



Fluoride volatility method for reprocessing of LWR and FR fuels

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ABSTRACT

Fluoride volatility method is based on direct fluorination of powdered spent fuel with fluorine gas in a flame fluorination reactor, where the volatile fluorides (represented mainly by UF_6 , partially NpF_6) are separated from the non-volatile ones (e.g. PuF_4 , AmF_3 , CmF_3 , fluorides of majority of fission products), the objective being to separate a maximum fraction of uranium component from plutonium, minor actinides and fission products. The current research and development work in the area of fluoride volatility method is focused on the experimental program carried out at the semi-technological line called FERDA, which is a follow-up of the previous FREGAT-2 technology. The experimental test program, launched in 2004 by the Nuclear Research Institute Řež plc, has been focused mainly to the study of flame fluorination process, which is considered to be the crucial unit operation of the technology. The fluorination experiments were realized in the first instance with pure uranium oxide fuel and later on with simulated spent oxide fuel. Follow-on tests are planned with oxide fuels with inert matrixes. The experimental program is further supplemented by the system studies focused mainly to the process flow-sheet design and calculations and to the requisite modification of some apparatuses for the future verification of the process with irradiated fuel in hot conditions.

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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 light-water reactors (LWRs) or generation IV fast reactors (FR), especially of fast breeders. The technology should be chiefly suitable for the reprocessing of advanced oxide fuel types, e.g. fuels with inert matrixes and/or fuels of very high burn-up, high content of plutonium and very short cooling time, which can be hardly reprocessed by hydrometallurgical technologies due to their high radioactivity.

Fluoride volatility method is based on a separation process, which comes out from the specific property of uranium, neptunium and plutonium of forming volatile hexafluorides whereas most of fission products (lanthanides) and higher transplutonium elements 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 BrF_3 , BrF_5 , ClF_3 or even by pure fluorine gas. Major former activities were carried out in 1950s and 1960s in US at Brookhaven, Argonne and Oak Ridge laboratories [1], in 1970s in France at Fontenay-aux-Roses [2] and in Belgium at Mol [1], in 1970s and

1980s in former Soviet Union at Dimitrovgrad [3] and in former Czechoslovakia at Řež [4].

Original intentions of the development of this dry reprocessing method of spent fuel were motivated in the past by the assumed commercial utilization of fast breeder reactors. Their application in the power industry can be economically efficient only in the case of a closed fuel cycle. However, reprocessing of fast reactor spent fuel brings about a number of specific difficulties in comparison to the reprocessing of spent fuel from thermal reactors. They are caused, for example, by higher burn-up, shorter cooling time resulting in a higher amount of energy released by the fuel, higher concentration and amount of plutonium, different cladding material, presence of metallic sodium, different fission products composition, etc. Therefore, countries that were planning the introduction of fast reactors also were attempting to develop suitable methods for reprocessing, because the industrial hydrometallurgical PUREX process, employing organic extractants and solvents, was not suited for the fast reactor spent fuel. Hence, the most intensive effort in the development of the FVM was in 1960s and 1970s together with the development of fast breeder reactors.

Nowadays, the renewed interest in the dry-pyrochemical reprocessing methods is motivated by requirements on the development of advanced fuel cycle technologies devoted to the planned 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.

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The reprocessing technology based on the fluoride volatility method consists of the following main operations:

1. Removal of the cladding material from spent fuel elements.
2. Transformation of the fuel into a powder with granulometric properties allowing the fluorination reaction.
3. Fluorination of the powdered fuel (the purpose of this operation is the separation of the uranium component from plutonium, minor actinides and most of fission products).
4. Purification of the products obtained.

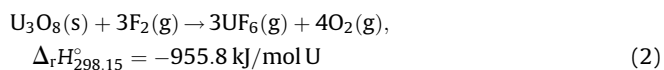
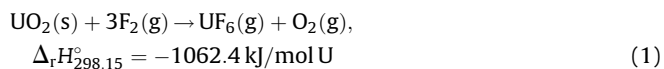
The first two steps represent preparatory stages for FVM itself and they can be realized separately from the FVM. Suitable technology of the cladding material removal is melting in high temperature furnace. The cladding material of oxide fuel is either zircalloy or stainless steel and both can be fully removed. Transformation of the fuel pellets into a powder is possible either mechanically by grinding or by partial oxidation of UO_2 into U_3O_8 . This chemical process is called voloxidation. Either flowing air or oxygen at 575–650 °C is used as oxidizing agent. The original voloxidation process was developed in ORNL in US and then further developed in several countries [5]. However, to prepare a uniform powder of required granulometry for subsequent fluorination by the voloxidation technique is rather difficult [4].

