

Waste Minimization Study on Pyrochemical Reprocessing Processes

H. Boussier, O. Conocar, J. Lacquement
CEA/DEN Valrho Marcoule/DRCP/SCPS/Pyrochemical Processes Laboratory
BP 17171 30207 Bagnols-sur-Cèze
France

ABSTRACT

Ideally a new pyroprocess should not generate more waste, and should be at least as safe and cost effective as the hydrometallurgical processes currently implemented at industrial scale.

This paper describes the thought process, the methodology and some results obtained by process integration studies to devise potential pyroprocesses and to assess their capability of achieving this challenging objective.

As example the assessment of a process based on salt/metal reductive extraction, designed for the reprocessing of Generation IV carbide spent fuels, is developed.

Salt/metal reductive extraction uses the capability of some metals, aluminum in this case, to selectively reduce actinide fluorides previously dissolved in a fluoride salt bath. The reduced actinides enter the metal phase from which they are subsequently recovered; the fission products remain in the salt phase.

In fact, the process is not so simple, as it requires upstream and downstream subsidiary steps. All these process steps generate secondary waste flows representing sources of actinide leakage and/or FP discharge.

In aqueous processes the main solvent (nitric acid solution) has a low boiling point and evaporate easily or can be removed by distillation, thereby leaving limited flow containing the dissolved substance behind to be incorporated in a confinement matrix. From the point of view of waste generation, one main handicap of molten salt processes, is that the saline phase (fluoride in our case) used as solvent is of same nature than the solutes (radionuclides fluorides) and has a quite high boiling point. So it is not so easy, than it is with aqueous solutions, to separate solvent and solutes in order to confine only radioactive material and limit the final waste flows.

Starting from the initial block diagram devised two years ago, the paper shows how process integration studies were able to propose process fittings which lead to a reduction of the waste variety and flows leading at an “ideal” new block diagram allowing internal solvent recycling, and self eliminating reactants. This new flowsheet minimizes the quantity of inactive inlet flows that would have inevitably to be incorporated in a final waste form. The study identifies all knowledge gaps to be filled and suggest some possible R & D issues to confirm or infirm the feasibility of the proposed process fittings

INTRODUCTION

In the seventies pyrochemical processes were considered as a possible alternative to hydrometallurgical PUREX process for spent fuel reprocessing ; at the time only uranium and plutonium recovery was aimed. Since late nineties with the Advanced Fuel Cycle Initiative (AFCI) and GENERATION IV, a renewed interest raised in pyrochemical processes but with new and more demanding objectives.

Not only uranium and plutonium but all minor actinides (i.e. neptunium, americium and curium) should be separated from fission products for recycling. In order to limit proliferation risks all actinides should be managed together. Lastly a particular attention has to be focused on waste management. Ideally a new pyroprocess should not generate more waste, and should be at least as safe and cost effective as the hydrometallurgical processes currently implemented at industrial scale.

Our process integration studies aim to devise potential pyroprocesses and to assess their capability of achieving these challenging objectives.

This paper describes the thought process, the methodology and some results obtained by these studies. As example the assessment of a process based on salt/metal reductive extraction applied to a GEN IV carbide fuel with SiC cladding, is developed.

PROCESS DESCRIPTION

A general process block diagram is given here after.

