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COPROCESSING OF THERMAL REACTOR FUELS

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ABSTRACT

The Nuclear Power Development Division (NPD) under the Assistant Secretary for Energy Technology in the Department of Energy (DOE) is responsible for examining alternative nuclear reactor fuel recycle systems which have potential for reducing the risk of proliferation of nuclear weapons. NPD is administering a base technology program of research and development and design studies which will provide a sound technical foundation for evaluating the nonproliferation potential and commercial feasibility of these alternatives.

The Savannah River Laboratory (SRL) has been assigned as the technical lead for those activities associated with the processing of thermal reactor fuel. In order to systematically identify technical requirements and design solutions, SRL periodically updates a Design Integration Study (DIS). The reference process being incorporated into the current DIS is coprocessing uranium and plutonium in a manner whereby pure plutonium is never available in a separate stream. As with other processes, coprocessing doesn't offer a technical fix for preventing proliferators. A flowsheet for this reference process is described with particular emphasis on technical issues and proliferation resistance advantages of coprocessing over conventional purex processing.

INTRODUCTION

On April 20, 1977, President Carter presented a new energy policy which committed the U.S. to the continued use of nuclear power from Light Water Reactors (LWR) but deferred indefinitely the commercial reprocessing of spent nuclear fuel due to the proliferation potential of separating and recycling fissile material. The Nuclear Power Development Division (NPD) responded to this new policy by redirecting our LWR Recycle Program to examine alternative fuel cycles with greater potential for proliferation resistance. This new program was renamed the Alternative Fuel Cycle Technologies Program and the program technical lead was assigned to Savannah River Laboratory (SRL) for reprocessing and Battelle Pacific Northwest Laboratory (PNL) for refabrication. The integrating mechanism for the results of the various R&D activities is a Design Integration Study which will incorporate the developed processes into a design of an integrated fuel cycle complex. The reference process for the Design Integration Study is coprocessed uranium and plutonium.

PROGRAM ORGANIZATION

The Nuclear Power Development Division has responsibility for Department of Energy (DOE) technology development programs associated with near-term power reactor concepts and their attendant fuel cycles. Within NPD, I am the Assistant Director for Fuel Cycle Development, having responsibility for Fuel Cycle Research and Development. The fuel cycle is matrixed into reprocessing and refabrication and by generic reactor type. The element which this paper will focus on is the coprocessing portion of the Alternative Fuel Cycle Technologies Program. The technical lead for this subprogram is the Savannah River Laboratory (SRL), whose direction is provided by the Director of the Fuel Cycle Program Office (FCPO) within the Savannah River Operations Office (SR). The program is divided into the following ten tasks within a Work Breakdown Structure (WBS):

Program Management
Studies and Analysis
Fuel Handling
Fuel Reprocessing
Conversion Processes
Fuel Refabrication
In-Plant Waste Treatment
Nonradioactive Systems Tests
General Support
Major Facilities

DuPont, the operating contractor at Savannah River, utilizes a Design Integration Study (DIS) to ensure that adequate design solutions are available to fulfill all technology requirements for a reprocessing complex. The responsibility for this effort is assigned to the Atomic Energy Division (AED) for the Company's Polymer Intermediates Division. Overall coordination is assigned to the Process Section of the AED. The Process Section is assisted by a DIS Task Force at Savannah River Plant which reports through the Separations Department of the AED's Manufacturing Division. The engineering studies will be conducted by the Design Division of the Company's Engineering Department. SRL and its contractors will prepare the Technical Data Summaries for the Design Division.

The major process operations within the Coprocessing Plant are: (1) receipt and storage of fuel; (2) end cropping and shearing of fuel; (3) off-gas treatment (including tritium); (4) dissolution of the fuel; (5) feed clarification; (6) solvent extraction; (7) waste handling and solidification and (8) product conversion. These processes will be discussed in detail in the balance of the report.

PROCESSES WITHIN THE COPROCESSING PLANT

Receipt and Storage of Fuel

Spent fuel transported in cooled shipping casks, is received at the plant and placed in temporary water basin storage prior to processing.

End Cropping and Shearing of the Fuel

Unfueled metal hardware is removed from fuel containing metal by cropping off end hardware and gas plenum regions in order to simplify the shearing process and minimize highly contaminated solid waste. The entire fuel elements are compacted (gagged) and then chopped into one to two inch lengths. Compacting maintains the alignment of the fuel rods and prevents pinched ends.

The technical issues here are remote maintenance of multiple shears, removal of decay heat, uniformity of sheared pieces, the prevention of a zirconium fire and protection of operating personnel from excess radiation.

Off-Gas Treatment

Tritium removal is based on voloxidation which is a process where UO_2 is oxidized to U_3O_8 in air and oxygen at a temperature of 450 to 550° C. The current concept for voloxidation utilizes a rotary kiln although further work is being done to examine batch or semi-continuous methods that do not involve rotary equipment inside containment. This process releases the tritium and a portion of the other volatile fission products into the off-gas system where they are trapped. The oxidation of the uranium minimizes the evolution of nitrogen oxide during dissolution, and the physical breakdown of the pellets into powder releases some of the krypton and carbon-14.