Whereas the early fluorination techniques of the FVM were fluidized bed processes, now the direct flame fluorination of powdered fuel is considered as the most promising unit operation for future industrial application. This method of fluorination in the frame of the FVM, which was firstly used in 1980s, is now under development by the company Hitachi Ltd. in Japan and by the Nuclear Research Institute Řež plc in the Czech Republic. Whilst Hitachi develops the FLUOREX process, which is based on the combination of dry fluoride technology with subsequent final hydrometallurgical partitioning [6], the technology developed by the Nuclear Research Institute can be considered as classical fluoride volatility method, where all steps of the separation technology are dry (non-aqueous).

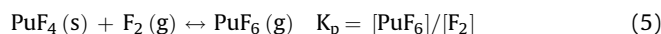
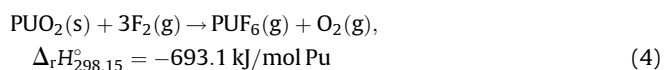
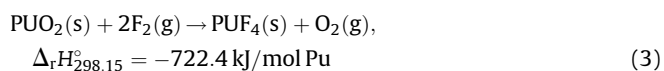
2. Description of the fluoride volatility process

Flame fluorination reaction of a 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. Usual temperature of ignition is over 250 °C. Subsequently the temperature in the flame can reach the range of 1500–1700 °C and therefore the walls of the reactor chamber and the whole reactor body have to be immediately intensively cooled. Principal fluorination reactions of main or significant fuel components are following:

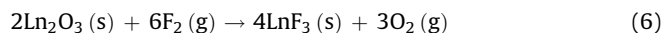
• Uranium:



• Plutonium:

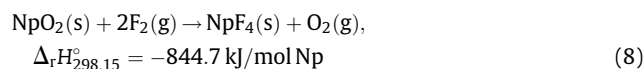
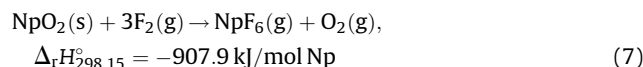


• Lanthanides:

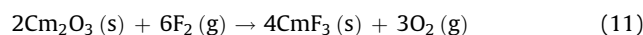
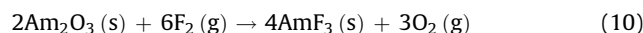


• Minor actinides

◦ Neptunium:



◦ Americium and curium:



The reaction enthalpies were determined from the thermochemical data of pure substances [7–9].

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 fluorinator bottom in the form of ash. The distribution of the spent fuel fluorination products according to their volatility is listed in Table 1. The further separation of most of individual components forming volatile fluorides is generally possible by sorption, condensation or distillation processes. However the separation of some volatile components is questionable owing to their chemical similarity.

While the fluorination of uranium to the volatile hexavalent form is spontaneous, plutonium hexafluoride is thermally unstable and can be obtained only at considerable oversupply of fluorine gas. Behavior of neptunium varies during the flame fluorination between uranium and plutonium based on the amount of surplus fluorine gas. However the thermal stability of neptunium hexafluoride is substantially higher than of plutonium hexafluoride so the thermal decomposition of NpF_6 is significantly lesser. Other chemical properties of neptunium, like reactions NpF_6 with NaF and the physical–chemical data of NpF_6 cause that both uranium and plutonium streams in the whole process could be contaminated by neptunium. Satisfactory solution of neptunium separation was not found yet, however the current effort in the further development of the FVM offers a chance to solve successfully this problem.

Uranium, plutonium and neptunium hexafluorides do not form a liquid phase at atmospheric pressure, their sublimation points are close: 56.5 °C for UF_6 , 55.2 °C for NpF_6 and 62.2 °C for PuF_6 . Certain possibility how to separate neptunium from uranium and plutonium within the FVM technology is by sorption–desorption methods on sodium and magnesium fluorides [4]. Sodium fluoride is commonly used for the decontamination of UF_6 . Uranium, neptunium and plutonium hexafluorides are completely sorbed on NaF at 100 °C. Whilst uranium and neptunium hexafluorides can be completely desorbed at 400 °C while passing fluorine gas through the bed, desorption of plutonium hexafluoride is impossible and formed complex $\text{PuF}_4 \cdot 3\text{NaF}$ is thermally stable even in the fluorine gas flow. Partial separation of neptunium from uranium is possible only via irreversible sorption of NpF_6 on MgF_2 at 100 °C. UF_6 is not sorbed on MgF_2 , but sorption of NpF_6 on this sorbent proceeds with the efficiency of 60–70%.

