Separations issues associated with ATW technology: State of the art and research needs

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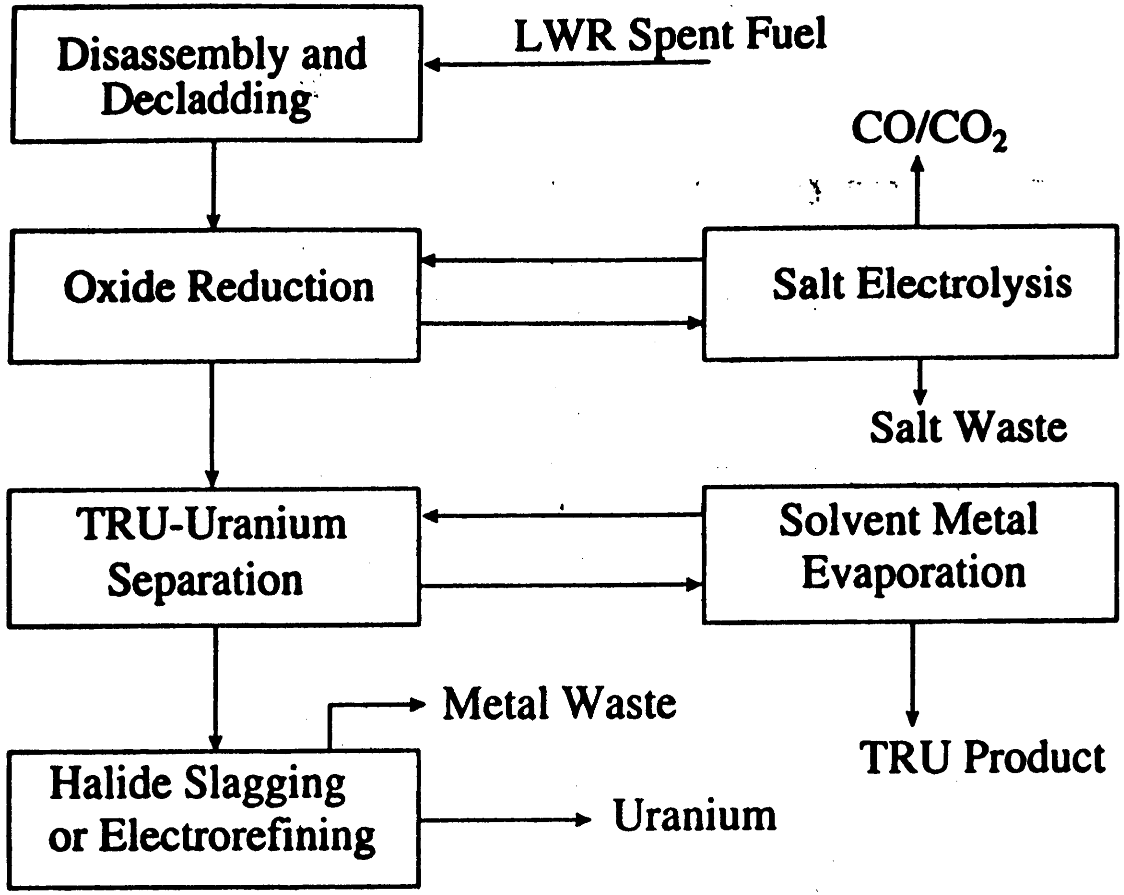
Molten Salt Processes - ATW

All but one of the several potential separations processes proposed by the accelerator transmutation of waste (ATW) project would use a molten mixed-fluoride salt as a carrier for the primary target loop. The molten salt would be circulated through a side stream external to the target region, and separations would be performed on the molten salt to produce targets for reintroduction into the nuclear reaction zone. Separations processes for use in the ATW concept must be very tolerant of the intense radiation fields produced by the fission products present in the target fluid because of the proposed short cooling times and consequent high radiation fields. It is doubtful that organic extractants could be used for these separations unless their process separation times could be reduced far below those achieved to date (It has yet to be demonstrated that molten salt process can achieve all the proposed separartions to the degree desired.)

Fluoride Volatility Processes

Isolation of uranium from bulk impurities or fission products by volatilization has been demonstrated to be a practical approach that could be scaled to industrial levels. The separation possibilities range from the recovery of uranium from ore concentrates (which is current practice) to the recovery of uranium from a molten salt (by using in-situ fluorination with elemental fluorine or perhaps the fluorinating agent O_2F_2) to produce volatile uranium hexafluoride. Since fluorides of other transuranic elements are not volatile and/or are unstable, some alternative processing technique would be needed to recover these transplutonium elements. A number of other elements of interest, such as molybdenum, technetium and iodine, also can be volatilized from spent fuel, introducing some complications into this isolation method. The individual elements may be separated by fractional distillation.

Previous research and development on fluoride-volatility and molten salt processes revealed several serious difficulties in developing metal alloys that would resist corrosive attack by the tellurium fission product. New techniques are needed for operating separation cascades in molten salt and molten metal systems to achieve some of the very high separations needed.



Actinide recycle pyroprocess concept.

Source: Argonne National Laboratory - Integral Fast Reactor Program, managed by the University of Chicago for the U.S. Department of Energy under Contract No. W-31-109-Eng-38.

Waste material generated during processing and maintenance operations for the ATW would have to be treated for recovery to degrees never before achieved in large-scale systems in order to reach the low overall system losses required by the stated ATW goals.

