

A CONCEPTUAL REPROCESSING AND WASTE MANAGEMENT SCHEME FOR ZIRCALOY-CLAD THORIA FUELS



H. S. LEVINE and R. L. SCHWOEBEL *Sandia Laboratories
Albuquerque, New Mexico 87115*

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A family of inorganic ion exchangers has been under development in this laboratory for stabilization of nuclides from various nuclear processing waste streams.¹ These materials are formed from hydrous oxides of titanium, zirconium, niobium, or tantalum and have a high affinity for all polyvalent cations in the wastes and a large ion exchange capacity. They consolidate and convert to nonvolatile, leach-resistant ceramic waste forms. While their effectiveness for high-level waste stabilization was demonstrated mainly with the titanium form of the ion exchanger, the zirconium and other forms can also be used. The large source of zirconium in the form of waste Zircaloy fuel hulls offers the particularly interesting possibility of combining this waste stream with others to mutual benefit. In fact, there is more than enough zirconium in this high-level solid waste to stabilize all the associated (e.g., Purex) wastes in the form of stable zirconates and to simultaneously reduce the resulting high-level volume by a factor of ~ 2 over the traditional calcine-glass approach. This observation has been investigated, and a conceptual process to convert this Zircaloy waste to ion exchange material was recently described.^{2,3} This process basically involved distillation of $ZrCl_4$ from the chlorinated waste, followed by reaction to form alkoxides, and then hydrolysis.

The Zircaloy conversion process is interesting not only from the point of view of stabilizing wastes associated with conventional fuels, but also in the reprocessing of thorium fuels. While thorium fuels can and have been processed by conventional aqueous techniques, it is necessary to add fluorides to dissolve the spent thoria fuel in reasonable lengths of time. The inclusion of fluorides influences the subsequent chemistry, since the Zircaloy cladding is also attacked and the presence of excess zirconium in the leachate markedly complicates the usual solvent extraction processes. This problem is avoided by the use of the Zircaloy conversion process. In this approach, the Zircaloy is chlorinated and separated from the fuel by volatilization. The fuel is then reprocessed by conventional methods without complication from Zircaloy dissolution. The volatilized zirconium, however, is readily converted to a zirconate ion exchanger for stabilization of wastes associated with reprocessing the fuel itself. The following paragraphs describe this conceptual reprocessing and waste management process in detail.

This integrated reprocessing and waste management

scheme for Zircaloy-clad thoria fuel is presented in flow-sheet form in Fig. 1, where the magnitude of the process streams has been estimated for discussion purposes only. As illustrated in this figure, the head-end process and the Zircaloy conversion process overlap with common chlorination and nonvolatile residue leaching steps. The overall integrated scheme is completed with the Thorex process for the fuel and a waste treatment process for the associated wastes.

As illustrated, the chopped fuel pins would be divided into two process streams by use of a mechanical decladding step. For example, mechanical rolling, crushing, or vibration might be suitable operations for achieving partial separation of fuel and cladding. Incomplete separation is expected and judged to be acceptable, since subsequent chlorination would effectively complete the separation process. It is estimated that 10% of the spent fuel would adhere to the Zircaloy hulls. The process stream containing the Zircaloy hulls and the adhering oxide fuel would then be fed into the Zircaloy conversion chlorinator.^{2,3} The chlorinating agent, refluxing $AlCl_3 \cdot NH_4Cl$, would react *endothermically* with the waste Zircaloy hulls to form some nonvolatile chlorides and $ZrCl_4$ that would distill from the reactor, as a slightly radioactive fraction, into the next stage of the Zircaloy conversion process. Subsequent reaction with isopropyl alcohol and then hydrolysis would form zirconate ion exchange material from this distillate. The oxide fuel carried into the chlorinator with the Zircaloy hulls would also react with the fused double salt, $AlCl_3 \cdot NH_4Cl$, to form additional chlorides and Al_2O_3 . Most of these products would remain in the chlorinator as a nonvolatile residue and would have no major effect on the conversion process.