Table 1
Distribution of fluorinated spent fuel according to the volatility [10]

Group I (highly volatile)			Group II (volatile)			Group III (non-volatile)		
Agent	mp (°C)	bp (°C)	Agent	mp (°C)	bp (°C)	Agent	mp (°C)	bp (°C)
Kr	-157.2	-153.4	IF ₇	5	4	AmF ₄	Subl.	513
CF ₄	-184	-129	MoF ₆	17.6	33.88	RhF ₃	Subl.	600
Xe	-111.8	-108.1	NpF ₆	54.8	55.18	SnF ₄	Subl.	705
TeF ₆	Subl.	-38.6	TcF ₆	37.9	55.2	ZrF ₄	912	918
SeF ₆	Subl.	-34.5	UF ₆	64	56.5	PuF ₄	1037	927
			PuF ₆	51.9	62.2	CsF	703	1231
			IF ₅	9.4	98	RbF	760	1410
			SbF ₅	6	142.7	UF ₄	1036	1450
			NbF ₅	80	235	AmF ₃	1427	2067
			RuF ₅	101	280	CmF ₃	1406	2330
			RuF ₆	51	70	YF ₃	1136	2230
			RhF ₅	95.5	n/a	BaF ₂	1353	2260
			RhF ₆	70	73.5	EuF ₃	1276	2280
						GdF ₃	1380	2280
						CeF ₄	838	Decomp.
						CeF ₃	1430	2330
						PmF ₃	1410	2330
						SmF ₃	1306	2330
						SrF ₂	1400	2460

Final purification of uranium hexafluoride from MoF₆, TcF₆, IF₅ and SbF₅, which tend to accompany UF₆ through the technology, 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 have uranium hexafluorides in liquid form. The technology was studied in 1980s with partial success, but the rectification process needs still further intensive development [4].

Suitable structural materials for FVM equipment are pure nickel and nickel alloys. The rates of corrosion of nickel by fluorine gas, anhydrous HF and volatile fluorides are acceptable up to 600–650 °C [1]. Although pure nickel exhibits very good corrosion

resistance, owing to difficulties by welding of pure nickel material, the use of high nickel content alloys could be often more appropriate for manufacture of several FVM apparatuses than the use of pure nickel metal [11].

3. Current status of R&D on fluoride volatility method

The Nuclear Research Institute Řež plc has been developing the FVM in the frame of fuel cycle devoted to Molten-Salt Transmutation Reactor. Here, the present day R&D represents the follow-up of the former long-lasting R&D activities in FBR fuel reprocessing

