

Development of Advanced Reprocessing Technologies

A. Introduction

Currently about 10 500 tHM (tonnes of heavy metal) of spent fuel are discharged annually from nuclear power reactors worldwide. Although this spent fuel still contains substantial fissionable material (uranium and plutonium) that can be reprocessed and recycled as fuel, only 15% is currently reprocessed. For most of nuclear power's history, reprocessing and recycling of the separated U and Pu in fast reactors has been the favoured strategy for the back end of the fuel cycle. While most countries have adopted a 'wait and see' strategy on this matter, some countries have decided, due to proliferation concerns and a lack of economic stimulus, to regard the spent fuel as waste and prefer to dispose of it after 30-40 years' storage without reprocessing. Lately, however, in some of these countries there has been a resurgence of interest in reprocessing and recycling as key components of developing future sustainable nuclear energy systems [Ref. 1, 2].

The main purpose of reprocessing is to better utilise natural resource by recycling the remaining uranium and plutonium, thus reducing demands on fresh uranium mining and milling and ensuring a more sustainable and long term use of nuclear energy. Reprocessing and recycling in fast reactors has the potential to reduce the uranium demand per kWh by a factor of 50-100. Reprocessing of fuel from light water reactors and gas cooled reactors and recycling of the separated plutonium as mixed oxide (MOX) fuel is today commercially available.

Table 1: Composition of spent fuel from thermal reactors: associated issues and plausible solutions

Constituent	Composition in percentage	Issue	Disposition path
Uranium	~ 95 - 96	An energy resource.	Separated uranium could be recycled as fuel in reactors.
Plutonium	~ 1.0	An energy resource, but also the major contributor to long term radio-toxicity (and heat-load) of the waste. Separated Pu constitutes a major proliferation concern.	Separated Pu could be recycled in reactors as fuel. Proliferation concerns could be reduced by not separating pure Pu.
Minor actinides (MAs) primarily Np, Am, and Cm	~ 0.1	Important contributors to long-term radio-toxicity of the waste. Proliferation concerns exist concerning separated Np.	MAs can be burnt alone or in combination with Pu in fast reactors.
Stable or short-lived FPs (fission products)	~ 3 - 4	Some FPs such as Cs and Sr are the primary contributors to the short term radio-toxicity and heat source in the waste. Other FPs, e.g. noble metals, could become valuable.	Storage of high level waste (HLW) for a few hundred years or separation of Cs and Sr for separate disposal after a few hundred years storage. Separated Cs has industrial applications.
Long-lived fission products (LLFPs) viz., Tc and I	~ 0.1	Contributors to the long term radio-toxicity of the waste.	No industrial process to limit the problem has been developed.

Figure IV-1 shows how the relative radio-toxicity¹ of the different components of spent nuclear fuel varies over time. For the first 100 years after spent fuel is discharged, its radio-toxicity is determined by the fission products. It is then determined by plutonium. If the plutonium is removed, the minor actinides determine the long-term radio-toxicity. It should be noted that both scales are logarithmic.

