



U.S. DEPARTMENT OF
ENERGY

Nuclear Energy

Fuel Cycle Research and Development

ADVANCED HEAD END FOR THE TREATMENT OF USED LWR FUEL

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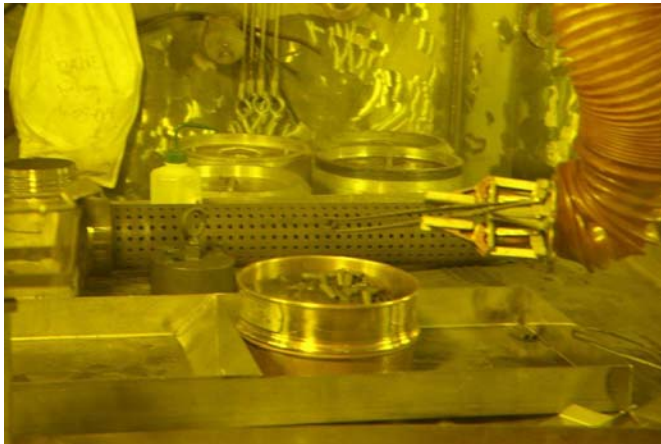
OECD Nuclear Energy Agency

**11th Information Exchange Meeting on Actinide and Fission Product
Partitioning and Transmutation**

Hyatt at Fisherman's Wharf, San Francisco, California, 1-5 November 2010



- **The voloxidation process was developed as a dry head-end method for removing tritium from segmented used fuel by oxidation of the UO_2 matrix into a fine U_3O_8 powder that can be easily separated from the cladding**
 - The voloxidation process takes place at 480°C to 600°C in the presence of air or oxygen.
 - *Conversion to the higher oxide results in expansion and restructuring of the grain-level crystallite accompanied by crumbling of the monolithic fuel pellet to a fine powder.*
 - Tritium, which may be present in the fuel in elemental form, diffuses to the surface of the particle where it reacts with oxygen to form water which enters the gas stream
 - *A fraction of the tritium is associated with the cladding as zirconium hydride (ZrTx)*



Kilogram-scale tests done with actual commercial LWR spent fuel ranging from low burnup and long cooling time to very high burnup and short cooling time indicated recoveries over 99%. Acid washing of the hulls extended the recovery to 99.9%



NO₂ Voloxidation

- A mixture of NO₂ and O₂ is used as an oxidant
 - UO₂ pellets treated with NO_{2(g)} readily transform into a fine brown powder
 - $3 \text{UO}_2 + 2 \text{NO}_{2(g)} \rightarrow \text{U}_3\text{O}_8 + 2 \text{NO}_{(g)}$ *t = significantly lower than for O₂ or air*
 - Faster than air or oxygen oxidation at t > 500 °C
 - Higher temperatures do not improve kinetics of NO₂ oxidation
 - Oxidation with the same mixture during cooling readily and completely converts the oxide powder into reddish-brown UO₃
 - *The generated UO₃ products will dissolve in just a few minutes using warm HNO₃ at a concentration of 0.25M or higher*
- The UO₃ powder produced treated with pure NO₂ (N₂O₄) gas or liquid at near room temperature produce metal nitrates, e.g.,
 - $\text{UO}_3 + 5 \text{NO}_{2(g)} \rightarrow \text{UO}_2(\text{NO}_3)_3 \text{NO} + \text{NO}(g)$
 - *Uranyl nitrosyl nitrate (UO₂(NO₃)₃NO) is yellow-green in color*