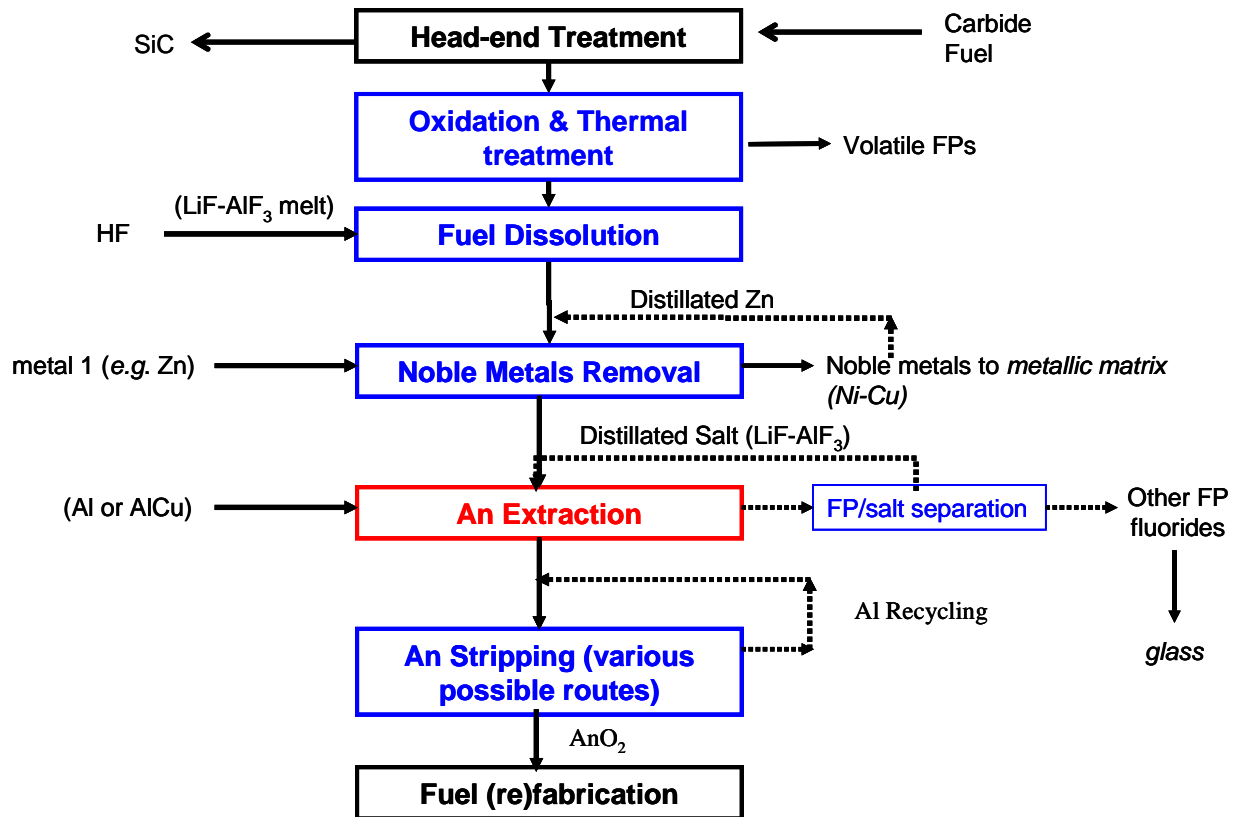


Fig. 1. Global process block diagram

Mechanical treatment

The process begins with a series of head-end operations on the fuel assemblies to obtain an oxide powder that is fine enough (50–100 μm) for the subsequent reductive distillation and fluorination steps. The main difficulty of this step is to limit material losses entrained with the SiC hulls. SiC is a ceramic material that is more brittle and should exhibit very different shearing behavior than ductile steel or Zircaloy cladding. Following the mechanical operations there may be relatively fine cladding debris mixed in with the fuel pellets and oxide fines. Complete separation of the cladding from the oxide exclusively through mechanical processes is difficult to imagine.

The mechanical treatment is highly dependent on the nature of the fuel and cladding. In view of the very preliminary status of this study and the fact that the form and nature of the fuel have not been clearly specified at this time, this process step will not be further discussed in this paper. It is assumed that only a small fraction of the SiC from the clads will be entrained with the oxide powder. The entrained SiC particles should be eliminated as volatile fluorides (SiF_4 and CF_4) during the hydrofluorination step [2].

During these operations some or all of the gaseous or volatile fission products (Kr, Xe, I, Br) are released and must be collected and trapped for disposal as an ultimate wastefrom.

Heat treatment

The resulting powder will be heat treated to eliminate the volatile elements. This involves distillation at high temperature (above 1000°C) in controlled atmosphere (argon + 5% hydrogen).

During this treatment all the cesium, rubidium and tellurium would be volatilized; the platinum-group metals and molybdenum would be on metal state. Some or all of the Tc, Cd, As, and Se would be also volatilized [3,4].

Hydrofluorination

The oxides are hydrofluorinated with HF as the fluorinating agent. HF generates fluorides at low oxidation states and thus prevents the formation of volatile uranium hexafluoride.

