Closing the CANDU Nuclear Reactor Fuel Cycle with a Modified PUREX Processing System: Reducing, Recycling and Refining CANDU Spent Fuel

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Summary

Currently, CANDU reactors in Canada utilize less than 1% of the potential energy in the fresh fuel bundles fed before storing the remainder as nuclear ‘waste’ at on-site nuclear waste management facilities. With the modified PUREX processing system, it is economically possible to close the fuel cycle by extracting and converting the remaining 99% to usable energy. The process is designed to mitigate proliferation efforts, as well as produce mixed-oxide fuel for reuse in CANDU reactors and metallic fuel for use in fast-neutron reactors. The multiple products generated create a profit centre.

1. Introduction

More than 50% of Ontario’s electrical energy usage is provided by the nuclear energy sector [1]. A by-product of this energy production is the accumulation of spent CANDU nuclear fuel bundles, which are currently considered unusable nuclear waste. There are approximately 45,000 tonnes of spent nuclear fuel in Canada and in Ontario alone this amount is projected to increase at a rate of 1,500 tonnes per year [2]. However, only 0.74% of the original incoming fuel in a fuel bundle is utilized to create energy, leaving approximately 99.26% of the original fuel as untapped potential energy [1]. This is equivalent to approximately 4,000 years of energy at current levels of nuclear energy production in Canada or $50 trillion of electricity at an average cost of 9.9 cents/kWh [2]. In order to capitalize on this large energy resource and reduce unnecessary long term storage of radioactive material, a processing system is needed to close the fuel cycle by producing recycled fuel for nuclear reactors. The processing system proposed is a modification of the traditional plutonium-uranium extraction (PUREX) process to better serve the fuel processing needs of Canada’s fleet of CANDU reactors.

2. Modified PUREX Process

2.1 Overview of conventional PUREX

The conventional PUREX process is a liquid-liquid extraction technique implemented to separate uranium (U) and plutonium (Pu) from a complex mixture of radioactive fuel elements dissolved in nitric acid. Separation is achieved by using an extracting agent, known as tributyl phosphate (TBP), in a normal paraffinic hydrocarbon diluent. Although effective, the process engenders concerns about proliferation due to the isolation of Pu and concerns about damage to the environment from the disposal of high-level liquid waste. Furthermore, it does not separate long-lived minor actinides from short-lived fission products (FPs). The former may be used as fuel in fast-neutron reactors (FNRs) with a fraction reused as CANDU fuel, while the latter decay to valuable metals. The original PUREX process has been modified and optimized to achieve these end products and overcome these concerns.

2.2 Process Flow of the Modified PUREX Processing System

The process flow and capabilities of the modified PUREX processing system are shown in Figure 1.

