Chemical Processing Associated with the Accelerator Transmutation of Nuclear Waste (ATW) Concept

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ABSTRACT

An accelerator-driven subcritical nuclear system is described that destroys both actinides and selected long-lived fission products by transmutation An application of this accelerator transmutation of waste (ATW) concept to the nuclear waste from commercial spent fuel is presented as an example. Particular attention is given to the chemical processing assodated with thii concept. Actinides are separated from their fission products and key long-lived fission products are separated and transmuted.

Researchers at Los Alamos have been developing a transmutation concept that utilizes an accelerator-driven neutron source to transmute actinides and long-lived fission products, thereby allowing reduced storage times for nuclear wastes. Neutrons are produced by spallation reactions when a medium energy, high current beam of protons strikes a heavy metal target. The actinides and long-lived fission products to be transmuted are circulated through a blanket region surrounding the target. The stable and short-lived transmutation products are removed from the circulating loops using advanced chemical separations. Some of these same chemical separations may be used to purify the actinides and long-lived fission products from nuclear waste in preparation for transmutation. The thermal power from fissioning the actinides maybe converted to electricity. A portion of this electrical power is used to drive the proton accelerator with the remainder directed to the commercial power grid. This concept is shown schematically in Fig. 1. Ultimately, we envision an accelerator-driven nuclear energy system of this kind that could be fueled with natural uranium or thorium, produce electrical power, and concomitantly destroy its own nuclear waste.

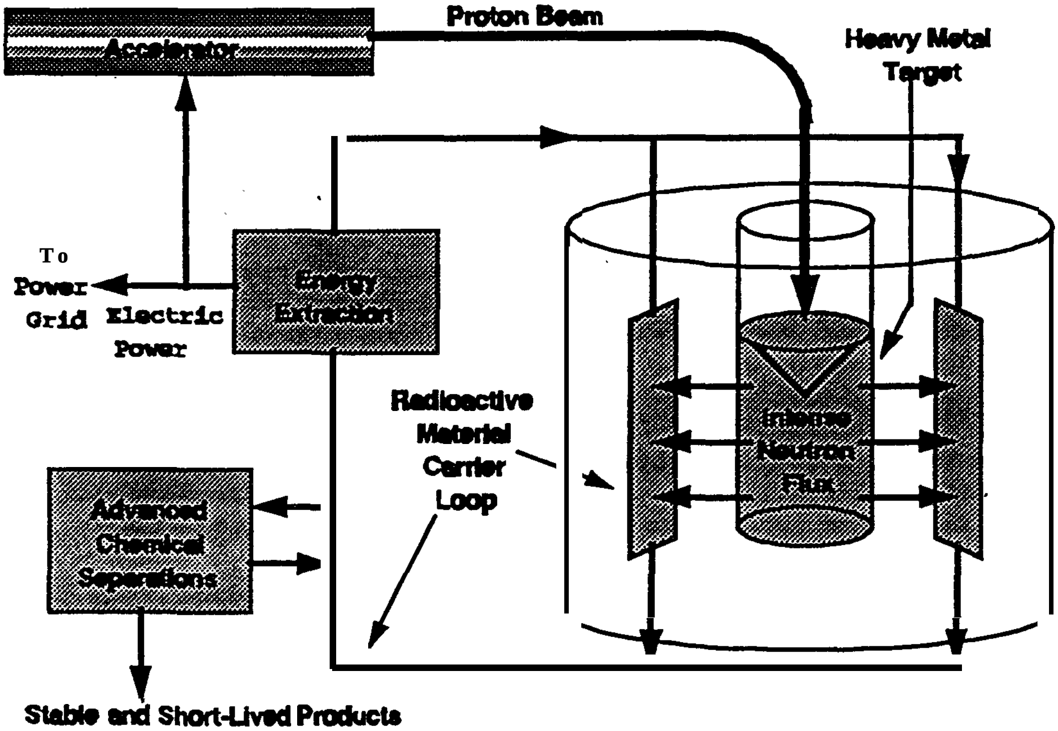

Figure 1. Schematic of accelerator transmutation of waste (ATW) concept

A key feature of the accelerator transmutation of waste (ATW) concept is the use of an intense flux of thermal neutrons for the transmutation. This enables significant transmutation rates with small blanket inventories of the species to be transmuted. We currently estimate that ATW systems can achieve neutron fluxes in the range of 10’S -10’6 neutrons cm^{-2} see"'. Fluxes in standard thermal reactors are typically one or two orders of magnitude lower than this. Fast reactors attain approximately the same flux as an ATW system, but cross sections for transmutation are generally more than an order of magnitude smaller m the fast spectrum. Consequently, for a given transmutation rate, ATW systems require an order of magnitude smaller inventories. This in turn permits the use of a small capacity chemical processing facility and results in smaller end-of-life residues in the overall system.