The off-gas system is designed to recover tritium, carbon-14, iodine-129, krypton-85, ruthenium-103,106, nitrogen oxides and radioactive particulates from the gaseous effluents throughout the plant. Physical and chemical traps are used for the recovery and storage of tritiated water iodine, ruthenium and carbon. Nitrogen oxides are absorbed to produce nitric acid for recycle to the process. A selective fluorocarbon absorption process using dichlorodifluoromethane (freon R-12) is specified for recovery of krypton-85. The krypton-85 is compressed and stored in gas cylinders which are accumulated on-site and periodically shipped to an off-site Federal repository.

Technical issues include percent of tritium released, optimized process variables and effect of voloxidation on dissolution.

Dissolution

The voloxidized fuel is transferred to a dissolver basket where it is dissolved in nitric acid. The reference process is batch dissolution in multiple dissolvers but both slow semi-continuous addition and continuous dissolution (rotary dissolvers) are being studied. Secondary dissolution will probably be necessary due to increased amounts of plutonium bearing insoluble residue in high-burnup fuels and mixed-oxide recycle fuels.

Cooperation with fuel fabricators to strive for homogeneous, solid-solution fuel will aid complete dissolution. Technical issues include maintaining a safe criticality margin, fission product plating and leached hull monitoring and disposal.

Feed Clarification

The feed clarification and adjustment system will incorporate centrifugation for removal of insolubles, and evaporation for reduction of process volumes in addition to having the flexibility necessary to alter nitric acid, uranium and plutonium concentration, adjust plutonium valence and evolve iodine. Concentration by evaporation of dilute uranium and plutonium solutions generated in secondary leaching and rinsing reduces processing flow rates. An organic flocculant will be used to form a scavenging precipitate which will coagulate insoluble particulate matter and zirconium fuels. These highly radioactive particles containing molybdenum, palladium, ruthenium, zirconium and niobium are often found in highly irradiated fuels. The precipitate will be removed by centrifugation providing a clarified feed solution to the first solvent extraction cycle. Savannah River has a great deal of experience in their canyons with these types of processes, but additional research into other flocculants and optimization studies are being performed.

Solvent Extraction

A modified Purex solvent extraction process has been specified to separate and purify plutonium and uranium from solutions of irradiated LWR fuel. Purex operating experience, laboratory experiments in miniaturized equipment, and computer calculations using experimental distribution data were used to develop these flowsheets and to predict the stage-to-stage transfer of uranium, plutonium, nitric acid, and fission products. The losses of plutonium and uranium will be less than those for Purex, but individual stage decontamination factors are estimated to be lower for the coprocessing flowsheet. This results from the choice of conditions to minimize Pu losses and also from the effects of increased radiolysis. However, the overall decontamination is better for coprocessing because of additional process steps.

Figure 1 presents a simplified overall flowsheet for the solvent extraction process.

The first cycle of the solvent extraction process effect primary decontamination of uranium and plutonium from the fission products and partially separates plutonium from uranium. The clarified feed to this cycle is valence-adjusted and fed to the center of the first, 1A, countercurrent multistage contactor. In the extraction section of the contactor the actinides are selectively extracted into the organic phase while the bulk of the fission products remain in the aqueous phase and leave the contactor in the 1AW aqueous waste stream. In the scrub section of the contactor the actinide-bearing organic stream is washed for additional fission product removal.

The organic product stream from the 1A contactor is center-fed to the 1A' contactor. The 1A' contactor provides different extraction conditions than those present in the 1A contactor to produce additional decontamination from difficult-to-separate fission products, i.e., Zr, Nb, and Ru.

The plutonium-uranium stream (12 percent Pu in U+Pu) is separated from the bulk of the uranium in the 1B contactor. A low-acid aqueous extractant stream containing a reducing agent to reduce the plutonium to the +3 valence state back-extracts plutonium and some of the uranium into the aqueous phase. The aqueous product stream, 1BP, containing essentially all the plutonium and about 5 percent of the total uranium is sent to the second and third plutonium/uranium cycles for further purification. The organic stream containing about 95 percent of the uranium is stripped by very dilute nitric acid and the aqueous product stream is sent to the second or third uranium purification cycles.