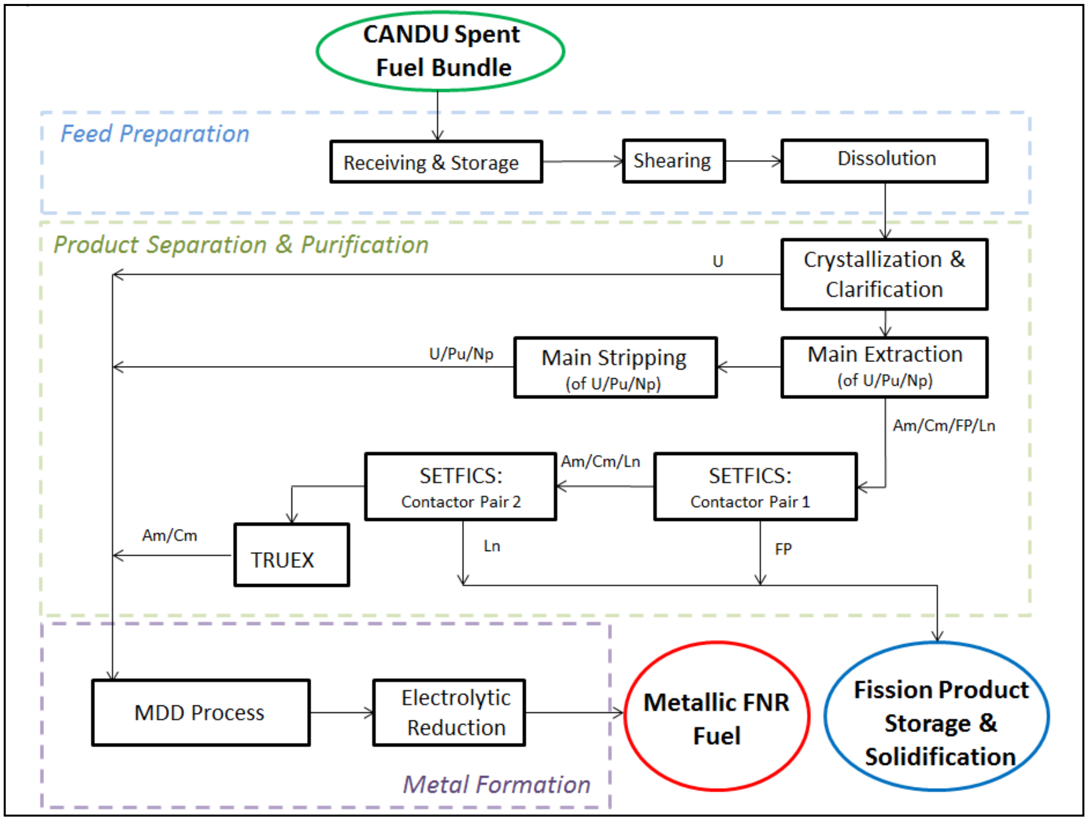

Figure 1: Overall Process Block Diagram for the Modified PUREX Processing Plan

2.2.1 Fuel Bundle Shearing and Dissolution

The modified PUREX process begins by removing the fuel rods from CANDU fuel bundles and mechanically shearing them into small segments [3]. The resulting uranium dioxide fuel pellets are dissolved in 4M nitric acid at 95°C in a counter-current flow, rotary dissolver. This dissolver operates continuously and provides effective mixing for dissolution at lower concentrations of acid [3].

2.2.2 Crystallization and Clarification

The uranium in the dissolver solution, present as uranyl nitrate, becomes less soluble at lower temperatures, such that at 10-20°C approximately 75% of it crystallizes out as uranyl nitrate hexahydrate (UNH) [4]. The crystallization, conducted in a temperature-controlled, continuous crystallization device, reduces the amount of aqueous and organic solution being processed by a factor of four, as well as the contaminated liquid waste requiring treatment.

2.2.3 Main Liquid-Liquid Extraction and Stripping – Extraction of U, Pu and Np as a Group

After crystallization the remaining solution is fed into a multistage centrifugal contactor to separate the residual actinides from FPs via counter-current, liquid-liquid extraction. Within any given stage of the contactor, mixing is achieved with a stationary agitation disc mounted on a central drum. The heavier and lighter liquids are separated by forces generated by a rotating bowl [5].

The extracting agent fed counter-currently to the dissolver solution is an organic of 30 vol% TBP in n-dodecane. Provided that a high acid concentration is maintained, tetravalent and hexavalent actinides (e.g. U, Pu and Np) are preferentially extracted into the organic TBP [6]. The reaction for U is shown:

$$UO_2^{2+} + 2NO_3^{-} + 2TBP = [UO_2(NO_3)_2{*}2TBP] \quad \Delta H_r^\circ = -23 \text{ kJ/mol} \qquad \text{(Rx. 3)}$$

The remaining FPs and minor actinides exit in an aqueous phase. The loaded organic is then fed into another multistage contactor containing 0.2M of nitric acid [6]. This strips the U, Pu and Np into an aqueous phase for further processing. Overall, the decontamination factor of FPs is $>10^5$ for U, Pu and Np [4], more than sufficient to qualify the actinides as FNR fuel.

2.2.4 Solvent Extraction for Trivalent f-elements Intra-group Separation in a Carbamoylmethyl phosphine oxide-complexant System (SETFICS)

The minor actinides and FPs leaving the main extraction are separated using SETFICS. The process is composed of two multistage contactor pairs. The first pair extracts both minor actinides and lanthanides into an organic phase of CMPO-TBP-n-dodecane and removes any nitric acid impurities using hydroxylamine nitrate (HAN) [6]. The remaining FPs are sent for product treatment and then storage.

The second contactor pair separates the lanthanide FPs from minor actinides with an aqueous chelating agent called diethylene triamine pentaacetic acid (DTPA). This reaction can achieve trivalent actinide-lanthanide separation with a decontamination factor >10 [4]. The lanthanides in the organic are stripped into an aqueous phase using dilute nitric acid and sent for treatment with the other FPs.

2.2.5 Transuranic Extraction (TRUEX)

The trivalent minor actinide product in DTPA is further treated in a process known as TRUEX. This works like the first contactor pair of SETFICS, where CMPO-TBP-n-dodecane extracts trivalent actinides in one contactor and then dilute nitric acid is used to strip them into an aqueous phase [6].

2.2.6 Actinide Oxide Formation

The non-FP outputs of the separation section of the process are in the form of a U/Pu/Np stream, a stream of minor actinides and UNH crystals. The U/Pu/Np stream is oxidized separately to re-form mixed oxide fuel suitable for CANDU reactors. As 75% of the initial U has been removed from the U/Pu/Np stream, the fissile material in concentrated from about 0.5% in spent CANDU [1] fuel to 1.31%. This is greater than the 0.72% in typical CANDU fuel [1]. The minor actinide stream can be oxidized along with the U/Pu/Np stream for CANDU fuel or oxidized separately and reduced to a metal (Section 2.2.7) for more efficient FNR fuel use. The UNH is oxidized to a relatively benign oxide that can be stored indefinitely, sold or used to produce FNR fuel.

A process called Modified Direct Denitration (MDD) is used for precipitation of actinides as oxides. The designated actinide stream is treated with ammonium nitrate in a ratio of ammonium ions to actinide of 2:2.6 [7] and then reacted in an electric kiln at temperatures of up to 500°C [8].