The ATW concept is being explored for both aqueous and nonaqueous carrier media Nonaqueous carriers such as molten salts allow the system to operate at high temperatures and near ambient pressures, allowing more efficient conversion of thermal power to electrical power. However, the chemical separations for such systems will require significant development. Aqueous systems, on the other hand, can draw from a wealth of chemical processing knowledge developed for nuclear fuel reprocessing. The remainder of this paper will focus on a concept that uses a heavy water carrier and moderator with particular attention to a possible approach to the chemical processing. The AIW concept might be applied to a number of nuclear waste problems including commercial spent fuel and wastes from nuclear weapons production. We will consider for this presentation an example based on the commercial spent fuel application. This particular system has been described in much more detail in presentations to the U.S. National Academy of Science panel on Separation Technologies and Transmutation Systems (STATS).[1] It consists of a 1600 MeV, 250 milliampere proton accelerator driving four target-blanket modules. Thus each module receives 100 MW of beam power. A number of possible target designs are being explored but the particular design used in this example consists of heavy water cooled tungsten surrounded by a lead annulus. A heavy water moderator blanket surrounds the target An array of tubes in the blanket carry the materials to be transmuted. Some tubes carry actinides as an oxide slurry or suspension in heavy water while fission products are circulated in separate tubes as heavy water solutions. Initial estimates indicate that this system could transmute the plutonium, higher actinides, and key long-lived fission products (Tc, 1) discharged from eight 3000 MWt light water reactors (LWRs). Most of the aqueous separations used in this example are well proven, having been deployed at significant scale. Such technologies were chosen so that overall material balances could be estimated. The system has not been optimized and there are numerous avenues for improvement

The excess neutrons generated in the spallation target allow any number of long-lived fission products to be transmuted. However, as more fission products are addressed, a greater fraction of the generated power is required to run the accelerator. Thus, the choice of which fission products to transmute must be based on analyses of costs and benefits. In this system, strontium and cesium have extremely small neutron absorption cross sections and are not considered for transmutation. We envision a nuclear waste management strategy in which these radionuclides would be placed in engineered storage for 10 half lives or more to allow them to decay to stable materials. It is generally agreed that of the remaining long-lived fission products ($\tau_{1/2}$ > 30 years), ^{99}Tc and ^{129}I represent the greatest risk.[2] We have chosen for this example to transmute only these two fission products. The system transmutes both the fission products from the LWR spent fuel as well as those created from actinide burning. In order to support eight LWRs, the system must transmute 2500 kg/yr of actinides, 250 kg/yr of technetium, and 79 kg/yr of iodine. For the technetium and iodine, approximately 80% of the material transmuted comes from the LWR waste while 200A is generated from actinide burning. The actinide burning produces about 90 kg/yr of other long-lived fission products that are not transmuted; primarily ^{107}Pd and

^{93}Zr with smaller amounts of ^{135}Cs, ^{126}Sn, and ^{79}Se. The actinide burning also produces 2410 kg/yr of stable and short-lived ($\tau_{1/2} \leq 30$ years) radioactive fission products. These include 75 kg/yr of ^{137}Cs and 14 kg/yr ^{90}Sr.

Each target-blanket module for this reference aqueous system produces about 1900 MW of thermal power. Using a thermal to electric conversion efficiency of 30%, similar to that for a pressurized water reactor, each module produces 570 MW electrical power. With recent advances in accelerator technology it is expected that "wall plug" efficiencies of 45°A can be attained for the proton accelerator. Thus, each of the four target/blanket modules must supply 220 MW of electrical power to run the accelerator, leaving a total of 1400 MWe for sale to the commercial grid.

The neutronics for transmutation of ^{99}Tc are particularly favorable. The thermal neutron capture cross section is relatively large (-20 barns), the initially formed ^{100}Tc decays rapidly (($\tau_{1/2} = 16$ see) to give stable ^{100}Ru, and this transmutation product is not easily activated because both ^{101}Ru and ^{102}Ru are stable isotopes.

