phosphate (or other) extractant, yielding:

- diluent wastes.

(f) Pu and U product evaporators

In each case:

- off-gas scrubber liquors, if not recycled;
- HEPA filters.

(g) Plutonium finishing

Plutonium oxide will be obtained by precipitation as the oxalate or as ammonium plutonyl carbonate for calcination, or directly by thermal denitration. Wastes will include those from off-gas control:

- off-gas scrubber liquors;
- HEPA filters,

and plant clean-out wastes

- wash liquors;
- possibly tissues.

(h) Uranium finishing

Finishing will be by precipitation as ammonium diuranate or as ammonium uranyl carbonate, for calcination, or by thermal denitration. Wastes will be similar to those from section 3(g).

(i) Uranium enrichment

Very briefly, UO_2 is converted to UF_6 for enrichment by reactions typically with hydrogen fluoride to form UF_4, and then fluorine to yield UF_6. Following enrichment, UF_6 is converted to UF_4 by reaction with hydrogen, and then to UO_2 by reaction with steam, or by the ammonium diuranate or ammonium uranyl carbonate routes.

This area is not discussed in detail as it is assumed that uranium recovery is not a prime objective. However, uranium contaminated wastes may arise from off-gas and plant clean-up operations, and as calcium or magnesium fluoride slag if uranium metal is required. The routes for neptunium and technetium in the reprocessing flowsheet should also be assessed.

(j) Mixed oxide fuel fabrication

UO_2 and PuO_2 will be mixed, ground, made into pellets, sintered, ground to size if appropriate, followed by assembly in fuel pins. Wastes may include:

- PuO_2 dust;
- grindings;
- contaminated tissues from cleaning operations;

- hypalon gloves;
- polyethylene;
- PVC bags, where bagless transfer is not feasible;
- off-gas scrub liquors where appropriate;
- HEPA filters.

(k) Uranium oxide fuel fabrication

$U0_2$ fuel fabrication may yield a comparable range of wastes to those from mixed oxide fuel fabrication. The alpha contamination will be much lower, but the waste volume may be higher.

(l) Actinide oxide fuel fabrication

This is not a current problem, but will need consideration when actinide recycle projects are implemented.

(m) Maintenance, refurbishing and decommissioning operations

- waste liquors from plant wash-out and decontamination operations for all previous stages.

4. SUMMARY OF POTENTIAL ALPHA CONTAMINATED SECONDARY WASTES

Section 3 attempts to identify potential sources of alpha active waste from the fuel cycle. Not all will occur: some will be eliminated by changes to the flowsheet, recycle, or by new technology. However, for the purpose of this note the secondary wastes can be grouped into three main classes.

(a) Organic wastes

- waste solvent (eg. tributyl phosphate/dodecane);
- diluent wastes (eg. dodecane);
- tissues;
- hypalon;
- PVC;

- polyethylene;
- HEPA filters;
- complexing agents used in decontamination operations.

(b) Solid wastes

- fuel hulls;
- undissolved PuO_2 rich residues;
- Pu-Pd type alloys in insoluble fission products;
- slags, eg. calcium fluoride (if uranium metal is required);
- PuO_2 or MOx waste:

    - from fuel production;
    - as sub-standard fuel or intermediaries.

(c) Liquid wastes

- MA, LA waste streams;
- solvent wash raffinates (SWR);
- off-gas scrubber liquors;
- plant washings;
- decontamination liquors.

Of these, the solvent wash raffinates will have high sodium nitrate concentrations, unless an alternative washing reagent can be developed.

5. TREATMENT OF ORGANIC WASTES

(a) Key requirements

The key requirements are:

(i) to destroy organic materials totally in order to minimise any risk of interference with subsequent actinide recovery processes.

(ii) to generate an aqueous waste stream from which actinide recovery is reasonably feasible; again, this needs avoidance of organic complexants; and where possible it implies a need to avoid the introduction of large concentrations of inorganic salts, and of inorganic ions that might interfere with separations, for example carbonate, fluoride and sulphate ions.

