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PLUTONIUM MANAGEMENT**

by

**Stacey Eaton, Carl Beard, John Buksa,
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DEVELOPMENT OF ADVANCED MIXED OXIDE FUELS FOR PLUTONIUM MANAGEMENT

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ABSTRACT

A number of advanced Mixed Oxide (MOX) fuel forms are currently being investigated at Los Alamos National Laboratory that have the potential to be effective plutonium management tools. Evolutionary Mixed Oxide (EMOX) fuel is a slight perturbation on standard MOX fuel, but achieves greater plutonium destruction rates by employing a fractional nonfertile component. A pure nonfertile fuel is also being studied. Initial calculations show that the fuel can be utilized in existing light water reactors and tailored to address different plutonium management goals (i.e., stabilization or reduction of plutonium inventories residing in spent nuclear fuel). In parallel, experiments are being performed to determine the feasibility of fabrication of such fuels. Initial EMOX pellets have successfully been fabricated using weapons-grade plutonium.

I. INTRODUCTION

Current conditions have created an increasing worldwide inventory of unseparated plutonium, which is a growing concern with regard to nuclear weapons proliferation. Although much attention has been given to the disposition of excess weapons plutonium, which is the more immediate concern, eventual attention will have to be focused on the much larger quantities of plutonium found in spent nuclear fuel. A fuel form is currently being developed at Los Alamos National Laboratory (LANL) that enables a near-term ability to manage these unseparated plutonium inventories. This new fuel form, referred to as Evolutionary Mixed Oxide (EMOX), is a slight perturbation on standard Mixed Oxide (MOX) fuel. EMOX is created by the addition of a nonfertile component (currently stabilized zirconia) to a uranium-plutonium oxide matrix. By controlling the nonfertile content, the amount of plutonium remaining in the spent fuel can be controlled. EMOX is unique in that it can evolve, through the addition of greater amounts of nonfertile material, from a standard MOX composition to EMOX compositions with increased plutonium destruction rates. Eventually, a pure nonfertile fuel (NF) form containing no uranium can be used for nearly complete plutonium destruction. The various compositions can be tailored to meet specific fuel-cycle goals, whether it be the stabilization or reduction of unseparated plutonium inventories. EMOX fuel development activities to date at LANL have focused on two main areas: modeling of in-reactor performance, and experimentation on EMOX fuel fabrication and EMOX fuel fabrication process development. This paper provides an overview of the current activities and provides a summary of the results obtained to date.

II. FUEL PERFORMANCE

Extensive calculations have been performed to assess the feasibility of incorporating the EMOX fuel form into existing pressurized water reactor (PWR) systems. For these

calculations, a PWR pin cell model was developed for use in the HELIOS¹ code. HELIOS is a collision probability based transport code, which supports general two-dimensional geometries and has the ability to perform burnup calculations. The cross-section library contains over 270 explicit materials and data for 115 fission products. A typical Westinghouse PWR² was used for the model development. As is done with conventional MOX in a UO₂ core, the fuel cycles examined consist of the addition of some fraction of EMOX (typically third-core, half-core, etc.) to a standard enriched UO₂ core. This EMOX core fraction comprises varying percentages of PuO₂, natural UO₂, and varying amounts of a nonfertile component of calcia-stabilized zirconia (the "nonfertile fraction"). Figure 1 provides a visual description of this nomenclature where, in this case, the EMOX core fraction is 18.4%, the initial plutonium loading in the EMOX is 5% and the nonfertile fraction is also 5%.

The EMOX performance has been assessed as a function of several variables, including the fraction of the core that is loaded with the new fuel, the initial plutonium loading in the EMOX component, and the nonfertile fraction used in each composition. Figure 2 is an example of some of the calculations performed to date. This figure shows the performance of a third-core loading of EMOX for varying initial plutonium loadings. The nonfertile fraction here was varied from zero (pure MOX) to the remainder of the EMOX composition (pure NF). Performance is measured in terms of percent change in the core-averaged plutonium inventory, a positive value indicating a plutonium-breeding system. Results show that greater plutonium destruction rates can be achieved with the addition of increasing amounts of nonfertile material. For example, several European countries recycle MOX fuel in their reactors in third-core configurations, typically at 5% plutonium loadings. This figure shows that such a system is actually a net breeder of plutonium when the core-averaged inventory is considered. The addition of a 30% nonfertile fraction to the EMOX composition (with the same 5% plutonium loading), however, greatly reduces the amount of plutonium breeding. A 50% nonfertile addition reaches the break-even point, while a 70% nonfertile addition creates a plutonium consuming system.

