Current progress in R&D of Fluoride Volatility Method

Jan Uhlíř*, Martin Mareček and Jan Škarohlíd

Nuclear Research Institute Řež plc, Husinec – Řež 130, CZ-25068, Czech Republic

Abstract

Fluoride Volatility Method is regarded to be a promising advanced pyrochemical reprocessing technology, which can be used for reprocessing mainly of oxide spent fuels coming from current LWRs or future GEN IV fast reactors. The technology should be chiefly suitable for the reprocessing of advanced oxide fuels with inert matrixes of very high burn-up and short cooling time, which can be hardly reprocessed by hydrometallurgical technologies. Fluoride Volatility Method is based on direct fluorination of powdered spent fuel with fluorine gas in a flame fluorination reactor, where the volatile fluorides (mostly UF₆) are separated from the non-volatile ones (trivalent minor actinides and majority of fission products). The subsequent operations necessary for partitioning of volatile fluorides are condensation and evaporation of volatile fluorides, thermal decomposition of PuF₆ and finally distillation and sorption used for the purification of uranium product.

Keywords: Fluoride volatility method; Pyrochemical reprocessing

1. Introduction

Fluoride Volatility Method (FVM) is regarded as a promising advanced pyrochemical reprocessing technology, which can be used for reprocessing mainly of oxide spent fuels coming from future Generation IV fast reactors, especially of fast breeders operated within the closed uranium – plutonium fuel cycle. The technology should be chiefly suitable for the reprocessing of advanced oxide fuel types e.g. MOX fuels with high content of plutonium, dispersed fuels with inert matrixes and/or fuels of very high burn-up and very short cooling

* Corresponding author. Tel.: +420-26617-3548; fax: +420-26617-3531.
E-mail address: uhl@ujv.cz.
time, which can be hardly reprocessed by hydrometallurgical technologies due to their high radioactivity or pure solubility in nitric acid.

Fluoride Volatility Method is based on a separation process, which comes out from the specific property of uranium, neptunium and partially plutonium to form volatile hexafluorides whereas most of fission products (lanthanides) and higher transplutonium elements (mericurium, curium) present in irradiated fuel form non-volatile trifluorides. This property has led to the development of several technological processes based on fluorination of irradiated fuel either by strong fluorinating agents like BrF₃, BrF₅, ClF₃ or even by pure fluorine gas. [1,2,3,4] Chiefly the fluorination by pure fluorine gas enables to conduct the process very fast and effectively as the flame reaction with very high efficiency.

The present interest in the dry reprocessing method is motivated by requirements on the development of advanced fuel cycle technologies devoted to the Gen IV nuclear reactor systems. Among the pyrochemical technologies under present development, the Fluoride Volatility Method is almost the only one, which is not based on the use of molten salt techniques.

2. Principles of the technology

Before the fluorination of the powdered fuel, the removal of cladding material and subsequent transformation of the fuel into a powdered form of a suitable granulometry for dosing has to be done. The technology of decladding is a melting in high temperature furnace. The typical cladding material of oxide fuel, which is either zircalloy (LWR) or stainless steel (Fast Reactors), can be fully removed. Suitable transformation method of the fuel pellets into a powder is either grinding or voloxidation when UO₂ is converted into powdered U₃O₈.[5] Then the reprocessing by the Fluoride Volatility Method is based on following main operations:

1. Fluorination of the powdered fuel (the purpose of this operation is partitioning of volatile fluorides from non-volatile ones)
2. Thermal decomposition of plutonium hexafluoride
3. Purification of the uranium product

Flame fluorination reaction of spent oxide fuel is a basic unit operation of the whole process. The reaction between the fuel powder and pure fluorine gas is spontaneous and highly exothermic. Principal fluorination reactions of main fuel components are following:

\[
\text{uranium:} \\
\text{UO}_2(s) + 3\text{F}_2(g) \rightarrow \text{UF}_6(g) + \text{O}_2(g) \quad \Delta_r H^0_{298.15} = -1062.4 \text{ kJ/mol U} \quad (1) \\
\text{or} \\
\text{U}_3\text{O}_8(s) + 9\text{F}_2(g) \rightarrow 3\text{UF}_6(g) + 4\text{O}_2(g) \quad \Delta_r H^0_{298.15} = -955.8 \text{ kJ/mol U} \quad (2)
\]

\[
\text{plutonium:} \\
\text{PuO}_2(s) + 2\text{F}_2(g) \rightarrow \text{PuF}_4(s) + \text{O}_2(g) \quad \Delta_r H^0_{298.15} = -722.4 \text{ kJ/mol Pu} \quad (3) \\
\text{PuO}_2(s) + 3\text{F}_2(g) \rightarrow \text{PuF}_6(g) + \text{O}_2(g) \quad \Delta_r H^0_{298.15} = -693.1 \text{ kJ/mol Pu} \quad (4) \\
\text{PuF}_4(s) + \text{F}_2(g) \leftrightarrow \text{PuF}_6(g) \quad K_p = \frac{[\text{PuF}_6]}{[\text{F}_2]} \quad (5)
\]

\[
\text{neptunium:} \\
\text{NpO}_2(s) + 3\text{F}_2(g) \rightarrow \text{NpF}_6(g) + \text{O}_2(g) \quad \Delta_r H^0_{298.15} = -907.9 \text{ kJ/mol Np} \quad (6) \\
\text{NpO}_2(s) + 2\text{F}_2(g) \rightarrow \text{NpF}_4(s) + \text{O}_2(g) \quad \Delta_r H^0_{298.15} = -844.7 \text{ kJ/mol Np} \quad (7) \\
\text{NpF}_4(s) + \text{F}_2(g) \leftrightarrow \text{NpF}_6(g) \quad K_p = \frac{[\text{NpF}_6]}{[\text{F}_2]} \quad (8)
\]

