

PYROCHEMICAL PROCESSING OF IRRADIATED TRANSMUTER FUEL

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Abstract

The US accelerator transmutation of waste program is directed toward the destruction of transuranic elements and long-lived fission products present in spent light water reactor fuel. Initial separation of these materials from the light water reactor spent fuel will be accomplished by conventional aqueous processing methods. The transuranic elements will be incorporated in blanket fuel assemblies that will be irradiated to burn-ups in the range of 30 atom percent, and the fuel assemblies will be processed to recover and recycle unburned transuranic elements and newly-generated long-lived fission products. The accelerator driven transmutation system will use a fuel type much different from light water reactor fuel, however, and the fuels under consideration are amenable to pyrochemical processing. Two different pyrochemical processing methods are described in this paper, both involving an initial chlorination of the irradiated transmuter fuel.

1. Introduction

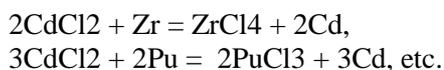
The present concept for partitioning and transmutation of selected radionuclides in the US accelerator transmutation of waste (ATW) program calls for the extraction of transuranic elements and certain long-lived fission products from spent light water reactor (LWR) fuel and their subsequent destruction in an accelerator-driven sub-critical system. Transmutation will be carried out in an accelerator-driven sub-critical assembly, providing an intense flux of high-energy neutrons produced by spallation reactions resulting from the impingement of high-energy protons on a liquid metal target. The technology development roadmap [1] for this program called for approximately 1 450 tons of spent LWR fuel to be treated per year, corresponding to some 14 tons of transuranics per year. The form of the targets to be used for long-lived fission product (i.e. ^{99}Tc and ^{129}I) transmutation is tentatively set as metallic technetium and sodium iodide, and the selection of the form of the transuranic-bearing blanket fuel elements seems to be converging on a design that comprises a dispersion of metallic transuranic elements in a metallic zirconium matrix. Uranium is excluded from the fuel in order to preclude the formation of additional transuranic elements by neutron absorption. The initial version of the fuel contains 23 weight percent transuranics and 77 weight percent zirconium. More recent studies suggest that a 50-50 composition may be preferred. An alternative to the metal dispersion/metal matrix fuel is a dispersion of transuranic nitrides or oxides in an inert matrix such as molybdenum, stainless steel, or zirconium nitride. Regardless of fuel type selected, the burn-up target for the transmuter blanket fuel is on the order of 300 MWd/kgHM, or approximately 30 atom percent burn-up of the TRU elements; the fuel must thus be processed to extract the significant concentrations of newly-generated fission products and to recover the unfissioned transuranics (as well as iodine and technetium) for recycle to the transmuter system. At this burn-up level, throughput requirements for the processing of the transmuter blanket fuel are in the range 4-35 tons (heavy metal) per year, depending on the fuel composition, transmuter operating cycle, and plant deployment scheme ultimately chosen.

2. Process selection

In the case of the metal dispersion/metal matrix fuel, the low throughput rate and the large concentration of zirconium in the fuel material, combined with a desire to minimize the generation of high-level radioactive wastes and secondary wastes, favor the use of a non-aqueous processing method. Conventional electrorefining methods, as applied to metallic fast reactor fuels, were considered inappropriate in this application because the high zirconium concentration would tend to reduce throughput to an unacceptably low level and require extensive replication of equipment to achieve throughput goals. The focus of process development has thus been on volatility processes, specifically chloride volatility processes that retain the non-volatile transuranic elements in a chloride salt that can be dealt with by means already developed for actinide extraction.

3. Primary chloride volatility process

The process concept under study, shown in Figure 1, involves the chopping of irradiated fuel elements, followed by chlorination of the constituents of the fuel in a salt bath containing added cadmium chloride that is formed by sparging chlorine gas through the liquid metal. The cadmium chloride reacts with the metallic constituents of the fuel by reactions such as:



The metallic cadmium product of the chlorination reaction drops back to the bottom of the chlorination vessel for subsequent reaction with chlorine. The temperature of the chlorination vessel is then increased to volatilize $ZrCl_4$. The primary purpose of the volatilization step is to remove the matrix zirconium, in order to facilitate the subsequent extraction of the transuranic elements. Experiments have shown the ready volatilization of $ZrCl_4$ at modest operating temperatures (500-700°C) whilst transuranic elements and the noble metal fission products are retained in the salt. Initial tests with a LiCl-KCl salt were not successful because the $ZrCl_4$ tended to complex with KCl, forming a non-volatile K_2ZrCl_6 compound. Removing the KCl from the bath resulted in full volatilization of the zirconium without loss of any of the transuranic elements. The recovered $ZrCl_4$ can be reduced to form zirconium metal, which can then be recycled to the fuel fabrication process.

The liquid cadmium at the bottom of the chlorination vessel contains the noble metal fission products (NMFP). The cadmium can be separated from the residual salt by freezing the metal and drawing off the salt bearing the transuranic chlorides and other fission product chlorides. Cadmium can then be recovered for recycle by distillation, sending the noble metal fission products to an extraction step where technetium is selectively removed and sent to transmutation target fabrication. The other noble metal fission products are immobilized by alloying with zirconium and iron to produce a highly durable metal waste form. This waste form will effectively immobilize technetium as well, should it prove disadvantageous to extract and transmute technetium.