Prior to extraction of the actinides by aluminum based alloy, one option could be to eliminate the zirconium fluoride by volatilization, by heating the fluorides above 800°C. This would be particularly advantageous since Zr represents about 3% of the total negative reactivity of the FP. The volatilization step has not yet been tested.

Dissolution in a LiF-AlF₃ salt phase

After the fluorination step the powder is contacted and dissolved at 830°C in a molten salt flow with a composition selected to obtain the required extraction performance. The process was initially based on a binary salt (from 85 mol% LiF, 15 mol% AlF₃ to 65 mol% LiF, 35 mol% AlF₃).

Digestion of platinum-group metals

The salt phase is then placed in contact with a mildly reducing metal phase containing zinc possibly or not alloyed with copper and nickel. The platinum-group metals and molybdenum are extracted to the metallic state; these elements, the noble metals, as well as Sb, Ge(?) and Nb(?) are dissolved in the metal phase [3]. Zinc is then recycled by vacuum evaporation; the extracted elements remain in the Ni/Cu alloy. The nickel/copper matrix could constitute an acceptable confinement matrix; this point must be confirmed by a specific study.

Other metal matrices could also be considered, for example Zr/Ni, Cu/Sn or Al. Although some of these have lower potential radionuclide loading capacities than Ni/Cu alloy, it could be advantageous to use a matrix that is entirely constituted by a process waste flow (Al from the metal loop).

Group extraction of the actinides

The salt is then contacted with an Al or Al/Cu metal phase in which aluminum is the reducing metal; copper is added to obtain a heavier metal phase and thus facilitate the separation of the salt and metal phases. It has no chemical role and tests carried out showed that Cu is not indispensable. During this stage almost all the actinides are extracted, together with a small fraction of the fission products present in the salt. A high actinide recovery yield and satisfactory fission product decontamination performance requires a multistage extraction system and suitable salt and metal flow settings. Simulations using the experimentally measured distribution coefficients showed that two theoretical countercurrent stages would be sufficient.

In order to minimize waste generation, salt phase have to be recycled, but to prevent accumulation of fissions products in the salt they have to be previously eliminated by an appropriate (read on, waste management flow chapter).

Recovery of the actinides and preparation of finished products

Two variants can be considered at this point:

- The extracted actinides and FP dissolved in the metal phase are transferred to a LiCl-KCl or NaCl-CaCl₂ salt phase by oxidizing stripping using CuCl₂. The actinides would then be precipitated as oxides by adding lithium carbonate and potassium carbonate, or sodium carbonate and calcium carbonate. The salt and oxide separated by settling (or possibly by filtration or centrifugation) supplemented by low-pressure distillation of the trace amounts of salt entrained with the precipitate. This variant has already been implemented under active conditions in the laboratory [5, 6] but has drawbacks because it generates two secondary waste flows: the Al/Cu phase drawoff, which could be a source of actinide losses in the event of insufficient stripping, and the chloride salt phase drawoff, which is a waste stream difficult to manage.
- If an Al metal phase without copper is used, hydrochlorination by gaseous HCl could be used to chlorinate the aluminum forming volatile AlCl₃ that can be evaporated and separated. The solid residue comprises the actinides, which are oxidized in air to oxide form. AlCl₃ can be recycled to the process head-end stage as Al via an electrolytic reduction step, as implemented for example in the ALCOA industrial process [7]. The behavior of zirconium in the process remains uncertain at this time; if the zirconium is not eliminated upstream, a great part will follow the actinides in the aluminum. The hydrochlorination step should eliminate Zr together with AlCl₃ in the form of volatile ZrCl₄. In this case the behavior of Zr in the aluminum recycling process must be examined to ensure this will not create a zirconium holdup loop. This variant has the potential drawback of attacking the solvent (aluminum) to recover the solute (actinides), and implies converting all the Al flow into AlCl₃. This would generate a substantial off-gas stream that would have to be managed and would probably produce a secondary waste flow. These flows have not been quantitatively assessed.

Overall process performance

The actinide and FP recovery yields and the quantity of FP entrained with the actinides were estimated using a model simulating the process. The negative reactivity supplied by the FP was also estimated as a fraction of the total negative reactivity of the FP initially present in the fuel.