Similar calculations were performed for half- and full-core loadings of EMOX, and the results are shown in Figs. 3 and 4, respectively. These figures show that greater destruction rates are achieved as the EMOX core fraction increases, and the systems can be utilized as plutonium consumers at lower initial plutonium loadings. In the full-core EMOX case (Fig. 4), only the compositions with initial plutonium loadings of >3% remain critical for the duration of the fuel lifetime. The pure nonfertile cases provide the best performance, with the EMOX cases providing a smooth transition between that and the standard MOX initial fuel.

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The EMOX fuel performance must not only be assessed in terms of plutonium destruction, but also specifically in terms of in-reactor behavior (i.e., safety performance). To this end, a preliminary assessment was performed of the temperature coefficients expected from the use of EMOX in a standard PWR. Temperature coefficients were predicted for both the fuel and moderator, and the results were compared with similar coefficients for MOX and NF cores. Figures 5 and 6, respectively, show the fuel and moderator coefficients for third- and full-cores of MOX, EMOX, and NF fuels. All of the coefficients are negative over the temperature range examined. The three different third-core cases exhibit similar behavior, as do the MOX and EMOX full-core cases. The full-core NF cases coefficients are significantly greater, but also remain negative over the entire temperature range. Of greatest importance is that while EMOX (with a 30% nonfertile fraction) shows a substantial improvement over MOX in terms of plutonium destruction, its in-reactor safety behavior is comparable.

III. FUEL FABRICATION DEMONSTRATION

A parallel effort has been ongoing to assess the feasibility of fabricating EMOX fuel ($\text{PuO}_2\text{-UO}_2\text{-ZrO}_2\text{-CaO}$) within the bounds of existing fabrication processes. This effort was designed to address the issues involved with the development of a complete fabrication process including the examination of such final sintered fuel pellet properties as phase distribution, grain size, and degree of densification.

The decision to use the $\text{ZrO}_2\text{-CaO}$ matrix as the nonfertile component of the EMOX fuel was made based on the substantial amount of information published from previous developmental and experimental programs. Experience shows that irradiation of $\text{UO}_2\text{-ZrO}_2$ fuel will result in rapid densification or void collapse because of phase transformation.^{3,4,5} The addition of a small amount of calcium oxide will stabilize a face-centered cubic crystal structure so that it will remain stable under irradiation conditions. This face-centered cubic structure also permits greater solubility of the plutonium oxide in the $\text{UO}_2\text{-ZrO}_2\text{-CaO}$ matrix.

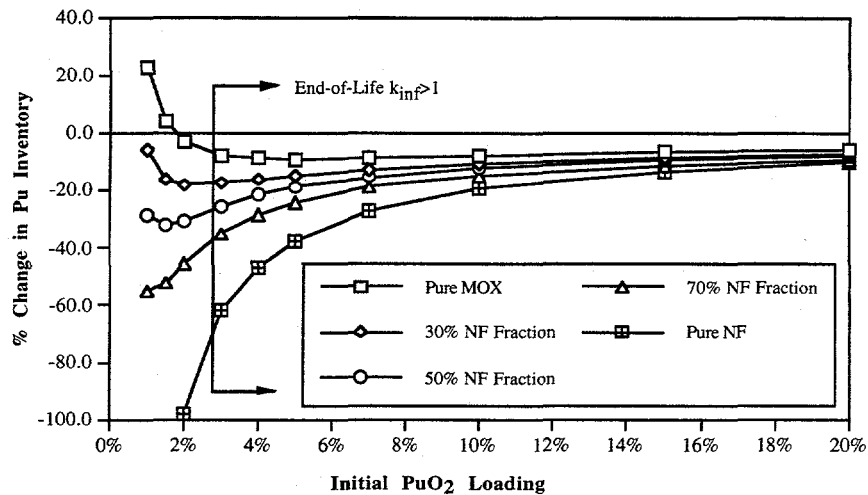


Fig. 4. Change in plutonium inventory for various full-core EMOX compositions as a function of initial plutonium loading.