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NO₂ Delivery System





Some Properties of NO₂

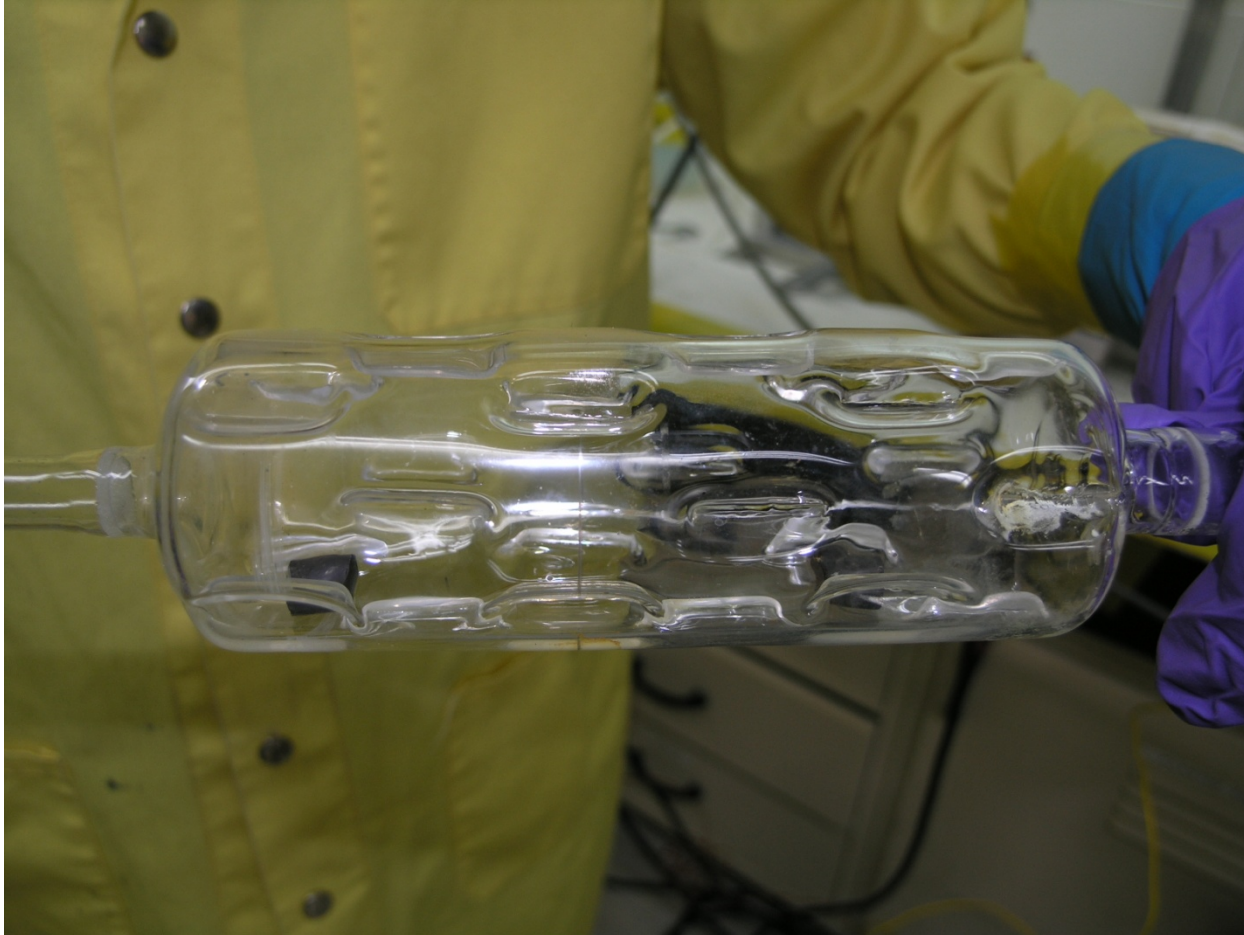
- **Dinitrogen tetroxide is a clear liquid (blue tint)**
 - Boiling point 21.1 °C
 - Melting point -9.3 °C
- **N₂O₄ (Clear blue, diamagnetic) ↔ 2 NO₂ (Brown, paramagnetic)**
 - Readily dissociates to NO₂
 - *16% dissociated at 21.1°C, 50% at 40 °C, and 99% at 135 °C*
- **NO₂ is an strong oxidizer more reactive than O₂**