The model can only take into account phenomena that have been observed experimentally or predicted thermodynamically. These results are subject to doubt since we have no direct experience with all the process steps.

The results (see table I) indicate that it is theoretically possible to obtain a satisfactory recovery yield (excluding head-end losses during the mechanical operations) but that significant quantities of fission products—mainly zirconium—is entrained with the finished products.

Given our currently incomplete knowledge of all the steps in the proposed process, we have been obliged to adopt several hypotheses in simulating the process; the hypotheses that could significantly impact process performance are discussed below.

- The stripping yield was assumed equal to 94%. This figure is based on a single unoptimized exploratory experiment, and our experience with this step is insufficient to assert that this is the definitive figure.
- We have assumed that the zirconium was eliminated either by volatilization of zirconium tetrafluoride during the process head-end step, or when the actinides are recovered from the aluminum metal phase by hydrochlorination of Al to AlCl₃, during which ZrCl₄ could be separated from the AlCl₃.

Table I. Overall balance of finished products

Overall balance of finished products	Volatilized Zr
Actinide recovery (wt%)	≥99%
FP recovery (wt%)	≈ 0.6%
FP/An (wt%)	≈ 0.06%
FP negative reactivity (%)	≈ 0.7%

If this were not the case, the FP decontamination performance could be altered as indicated in following table:

Table II: Overall balance of finished products (unvolatilized Zr)

Overall balance of finished products	Unvolatilized Zr
Actinide recovery (wt%)	≥ 99%
FP recovery (wt%)	≈ 8%
FP/An (wt%)	≈ 0.9%
FP negative reactivity (%)	≈ 3.7%

This would be near the upper permissible limit for FP contamination.

WASTE FLOW MANAGEMENT

Recycling the salt and metal phases may be advantageous for minimizing the waste flows [1]. However, both reductive extraction and oxidizing stripping involve the transfer of the reducing or oxidizing agent from one phase to the other, thereby modifying the composition of each phase; recycling the phases would thus require online adjustments to maintain a constant composition and holdup in the loops. This generates secondary waste flows representing sources of actinide leakage and FP discharge. The nature and volume of the waste flows are examined in the following sections.

Fluoride salt flow

Recycling the salt phase generally minimizes the waste flows. To prevent excessive accumulation of fission products in the salt which could jeopardize FP/An decontamination factor it must be decontaminated by extracting the fission products. For this purpose two routes can be considered:

- The chemical one by extracting all the radionuclides except the alkaline earths using Al/Bi alloys.
- The physical one by distillation under vacuum.

Extraction with Al/Bi alloy

The loop behavior was simulated, and three aspects were considered:

- once-through operation (100% drawoff) without decontamination,
- loop operation (20% drawoff) without decontamination,
- loop operation (10% drawoff) with decontamination.

The results of waste flow assessment are summarized and discussed in Table III

The fluoride salt flow containing FP, and traces of actinides is not an acceptable ultimate wasteform, and must be conditioned in a glass matrix, which is very well known and has been used industrially since 1978. Preliminary study showed that glass matrix could accommodate up to 15-20wt% of fluoride salt.

Table III . Waste Flow Assessment

Aspects	Salt waste flow Kg/tHM	Minimum glass mass produced kg/tHM	FP+An glass content wt%	Comments
Once-through operation (100% drawoff)	7 000	35 000	0.12%	Not compatible with industrial implementation
Loop operation (20% drawoff) without decontamination	1580	7900	0.43%	Not compatible with FP/An decontamination factor requirements
Loop operation (10% drawoff) with decontamination	750	3740	0.22%	Additional Al/Bi metallic waste flow.

The limiting parameter for glass is the maximum fluoride salt mass. Assuming a maximum fluoride content of 20 wt%, the glass quantity produced would be about 35 000 kg/tons with a FP +actinide content of about 0.12% for the once-through aspect and about 3740 kg/tons with a FP +actinide content of about 0.22% for the once-through aspect

This glass flow represents about 4300 kg. of glass per Twhe with loop operation management. (10% drawoff) with decontamination.