\[
\text{americium and curium:} \\
2\text{Am}_2\text{O}_3(s) + 6\text{F}_2(g) \rightarrow 4\text{AmF}_3(s) + 3\text{O}_2(g) \quad (9) \\
2\text{Cm}_2\text{O}_3(s) + 6\text{F}_2(g) \rightarrow 4\text{CmF}_3(s) + 3\text{O}_2(g) \quad (10)
\]
Based on these reactions, the main partitioning of spent fuel is realized directly in the fluorination reactor. Whereas the volatile products of the fluorination reaction leave the apparatus, the non-volatile fluorides remain caught in the bottom part of fluorinator in the form of ash. The further separation of most of individual components forming volatile fluorides is generally possible by condensation at different temperatures, sorption and distillation processes. While the fluorination of uranium into volatile hexavalent form (UF₆) is spontaneous, plutonium hexafluoride is thermally unstable and can be obtained only at considerable surplus of fluorine gas. Behavior of neptunium during the process varies between uranium and plutonium, however the thermal stability of NpF₆ is substantially higher than of PuF₆.

Separation of plutonium is possible by thermal decomposition of gaseous PuF₆ into solid PuF₄ at about 450 °C, separation of neptunium is possible by sorption of NpF₆ on MgO. Final purification of uranium hexafluoride from MoF₆, TeF₆, IF₅ and SbF₅, which tend to accompany UF₆ through the system, could be done by rectification process. Distillation of UF₆ is usually done in temperature range from 75 °C to 90 °C at pressure of about 2 atm in order to keep uranium hexafluoride in liquid form. The process flow-sheet of the FVM is shown in Fig. 1.

![Process flow-sheet of Fluoride Volatility Method](image)

3. Main results of existing development

Nuclear Research Institute Řež plc has been developing the FVM in the frame of fuel cycle program devoted to selected Generation IV reactor systems. The process flow-sheet of investigated technology is based on the direct fluorination of powdered spent fuel by fluorine gas and on the subsequent purification of volatile products by condensation, sorption, thermal decomposition and rectification.

Experimental verification of the technology has been realized at the semi-pilot level. The technological line called FERDA (shown in Fig. 2) was built in the radiochemical laboratory of NRI Řež plc. FERDA is an...
experimental technology of the batch character with the short-time capacity 1-3 kg of powdered fuel per hour. The maximum capacity of volatile fluorides (UF₆) accumulated in the technology is about 7 kg. Main structural material of the FERDA line is nickel or nickel alloys.

The main aims of existing experimental development have been pre-hot test verification of individual apparatuses and process control before emplacement of the technology into hot cell. The crucial experimental effort has been focused to the mastering of flame fluorination process as the previous historical laboratory investigations of the Fluoride Volatility Method used primarily slow gradual fluorinations of the fuel poured on the reaction boat or quasi fluidized bed technique. Diluted fluorine gas was usually used for these fluorinations.

Several experiments with uranium fuels (UO₂ and U₃O₈) and with simulated spent fuel (uranium oxides and selected non-active oxides of lanthanides) were done to obtain data for optimization of the design and construction of scroll feeder and flame fluorination reactor. The final design of flame fluorinator was verified by long run fluorination tests (several hours) with uranium oxides and with simulated spent fuel mixtures. The objective of the experiments with uranium oxide was to achieve maximum conversion factor; the objective of experiments with simulated spent fuel was to verify the partitioning of volatile and non-volatile products of fluorination reaction. The fission product simulants were mixtures of non-radioactive oxides of Y₂O₃, Nd₂O₃, CeO₂, Sm₂O₃, BaO and SrO, which represented about 3 – 5 % of fuel. [6]

The maximum conversion factor (fluorination efficiency) with pure uranium fuel reached 92 % with U₃O₈ and 97 % with UO₂. The presence of fission product simulants had no measurable effect on the flame fluorination reaction and fully verified the capability of flame fluorinator to separate non-volatile products of fluorination. The photo and schematic draft of the flame fluorination reactor with scroll feeder on the top and removable container of solid products in the bottom part are shown in the Fig. 3.
4. Conclusions

Existing development of the Fluoride Volatility Method successfully verified the basic functionality of main tested apparatuses in non-active conditions with uranium and simulated fuels. The subsequent step of the verification should be realized in hot cell with irradiated fuels. Although the basic construction of apparatuses was designed for hot cell requirements, there will be necessary to do some modifications simplifying the manipulation by remote control. However these changes should not affect the basic parameters of apparatuses.

Fluoride Volatility Method has a good potential to be used within the fuel cycles of advanced reactor types for reprocessing of modern oxide fuel types. The main attractiveness of the technology can be found in the reprocessing of fast breeder reactors spent fuel owing to the extreme radiation resistance of the used chemical agents (fluorine gas, inorganic fluorides), which allows to reprocess the spent fuels after short cooling time and the avoidance of any moderating agent, which enable to reprocess fuels with high content of fissile material. Moreover this technology should be attractive for reprocessing of dispersed (inert matrix fuels), which cannot be processed by hydrometallurgical methods due to theirs insolubility in nitric acid. However the technology still needs exacting development to reach full industrialization.
Acknowledgements

Existing R&D on the Fluoride Volatility Method in the Nuclear Research Institute Řež plc was realized thanks to financial support of the Ministry of Industry and Trade of the Czech Republic.

References