AECL'S PROGRESS IN DEVELOPING THE DUPIC FUEL FABRICATION PROCESS

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ABSTRACT

Spent Pressurized Water Reactor (PWR) fuel can be used directly in CANDU* reactors without the need for wet chemical reprocessing or reenrichment. Considerable experimental progress has been made in verifying the practicality of this fuel cycle, including hot-cell experiments using spent PWR fuels and out-cell trials using surrogate fuels. This paper describes the current status of these experiments.

INTRODUCTION

Atomic Energy of Canada Limited (AECL), the Korean Atomic Energy Research Institute (KAERI) and the United States Departments of State and Energy (US DOS/DOE) are involved in a joint program to develop a process for the Direct Use of spent PWR fuel in CANDU* reactors (DUPIC). This involves reconfiguring spent PWR fuel into a form that can be used in a CANDU reactor without using conventional, wet reprocessing technology. This provides a proliferation-resistant fuel cycle that does not involve wet chemistry at any stage of the process.

The reference PWR fuel for this project is 3.5% U-235 at start of life, with a discharge burnup of 35 MWd/kgU. This is typical of Korean spent PWR fuel. The residual fissile content of this spent fuel is sufficient to burn in a CANDU reactor without the addition of more fissile material. Although the achievable burnup with this fuel will depend on details of the bundle design, the burnup is approximately 18 MWd/kgHM, which compares to natural uranium burnups in CANDU of around 7.5 MWd/kgU.

A Phase I study, looking at various reconfiguration methods, has been completed. The process that was recommended is OREOX, a process in which dense UO_2 pellets are broken down into a ceramic-grade powder by cyclic oxidation and reduction, and the resulting powder is pressed and sintered into CANDU-quality pellets that are assembled into CANDU bundles.

Phase II, an experimental verification to demonstrate the feasibility of the OREOX process, is now underway. There are a number of issues being addressed, including:

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* CANDU = Canada Deuterium Uranium, a registered trademark

- a decladding technology to separate spent PWR fuel from its cladding,
- optimizing the OREOX cycle to produce a sinterable powder,
- remotely fabricating CANDU-quality pellets, elements and bundles,
- trapping and disposing of volatile fission products throughout the process,
- irradiation testing DUPIC fuel to measure fuel performance,
- extending modelling codes to include DUPIC fuel, and
- establishing safeguards procedures for the entire process.

All of the processing and fabrication activities must be performed in a hot-cell environment.

The workscope for this phase of the project is divided among the various members as follows:

• Development of fuel-element fabrication technology.....	AECL
• Development of fuel-bundle fabrication technology.......	KAERI
• Reactor physics and safety analysis	Joint AECL/KAERI
• Verification of irradiation behaviour	KAERI (with AECL)
• Safeguards	US/KAERI

The results described here focus on advancements by AECL in optimizing the OREOX cycle.

OREOX PROCESS

A number of possible reconfiguring technologies were assessed during Phase I, and the one chosen for further study was OREOX. The OREOX process uses crystallographic phase transitions in uranium oxides to break the initial UO_2 pellets into fine powders. Oxidizing UO_2 into U_3O_8 results in a transition from a cubic to an orthorhombic structure, with an associated volume increase of 32%. The cyclic transformation between cubic and orthorhombic phases causes microcracking in the matrix, and the production of a fine powder. If the powder can be made fine enough, it can be processed as a ceramic-grade powder into CANDU-quality fuel pellets, for assembly into CANDU fuel bundles.

The OREOX process has a number of steps, including:

- decladding the spent PWR fuel,
- subjecting the exposed fuel to alternating cycles of oxidation and reduction, to produce a fine powder,
- any subsequent powder conditioning (i.e., milling) required to improve the sinterability of the powder,
- fabricating CANDU-quality fuel pellets from that powder,
- loading the pellets into sheaths,
- assembling the CANDU bundles,
- disposing of irradiated PWR assembly hardware, and
- trapping and disposing of volatile fission products released during the decladding, OREOX and sintering processes.

A schematic flowsheet of the OREOX process is shown in **Figure 1**.

Hot-cell and pilot-scale out-cell experiments are being performed in parallel during the development phase of this project.