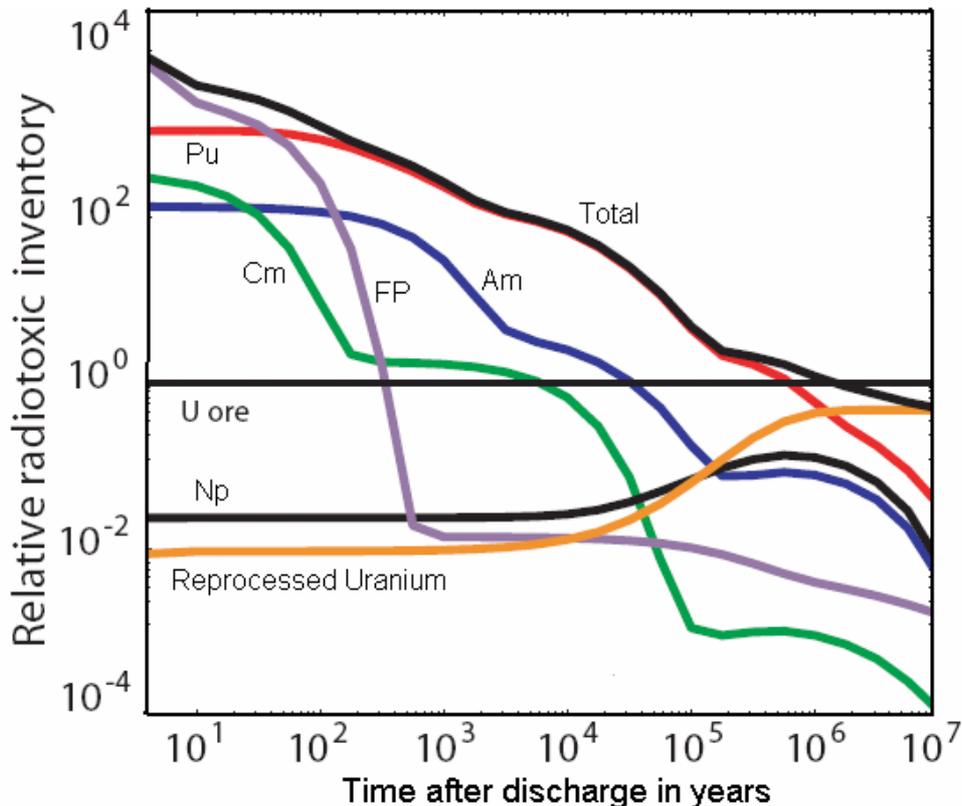


FIG. IV-1. Relative radio-toxicity of the different components in spent nuclear fuel from a light water reactor irradiated to 41 MWd/kgU with respect to the radio-toxicity of the corresponding uranium ore. [Ref. 3,4]

In comparison with direct disposal of spent fuel, present day reprocessing also provides some positive effects on the remaining radioactive waste that needs disposal. These include:

- Long term radio-toxicity is reduced. This reduces long term concerns for the repository, which could simplify the repository design and increase public acceptance.
- Long term heat production is reduced, which increases the capacity of a repository, as the packaging density in most cases is determined by the heat load.
- The volume of high level waste is reduced.

These effects can be further enhanced in advanced reprocessing systems, where minor actinides are also separated with the purpose of burning them, thereby further reducing the long term radio-toxicity and heat load in the remaining waste. In addition, some valuable fission product materials, e.g. caesium and platinum group metals, could be extracted for industrial use. Heat reduction is mainly achieved by removing the caesium and strontium followed by plutonium and americium.

¹ Radio-toxicity is calculated by dividing the radioactivity (Ci) of a nuclide in the spent fuel by the maximum permissible concentration (Ci/m³) of that radionuclide in drinking water.

B. PUREX – current industrial reprocessing technology

All current commercial reprocessing plants use the PUREX² process. It was developed for civil applications during the 1960s, following experience gained from military programmes.

In the PUREX process (which is summarized in Fig. IV-2), the spent fuel is first chopped into small pieces and then dissolved in nitric acid and subjected to a solvent extraction process using tri-n-butyl phosphate (TBP). Uranium and plutonium are selectively taken up in the TBP phase resulting in good separation from the rest of the fission products and minor actinides³, which are retained in the initial acid medium. The U and Pu are then separated in multistage extraction cycles and purified. The present state of the art in PUREX reprocessing provides a 99.9 % separation of U and Pu. In some variants of the PUREX process the Pu is coprecipitated with uranium to avoid the separation of pure plutonium. This is the case in the Japanese reprocessing plant at Rokkasho. The waste stream (the liquid high level waste) that contains fission products, minor actinides and activation products, is processed and vitrified, i.e. mixed with glass material to form a borosilicate glass, and encapsulated in a steel container.