For this coprocessing flowsheet, the uranium and plutonium are only partially separated from each other in the first cycle partitioning contactor (1B). The modification of the standard Purex flowsheet proposed to accomplish this involves eliminating the back-extractant stream (1BS) and moving the stage where organic feed enters from the center of the contactor to the stage where the aqueous strip solution leaves the contactor. These changes ensure that some uranium is always in the plutonium product stream. The quantity of uranium in the aqueous product is controlled by temperature, flow rates of organic (1BF) and aqueous (1BX) streams, nitrate concentration in the strip solution (1BX), uranium concentration in the organic feed, and TBP concentration of the organic phase. Ordinarily, the temperature, flow rate of organic stream, uranium concentration, and TBP concentration will be constant, so the uranium concentration in the aqueous product will be controlled by varying the nitrate concentration and flow rate of the aqueous strip stream. The plutonium concentration in the feed to first cycle will vary depending on fuel burnup from ~0.5 wt % for initial LWR fuel charges to ~1.0 wt % for nominal fuel. Therefore, the strip concentrations and/or flow rates will change, depending on the plutonium concentration in the feed, to attain a final nominal concentration of 12 wt % Pu in the uranium-plutonium product. Due to design characteristics, the upper bound for Pu concentration is 20 percent Pu in U+Pu.

The technical issues for coprocessing solvent extraction are inherited from conventional purex solvent extraction and include: Pu polymer formation, solvent degradation, solvent cleanup, nuclear criticality safety and flow rate and mass balance optimization for the coprocessing flowsheet.

Waste Handling and Solidification

Liquid waste from the coprocessing plant will be handled in a separate Waste Solidification Facility. In general, the facility will receive acidic high- and intermediate-level liquid wastes (HLLW and ILLW) from stainless steel waste tanks, concentrate by evaporation to reduce volume, solidify the waste into a glass form and package the waste into metal containers for disposal at a national repository.

Conversion

A coprecipitation process for plutonium and uranium uses ammoniumhydroxide or ammonia as the precipitant. When the precipitation is performed under suitable conditions, the mixed-oxide produced is soluble in nitric acid-water solution, eliminating the use of fluoride for the dissolution of the mixed-oxide, both in scrap processing and in fuel processing. Also, in line with recent policy, the Pu is not separated from the uranium at any point in the processing.

The latest variation of this process was developed by the General Electric Company, given the acronym "Coprecal" and adopted for use in the Design Integration Study.

The "Coprecal" process involves the following steps:

- Addition of ammonium hydroxide to concentrated plutonium-uranium nitrate solution to produce a finely divided slurry of ammonium diuranate and plutonium hydroxide.

- Introduction of the entire slurry to an elutriative fluid unit bed where it is calcined to form UO_3-PuO_2.

- Reaction of the calciner powder with 6 percent hydrogen in nitrogen at elevated temperatures to produce UO_2-PuO_2.

- Treatment of the reduced powder with hot carbon dioxide gas to "stabilize" the powder to inhibit its reoxidation when contacted with air.

Technical issues for "Coprecal" are defining the additional requirements on the calcination process and the off-gas handling system due to calcination of the whole slurry and solving the materials handling and transfer problems for the variety of phases.

DISCUSSION

The transition from a uranium/plutonium separations concept to coprocessing as a reference process, does not suggest coprocessing or any variation thereof is a technical "fix" to prevent proliferation of nuclear weaponry. Coprocessing as described in this paper does, however, introduce a complication for a potential proliferator; he must make substantial changes in the "hot" part of the plant in order to effect a pure plutonium stream. In addition, he must then cope with criticality control in the downstream process steps. Such modifications take time and require overt action.

The description of a coprocessing flowsheet presented in this paper is the initial design based on the best available information. It should be noted that it is a change in perspective to convert a processing system initially designed to produce pure plutonium to a processing system which must diligently avoid any pure plutonium streams. The magnitude of this change will allow fine tuning of equipment and process variables to enhance proliferation resistance. Some possible modifications which are being considered include: (1) total remote operation of reprocessing and refabrication processes which greatly limits access to materials, (2) partial decontamination from the fission products which eliminates solvent extraction steps which could be used to purify the plutonium stream (in addition, the presence of fission products increases the detectability of the material), (3) computer controlled valves and flow controls with software interlocks which could immobilize process material, and (4) improved safeguards and physical protection which would both decrease the probability of individuals gaining access to the material and increase the probability that a diversion would be detected quickly. Before a modification can be incorporated, there must also be verification that it does not interfere with the operability and maintenance of the plant.

Many factors affect the proliferation resistance of a fuel reprocessing plant, and in some cases proliferation resistance engineering must cope with plant operability. For example, the plant must be flexible enough to process fuels of varying burnups, compositions, age and radiation levels, and yet inflexible enough so that it is very difficult to produce weapons-usable material. The plant needs to have the flexibility to recycle off-spec material back through the first cycle; this same flexibility might also give proliferators an opportunity to purify a plutonium stream by repeating passes through the same cycle. Another example of a potential problem is in the master blend composition. Feed material could have anywhere from 0.5 to 1.0 percent Pu, depending on burnup. However, the specification for the product is 12 percent Pu in U and the solvent extraction system must have enough flexibility in flow and concentration to dampen the effect of the factor of two difference in feed concentration. This same flexibility when misused could increase the Pu composition in the product above the 12 percent limit. There are other examples of these types of tradeoffs and one of the goals of the NPD program is to identify acceptable compromises.

Figure 1

COPROCESSING SOLVENT EXTRACTION FLOWSHEET