

Evaluation of Various Methods for Converting Spent Nuclear Fuel into Fluoride Salts

P. A. Taylor, A. D. Braatz, G. D. Del Cul, B. B. Spencer

*Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6243,
taylorpa@ornl.gov, braatzad@ornl.gov, delculgd@ornl.gov, and spencerbb@ornl.gov*

INTRODUCTION

Used nuclear fuel (UNF) resulting from the operation of light water reactor power generating stations contains significant amounts of residual fuel, and thus, exploitable energy. Concerns about the cost and proliferation potential of recycling the fuel using conventional reprocessing methods, where many of the fuel components are separated and purified, have hindered implementing the recycle of the UNF. This has led to the indefinite storage of large quantities of UNF that lacks a final disposition pathway.

A new concept for an advanced molten salt reactor capable of using the UNF requires only that the UNF be converted to fluoride salts, without the need for separating the various actinides from the fission products. These salts can be used as nuclear fuel in an accelerator-driven molten-salt nuclear reactor. An accelerator produces the extra neutron flux needed to produce a sustained nuclear reaction in the low enrichment fuel salt. Turning off the accelerator immediately stops the nuclear reaction. A flow of helium over the operating reactor core would continuously remove volatile radionuclides, which would be recovered if valuable (e.g., tritium) or retained for decay (e.g., krypton-85). Continuous removal of volatile radionuclides would keep the inventory in the core almost 6 orders of magnitude lower than a typical light water reactor's inventory. The concentration of long-lived actinides in the core is also reduced over time.¹

APPROACH

Various processes to produce the fluoride salt fuel from UNF are being evaluated. The plan is to convert all of the spent fuel, including fission and activation products, into fluoride salts. Some volatile species are inevitably released as the fuel is converted from a monolithic form to a granulated salt (e.g., krypton and xenon). There exists a large body of information on preparing fluoride salts for use in molten salt reactors, much of which originated with supporting research for the Molten-Salt Reactor Experiment (MSRE), which was operated at Oak Ridge National Laboratory from 1965 to 1969. The MSRE fuel salt was composed of fluoride salts of lithium, beryllium, zirconium, and uranium. The project demonstrated the key aspects of using molten salt fuel, including the chemical stability of the salt and the compatibility of the molten salt with the graphite and Hastelloy-N construction materials.

DESCRIPTION OF STUDIES

A wide range of processes are being evaluated for converting the UNF into fluoride salts. One alternative is to modify conventional aqueous processing. Beginning with the most widely used process, the initial steps would remain largely unchanged (i.e., mechanically chop the fuel into segments and then leach the fuel from the cladding using nitric acid, typically using concentrated acid near its boiling point). Processing beyond this point would be greatly different. Most of the salts could then be precipitated using ammonium hydroxide, denitrated, and then fluorinated using hydrogen fluoride (HF). An alternative to precipitation would be evaporation of the solution, followed by denitration and fluorination. Another alternative to acidic leaching is to use voloxidation, which converts the fuel pellets to a free-flowing oxide powder that can be mechanically separated from the cladding and then fluorinated.

More direct methods avoid the aqueous processing altogether. The cladding can be removed chemically using anhydrous hydrogen chloride (HCl) or chlorine (Cl₂) to convert the zirconium in the Zircaloy® to volatile zirconium tetrachloride (ZrCl₄). HCl produces a cleaner ZrCl₄ product for potential reuse than does Cl₂, but this process also produces hydrogen gas as a by-product.² Both HCl and Cl₂ can be used at about 350°C and atmospheric pressure. Once the cladding is removed, the fuel pellets can be oxidized (i.e., voloxidation), producing a fine oxide powder that can be fluorinated with HF, or the pellets can be fluorinated directly using HF at a temperature of about 550°C and atmospheric pressure.³

For each of these alternatives, the required reaction conditions are being evaluated, including temperature, pressure, materials of construction, off-gas composition and treatment requirements, and reaction by-products. A flow sheet and material balance are being produced, and estimated capital costs will be developed.

RESULTS

The available literature indicates that the processing chemistry to convert UNF to fluoride salts is quite feasible. High-level flow sheets and material balances will be presented to show the fuel salt compositions expected to arise from the most promising processes. Initial assessments of the characteristics of the spent fuel salt will also be discussed.

REFERENCES

1. C. D. BOWMAN, et al., GEM*STAR: The Alternative Reactor Technology Comprising Graphite, Molten Salt, and Accelerators, p. 2877, D. G. CACUCI (ed.), *Handbook of Nuclear Engineering*, Springer Science+Business Media LLC, New York, NY (2010).
2. E. D. COLLINS, et al., "Process Development Studies for Zirconium Recovery/Recycle from Used Nuclear Fuel Cladding," *Procedia Chemistry*, **7**, 72–76 (2012).
3. E-H. KIM, et al., "Fluorination of UO₂ and CeO₂ Under the Atmosphere of HF and H₂," *J. Ind. Eng. Chem*, **8**, 98–102 (2002).