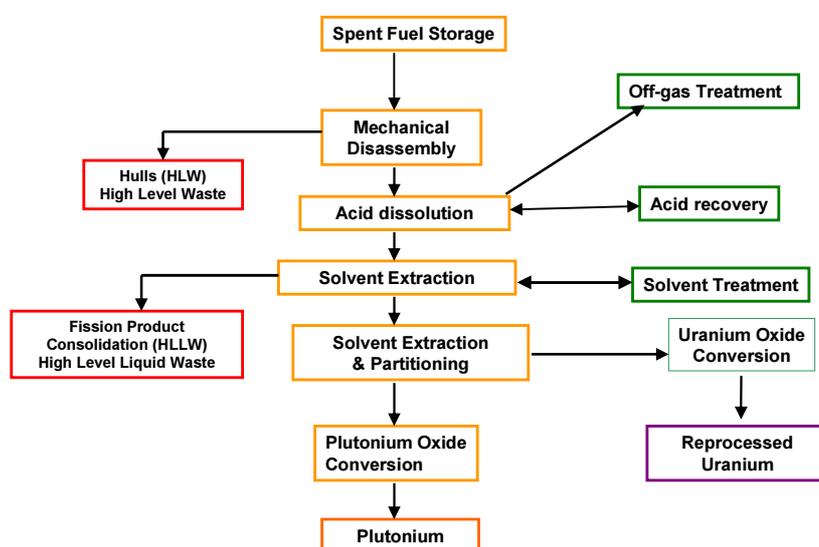


FIG. IV-2. Key steps in the PUREX process.

In a PUREX reprocessing facility the spent fuel is thus separated into its four components: uranium, plutonium, high level waste containing fission products and other transuranic elements, and metallic waste from the fuel rods and assemblies.

The PUREX technology is actively used on a large scale in France, Japan, India, Russia, and the United Kingdom. It is used to reprocess uranium and mixed oxide (MOX) fuel from different types of reactors (LWR, PHWR, GCR and LMFR⁴) and also fuel with different chemical forms and enrichments, e.g. from research reactors. Around 90 000 tHM have been reprocessed in civilian

² Plutonium-Uranium Extraction (PUREX)

³ The main minor actinides are neptunium, americium and curium

⁴ LWR = light water reactor, PHWR = pressurized heavy water reactor, GCR = gas cooled reactor and LMFR = liquid metal cooled fast reactor.

reprocessing facilities. The current annual industrial reprocessing capacity is around 4600 tHM globally, and it is expected that an additional 2000 tonnes might be added in the next 10 years.

C. Developments in reprocessing technologies

The current generation of reprocessing plants has been continuously improved in regard to the following [Ref. 5]:

- i) flexibility (adaptations to increased burn-up, MOX treatment);
- ii) reduction of effluent discharges and impacts on the environment;
- iii) reduction of occupational exposure (e.g. during preventive maintenance and inspections);
- iv) reductions in waste volumes (of both HLW and intermediate level waste (ILW));
- v) simplification of the process (e.g. through reducing the number of cycles needed);
- vi) increased safety through reduced criticality hazards, and better proliferation resistance by real time accounting of nuclear materials.

Nevertheless reprocessing systems still have to address some more challenging concerns, namely:

- i) proliferation issues associated with producing separated plutonium;
- ii) issues associated with high level waste, owing to the presence of minor actinides and long-lived fission products (LLFP);
- iii) economics and costs; and
- iv) the processing of transuranic-rich fuels that are being developed for future advanced nuclear reactors.

Much of the ongoing development work for reprocessing technologies deals with these issues. The economic competitiveness of reprocessing and recycling of fissile materials depends on the price of natural uranium and on the possible gains from reduced demands for repositories.

Collaborative international efforts are underway, including INPRO and GIF⁵, for developing innovative reactors and fuel cycles that are competitive and safe, with simplified procedures for managing radioactive waste and with features to increase the proliferation resistance of nuclear materials. Similar to the evolution of innovative nuclear reactor development, reprocessing technology is evolving in stages.