This is a major flow compared with the glass flow produced by PUREX reprocessing (about 800 kg/Twe.h). This aspect is a major weakness in the process and must be improved.

Distillation under vacuum

Ideally, the FP would be separated from the salt bath and recovered in oxide form, then vitrified, leaving a decontaminated salt bath. However, it could be very difficult or even impossible to selectively extract the alkali and alkaline earth FP from the salt bath. One possibility for separating them might be based on the differences in the boiling temperatures of the different fluorides.

Plotting the calculated vapor pressure values¹ for the fluorides versus the temperature suggests that there might in fact be a possibility:

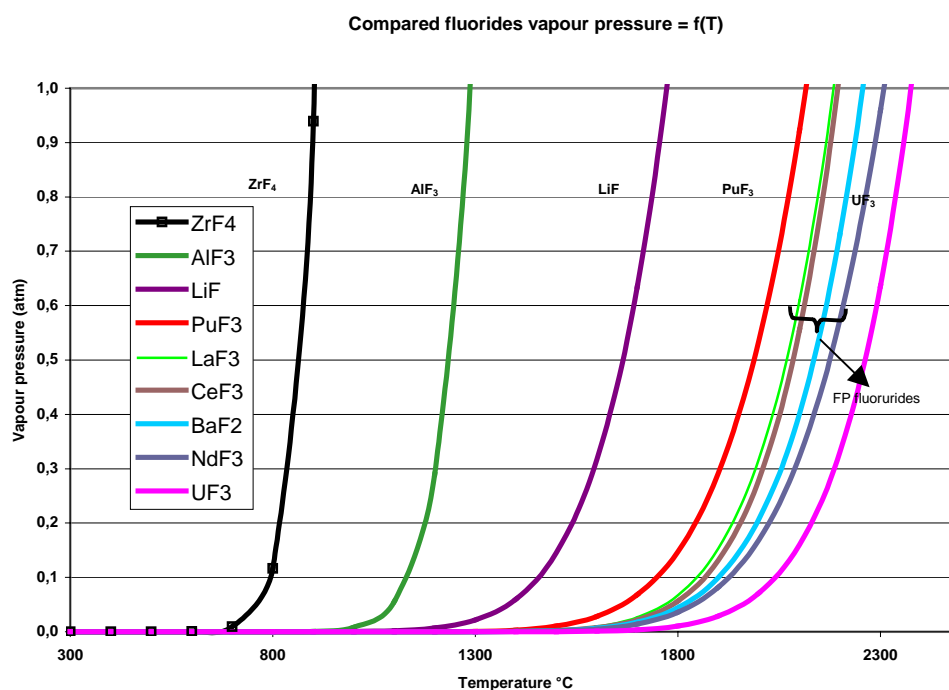


Fig. 2. Fluoride vapor pressure versus temperature

Following the extraction step, the main salt components AlF₃ and LiF could possibly be distilled without affecting the fission product fluorides, which could be vitrified separately resulting in a smaller glass production than if the salt were conditioned as well. The decontaminated salt without FP could then be recycled in the process head-end.

¹ Calculated from thermodynamic data using HSC Chemistry software version 4.1 from Outokumpu Research Oy. The simplified calculation did not take into account the fact that the FP are in solution.

- A rich AlF_3 flow could possibly be separated; a fraction of this flow, estimated at about 600 kg/tHM should be drawn off to adjust the AlF_3 concentration in the salt. The AlF_3 drawoff could either constitute a waste salt (preferably lightly contaminated) or be recycled as aluminum and then converted to a chloride (AlCl_3) for use as the oxidizing agent in the oxidizing stripping step. Recycling AlF_3 as AlCl_3 would make the process more complex and must be weighed against the drawback of managing a lightly contaminated AlF_3 waste flow. As no evaporation test has been carried out under realistic conditions, it is impossible to estimate the residual FP contamination level in the salt.

If the potential for fractional distillation of the salt is confirmed experimentally, the ultimate glass waste flow arising from the salt loop would be significantly reduced. The glass mass produced (460 kg/tHM) would then be comparable to the quantity generated by a hydrometallurgical process for the same type of fuel.

The investigation of these routes should be a medium-term focus of research for the reductive extraction process.