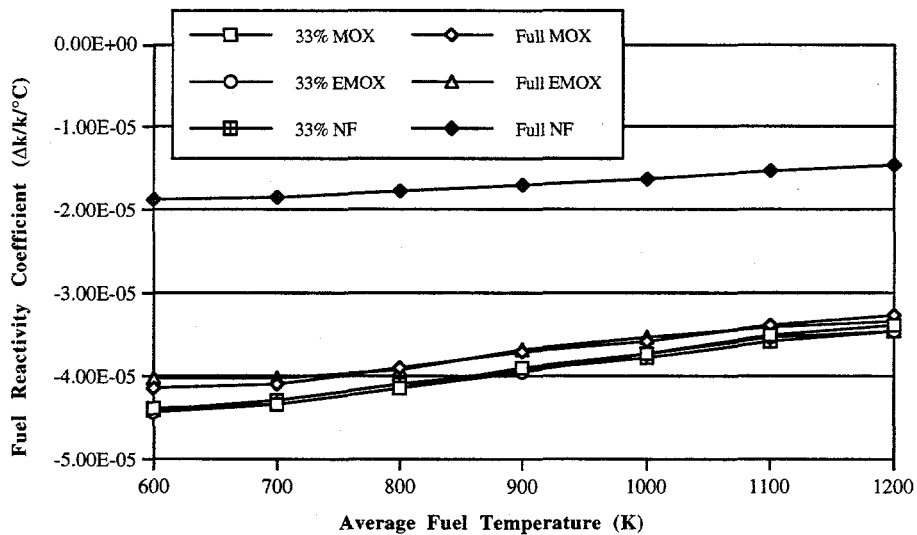


Fig. 5. Fuel temperature reactivity coefficients of various fuel forms (6% PuO_2).

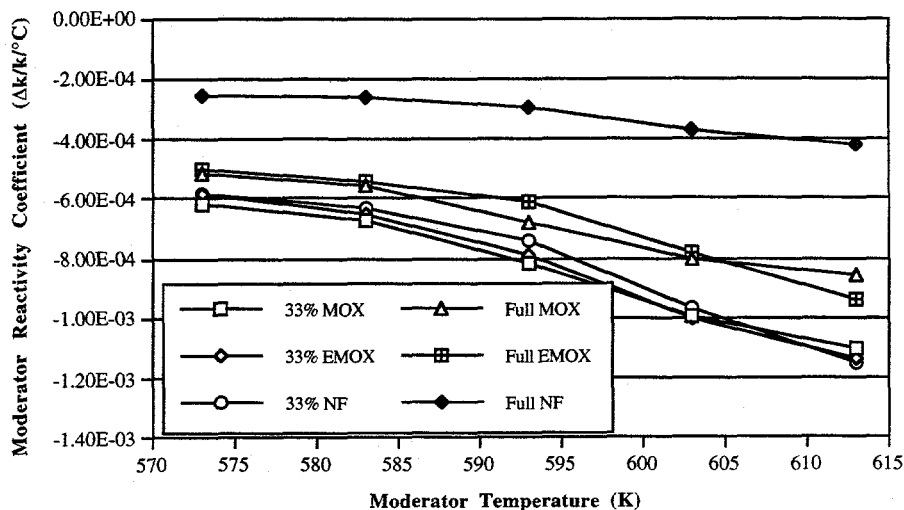


Fig. 6. Moderator temperature reactivity coefficients of various fuel forms (6% PuO₂).

Extensive experimental work has been performed on a uranium ternary fuel (UO₂-ZrO₂-CaO).⁵ In the Shippingport PWR, side-by-side irradiation was performed on ternary (UO₂-ZrO₂-CaO), binary (UO₂-ZrO₂), and uranium oxide (UO₂) plate-type elements. The UO₂ and ternary fuels performed similarly, with no reported fuel failures. The binary fuel, however, exhibited rapid densification because of the induced phase instability. Solid ternary fuel pellets were irradiated at the Power Burst Facility, a transient test reactor, and no fuel rod failures occurred with over 1000 hr of operational experience. Finally, the Light Water Breeder Reactor Fuel Development Program performed side-by-side irradiation of ternary, binary, and UO₂ duplex fuel pellets (annular pellets with thorium center for breeding). Again, the UO₂ and ternary fuels performed similarly, both being successfully irradiated to high burnup. This experimental work not only provides valuable irradiation data, but also developed a substantial base of fabrication and reprocessing technologies for this ternary fuel.