The aqueous ATW has very short cooling times so the separations must take place in very high radiation fields that would cause serious degradation of both water and organic agents. Processing using molten metals or salts avoids the problems of radiation degradation because these systems are very resistant to radiation damage.

Other severe problems are shared by both the aqueous and molten salt processing proposals. They include severe decay heating from some of the separated actinides and nonuniform phase and thermal mixing in both slurry and molten salt.

Electrorefining may be used merely for a rough separation of uranium before counter-current reductive extraction, but can afford a more complete separation between transuranic and rare earth elements. A small-scale experiment showed that over 99% of each actinide could be recovered from a simulated waste. The LiCl-KCl mixture can be recycled after purification, while the salts of fission products are electrolytically decomposed and converted to oxides for vitrification in borosilicate glass.

The process investigated at CRIEPI to recover transuranic elements from high-level PUREX wastes consists of denitration to oxides, chlorination, reductive extraction and electrorefining in a LiCl-KCl/Cd or LiCl-KCl/Bi system. After denitration and leaching with water to remove the soluble alkali metal nitrates, the undissolved oxides (mainly of actinides, rare earths and transition metals) and platinum group metals are converted into chlorides in a bed of LiCl-KCl at above 700 °C.

The mixed chlorides are reductively extracted or electrorefined in contact with liquid cadmium or bismuth. Thermodynamic data for actinides and rare earth elements in this system are needed to establish the separation process.

The chemical similarity of neptunium with plutonium in molten chloride salts is used for its pyrochemical reprocessing. Neptunium (as oxychlorides or tetrachloride) will co-deposit with UO_2 or co-precipitate with PuO_2 by supplementary electrorefining for UO_2-PuO_2 recovery. That behavior was demonstrated during the BOR-60 spent MOX fuel reprocessing. The process for Np pyrochemical co-deposition with UO_2 and UO_2-PuO_2 from molten NaCl-KCl was developed for Np fuel production and experimental fuel pins are under irradiation in the BOR-60 fast reactor.

Americium and curium behave in molten chloride systems similarly to the rare earth elements. So their recovery and separation from molten salt with rare earth is difficult. It could be possible for americium to exist in the salt as AmO^+ species under high oxygen partial pressure. This phenomenon is used for the co-deposition of americium with UO_2-PuO_2 during electrolysis. A method for americium co-deposition with MOX fuel by electrolysis is under development.

Technetium and neptunium are targeted due to their solubility in the oxidizing conditions at Yucca Mountain. The problems associated with these elements stem from the repository choice, not their inherent chemical behavior. Selection of a repository with reducing conditions would eliminate the need to address these elements since they would be insoluble in the tetravalent state. Care should be taken in future presentations to explain that the concern is due to oxidizing conditions at Yucca Mountain.

Radiation effects were not discussed, but may be important. True, the use of pyrochemistry reduces radiation effects. However, much is made of the relatively small volumes used. These small volumes will have extremely large radiation doses. The effect on the chemistry and equipment may be considerable and needs to be investigated.

The separation of iodine is required so that I-129 can be transmuted. The volatility of the iodine can be used to achieve separation, but also requires attention to avoid losses during reprocessing. Supplementary information received after the review indicates that at present the pathway for separating iodine is by exploiting its volatility. For incorporation into the target, the use of chromium iodide or lanthanum iodide is proposed. If this route is to be used, separation of iodine from chlorine needs some exploration. More importantly, more attention is needed to evaluate the proposed target material. As a soft base, I preferably forms complexes with soft acids such as Cu^+, Ag^+, Au^+, Cd^{2+}, Hg^+ or atoms in the metallic state. Chromium and lanthanum are hard acid metal ions, which may not be the best metal ions for forming stable iodide complexes under the conditions experienced by the target. Choosing a suitable target material incorporating iodine is complicated due to the neutronic, thermal, and chemical stability considerations and requires a more concerted research effort.

R & D status of Partitioning

Significant technical achievements: demonstrated on lab scale
Industrial feasibility : to be demonstrated

- ***Problems to be solved***

✓ Separation of Am and Cm from lanthanides
✓ Minimization of secondary wastes
✓ Corrosion resistance materials in dry process
except for ANL process
✓ Scale-up & Demonstration of a whole process
✓ Safety assessment

It is improbable that the ATW system would be able to achieve the goal of no long-lived HLW output because the unavoidable process losses would lead to contamination of various parts of the system. Eventually, these items would have to be treated as HLW or treated by additional expensive processes.

Conclusion

A number of the LWR and ALMR goals that depend on separations technology have yet to be fully demonstrated. Of particular importance is a reduction in the overall process losses during separations. Thus, research and development in separations technology must be an essential part of any program to develop S&T.

For ATW, processes based on molten salt and molten metal systems are very radiation-resistant and would not be subject to radiation-induced reagent degradation as in the case for aqueous systems. The ATW separations concepts that have been proposed are beyond demonstrated technology and are questionable in the intermediate term.

The separations research and development necessary for these accelerator-based transmutation schemes would be more extensive than that required by the IFRs because a wider variety of separations options must be considered. A circulating molten salt that is processed by pyrochemical techniques may be the best solution for operating in the very high neutron flux and with the short-cooled materials in the ATW system, and it is this approach that has been receiving major emphasis at the Los Alamos National Laboratory. No demonstration of this technique has yet been performed. Extensive laboratory study followed by demonstration of the technology would be required, as there has been little experimental research on the proposed ATW schemes.