

THE ROLE OF FLUORIDE VOLATILITY METHOD IN MOLTEN SALT REACTOR FUEL CYCLES

T. SHIBUYA
NEC Corporation
Kawasaki, Japan
Email: taizo@nec.com

R. YOSHIOKA
International Thorium Molten-Salt Forum
Yokohama, Japan

M. KINOSHITA
International Thorium Molten-Salt Forum
Yokohama, Japan

T. FUKASAWA
Nippon Nuclear Fuel Development Co., Ltd
Ibaraki, Japan

Abstract

Molten Salt Reactors (MSRs) feature highly diverse fuel cycles, necessitating a common reprocessing technology. The paper evaluates the Fluoride Volatility Method (FVM), an industrially established process, as a potential common platform for three distinct fuel types: spent oxide fuel, liquid fluoride fuel, and solid fuel from Fluoride-salt-cooled High-temperature Reactors (FHRs). Although further development is required for its application to liquid and solid fuels, FVM is a realistic common platform technology for these varied fuel cycles. The study also highlights the ongoing research into predicting chemical potentials using machine learning, which aims to further advance future fuel reprocessing technologies.

1. INTRODUCTION

A key feature of Molten Salt Reactors (MSRs) is the diversity of their fuel cycles. The fuel forms range from solid to liquid, the salts utilized can be either fluorides or chlorides. The nuclear fuel materials include uranium (U), plutonium (Pu), and thorium (Th), with the co-utilization of Minor Actinides (MAs) also under consideration. Reprocessing options range from a once-through cycle to various closed-cycle schemes, which may be performed online, offline, or as a combination of both. The development of MSRs is accelerating, with fluoride-salt-cooled solid-fuel reactors and liquid fluoride-fueled reactors showing momentum for commercial deployment in the 2030s. One realistic approach to address these diverse development scenarios is to construct flowsheets centered on a mature, common technology. The Fluoride Volatility Method (FVM) is not only established as a key industrial technology for uranium enrichment but has also been researched for processing oxide and fluoride fuels [1-3]. The FVM also shows potential for application in treating fuel debris [4]. In this study, we discuss the role of the FVM and demonstrate its applicability as a common technology for the fuel cycles of three specific fuel types: oxide fuel, liquid fluoride molten salt fuel, and molten salt-cooled solid fuel..

2. OXIDE FUEL

The FVM can be utilized as a front-end process to convert spent fuel from LWRs into fresh fuel for MSRs. An example flowsheet is shown in Figure 1. This flowsheet is composed of FVM and post-FVM processes and is almost identical to the FLUOREX method proposed by Kani et al. [1]. In this context, the FVM refers to the fluorination process using fluorine gas within a flame reactor and the subsequent UF₆ purification steps, which are essential for the product to be handled safely at enrichment plants.

Decladded oxide fuel, along with fluorine gas diluted by an inert gas such as argon, is fed into the top of the flame reactor. Inside the reactor, volatile fluorides, including UF_6 , are generated. The proportion of UF_6 among the volatile fluorides is increased by controlling the temperature, reaction time, and fluorine concentration. The lower part of the flame reactor is equipped with a thermal decomposition chamber. In this chamber, PuF_6 decomposes into PuF_4 , allowing most of the volatile Pu to be recovered in solid form. The volatile fluoride stream exiting the flame reactor is purified into UF_6 by passing through a series of traps. These traps use materials such as UO_2F_2 , MgO , and alumina to remove various contaminants, including Pu, MAs like neptunium (Np), and fission products (FPs) such as technetium (Tc), molybdenum (Mo), and ruthenium (Ru). After purification, the UF_6 can be enriched if needed and then reduced to become fuel for fluoride-salt MSR.

The residue from the fluorination process is composed of fluorides, oxyfluorides, and oxides of U, transuranic elements (TRU), and fission products (FPs). This residue, along with materials recovered from the UF_6 purification step, is treated in the post-FVM process. As shown in the figure, this process consists of oxide conversion and solvent extraction. During oxide conversion, fluorides are converted into oxides via hydrolysis with high-temperature steam. These oxides are then dissolved in nitric acid and treated using a solvent extraction method such as the well-known PUREX process. The PUREX process can be replaced by the SELECT process [5] to recover MAs in the future. The oxides produced after solvent extraction can be used directly as Mixed oxide (MOX) fuel or, following halogenation, as fuel for MSRs. Alternatively, the post-FVM stage could consist of pyroprocessing technologies that utilize molten salts and liquid metals.