A preliminary surrogate study successfully determined the feasibility of preparing a nonfertile fuel by the solid-state reaction method using calcia, zirconia, and ceria (as the plutonium surrogate) as oxide precursors. In the surrogate study, reagent-grade ZrO₂ (87.19 wt%), CaO (10.12 wt%), CeO₂ (2.69 wt%), stearic acid (1 wt%), and polyethylene glycol (1 wt%) were dry ball milled for 24 hr. The milled powder was uniaxially pressed into pellets (6.5 mm x 6.0 mm) at a pressure of 310 MPa. The green pellets were then sintered for 5 hr in an 80% N₂, 20% O₂ atmosphere at three temperatures (1200, 1400, and 1700°C). Pellet samples were cooled from the sintering temperature at an average rate of 10°C/min. As shown in Fig. 7, a significant increase in the bulk density of the surrogate fuel pellet occurred between the sintering temperatures of 1200 and 1400°C. This increase in density from 2.94 to 4.24 g/cm³ corresponds to a decrease in open porosity (vol%) from 47.3 to 20.3%. An additional increase in bulk density occurred between the sintering temperatures of 1400 and 1700°C. This increase in density from 4.24 to 4.67 g/cm³ corresponds to a significant decrease in open porosity (vol%) from 20.3 to 0.281%. Figure 8 shows the x-ray powder diffraction pattern of the surrogate fuel sintered at 1200, 1400, and 1700°C. The cubic crystalline phase, Ca_{0.15}Zr_{0.85}O_{1.85} is present in the surrogate fuel sintered at 1200, 1400, and 1700°C. This cubic phase is the calcia-stabilized form of zirconia corresponding to a CaO content of approximately 20 mole%. The orthorhombic crystalline

phase, CaZrO₃, is present in the surrogate fuel sintered at 1200 and 1400°C. The CeO₂ precursor is present in the surrogate fuel sintered at 1200 and 1400°C. For a sintering time of 5 hr, the x-ray diffraction data indicate that a sintering temperature of between 1400 and 1700°C is required to form a solid solution of CeO₂ in calcia-stabilized zirconia.

Nonfertile fuel containing weapons-grade plutonium (obtained from the hydride/oxidation process at LANL), was fabricated using the solid-state reaction method. Reagent-grade ZrO₂ (87.19 wt%) and CaO (10.12 wt%) were blended with weapons-grade PuO₂ (2.69 wt%) by dry ball milling for 4 hr. Stearic acid (0.2 wt%) and polyethylene glycol (0.2 wt%) served as a lubricant and binder, respectively. The powder mixture was subsequently cycled six times through a high-energy vibratory mill containing ZrO₂ milling media. The milled powder was granulated and subsequently pressed into green pellets (9.27 mm x 10.16 mm) using a uniaxial hydraulic press. The green pellets were sintered for 6 hr in a 94% argon, 6% hydrogen atmosphere at a temperature of 1700°C. Density measurements indicate that the nonfertile fuel pellets were sintered to a density of 4.77 g/cm³. This final density corresponds to 89.7% of theoretical. The grain size for the sintered pellet ranges from 10 μm to >50 μm. The x-ray diffraction pattern of the sintered fuel pellet shows the phase structure to have two components of a face-centered cubic lattice structure. These major and minor components have lattice constants of 5.147 and 5.09 Angstroms, respectively. The minor component lattice constant is characteristic of calcia-stabilized zirconia. From peak height measurements, the minor component can be estimated to be ~10% of the major component.