The residual salt containing the transuranic chlorides, strontium and caesium chlorides and lanthanide chlorides is transferred to an electrowinning vessel, where the transuranic elements are extracted by electrowinning. It appears that the iodine can also be extracted by electrowinning, but that step has yet to be proven. The transuranic elements are sent to the fuel fabrication step, and the iodine to transmutation target fabrication after converting it to sodium iodide. The recovery of TRU elements has been demonstrated and it is planned to conduct experiments with iodine extraction during the year 2001.

Because the thermodynamic properties of technetium are not well known, it is not clear that the technetium will be volatilized along with the zirconium, but the expectation is that it will remain in the salt. Experiments are necessary to validate this assumption. The fate of iodine in this process is also not clear, and there may be multiple routes for recovery of iodine for subsequent transmutation. Testing of the complete flow-sheet in 2001 will serve to answer many of these questions.

4. Alternative fuel processing

Figure 2 shows a schematic flow-sheet for a process to treat those alternative transmuter blanket fuels incorporating an inert matrix material that will not form a volatile chloride. This process would be applicable to oxide or nitride fuel dispersions, with the added restriction in the case of nitride fuels that the nitrogen may be fully enriched in ^{15}N , to preclude the formation of excessive amounts of ^{14}C by the (n,p) reaction with the more common isotope of nitrogen, ^{14}N . This necessitates recovery and recycle of the enriched nitrogen. The process would also be useful in treating LWR fuels designed with inert matrices for burning plutonium. The initial part of the flow-sheet is much the same as that for treatment of TRU-Zr alloy fuel described above, with the exception that no species are volatilized in the course of the chlorination step. The noble metal fission products will not be chlorinated, and they will be sent to the metal waste form along with the inert matrix material (molybdenum or stainless steel), which will also not be chlorinated by $CdCl_2$. The transuranic chlorides, rare earth fission product chlorides, strontium and caesium chlorides, and the LiCl-KCl carrier salt are then contacted with a dilute alloy of lithium in cadmium in a series of centrifugal contactors operating well above the melting temperature of the salt mixture. By appropriate control of the lithium activity, the

transuranics will be reduced to the metallic state and transferred into the cadmium phase, while the fission product chlorides remain in the salt phase. The fission product bearing salt is directed to the ceramic waste form production process, resulting in a glass/sodalite composite waste form that has been shown to be highly resistant to leaching by groundwater.

The transuranic elements in the cadmium phase are oxidized by sparging chlorine through the melt, and the resultant transuranic chlorides (together with a trace amount of rare earth chlorides formed from the small amount of rare earth fission products that extract with the transuranics in the reductive extraction step) are separated from the metal phase. They are then placed in a LiCl-KCl salt bath, where the transuranics are reduced with metallic lithium and recovered as metals. The metallic transuranic elements are then sent to the fuel fabrication process for recycle to the transmuter. The trace amount of rare earth contamination of the transuranics will not cause any neutronics problems in the high neutron energy spectrum of the transmuter.

Figure 1. Schematic flow-sheet for the chloride volatility process for treatment of irradiated transmuter blanket fuel of the general composition 30-50% TRU, 70-50% Zr