(iii) to avoid the generation of solid materials from which actinide recovery could be difficult.

While incineration type processes will meet the first requirement, they do not generate an aqueous product, and incinerator ash can be very difficult to process. 'Acid digestion' introduces large quantities of sulphate ions. Treatment with hydrogen peroxide avoids many of the difficulties, but may not give complete destruction of the organic components.

The process that meets the requirements most closely appears to be electrolytic oxidation in nitric acid using a catalyst.

(b) Summary of Silver (II) process

In the silver (II) process, organic materials are destroyed in an electrochemical cell. The cell is similar to those used in chlorine manufacture. It is divided into anode and cathode compartments by a membrane which allows the flow of ions which carry the current, but prevents gross mixing of the contents of the two compartments. Silver (I) is oxidised to silver (II) at the anode. Silver (II) is a very powerful oxidising agent, and reacts with water to form oxidising and reactive radical species. These species react with organic materials fed to the anode compartment, and oxidise them to carbon dioxide, some carbon monoxide, water, and inorganic acids from any hetero atoms such as nitrogen, phosphorus or sulphur present in the organic wastes. The silver (I) is reoxidised at the anode, so there is no net consumption of silver in the process.

(c) Application to organic waste arisings

The silver (II) process can destroy all the organic materials listed in 4(a), with the exception of some HEPA filters and PVC; however, these two exceptions would be decontaminated.

Some of these organic materials contain inorganic fillers. For example, hypalon can yield 30% by weight of ash after incineration: mainly alumina, silica and titania, with smaller quantities of Ca, Fe, Mg, Na and Zn. If these fillers were to dissolve, they would set further targets for the aqueous treatment process. In practice, it is more likely that they will have been incorporated into the plastics as fine ceramic grade pigments, etc. These remain as undissolved fine particles, and can be removed by cross-flow filtration.

6. TREATMENT OF SOLID WASTES

(a) Key requirements

The key requirements are to dissolve PuO_2 rich residues, and plutonium from other contaminated wastes, and to generate an aqueous stream, preferably in nitric acid.

(b) Treatment

Any plutonium contamination of the organic wastes listed in section 4(a) will have been dissolved by the silver (II) process. A similar silver (II) scheme can be applied to plutonium rich residues and scrap from mixed oxide fuel fabrication but probably with a different operating regime.

The silver (II) process can be used to decontaminate hulls. The separation of plutonium from Pu-Pd alloys or from slags is unlikely. However, the slags will be from uranium processing, where the quantities of other actinides should be small.

If the quantities of plutonium in Pu-Pd and similar alloys are significant, an alternative electrochemical process may be feasible as a separate small scale batch operation. This requirement is unlikely for thermal reactor fuel, but may need consideration for high burn-up fast reactor fuel.

7. TREATMENT OF AQUEOUS WASTES

(a) Key requirements

The key requirements are:

(i) to separate actinides from all other ionic components, preferably in a nitric acid solution.

(ii) to suit operation on:

- solutions containing significant quantities of phosphate;
- aluminium solutions containing silicon and titanium ions if these are dissolved instead of being removed by filtration;
- the liquid wastes arising directly, as listed in 4(c); these will contain significant quantities of sodium ions; complexing agents in decontamination liquors are assumed to have been destroyed.

(iii) if feasible, to offer options for the removal of key anions, for example pertechnetate and iodide, to support improved management of long-lived fission products.

(iv) to avoid or minimise the generation of secondary wastes for recycle.

(b) Summary of the electrochemical ion exchange process

Of the various processes available, electrochemical ion exchange is a very promising, selective and flexible technique. The following section gives a brief description of the process.

Electrochemical ion exchange (EIX) is an advanced ion exchange process. An electrical driving force is used to enhance both the adsorption and elution reactions: the process is controlled by the direction of electric current flow.