2.2.7 Electrolytic Reduction

After MDD, the oxides are transferred into porous ceramic baskets and loaded into a large electrolytic cell. The metal oxides in the basket act as a cathode. An inert, conductive ceramic serves as an anode, and a $LiCl/Li_2O$ (3 wt. %) molten salt at 650°C is the electrolyte. When a voltage of about 2.40V is applied, the metal ions of the oxides are reduced to their base metals [9]. Typical efficiencies are 99.7% for U, >97.8% for Pu, 98.8% for Np and >90% for Am [10]. After reduction, the cathode material is in the form of a metallic lump of actinides. This metal may be transferred to a metallurgical facility to be smelted, casted into FNR fuel pins and sealed into FNR fuel bundles.

2.2.8 Process Efficiency

Using lab, pilot and industrial scale process data, the process efficiencies have been estimated. The overall recovery of fission products and actinides is about **98.02%** and **99.70%** respectively. The actinide product stream is about **99.13%** pure, while the fission product stream is **99.95%** pure.

3. Waste Mitigation

During operation NO_x gas is produced and recycled to make more nitric acid for process solvent. This is accomplished by feeding NO_x counter-currently to oxygen and water in an absorption tower.

Non-recyclable liquid streams containing FPs need to be treated before being transported and stored. The most developed process for PUREX high-level waste is vitrification, which incorporates the liquid into stable borosilicate glass blocks. The solution is calcined in a kiln at about 600°C and then fed into a glass-making furnace where it is mixed with glass frit. After heating at 1150°C, the molten product is poured into stainless steel containers, which are sealed and loaded into transportation flasks [11].

4. Economics

An economic analysis was performed on the preliminary design of the modified PUREX process. The analysis included looking at the capital cost, operating cost and revenue generated by the plant. A cash flow analysis was done for an assumed 40-year plant life [12], and economic metrics such as net present value (NPV), internal rate of return (IRR) and payback period were calculated to determine if the processing plant design was economically feasible. The analysis was done based on processing approximately 16,000 CANDU fuel bundles per year (equal to 304 tonnes of heavy metal per year).

The capital cost included each major piece of equipment (including the associated installation, piping, electrical and instrumental costs), the cost of building the plant (including land, material, and shielding), as well as indirect costs (such as contractor fees) and a contingency. The operating cost included the cost of raw materials, utilities, and both direct and indirect labour costs, which includes an allowance for equipment replacement. The revenue was calculated by assuming that all of the metal actinide products would be sold at a price based on the price of U. Thus, calculating the yearly cash flow with depreciation, taxes and inflation, a cash flow analysis was generated. From this cash flow a NPV calculation showed the project was profitable at an IRR of 12%, which was above the minimum acceptable rate of return of 10% often used by the nuclear industry [13]. From this cost analysis, the project was economically feasible and could be made more profitable if the throughput or the price at which the product is sold is increased.

5. Future Benefits and Recommendations

The ability of the modified PUREX facility to process a wide variety of fuels and have the output fuel be used in both CANDU and FNR reactors closes the nuclear fuel cycle, thus extracting the maximum energy with minimal losses and waste. Furthermore, spent fuel contains the fissile isotopes U-235, Pu-239 and Pu-241. The process has been designed to ensure that Pu is always present with other actinides or fission products at concentrations that preclude their use as explosives. At no point is Pu separated from other fuel elements, which follows proliferation resistance efforts by the CNSC and the IAEA.

Areas recommended for further investigation include the recycle of waste streams to determine the efficiency increase with the addition of recycling tanks. A more detailed analysis would also have to be performed to accurately determine the economic feasibility of the process, as capital and operating costs estimated were on the order of 100 times lower then costs stated from other PUREX processing economics reports [14] [15]. Finally, the extraction of stable fission products like ruthenium and rhodium should be considered, as they may be sold as commodities without the approximately 300 year wait time required for the unstable FPs to decay to background levels [2].

6. Conclusion

The proposed modified PUREX process is designed to extract a spectrum of valuable products. These include zirconium, purified FPs, major and minor actinides, as well as metal and metal oxide nuclear fuel. Reprocessing these spent nuclear fuel bundles has multiple purposes, as it will not only decrease the amount of nuclear waste requiring storage in Canada but will recover the actinide components of the spent fuel to close the fuel cycle. A further motivation arises due to the economic benefits from the potential revenue stream due to energy production and the isolation of the FPs in the spent fuel. The process proposed to accomplish these benefits offers simplicity and reliability through the use of liquid-liquid extraction techniques, most of which have a long track record of implementation on an industrial scale. It also offers high separation efficiency, producing an actinide product and fission product stream with purities of **99.13%** and **99.95%** respectively. Overall, this option should provide the processing system with multiple products to allow for economic operation regardless of market price fluctuation or the construction of an FNR within Canada, as well as aid in the public perception of the nuclear industry as a more sustainable energy sector.

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