HOT-CELL EXPERIMENTS

Hot-cell experiments using small quantities of irradiated PWR fuel (between one and three pellets), have investigated fission-product (FP) release during various OREOX thermal cycles. Volatile FP's are expected to be released during the OREOX process, including noble gases (krypton and xenon), cesium, iodine and possibly ruthenium. It would be desirable to have volatile FP's removed in the (relatively low temperature) OREOX furnace, rather than in the (more complex and sophisticated) sintering furnace. To facilitate this, various OREOX schedules were examined to investigate FP release.

A horizontal tube furnace with a 7.5 cm diameter alumina tube was used for these experiments. Fuel samples were contained in alumina boats mounted in alumina trays that were inserted into the furnace tube. Appropriate gases (air, Ar/4% H_2, Ar/12%CO or CO_2) were flowed into the furnace tube and out into the hot-cell ventilation system after scrubbing through an appropriate filter system. Because of safety constraints in the hot cells, the hydrogen content of reduction gases did not exceed 4%.

Two spent PWR fuels were used for the in-cell tests. Fuel A had an initial enrichment of 2.55% U-235, achieved a burnup of 28 MWd/kgU (672 MWh/kgU), and was discharged in 1974 May. Fuel B was initially 3.5% U-235, achieved 57 MWd/kgU (1375 MWh/kgU), and was discharged in 1988 February. Although neither fuel duplicates the reference spent PWR fuel specifications, they do bracket the conditions (one a lower initial enrichment and burnup, the other the correct initial enrichment but a higher burnup). The trend in nuclear power is to higher burnups, making this high-burnup information important.

OREOX trials were conducted using a number of thermal cycles. It was found that Fuel A (28 MWd/kgU) was rapidly oxidized at approximately 400°C (which is consistent with 4-atom% SIMFUEL** results), and only partially oxidized at 350°C. Fuel B (57 MWd/kgU) did not appear to be oxidized until the temperature was raised to 500°C. Thus the burnup of the fuel has a significant impact on the OREOX schedule to be used.

FP release was monitored during the various OREOX cycles. 98% of the cesium was released after 3.9 hours at 1400°C, whereas 76% was released after 1.4 hours at 1320°C. Approximately 3.5% of the krypton was released from Fuel A at 400°C, whereas 30% of the krypton was released from Fuel B under similar conditions. Ruthenium was released rapidly during heating to 1400°C, whereas no europium was released during any of these tests. There was no release

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** SIMFUEL is UO_2 containing stable chemical additives that simulate the composition of irradiated fuel.

of FP's during the reduction portions of the schedules (except for a small amount of krypton released during the first two cycles). FP release is summarized in **Table I.**

Resultant powder morphologies were similar to those found in initial out-cell trials during commissioning of the apparatus. Equipment was not available for these first in-cell trials, to investigate powder sinterability.

PILOT-SCALE PROCESSING

Powder and pellet fabrication properties were examined during out-cell pilot-scale processing. These experiments looked at variables such as cycle temperatures, powder bed depth, gas-flow rates and dwell times at temperature. Powder characterization was performed on all powders. The important powder parameters are: particle-size distribution, surface area, and sinterability. Scanning Electron Micrograph (SEM) analysis is the best method of characterizing irradiated fuel powder, and this method was therefore also used to "bench-mark" powders produced during pilot-scale OREOX trials.

All out-cell tests used SIMFUEL simulating fuel with 4 atom% burnup (approximately 35 MWd/kgU). The composition of the SIMFUEL is listed in **Table II**. Because SIMFUEL is a sintered product composed of stable additives, it contains no volatile elements. The primary importance of SIMFUEL tests in these experiments is to determine the sinterability of powders fabricated by various OREOX cycles.

During the initial pilot-scale trials, a high-temperature oxidation stage (1100°C) was included in the first cycle. Subsequent cycles were: reduction in Ar/4%H2 at 700°C and oxidation in air at 400°C. The intent of the high-temperature oxidation was to drive off volatile FP's before reaching the sintering furnace. Note that, although these experiments were performed out-cell, the hydrogen content of reduction gases was kept down to 4%, to be consistent with the small-scale hot-cell and future pilot-scale experiments that will be done in-cell.

The initial oxidation at 1100°C was performed in a regular box furnace. All subsequent processing was in a box furnace with an extended hot zone and a stainless-steel hydrogen retort. Alumina trays 18 cm x 14 cm x 6 cm were used to contain the pellets and powder in the furnace during processing. A tray of as-fabricated SIMFUEL pellets is shown in **Figure 2A**). The same pellets after the OREOX process are shown in **Figure 2B**).