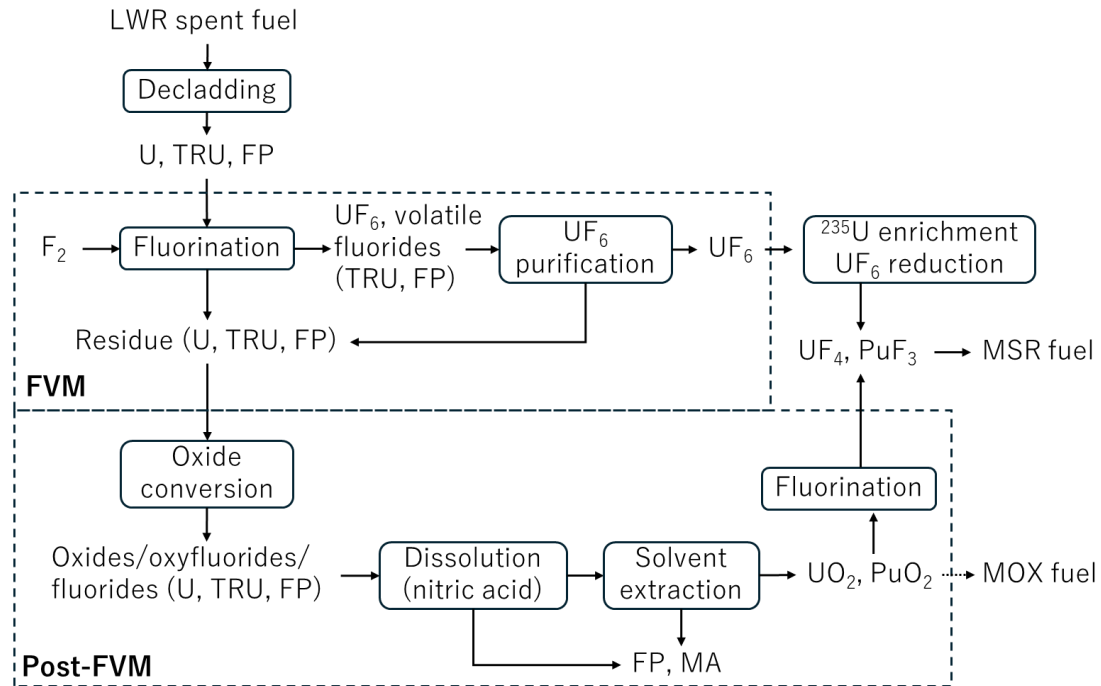


FIG. 1. Example flowsheet for oxide fuel reprocessing.

3. FLUORIDE SALT FUEL

Liquid-fueled MSRs utilize a fuel salt consisting of nuclear material (e.g. UF_4) dissolved in a carrier salt such as LiF-BeF_2 (FLiBe). While the ability to remove volatile FPs like xenon and krypton during operation represents an advantage of liquid fuel, the primary challenge remains the removal of non-volatile FPs. The technology to selectively achieve this is, however, still in its early stages of research [6]. This necessitates a more comprehensive procedure to remove elements such as actinides, lanthanides, and noble metals either simultaneously or sequentially from the carrier salt, and then return the fuel components to the salt. Figure 2 shows an example flowsheet for fluoride MSR fuel reprocessing. It consists of the FVM followed by carrier salt purification and the separation of TRU, Th, and FPs.

While the fluorination of the fluoride salt was demonstrated by sparging fluorine gas in a liquid salt, the high corrosion rates of vessels are considered a major issue [3]. This led to the concept of a "frozen wall," a technique pioneered in early studies at Oak Ridge National Laboratory (ORNL), which protects equipment walls with a layer of solidified salt by lowering the wall temperature [7]. In contrast to the online processing considered at ORNL, it is also possible to process the fuel offline in batches [8]. Since such batch processing allows for a cooling period for the decay heat to decrease, partial melting—an option proposed during the fuel decommissioning of the MSRE [9]—may become a viable choice. Additionally, feeding the salt into a flame reactor is another conceivable option. In fact, industrial flame reactors employ water-cooling on their walls to reduce corrosion. For UF_6 purification, the same technologies used for oxides should be applicable.

Options for carrier salt purification include vacuum distillation and reductive extraction. While tests on FLiBe purification using vacuum distillation were conducted at ORNL [10], challenges remain in finding container materials that can withstand high temperatures around 1000°C . Reductive extraction is a technique where the molten salt is brought into contact with a liquid metal, such as Bi containing a reductant like Li, to reduce elements other than the carrier salt constituents and extract them into the liquid metal phase. Other materials such as Al and Ga have also been proposed as reductants or carrier metals [11,12].