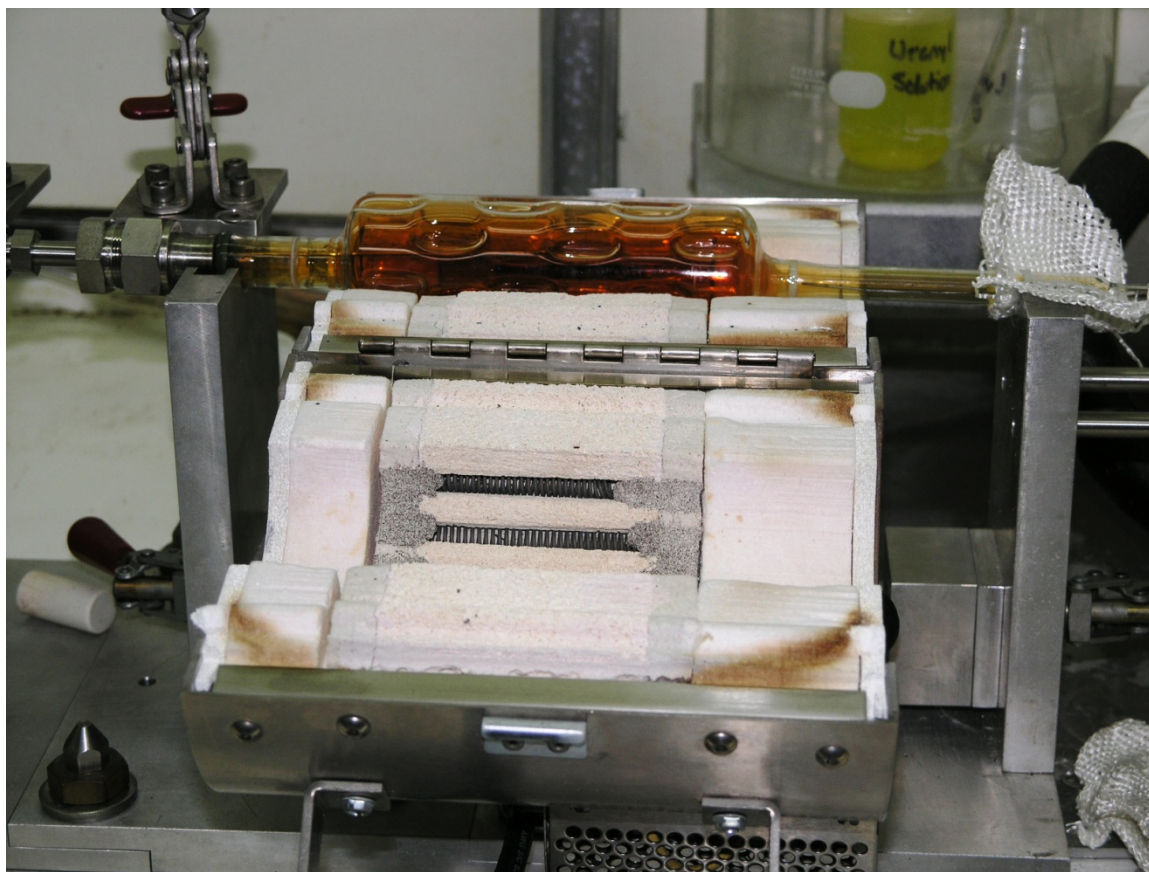
Some Properties of NO₂ and related species

- **NO₂ readily react with O₃ to form N₂O₅ and possibly NO₃ as an intermediate species**
 - At room temperature and in the pure form, N₂O₅ is a colorless solid with a very high vapor pressure. It is also a very strong oxidizing agent
 - *Using a mixture of NO₂ (N₂O₄) and O₃/O₂ produced with a commercial ozone generator. showed to improve the kinetics of the voloxidation process*
 - NO₂ (g) + O₃ (g) → NO₃ (g) + O₂ (g)
 - 2 N₂O₄ (g) + O₃ (g) → N₂O₅ (g) + O₂ (g)
 - The tests showed that the oxidation of pellets into a fine red UO₃ powder was faster than with NO₂ alone
 - *This finding represents a significant potential improvement, because voloxidation with NO₂ alone is considerably faster than the reactions in air or oxygen at much lower temperatures*
- **Stainless steel and nickel are compatible with NO₂, O₃ and N₂O₅**
 - Copper based alloys including Monel are not
 - Also compatible are fluorinated polymers, such as Teflon; elastomers, such as Kalrez; glass; and quartz.