SEM investigation of as-produced powder indicated that it was very coarse (>5 µm), with a smooth surface and some indication of laminations in particles. A SEM of this powder is shown in **Figure 3**. Pellets made from this powder crumbled on exit from the die and it was not possible to make sintered samples.

To increase the sinterability of the powder, it was subjected to dry vibratory milling for 1 hour using cylindrical zirconia media (12.5 mm dia x 12.5 mm tall). Pellets fabricated from this powder sintered to a density of 9.9 g/cm^3 (approximately 92% of the theoretical density of 4 atom% burnup SIMFUEL). The poor sinterability of this powder is attributed to the coarseness introduced during the initial high-temperature oxidation stage.

The second set of pilot-scale trials did not include the high-temperature oxidation, and used only three cycles of oxidizing in air at 400°C and reducing in Ar/4%H_2 at 700°C. All oxidation and reduction was done in the large box furnace with the stainless-steel retort. The as-produced powders had a mean particle size of 2.4 µm (50% mass level as measured by sedimentation) and a surface area of 4.0 m^2/g. A SEM is shown in **Figure 4**. Some of this powder was also vibratory milled, as above. After milling, the particle size was 1.7 µm and the surface area was 6.5 m^2/g.

Pellets were fabricated from both powders and sintered. The sintered densities were: as-produced 96.5% of the theoretical density of 4 atom%-burnup SIMFUEL, after milling 97.9% of theoretical density. Both are within the CANDU-specified window of 95.3% to 98.1% of the theoretical density (of fresh UO_2).

Overall, it was found that OREOX pellets made from SIMFUEL powders that had been subjected to a high-temperature oxidation stage did not sinter to a high density, whereas those that did not experience this step had adequate sinterability.

CONCLUSIONS

Although high-temperature oxidation is effective in driving off volatile fission products, it causes the formation of coarse granules that are resistant to further size reduction and have poor processing/sintering characteristics.

The hot-cell FP release results can be summarized as:

- 98% of the cesium was released after 3.9 hours at 1400°C, whereas 76% was released after 1.4 hours at 1320°C.
- Approximately 3.5% of the krypton was released from Fuel A at 400°C, whereas 30% of the krypton was released from Fuel B under similar conditions.
- 100% of the ruthenium was released rapidly during heating in air to 1400°C.
- No europium was released during any of these tests.
- There was no release of FP's during the reduction portions of the schedules (except for a small amount of krypton released during the first two cycles).

These results imply that restricting the oxidation temperature to less than 500°C will result in significant quantities of cesium remaining in the fuel during the OREOX process and being released in the sintering furnace. There is no indication yet of how ruthenium, europium or cesium will behave in a sintering furnace.

Dry vibratory milling was found to improve the sinterability of as-produced powders.

High-density pellets, meeting CANDU specifications for sintered density, can be produced on a pilot scale using an OREOX cycle and SIMFUEL.

FUTURE ACTIVITIES

The DUPIC project has had a very promising start and is gaining momentum. Future work will continue to optimize the OREOX cycle on both a small scale, using spent PWR fuel, and on a pilot scale, using SIMFUEL.

In parallel with this, in-cell efforts will be scaled up, leading to the fabrication, using spent PWR fuel, of both OREOX fuel elements (by AECL) and bundles (by KAERI) for a research reactor irradiation. These elements and bundles will then be subjected to post-irradiation examination. Fuel performance modelling codes will then be extended to include DUPIC fuel.

All partners in the project (AECL/KAERI/DOS/DOE) will continue to work towards the establishment of safeguards procedures and equipment.

ACKNOWLEDGEMENTS

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Table I. Fission-product removal from spent PWR fuel

	Low Temperature (400°C)		High Temperature (1400°C)
	Fuel A	Fuel B	
Cesium	<1%	<1%	98%
Krypton	3.5%	30%	100%
Ruthenium	<1%	<1%	100%
Europium	0%	0%	0%

Table II. Composition of 4 atom%-burnup SIMFUEL

Element	Also Representing	g/gU %
Ba		0.22
Ce	Np	0.28
La	Am, Cm	0.14
Mo		0.40
Sr		0.08
Y		0.05
Zr		0.40
Rh		0.05
Pd		0.22
Ru	Tc	0.29
Nd	Pr, Pm, Sm	0.47