EMOX fuel containing weapons-grade plutonium was fabricated using the solid-state reaction method. The flow diagram for the fabrication of EMOX fuel is shown in Fig. 9. Reagent-grade ZrO₂ (4.63 wt%) and CaO (0.462 wt%) were blended with weapons-grade PuO₂ (10.97 wt%) and depleted UO₂ (83.94 wt%) by dry ball milling for 4 hr. Stearic acid (0.2 wt%) and polyethylene glycol (0.2 wt%) served as a lubricant and binder, respectively. The powder mixture was subsequently cycled six times through a high-energy vibratory mill containing tungsten carbide milling media. The milled powder was granulated and subsequently pressed into green pellets (9.27 mm x 10.22 mm) using a

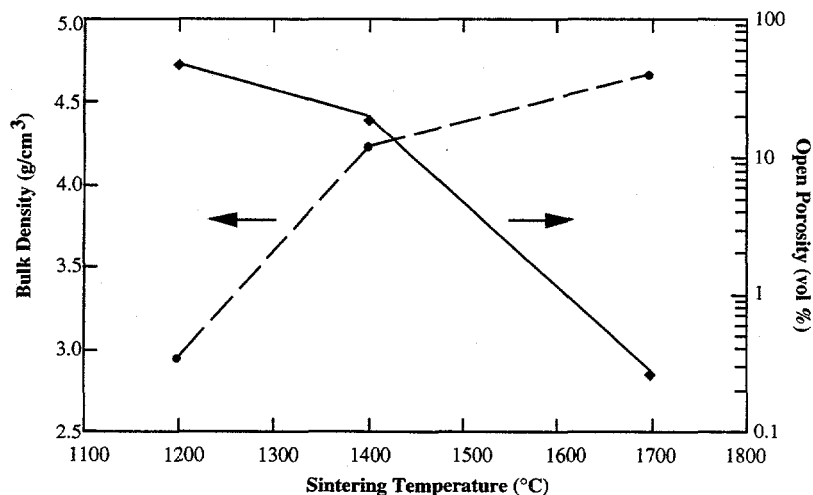


Fig. 7. Densification behavior of surrogate nonfertile fuel pellets.

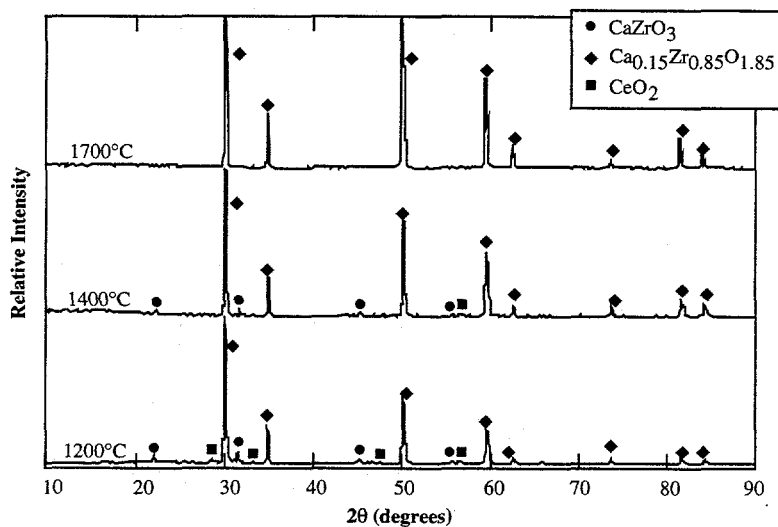


Fig. 8. X-ray diffraction pattern of sintered surrogate nonfertile fuel pellet.

uniaxial hydraulic press. The green pellets were sintered for 6 hr in a 94% argon, 6% hydrogen atmosphere at a temperature of 1700°C. Figure 10 shows a typical sintered pellet of EMOX fuel. Density measurements indicate that the EMOX fuel pellets were sintered to a density of 10.12 g/cm³. This final density corresponds to 96.8% of theoretical. The grain size for the sintered pellet is approximately 10 μm. The x-ray diffraction pattern of the sintered fuel pellet shows the phase structure to have a single face-centered cubic lattice structure with a lattice constant of 5.4405 Angstroms.