After chlorination, the $AlCl_3 \cdot NH_4Cl$ would be removed by distillation and the nonvolatile chlorinated residue recovered. The soluble chlorides would be removed by a dilute HNO_3 leach, leaving a residue of Al_2O_3 and perhaps some stainless-steel and Inconel shards. The leached chlorides would then be precipitated by raising the pH, rinsed, and subsequently fired at an intermediate temperature to remove the last traces of chloride. The fired chloride-free product would then be recombined with the oxide fuel process stream for fluoride-catalyzed acid dissolution and further processing. Aqueous radioactive wastes from the Thorex process would then be decontaminated using packed zirconate ion exchange columns or stabilized by

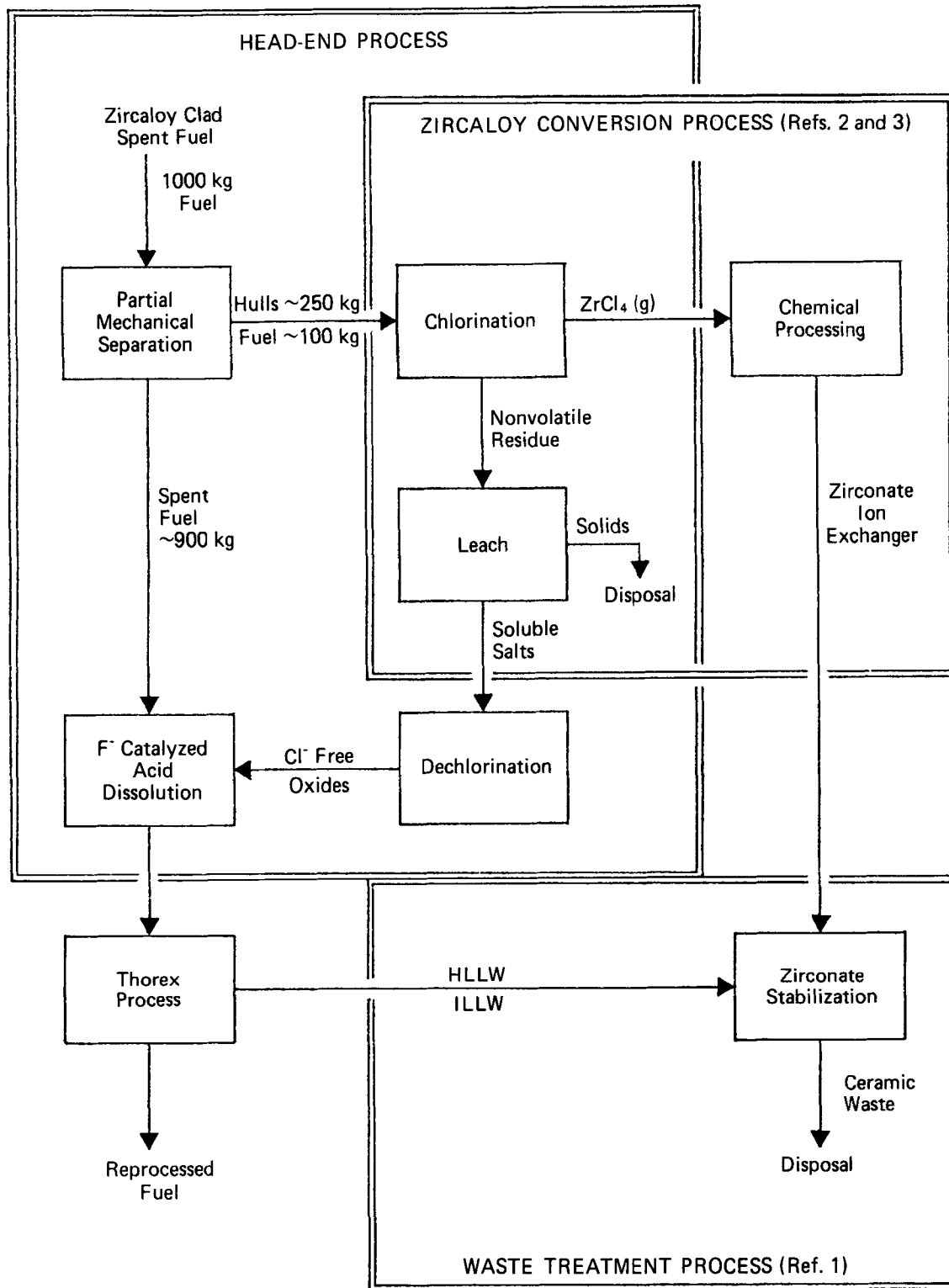
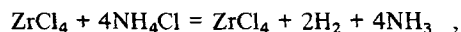


Fig. 1. Reprocessing and waste management scheme for Zircaloy-clad thorium oxide fuel.