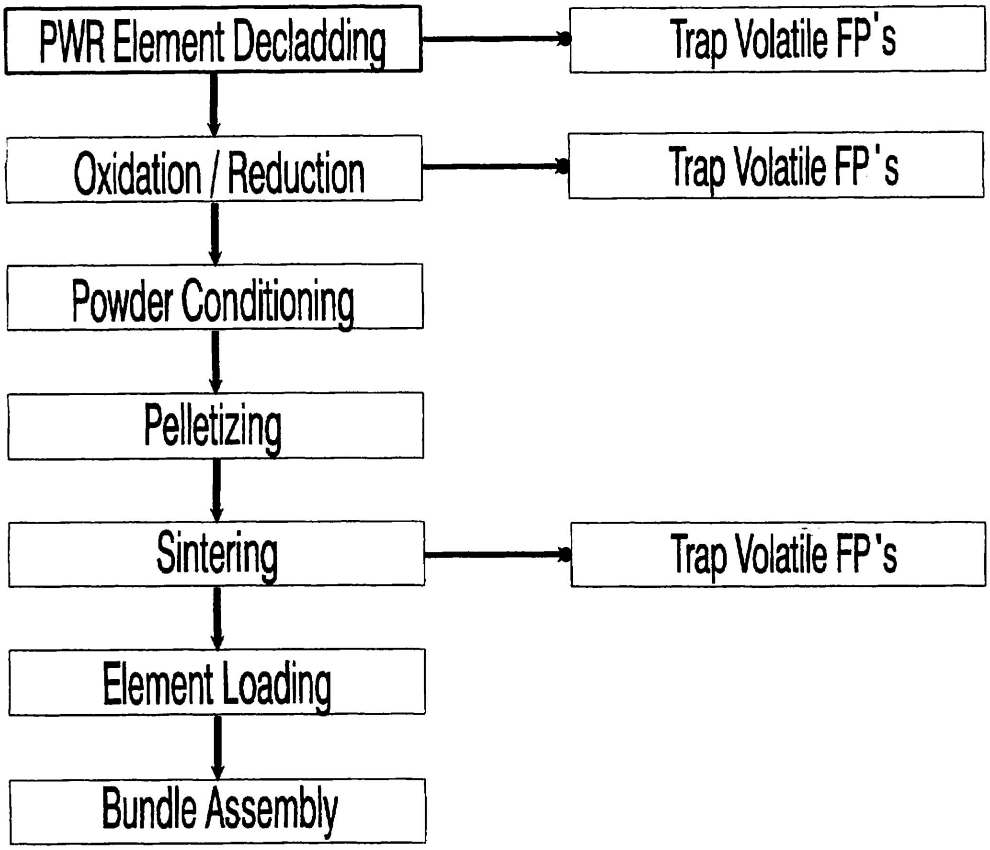
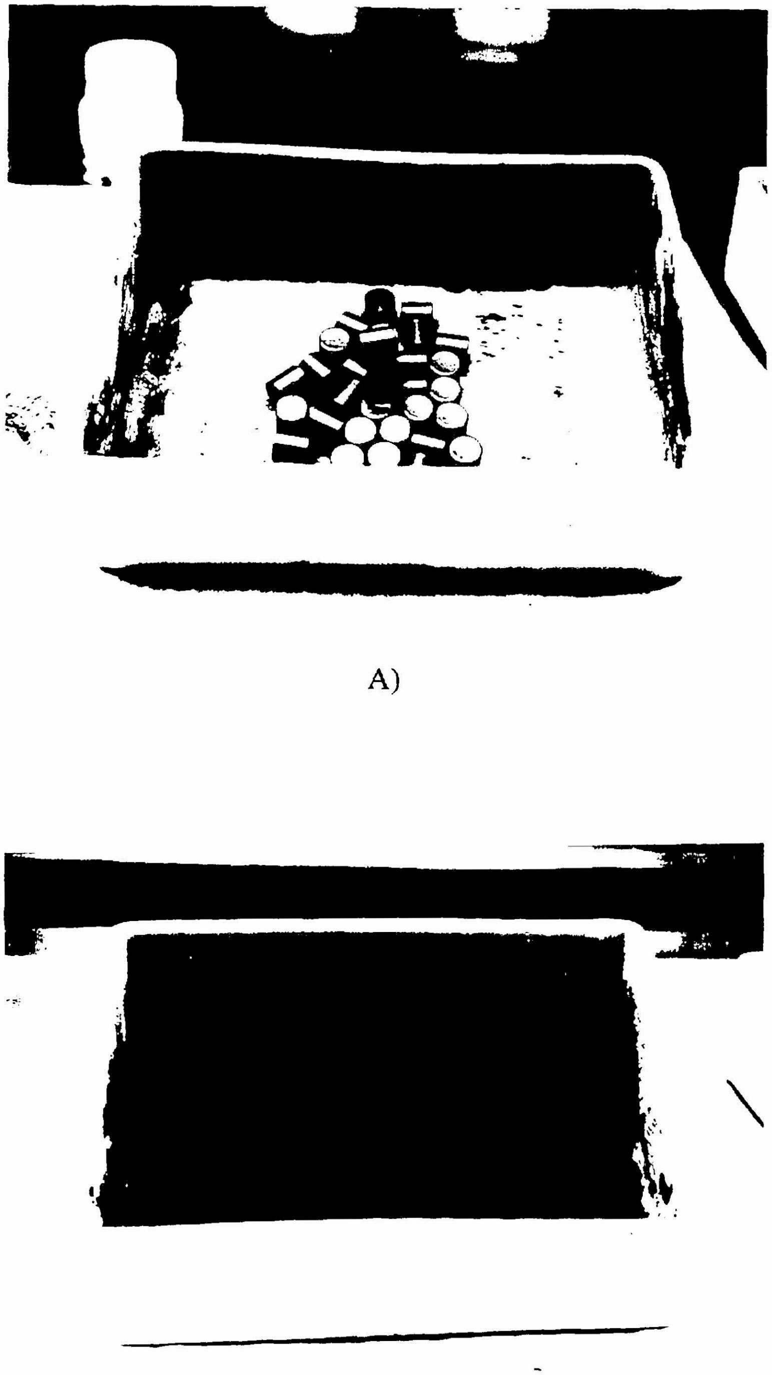