Several factors contribute to the importance of fission product technetium in nuclear waste management First, it is produced with a relatively large yield. In addition, long term risks are associated with its long half life (2.13 x 10S yr) and environmental mobility as the highly water soluble pertechnetate anion, TcO_4^-. In this form, technetium can leach from glass, grout, or mineral repositories. Finally, technetium can form a volatile oxide, Tc_2O_7, that must be dealt with in proposed vitrification schemes.

The chemistry of technetium and ruthenium is complex. Both elements can exist in a variety of oxidation states and both tend to form complex ions in aqueous solutions. In addition, the them.Wry of technetium has not been studied as extensively as most other transition metals due to the fact that it has no stable isotopes. After review-rig the chemistry of technetium we have chosen to transmute it as a heavy water solution of $^7LiTcO_4$.

During transmutation, the ruthenium product must be removed to prevent eventual activation of the ruthenium and also to minimize neutron losses. Options that we have examined for effecting the separation of ruthenium from technetium include ozonolysis, ion exchange, precipitation and filtration, magnetic separation, solvent extraction, electrodeposition, and fluorination. These options are briefty discussed in Los Alamos report LA-UR-92-39.[3] At the present time, ozonolysis and ion exchange appear to be the most promising approaches. Ion exchange has been demonstrated on a relatively large scale,' but suffers from a waste management perspective in that it generates a significant stream of radioactive spent resin. The ozonolysis approach appears attractive in terms of waste generation but has only been demonstrated at laboratory scale. Fig. 2 illustrates this approach. It involves sparging the pertechnetate solution with ozone to produce volatile ruthenium tetroxide. The $Ru0_4$ is swept out of solution as a gas and trapped in caustic solution where it is rapidly reduced to perruthenate (RuO_4^-) or ruthenate (RuO_4^{-2}). The ozone that reacts to form ruthenium tetroxide produces oxygen. Thii oxygen may be converted back to ozone and reused. The high neutron flux in the transmute is likely to generate significant radiolysis of the heavy water to deuterium and oxygen. A catalytic recombine would be used to prevent their buildup.

The viability of the ozonolysis approach has been tested at laboratory scale using ^{106}Ru as a tracer. 2-5 g/hr of ozone was sparged through a 5 x 10^{-4} M solution of lithium pertechnetate containing tracer amounts of ^{106}Ru. After exiting the reaction pot, the gas stream was bubbled through two consecutive 4 M LiOH traps. The amounts of technetium and ruthenium carried into the caustic traps was determined using liquid scintillation counting techniques. The results indicated a separation factor in excess of 10^s. It seems quite likely that the low levels of technetium carried into the trap were due to aerosol