The EIX electrode is made by coating a thick layer of ion exchange resin onto a mesh electrode using a suitable binder. The ion exchanger can be organic or inorganic, although the latter is normally favoured for nuclear applications. An expanded mesh counter electrode is mounted close to the surface of the ion exchanger which is exposed to the waste stream.

For cation removal the EIX electrode is the cathode, and the counter electrode is the anode. Cations are absorbed from the waste solution, and replaced by hydrogen ions generated at the anode. Thus the EIX system can be used to treat very large volumes of dilute effluent in this way. Modified schemes are used for concentrated or high salt content streams.

When absorption on the ion exchanger is close to capacity, the EIX electrode is regenerated by discharging the ions into usually one column volume of liquid. This is achieved by reversing the cell polarity, when the separated cations are driven off from the ion exchanger back into solution in a selected eluant, often water. The pH of the eluant can be adjusted to prevent precipitation of metal hydroxides.

In trial systems, over 2000 absorption/elution cycles have been performed without loss in system performance.

(c) Application to liquid waste streams

EIX appears to match all the requirements listed in 7(a):

- the ion exchange units are recycled many times (several thousand) so the quantity of the main process waste is small, and it has been decontaminated before discharge;
- in principle, actinide elements might be separated as a group (U, Np, Pu, Am, Cm), or as separate streams;
- anion separation is feasible to generate key fission product streams (eg. TcO_4^-, I^- have already been separated in trials);
- separation can be made from main components such as high concentrations of sodium or phosphate;
- anion and cation EIX units can be operated in parallel within a single module;
- units for different separations can be operated in series.

8. CONCEPTUAL PROCESS FOR TREATMENT OF MEDIUM AND LOW LEVEL SECONDARY WASTE STREAMS

(a) Outline of conceptual process

The treatment of all secondary waste streams from the fuel cycle to recover actinides is a very complex problem. Ideally, it should be planned in parallel with a reconsideration of the reprocessing and fabrication processes in order to optimise the complete system. However, based on waste streams from current reprocessing and fabrication practice, a conceptual scheme might be developed as follows:

- organic waste pre-treatment to suit the silver (II) process;

- destruction of organic materials by the silver (II) process;
- treatment of plutonium rich residues or scrap by a silver (II) process;
- separation of any particulate fillers remaining from organic waste by cross-flow filtration;
- an optional initial actinide separation by solvent extraction from the silver (II) cell is feasible; any waste solvent remaining in the cell after separation would then be destroyed by reactivating the silver (II) process;
- any essential aqueous waste pre-treatment;
- separation of actinides by EIX.

(b) Status

Nearly all of the key steps have been performed in isolation, but they have not yet been integrated into a single process.

There are many operational uncertainties that need consideration. For example:

- will uranium be separated?

This could have a very significant effect on throughput requirements;

- will the aim be to have one common plant, or a set of smaller plants for each fuel cycle facility or waste stream?

This will affect the duty expected of any single unit both on throughput and on separation targets. However, note that both the silver (II) and the EIX processes are modular in concept. Throughput is increased by adding more cells to operate in parallel.

(c) Other points

While the main aim of this note has been to focus on actinide recycle, the process should be adaptable for the removal of key fission product species, including technetium-99 as the pertechnetate anion, and iodine-129 as the iodide anion.

If required for the pre-treatment of aqueous waste, other electrochemical processes might be introduced for the adjustment of nitric acid concentration and for the destruction of ammonium and oxalate species.

A further electrochemical scheme might be feasible to enable the recovery of actinides (mainly Pu) from the insoluble fission product metal alloy particles from the dissolver. This may merit consideration for high burn-up fast reactor fuel.

This note is based on wastes from current reprocessing and fabrication practices. If partition-transmutation is introduced by extraction of actinides from the highly active aqueous waste stream and fabrication of fuel elements containing minor actinides, there will be many new waste streams that will need consideration. However, in principle they should be amenable to treatment by the conceptual scheme outlined in this note.