New wet processes are under development in which also the minor actinides and some LLFPs are separated for later destruction (incineration) in different types of reactors, including fast reactors and accelerator driven systems. Other methods are also being developed in which plutonium is never separated in a pure form but always mixed with minor actinides for proliferation resistance. In a longer time perspective different dry reprocessing technologies are also being developed, e.g. pyro-processing, which could provide benefits in terms of economics, size and fuel cycle flexibility through their higher radiation resistance. Several different lines of development are being considered and tested on a laboratory scale. In some cases the step towards industrial implementation is fairly short, while others will require substantial work before they can be introduced at an industrial level. The following section gives some examples of advanced processes.

⁵ INPRO = International Project on Innovative Nuclear Reactors and Fuel Cycles; GIF = Generation IV International Forum

C.1. Wet processes developments

For wet processes there are two different lines of approach: (i) advanced separation of different components in the high level liquid waste (HLLW) generated by the PUREX process (advanced separation) or (ii) changing the chemistry in the first separation step so that only uranium is separated, while keeping plutonium, minor actinides and fission products in the waste solution for later processing (e.g. UREX⁶).

Advanced separation

The purpose of the ongoing development work on advanced separation methods is to remove minor actinides and some fission products from the HLLW in order to reduce the radio-toxicity and heat load in the final high level waste. The minor actinides will be incorporated in reactor fuel for transmutation (nuclear incineration), while the separated fission products are conditioned for long term storage or separate disposal.

The processes typically involve the following steps:

- recovering minor actinides (MA) and lanthanide fission products
- purifying the MAs from the lanthanides
- individually separating the MAs
- recovering Cs and Sr

Several processes using different types of extractants and solvents have been studied in different countries and tested in hot facilities. Some examples are listed in Table 2. Each process uses its specific extractant and solvent. Very high separation efficiencies will be required to reduce the long term radio-toxicity of the remaining HLLW by a significant factor. In addition to high separation efficiency the minimisation of secondary process waste, e.g. by using amides instead of phosphorous reagents, is also an important goal.

Table 2: Review of advanced aqueous partitioning methods [Ref. 1, 6, 7, 8, 9, 10]

Process	Purpose	Country	Special aspects
DIAMEX	Extraction of minor actinides and lanthanides from HLLW	France	Diamide Extraction Process Solvent based on amides as alternate to phosphorous reagent Generates minimum organic waste as the solvent is totally combustible

⁶ URanium EXtraction

TODGA	ditto	Japan	Tetra-octyl-diglycol-amide Amide similar to DIAMEX
TRUEX	Transuranic elements (TRU) Extraction from HLLW	USA, Russia, Japan, Italy, India	Extraction by using Carbamoyl Methyl Phosphine Oxide (CMPO) together with TBP
SANEX-N	S elective A ctinide E xtraction process for group separation of actinides from lanthanides	France, Germany (Institute for Transuranium Elements (ITU))	Process for separating actinides from lanthanides from HLLW by using neutral N-bearing extractants, viz. Bis-triazinyl-pyridines (BTPs)
SANEX-S	ditto	China, Germany, India	Use of acidic S-bearing extractants, for example synergistic mixture of Cyanex-301 ⁷ with 2,2-bipyridyl
TALSPEAK	ditto	USA, Sweden	Trivalent Actinide Lanthanide Separation by Phosphorus Extractants and Aqueous Komplexes Use of HDEHP as extractant and DRPA as the selective actinide complexing agent
ARTIST	ditto	Japan	Amide-based Radio-resources Treatment with Interim Storage of Transuranics This process is made-up of: 1.) Phosphorus-free branched alkyl monoamides (BAMA) for separation of U, Pu; 2.) TODGA for actinide and lanthanide recovery and 3.) N-donor ligand for actinide / lanthanide separation
SESAME	Selective Extraction and Separation of Americium by Means of Electrolysis	France, Japan	Process for separating Am from Cm by oxidation of Am to Am(VI), subsequent extraction with TBP for separation from Cm
CSEX	Cs Extraction	USA, France	Using Calix-crown extractants
CCD - PEG	Extraction of Cs and Sr from the raffinate	Czech, EU, Russia, USA	Chlorinated cobalt dicarbollide and Poly-ethylene glycol (CCD-PEG) in sulfone based solvent is planned for extraction of Cs and Sr from UREX raffinate
SREX	Sr Extraction	USA	Using dicyclohexano 18-crown-6 ether
GANEX	Uranium extraction followed by group extraction of all actinides	France	Group recovery of all actinides based on branched amide compound N,N-di-(2-ethyl-hexyl)-iso-butanamide (DOiBA) and subsequent DIAMEX / SANEX
UREX +	Uranium Extraction + other processes for further separation	USA	A series of five solvent-extraction flow-sheets that perform the following operations: 1) recovery of Tc and U (UREX), 2) recovery of Cs and Sr (CCD-PEG), 3) recovery of Pu and Np (NPEX), (4) recovery of Am, Cm, and rare-earth fission products TRUEX, and 5) separation of Am and Cm from the rare earth fission products (Cyanex 301).