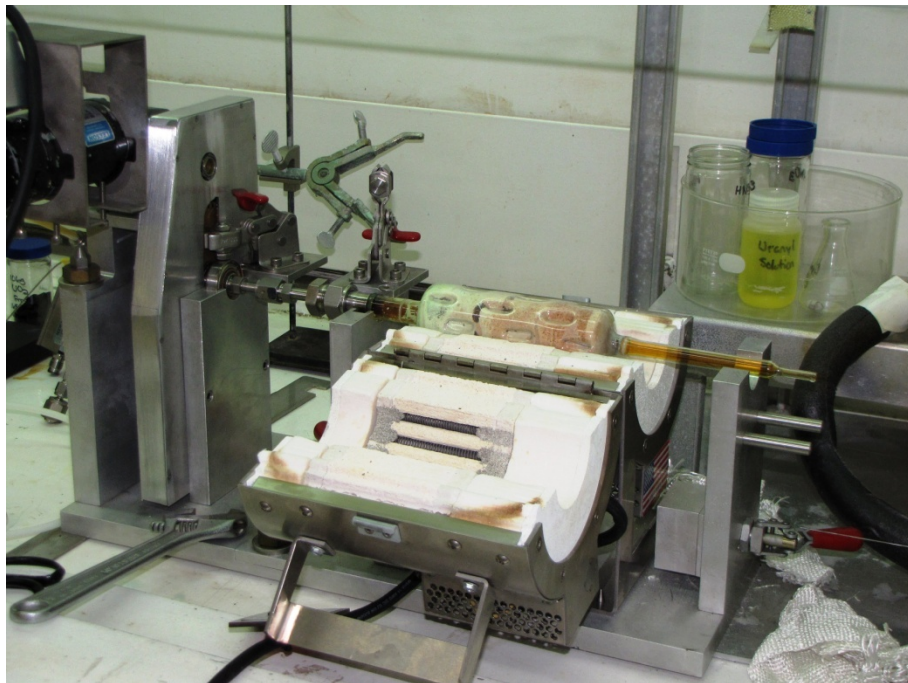
Quartz rotary reactor vessel showing two pellets of UO_2



Rotary Furnace, Quartz Container and uranium oxide powder



Room temperature nitration of U_3O_8 or UO_3 powders readily produces a yellow powder determine to be Uranyl Nitrosyl nitrate