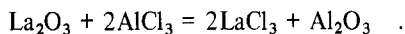
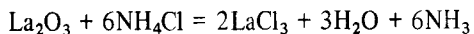
use of batch solidification processes with the zirconate material.⁴

The fused salt $\text{AlCl}_3 \cdot \text{NH}_4\text{Cl}$ is an effective chlorinating agent and reacts rapidly with Zircaloy in the 350 to 400°C temperature range to form ZrCl_4 and other products.^{5,6} The overall reaction, typically, can be written as



and it is a liquid-phase endothermic process. As such, it differs from past gas-phase, exothermic hydrochlorination efforts that suffered from heat dissipation problems. Calculation of free energy and enthalpy changes show that

oxides such as ThO_2 , ZrO_2 , SiO_2 , and UO_2 should react, barring kinetic effects, with the AlCl_3 component of the double salt, whereas other oxides should react with both components. All the oxide reactions are exothermic and can be written, typically, as



The overall net heat effect of the combined oxide and Zircaloy chlorination reactions, however, would still be endothermic for the expected range of relative amounts of material involved.

Some prior work on mechanical head-end processes has been performed,⁶⁻⁸ but additional design and development would probably be required. These mechanical operations could produce, in addition, a spent oxide fuel particle size small enough to enhance subsequent acid dissolution rates.

There is no prior experimental base relating to the chlorination of mixed-oxide fuel with fused $\text{AlCl}_3 \cdot \text{NH}_4\text{Cl}$. However, chlorination of SnO_2 , $\text{PbO} \cdot \text{SnO}_2$, TiO_2 , $\text{CaO} \cdot \text{TiO}_2$, GeO_2 , Na_2GeO_3 , Sb_2O_5 , As_2O_3 , and NaAsO_2 was successfully accomplished in a fused $\text{AlCl}_3 \cdot \text{NaCl}$ eutectic, a reaction analog of fused $\text{AlCl}_3 \cdot \text{NH}_4\text{Cl}$ (Ref. 9). No chlorination reaction occurred with SiO_2 , $\text{Na}_2\text{O} \cdot \text{SiO}_2$, B_2O_3 , and $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$, and all reactions were carried out in a Vycor reaction cylinder that was apparently unaffected. SiO_2 (as α -quartz) should react with the fused salt, however, because the free energy change for the reaction is negative but small. Additional chlorination studies are clearly needed to clarify the extent and kinetics of reaction with representative materials. Detailed chlorination reactor designs are not now possible because reaction kinetics and material problems are still not well defined. Promising candidate materials for this purpose, however, include molybdenum, gold, Al_2O_3 , Pyrex glass, Vycor, and other forms of vitreous silica.

Aqueous processing of the chlorinated fuel and Zircaloy residue appears to be relatively straightforward and is designed to remove chloride ions by precipitation, rinsing, and firing, so that chloride corrosion will not occur in subsequent fuel reprocessing. Studies would be required to optimize this aqueous processing, and some further refinements may be required. It is judged, however, that acceptable impurity chloride levels could be achieved.

The Zircaloy conversion process has undergone evaluation for high-level liquid waste (HLLW) management.^{2,3} Further development of this process would involve studies on chlorination of Zircaloy waste, desublimation of gaseous ZrCl_4 , alkoxide and ion exchange preparation, overall process evaluation, and evaluation of the effect of oxide fuel carry-over on the chlorination of Zircaloy hulls.

We conclude that this reprocessing and waste management scheme is conceptually simple and direct. It depends on the use of a strong chlorinating agent to convert the Zircaloy waste and adhering oxide fuel to nonvolatile

chlorinated residue and volatile ZrCl_4 fractions. The latter product would then be converted to an inorganic ion exchanger, which has a very high affinity for fission products, and combined with HLLW from subsequent fuel reprocessing to produce a stable and refractory waste form. The nonvolatile chlorinated fraction would be recovered and processed to remove chloride ions. This chloride-free fraction would then be recombined with the main oxide fuel process stream for further reprocessing. This approach eliminates the problems associated with concurrent dissolution of the fuel and cladding in a chop-leach head-end step. It also converts the otherwise waste fuel hulls to a highly effective ion exchanger that can be used to stabilize the associated HLLW into a stable waste form of about half the volume that would result in using calcine-glass technology.

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