IV. ONGOING ACTIVITIES

Work is continuing on the EMOX concept in both the fuel performance and the fuel fabrication demonstration areas, in addition to some new efforts. Assembly-level models have been developed to further assess the EMOX performance, and the results, while similar to those achieved using the pin cell model, are of a higher fidelity and more accurately

represent the heterogeneous nature of the fuel (and assembly) composition. New efforts have been initiated in the area of global inventory modeling. Results obtained from the fuel-performance assessment efforts are being further used in global energy models to assess the effect of EMOX fuel cycles on worldwide plutonium inventories. Additional EMOX fuel compositions containing nonfertile fractions of 30, 50, and 70 wt% will be fabricated to further demonstrate the feasibility of using the EMOX concept as a plutonium management tool.

V. CONCLUSIONS

Preliminary analyses have shown that the EMOX concept can be an attractive plutonium management tool. Small additions of the inert material to standard MOX fuel increase the overall plutonium destruction within the system, and the composition can be tailored to suit a particular management strategy, including zero net plutonium production or high plutonium destruction options. Initial compositions can be

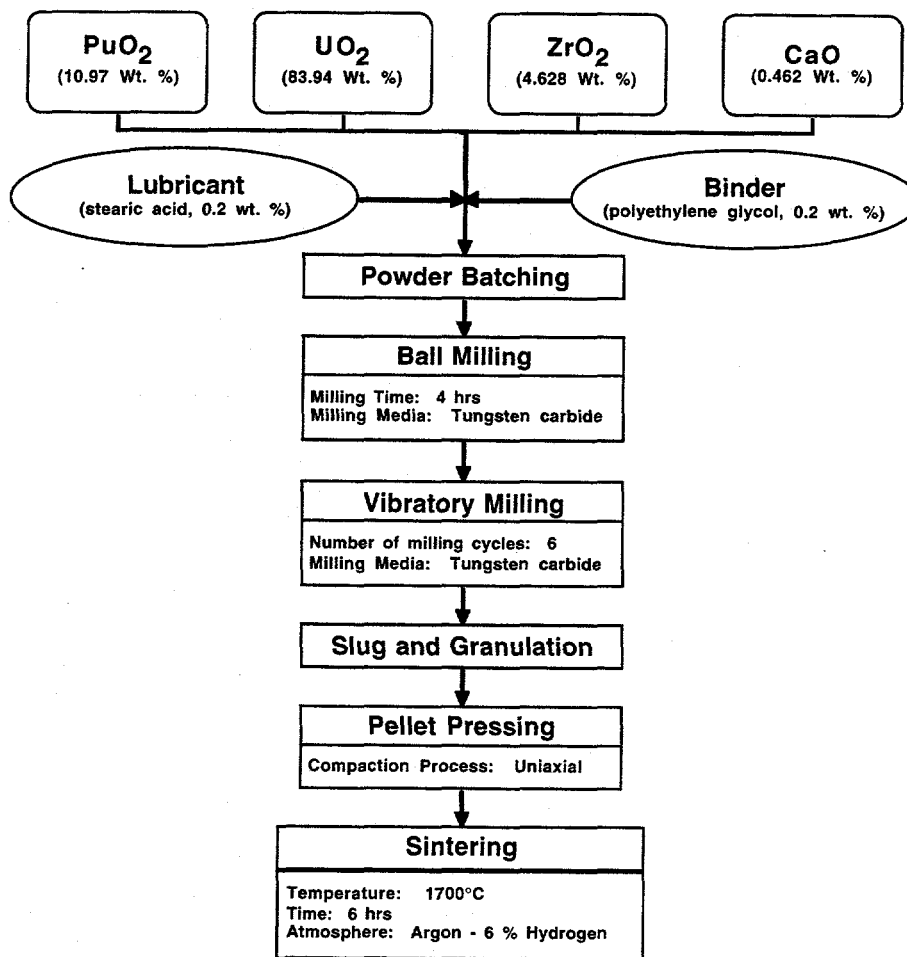


Fig. 9. Flow diagram for fabrication of EMOX fuel pellet.



Fig. 10. Sintered EMOX fuel pellet.

designed as slight perturbations from standard MOX fuel for ease in licensability, and then modified accordingly to provide a smooth transition to implementation of higher plutonium destruction nonfertile fuels. Preliminary calculational results predict satisfactory EMOX in-reactor performance, and preliminary fabrication analyses demonstrate successful fabrication of EMOX compositions. Additional analyses in both areas, in conjunction with the global plutonium inventory modeling efforts should further demonstrate the applicability of the EMOX concept to plutonium management strategies.

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