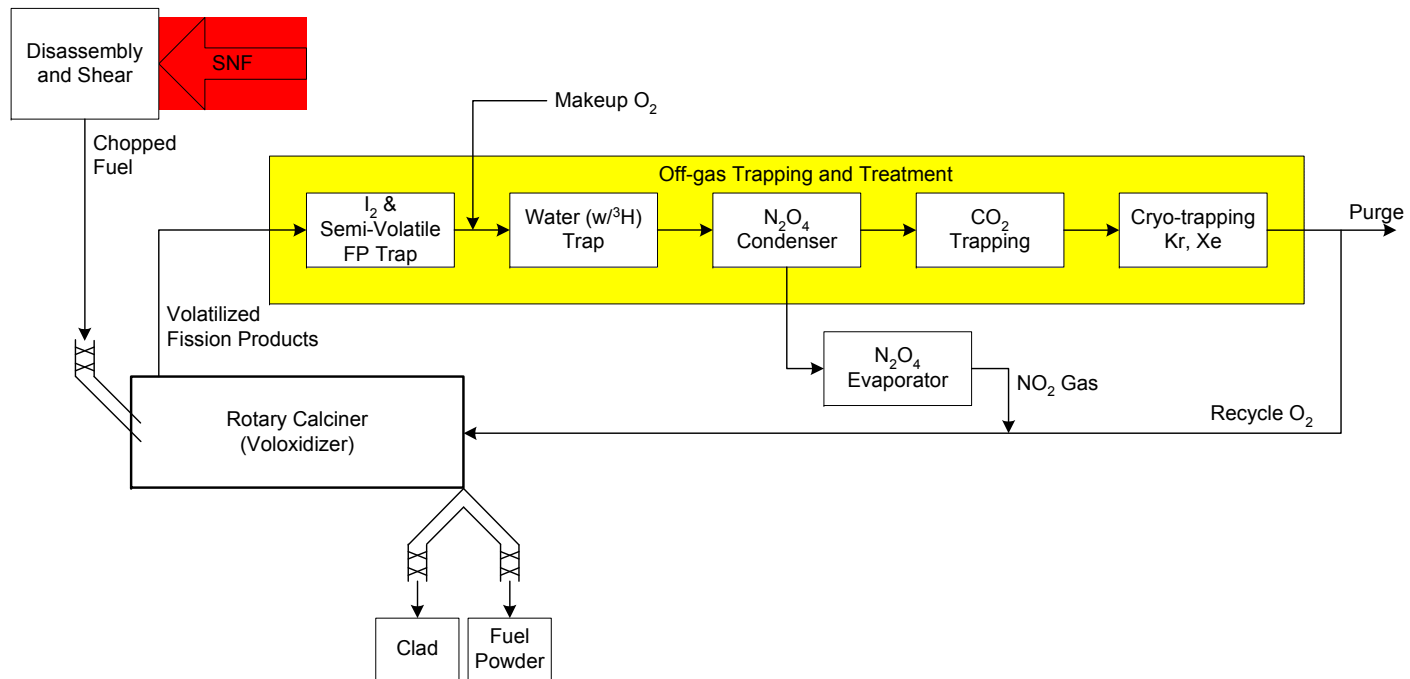


- $UO_3 + 5NO_2 \rightarrow UO_2(NO_3)_3 + NO + NO(g)$
- Gaseous or liquid NO_2 (N_2O_4) effective



NO₂ Voloxidation

- The NO_(g) byproduct readily reacts with O₂ during cooling to regenerate NO₂
 - $2 \text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2 \text{NO}_{2(g)}$
 - Overall the process can be autocatalytic with gaseous NO₂ being recycled while O₂ is consumed