Three other waste flows must be considered for the variant flowsheet: the noble metal containment matrix, the Al/Cu drawoff and the chloride salt drawoff.

Metal matrix for immobilizing the platinum group + Mo

An exploratory R&D program is now in progress to select more promising matrices. Although the studies have not been completed, we have nevertheless estimated the waste mass produced assuming 10 wt% waste loading—a minimum value that appears to be accessible based on the work done to date.

With this hypothesis the mass flow of metal waste immobilizing the platinum group + Mo would be about 280 kg/year/reactor.

Al/Cu flow management

Part of the Al/Cu flow must be drawn off to adjust the aluminum composition in the loop and prevent any accumulation of copper from the oxidizing stripping step using CuCl_2 . This flow is estimated at about 860 kg /tHM based on simulations using a model of the process, and could constitute the main source of actinide losses to the waste.

Prospects for improvement of metal flow management

AlCl_3 could be used as the oxidizing agent instead of CuCl_2 for the oxidizing stripping step. In this case, the quantity of aluminum transferred into the metal phase by reducing AlCl_3 would correspond exactly to the quantity of aluminum transferred into the salt phase during the reductive extraction step; the composition of the metal phase would remain unchanged with no need for adjustment by drawing off the fluoride.

AlCl_3 is a gas at the working temperatures imposed by Al/Cu alloy, i.e. about 670°C (or 100°C above the alloy melting temperature). This issue must be taken into account in implementing this step and in the equipment design. Nevertheless, this difficulty should not be impossible to overcome.

Chloride salt flow

This secondary waste flow arises mainly from the fact that oxide precipitation by carbonates adds K and Li cations to the process, increasing the chloride salt inventory. The excess salt must then be eliminated.

Prospects for improvement of chloride salt flow management

Two routes could be investigated to avoid managing a secondary waste flow consisting of chloride salt:

- Distill the quantity of LiCl/KCl salt necessary to compensate for the additional carbonates. The distilled salt should be sufficiently decontaminated to make it acceptable for surface disposal.
- Supply the oxygen necessary to precipitate the oxides using a gaseous reactant that does not add any cation to the salt. This route avoids managing a secondary waste flow consisting of chloride salt. This issue will be addressed by a research program.

Overall waste flow assessment

The waste quantities produced by reprocessing GEN IV carbide fuel have been evaluated. The values were calculated for two process variants. The first calculations, have been done with the initial process diagram(Fig. 3).