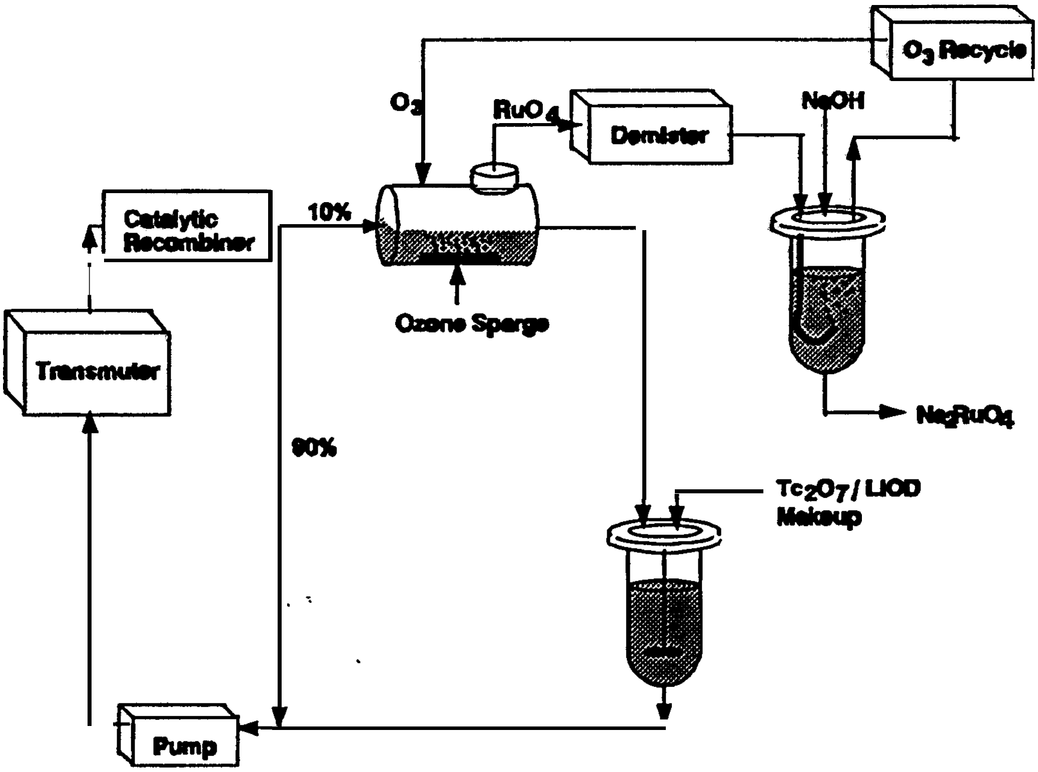

Figure 2 Separation of ruthenium from technetium using ozonolysis

formation and even larger separation factors may be possible using a demister. It was also determined that the rate of ruthenium transport was independent of pH in the range from 1 to 14. These preliminary results are quite encouraging.

The neutronics of iodine transmutation are slightly more complex than those for technetium, but nonetheless quite favorable. Unlike technetium, fission product iodine is not monoisotopic and, after cooling to allow the ^{131}I to decay, contains approximately 75% long-lived ^{129}I with the remainder being stable ^{127}I. The long-lived isotope transmutes cleanly and efficiently to stable ^{130}Xe. The stable ^{127}I absorbs a neutron to produce the 25 min ^{128}I. Most of this nuclide decays to produce stable ^{128}Xe. However, a small fraction undergoes electron capture or positron emission to produce stable tellurium.

Like technetium, iodine can exist in a variety of oxidation states. In addition, iodine and its compounds tend to be rather corrosive. Although the transmutation product xenon is relatively inert, it does form explosive oxides that must be avoided. After these considerations, we initially chose to transmute the iodine as solid elemental I_2, following the suggestion of Dincklange.[5] Iodine would be contained in zircalloy tubes, perhaps with a ceramic liner to prevent corrosion. In the proposed scheme the tubes are manifolded together and the gaseous xenon pumped out as it is formed. The array of tubes would be cooled by flowing heavy water. Preliminary engineering analysis indicates severe problems in conducting heat out of the iodine. The low thermal conductivity of iodine may cause it to vaporize along with the xenon transmutation product. We are currently examining other approaches to iodine transmutation.

The chemical processing needed for actinide transmutation is similar in many respects to that associated with spent fuel reprocessing. A major difference between conventional spent fuel reprocessing and AIW actinide processing is the requirement for ATW that chemical separations be performed shortly after irradiation. This requirement derives from a need to keep inventories of actinides as low as possible throughout the entire system. Without the benefit of long cooling periods, radiolytic decomposition of solvents and chemical reagents is a major concern and is an important consideration in selecting separation approaches. We have also been guided by the conviction that, where possible, we should propose separation technologies that have been operated at significant scale. By using such proven technologies, uncertainties with respect to waste generation are minimized. Guided by these considerations, we have proposed a baseline actinide processing flowsheet discussed in Los Alamos report LA-UR-92-63[6] and shown in Fig. 3.