⁷ Cyanex refers to compounds belonging to the family of organo-dithio-phosphinates (R₂PS₂).

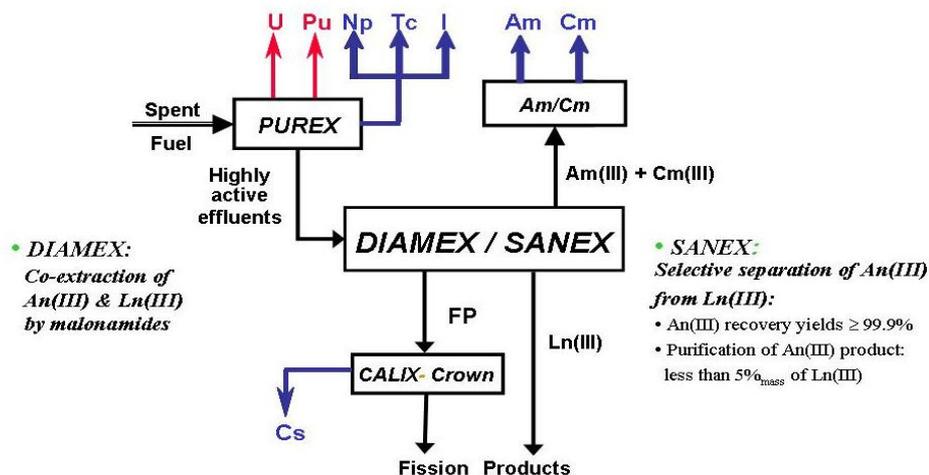


FIG. IV-3. One of the strategies for treating PUREX raffinate under development at Commissariat à l'énergie atomique (CEA), France.

Figure IV-3 shows the stepwise combination of different processes developed by CEA in France. For the first 'post-PUREX' step, the co-extraction of minor actinides (americium and curium) and lanthanides, the DIAMEX process is used [Ref. 7]. In the second step, SANEX, the actinides are separated from the lanthanides, and in the third step americium is separated from curium. A process called SESAME is under development for this. In the last step caesium and strontium are extracted from the remaining waste stream.

During current reprocessing operations, neptunium is partly discharged with the fission products into the HLLW and partly associated with the U and Pu stream. The purification of U and its separation from Np is achieved in the second extraction cycle of the PUREX process. An advanced PUREX process, PARC (PARTitioning Conundrum), is being developed with the main objective of separating Np and Tc in the first extraction cycle.

Pure uranium separation

As an alternative to PUREX-based processes a series of new processes are being developed that separate uranium (UREX) while keeping plutonium, minor actinides and fission products in the waste solution [Ref. 10]. Subsequently all actinides can be recovered as a group. Also caesium and strontium can be separated. These UREX based separation processes have become one of the key emphases in the US DOE's Advanced Fuel Cycle Initiative (AFCI), which provides the technical foundation for the Global Nuclear Energy Partnership (GNEP). A similar process, GANEX⁸, is being developed in France.