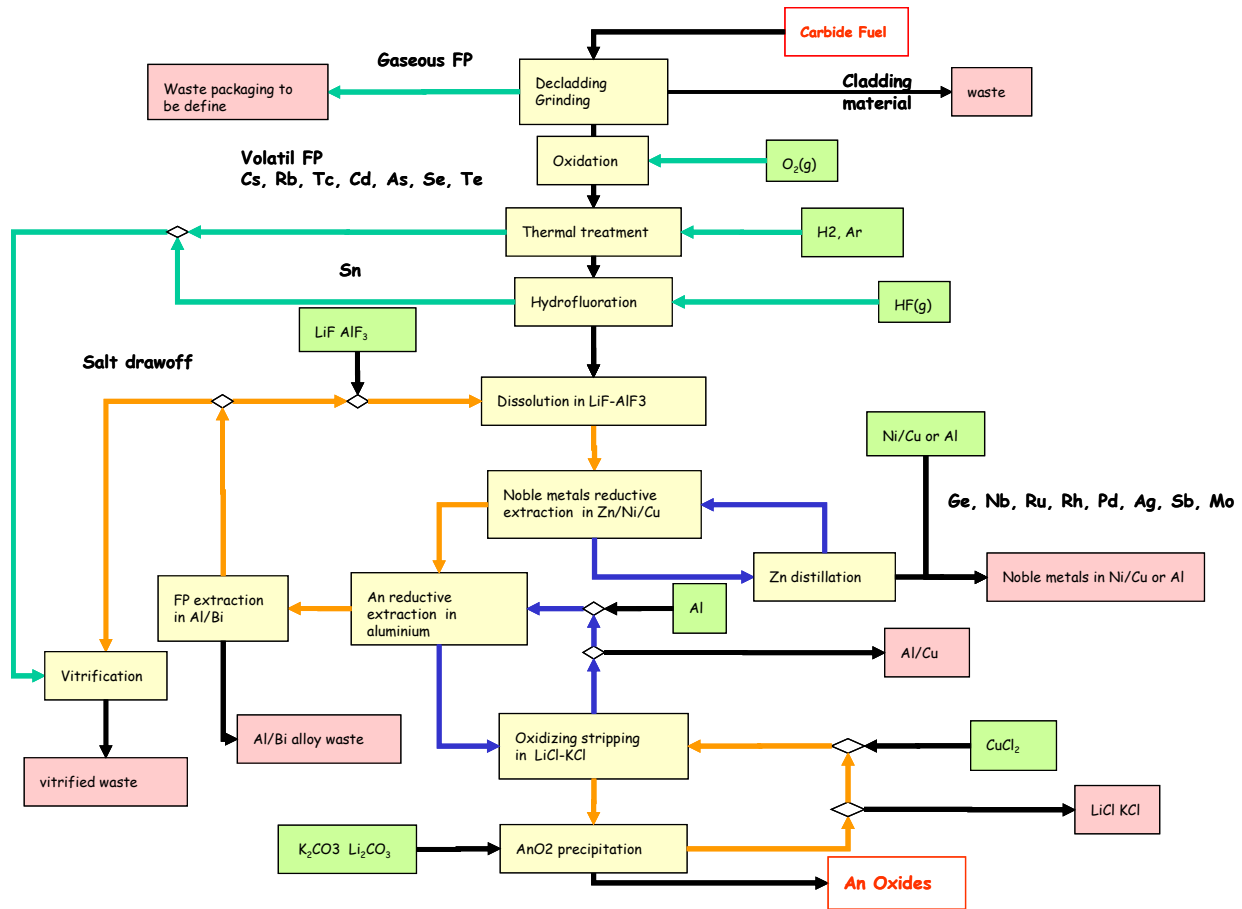


Fig. 3. Initial block diagram

In a final calculation we assumed that the potential improvements described in the preceding paragraphs were feasible and had been applied (Fig. 4). The result thus gives the minimum waste flow that can be expected in the present state of knowledge.

For the process head-end, fluoride salt is initially counted as primary waste; it is then assumed to be incorporated in a glass matrix as an ultimate wasteform. During this operation, the FP volatilized during the head-end heat treatment is incorporated in this flow without affecting the quantity of glass.

All the calculations were carried out on the basis of the material flows produced by reprocessing of one metric ton of heavy metal (black figures). In order to facilitate results inter comparisons, another figure is given, the flows normalized to the production of 1 Tweh (**red figures in bold**).