Sketch of closed-loop NO₂ voloxidation

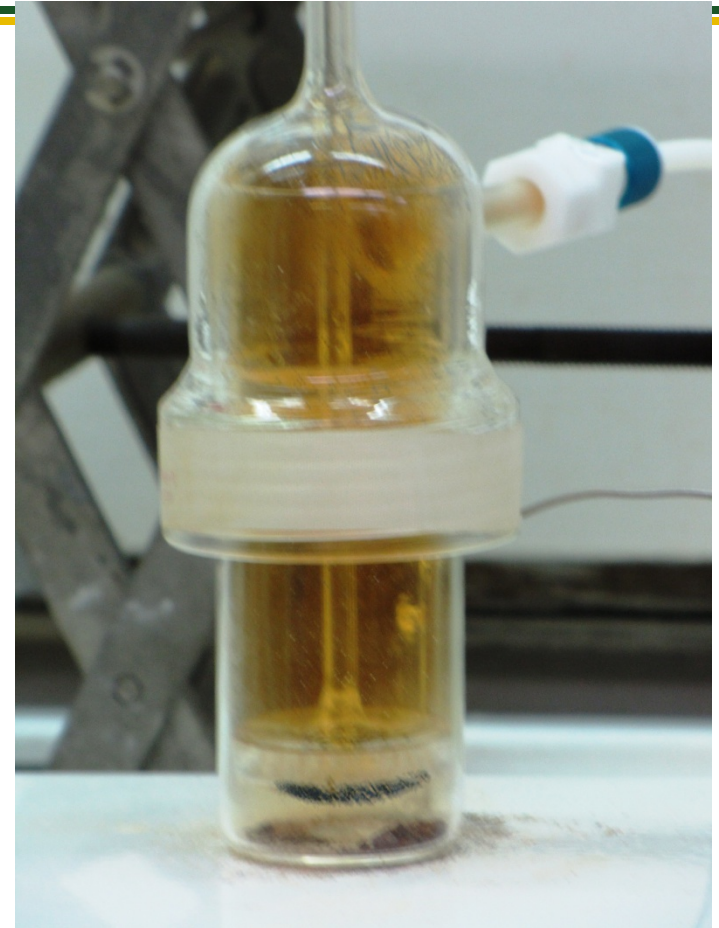


- Preliminary tests were conducted flowing NO_2
 - Over CsI powder
 - *On first contact of CsI with NO_2 the solid surface becomes black*
 - Over a finely dispersed mix of CsI (5%) and U_3O_8 powder, obtained by voloxidation of UO_2 pellets
 - *Two main deposits were collected.*
 - shiny-gray needles that decomposed over time to a black deposit.
 - *Most probably unstable nitrosyl iodide INO that decomposes to NO and I_2*
 - typical small dark crystals associated with elemental iodine

- To quantify the residual iodine, a test was conducted using a 1 g sample of U_3O_8 that was impregnated with a solution containing 10 mg of normal CsI spiked with 27 μCi of ^{125}I
 - *The sample was counted at 35keV before and after treatment. The sample was contained in a small alumina boat and treated with a gas mixture of NO_2/O_3 for 2 h producing bright red UO_3*
 - The activity of the post treatment sample at 35 keV was 5.7% of the original
 - *A second treatment was conducted using a small rotary calciner for an additional 2h.*
 - The residual activity was 1.2% of the original



Iodine Removal by NO₂ Voloxidation



Iodine, which is mostly present in the spent fuel as CsI, is released as I₂ vapor
$$\text{CsI} + x \text{NO}_2(\text{g}) \rightarrow \text{CsO}_x + \text{NO}(\text{g}) + 0.5 \text{I}_2(\text{g}) \quad (x = 0.5, 1 \text{ or } 2)$$



■ Our novel integrated process

- Results in the dry removal of tritium and iodine at a relatively low temperature
- Simplifies the off-gas trapping system
- Produces a fine powder amenable to several separation schemes
 - *Can be integrated with other processes*
 - Aqueous
 - Electrochemical
 - Dupic like processes
 - Halide volatility
 - Supercritical CO₂ dissolution
 - Alkaline separative schemes

■ Depending of the conditions the powder consists of UO₃ and oxides, or UO₂NO(NO₃)₃ and nitrates

■ Oxide and nitrate forms can be easily dissolved and enable design and use of continuous powder dissolver



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- **Kinetic studies and modeling of the NO₂-voloxidation and nitration processes**
 - Build macro-TGA to evaluate kinetics of nitration reactions using unirradiated surrogate fuels.
 - Measure reaction rates of nitration at previously determined favorable conditions.

- **Demonstration of the process on one or a few pellets of authentic commercial LWR spent fuel**
 - Build small rotary calciner capable of processing used fuel at the one or two pellet scale in a hot cell
 - Demonstrate nitration process on authentic used fuel pellet and initiate analysis of solid and gaseous products

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- **A novel dry head-end process is being developed**
- **The main goals are the separation of cladding from fuel and the upfront removal of problematic fission products while facilitating the downstream processing**
- **Cold tests using surrogate pellets and tests on a scale of tens of milligrams using actual used fuel are very promising**
 - The initial tests showed that the process can be performed at significantly lower temperatures than those for standard voloxidation by using a mixture of NO_2/O_2 or NO_2/O_3 to produce a fine red powder of UO_3 and to release all the tritium and iodine.
 - This powder—containing the uranium as UO_3 , transuranium actinides, and nonvolatile fission product oxides—is readily soluble in dilute acids
 - *Alternatively, the tests showed that the UO_3 powder can be contacted with NO_2 (N_2O_4) gas or liquid at room temperature to produce metal nitrates*