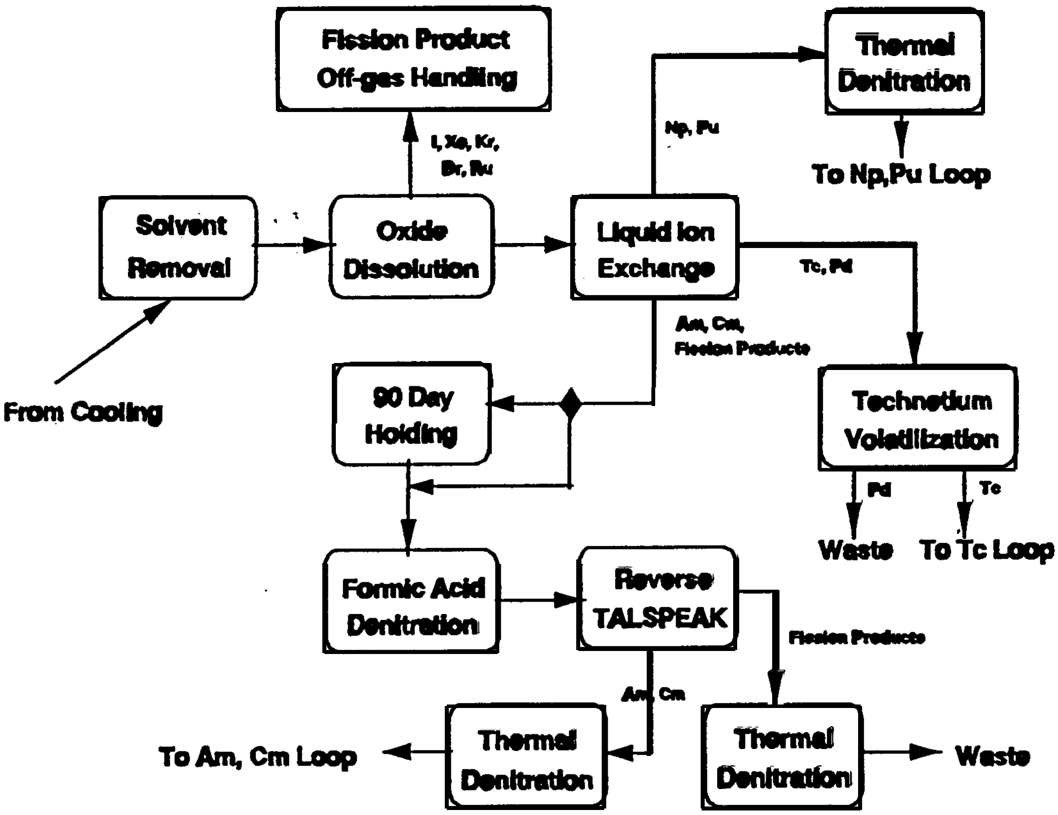

Figure 3. Actinide processing flowsheet

The actinides are suspended in heavy water as an oxide slurry and circulated through the transmute. The americium and curium are fissioned more slowly than the plutonium and neptunium and are also more difficult to process. Thus, by using separate recirculating loops with americium and curium in one and neptunium and plutonium in the other, we are able to process the americium and curium less frequently and allow it to cool for longer times before processing. This approach reduces the actinide inventories in the overall system.

The first step in the actinide flowsheet involves removat of the D_20 carrier by evaporation and sparging to remove tritium. The actinides and fission products are then dissolved in n-tic acid using an ozone sparge. Concentrations of the actinides and fission products are chosen so that the thermal loads in the resulting solutions do not exceed 10 watts/liter. The acid dissolution step releases some of the fission products (Kr, Xe, I_2, Br_2, and RuO_4) as gases and these are directed to an off-gas handling system. Iodine is recovered for subsequent transmutation to stable xenon. A quatemary amine liquid ion exchanger, aliquat 336 nitrate (trialkylmethylammonium nitrate with alkyl = C_8 and C_{10}, $C_8 > C_{10}$), is used to extract untransmuted neptunium and plutonium from the nitric acid solution for fast recycle back to the transmute. The aliquat 336 is even more radiation resistant than tributylphosphate (TBP) and spent extractant can be incinerated to water, nitrogen, and carbon dioxide. Neptunium and plutonium are stripped from the organic phase with dilute nitric acid, thermally denigrated back to their oxide form, and returned to the transmute. The aliquat 336 also extracts technetium and palladium into the organic phase. After the actinide back extraction, technetium and palladium fission products are stripped from the organic phase with a 1 M solution of ammonium hydroxide. The technetium is separated from the palladium by volatilization as Tc_2O_7, converted to $^7LiTcO_4$ by reaction with ^7LiOD, and sent to the technetium transmutation flowloop. The raffinate, containing trivalent higher actinides, lanthanides, and other fission products, is cooled for 90 days. After cooling, the acidity is adjusted to pH 3 with formic acid and the aqueous solution is extracted using the reverse-TALSPEAK (Trivalent Actinide-Lanthanide Separations by Phosphorous reagent Extractant from Aqueous Complexes) process.’ The trivalent actinides and lanthanides are extracted into the organic phase, leaving the other fission products in the raffinate. Thii raffinate is spray cakined and institutes a major waste stream. The actinides are selectively back extracted with 1 M lactic add and 0.05M diethylenetriaminepentaacetic acid, thermally denigrated, and returned to the transmute. The lanthanides are then stripped from the organic phase with 6M nitric add and disposed of as waste. The entire actinide processing flowsheet has been modeled using the commercial ASPEN PLUS simulation software and the results from this analysis are available in Los Alamos report LA-UR-92-1 241.6

The proposed approach to chemical processing internal to the aqueous transmutation system is credible. We have begun the experimental validation of the technetium and ruthenium separation chemistry. The proposed actinide processing uses demonstrated technology for each unit operation in the flowsheet. However, testing and demonstration of an integrated flowsheet is crucial and will undoubtedly lead to changes and improvements.

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