FIGURE 1 SCHEMATIC FLOW SHEET FOR THE OREOX PROCESS



A)

B)

FIGURE 2 ALUMINA TRAY WITH SIMFUEL PELLETS A) BEFORE AND B) AFTER THE OREOX PROCESS

FIGURE 3 SCANNING ELECTRON MICROGRAPH OF OREOX POWDER AFTER A SERIES OF HEAT TREATMENTS, INCLUDING A HIGH-TEMPERATURE OXIDATION

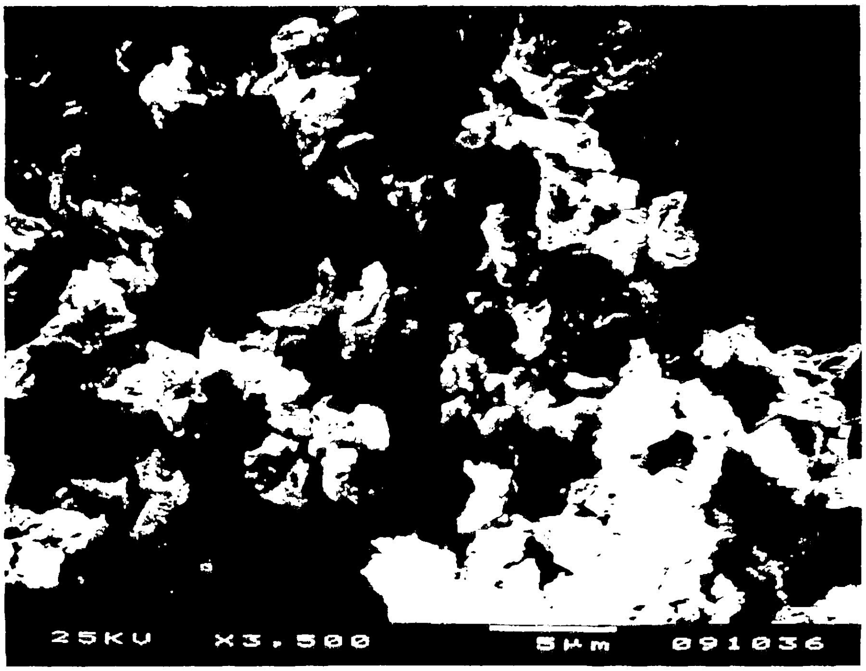


FIGURE 4 SCANNING ELECTRON MICROGRAPH OF OREOX POWDER AFTER ONLY LOW-TEMPERATURE OXIDATIONS