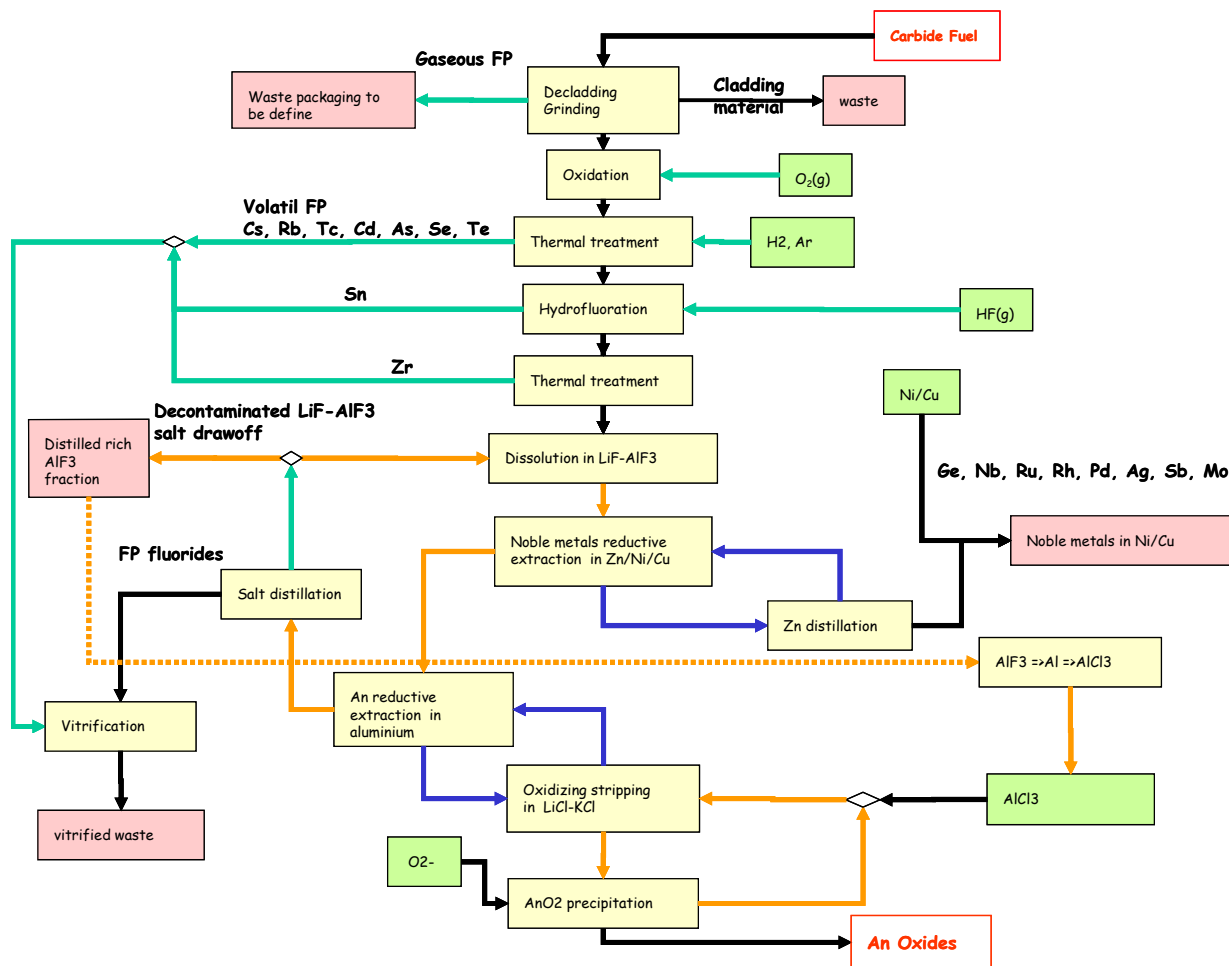


Fig. 4. Final block diagram

Table IV: Waste flow assessment (initial scheme)

Process version	Initial Scheme				
	Al/Bi	Glass	Nickel/copper matrix	Al/Cu alloy	Chloride salt
Wasteform	FP	FP	Platinum-group metals	Actinide losses	Low actinide activity
Main radionuclides	FP	FP	Platinum-group metals	Actinide losses	Low actinide activity
Mass produced					
kg/tHM	165	3750	280	860	700
Kg/Tweh	190	4250	320	975	790

The last table shows that both the quantity and the number of waste flows produced by the reductive extraction process can potentially be reduced by a significant amount.

Table V. Waste flow assessment (ideal scheme)

Process version	Ideal enhanced waste management process				
Wasteform	Distilled AlF3 fraction	Glass	Nickel/copper or Al matrix	Al/Cu alloy	Chloride salt
Main radionuclides	FP	FP	Platinum-group metals		
Mass produced	Could be recyclable				
kg/tHM	600	470	280		
Kg/Tweh	680	520	320	None	None

Ideally, the process would generate only two types of high-level waste—glass and metal— together with a low-level salt waste (it is too early to quantify the waste radioactive contamination level) that could be recycled in the process.

CONCLUSION

The study shows that primary waste management must be improved since the expected process flows—especially the fluoride salt—are too large, but promising options exist and will be investigated.

Starting from the initial block diagram devised two years ago, the paper shows how process integration studies were able to propose process fittings which lead to a reduction of the waste variety and flows leading at an “ideal” new block diagram allowing internal solvent recycling, and self eliminating reactants. This new flowsheet minimizes the quantity of inactive inlet flows that would have inevitably to be incorporated in a final waste form . The study identifies all knowledge gaps to be filled and suggest some possible R & D issues to confirm or infirm the feasibility of the proposed process fittings.

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