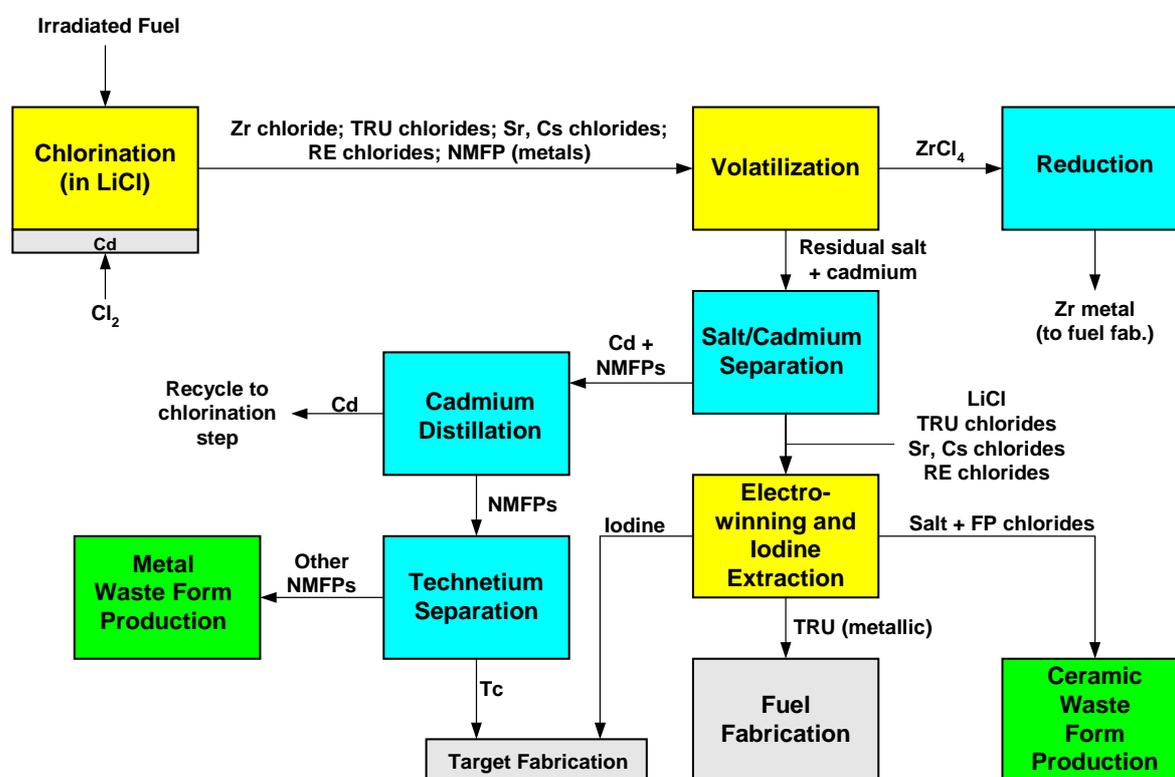
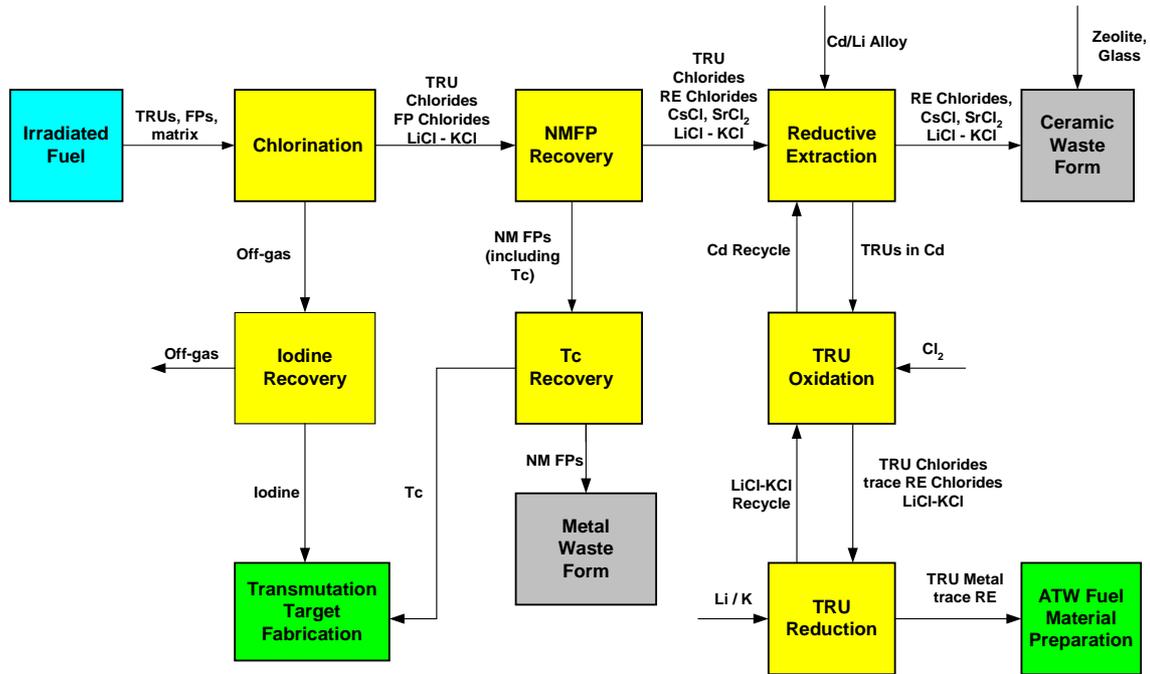


Figure 2. Schematic flow-sheet for the chlorination process for treatment of irradiated transmuter blanket fuel containing inert matrix material that will not form a volatile chloride. This process could be used for treatment of fuels with, for example, stainless steel or ceramic matrices.



5. State of process development

Both processes described here have been demonstrated with simulated irradiated fuel containing representative transuranic elements and non-radioactive fission product elements. The recovery of technetium and iodine has not, however, been shown, and remains to be accomplished with the next year. Experiments with irradiated fuels are necessary for final validation of process chemistry, but; the absence of an operating fast reactor test facility in the United States imposes a delay on access to irradiated fuel samples. In the meantime, tests will be conducted with fuel samples irradiated in thermal reactors. Even though the burn-up levels in thermal reactors will be somewhat less than would be achieved with fast reactor irradiations, the initial experiments will comprise a reasonable test of process designs and should be adequate for flow-sheet adjustment and discrimination among competing processes. Scale-up to prototype equipment sizes will occur within the next three to five years, with initial tests to be performed with simulated irradiated fuel.

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REFERENCE

- [1] *A Roadmap for Developing Accelerator Transmutation of Waste (ATW) Technology – A Report to Congress*, DOE/RW-0519, October 1999.