C.2. Pyro-chemical processes

Pyro-chemical processes were first investigated in the 1950s as an alternative to PUREX to increase the radiation resistance and stability of material used in extraction processes. An initial pyro-chemical process was constructed at the Experimental Breeder Reactor II (EBR-II) in the USA during the 1950s. Later many concepts for pyro-chemical partitioning were developed, and in some cases pilot plants were built and operated. The techniques were based on using metals and salts at high

⁸ Group ActiNide EXtraction

temperatures: melt-refining, volatilisation, gas-solid reaction, fractional precipitation, vacuum distillation, electro-deposition, electro-refining, electro-winning⁹ and others. This technology, which has a lower separation factor, can possibly decrease reprocessing costs nonetheless by taking advantage of the ability of fast reactors to use fuel with more impurities than would be acceptable in thermal reactors. The advantages of some of these pyro-processes are:

- Adaptability to reprocess spent fuels, including MA based fuels, with shorter cooling periods (this advantage relates principally to future fuel cycles),
- Ability to co-recover actinides largely in a single process,
- Compact plants that can accept several forms of fuel,
- Very short turn-around time for the fuel, and associated cost savings from the resulting reduction of otherwise large fissile materials inventories,
- Generation of minimum transuranic waste,
- Very high intrinsic proliferation resistance for the fissile materials owing to:
 - Limited purity of the end product, which limits its direct use in nuclear weapons,
 - A built-in isotopic barrier because of the presence of isotopes with high decay heat, high spontaneous neutron yield and lethally high radio-toxicity,
 - Co-location of reprocessing and fuel fabrication facilities with the reactor.

However, the main challenges facing pyro-processes are the requirement for an oxygen- and moisture-free plant environment, and the need to develop materials that will not only withstand high radiation levels but have excellent resistance to high temperature corrosion in molten metals and molten halide salts.

The common features of pyro-chemical processes are dissolution of spent fuel elements in a molten salt bath around 500 to 800°C, followed by some degree of selective recovery of constituent elements for recycling or conditioning. Semi-industrial scale reprocessing technologies based on electro-refining processes (ERPs) were developed in the USA in the 1980s for U as well as (U,Pu) metal fuels. Likewise, for UOX and MOX fuels Russia has developed the electro-winning process combined with remote vibro-pack technology for fuel rod fabrication. These were tested in fast reactors in the 1990s. A schematic diagram of the electro-refining cell and a flow-sheet for the ERP are shown in Fig. IV-4b.

In the molten salt refining process developed in the USA, the spent metallic fuel (U-Zr or U-Pu-Zr alloys) is chopped into small pieces and loaded in the anode basket of an electro-refining cell with, as the electrolyte, molten LiCl/KCl eutectic mixtures at around 773K. A cylindrical rod of low carbon steel is used as the cathode. CdCl₂ is added to the electro-refining cell to transfer most of the actinides and fission products as chlorides to the electrolyte bath. On passing a current through the cell, the uranium in the anode forms uranium ions in the molten salt electrolyte and then the uranium is reduced and deposited as uranium metal on the cathode. After uranium recovery, the solid cathode is replaced by a liquid cadmium cathode. Under this condition, electrolysis leads to co-deposition of U, Pu, MAs as well as some lanthanide elements into the liquid cathode. More reactive fission products remain dissolved in the salt phase. Fission products less reactive than actinides, namely noble metals and zirconium, are not dissolved and remain in the anode basket (see Fig. IV-4a).

⁹ Electro-winning and electro-refining processes are standard metallurgical processes for extracting and purifying metals. In electro-winning a current is passed from an inert anode through a liquid leach solution containing the metal so that the metal is deposited onto the cathode. In the electro-refining process, as the current passes through the anode, which is made of impure metal, the metal dissolves into the solution and gets deposited as refined metal onto the cathode.