Methods such as reductive extraction and electrolysis have been proposed for the separation of TRU and FPs. Techniques like electrolysis are also being researched for Th/FP separation [13]. Another option is to subject the residue from the carrier salt purification to oxide conversion and solvent extraction.

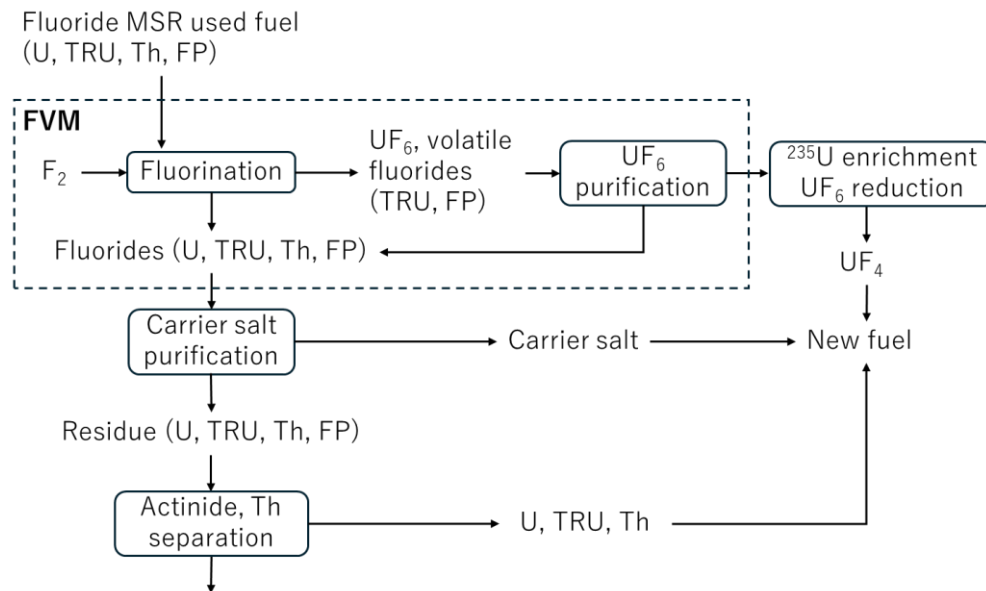


FIG. 2. Example flowsheet for fluoride MSR fuel reprocessing.

4. SOLID FUEL

Fluoride-salt-cooled High-temperature Reactors (FHRs) utilize solid fuel composed of numerous TRISO (TRI-structural ISOtropic) fuel particles compacted within a graphite matrix. Each TRISO particle consists of a fuel kernel, such as UO_2 , coated with layers of pyrolytic carbon (PyC) and silicon carbide (SiC). While several methods have been proposed for processing this solid fuel, a typical approach combines combustion with oxygen, mechanical crushing of the SiC coating, and solvent extraction. In this method, the graphite matrix and PyC layers are first burned off with oxygen. The particles, with their SiC coatings now exposed, are then mechanically crushed, and the resulting powder is treated with solvent extraction. However, the mechanical crushing step presents challenges, including equipment wear and the generation of radioactive fine particles. Since fluorine gas can react with SiC, the FVM has the potential to replace this mechanical process. Indeed, fluorination tests on UO_2 -SiC powder, simulating debris from Accident Tolerant Fuel (ATF) for LWRs with a SiC cladding, have shown that nearly the entire sample can be volatilized [14]. Volatile fluorides derived from

SiC can be easily separated from the product stream using a cold trap due to the difference in their boiling points.

5. CONCLUSION AND FUTURE WORKS

We have investigated the role of the Fluoride Volatility Method (FVM) in MSR fuel cycles for the following three cases: (1) the reprocessing of oxide fuel from LWRs as a front-end process for fluoride MSRs, (2) the reprocessing of fuel from liquid-fueled fluoride molten salt reactors, and (3) the reprocessing of solid fuel from Fluoride-salt-cooled High-temperature Reactors (FHRs). While the application of FVM to the first case has no fundamental challenges, its application to the latter two cases involves several development areas. Nevertheless, the FVM remains a realistic candidate as a platform technology. In the presentation, we will also introduce our ongoing research on the prediction of chemical potentials using machine learning interatomic potentials to advance fuel reprocessing technology.

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