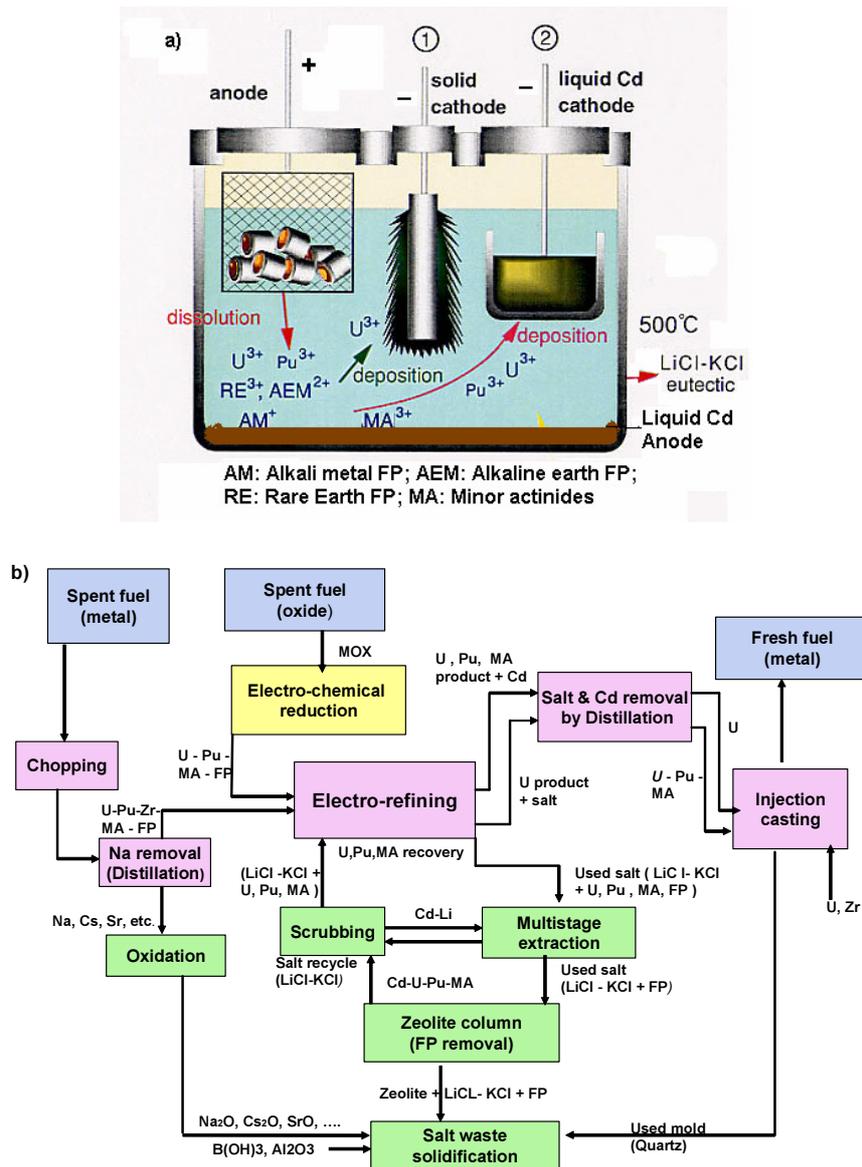


FIG. IV-4. a) Schematic of an electro-refining cell and b) the process flow sheet for an electro-refining process under development at Idaho National Laboratory (INL), USA and Japan Atomic Energy Agency (JAEA), Japan and ITU, EC

Recent technological development efforts [Ref. 11] in the USA range from laboratory-scale studies of new processing concepts such as the electrolytic reduction of spent LWR oxide fuel to the engineering-scale demonstration of high-throughput uranium electro-refining. Japan has a laboratory scale facility for electro-refining metallic fuel [Ref. 12]. In addition, development work is underway on extracting transuranic elements (TRUs) by pyro-chemical methods from HLLW generated from the PUREX process applied to LWR fuels. Other Member States (China, Czech Republic, France, Korea, India), as well as EC/ITU have also embarked on some of these pyro-chemical methods on a laboratory scale. At the Research Institute of Atomic Reactors (RIAR) at Dimitrovgrad, Russia the recycling of fuel at tonnage scale has been successfully demonstrated using a pyro-chemical method based on the electro-winning process as part of demonstrating a closed fuel cycle with mixed oxide fuels for the BOR-60 fast reactor. Another promising method is fluoride volatilization for processing the TRU-rich fuels or targets that are being considered for a future generation of dedicated burner reactors or accelerator-driven systems (ADSs).

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