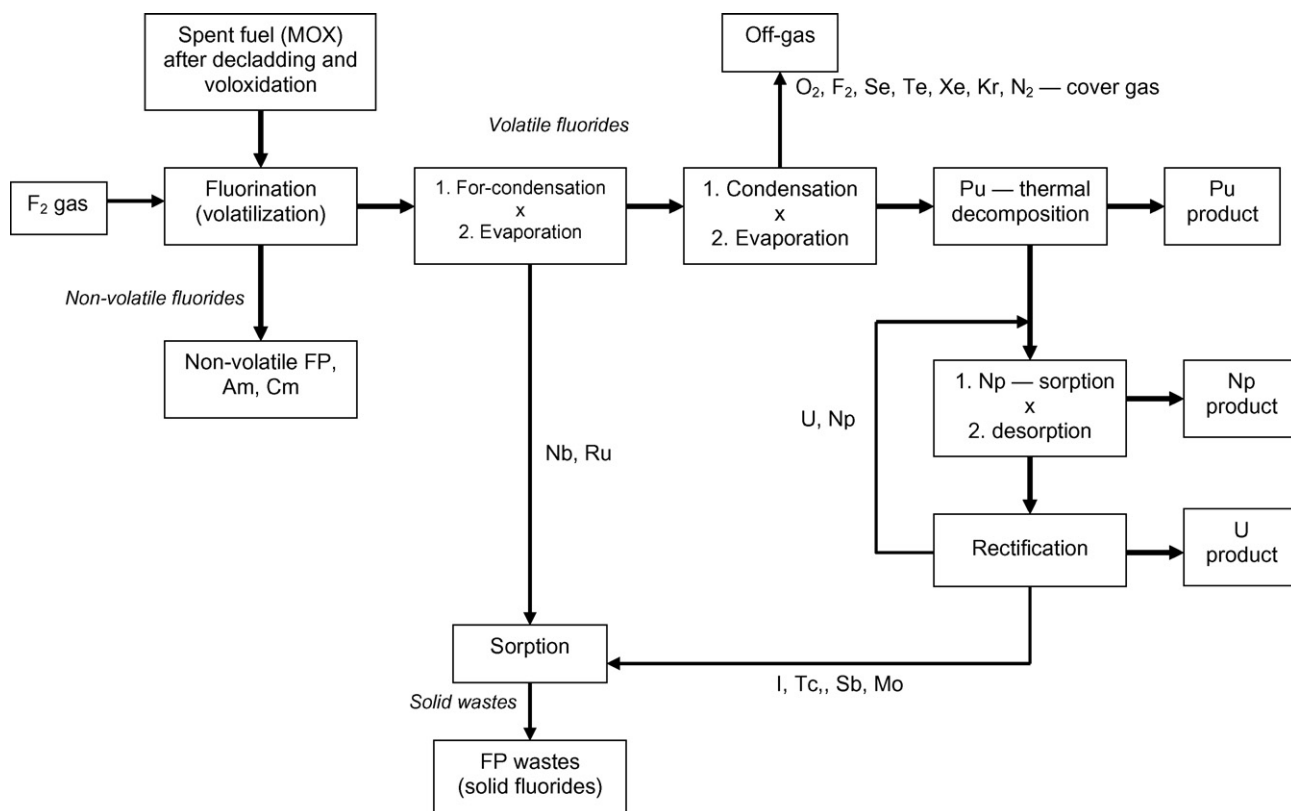


Fig. 1. Process flow sheet of fluoride volatility method.

running in 1980s during the FREGAT-2 program [4]. The FREGAT-2 technological line, which was realized in RIAR Dimitrovgrad hot cell was an attempt to reprocess the spent fuel from BOR-60 experimental fast reactor. Unfortunately the FREGAT-2 program was interrupted before the full verification of the equipment due to financial problems. The main apparatuses of FREGAT-2 line were in the ownership of NRI Řež plc and therefore they were returned back. Now, after substantial reconstruction they comprise the basic part of the FERDA line.

The current experimental R&D program of the verification pyrochemical reprocessing of current and advanced oxide fuel types was launched in 2004 by the NRI Řež plc. The aim of the nowadays activities is to develop the suitable pyrochemical technology, which should be used either for reprocessing of LWR spent mixed-oxide fuels (MOX) or for reprocessing of advanced types of fast reactor spent fuel, which cannot be reprocessed by common hydrometallurgical technology PUREX due to the high radioactivity of the spent fuel, poor solubility of some components (e.g. ZrO_2) of the fuel in nitric acid or due to high content of plutonium, which cause a criticality problem in case of hydrometallurgical technology.

The process flow sheet of investigated FVM technology is based on the direct fluorination of powderized spent fuel by fluorine gas and on the subsequent purification of volatile products by condensation, sorption, thermal decomposition and distillation is shown in Fig. 1. Here the main partitioning of spent fuel components is done in flame fluorinator during the fluorination reaction, when the group of non-volatile fluorides (most of fission products (FP) and americium and curium) remains caught in the ashpan in bottom part of the apparatus whilst the volatile fluorides of uranium, neptunium, plutonium and some fission products are successively trapped in the series of condensers or sorption columns. Here mostly ruthenium and niobium are separated from U, Np and Pu. After subsequent evaporation of uranium, neptunium and plutonium hexafluorides from second condenser, plutonium can be separated from uranium and neptunium by thermal decomposition of volatile PuF_6 according to Eq. (5). Neptunium is then separated by multiple sorption of NpF_6 on MgF_2 trap. Finally the purification of uranium from remaining volatile fission product fluorides (IF_5 , TcF_6 , MoF_6 , and SbF_5) is proposed by multiple distillations or by rectification of rough UF_6 . Main desired product of the reprocessing technology, which are uranium and plutonium are obtained in the form of volatile UF_6 and solid PuF_4 .

The current experimental R&D program is focused mainly to the technological verification of individual unit operations, apparatuses

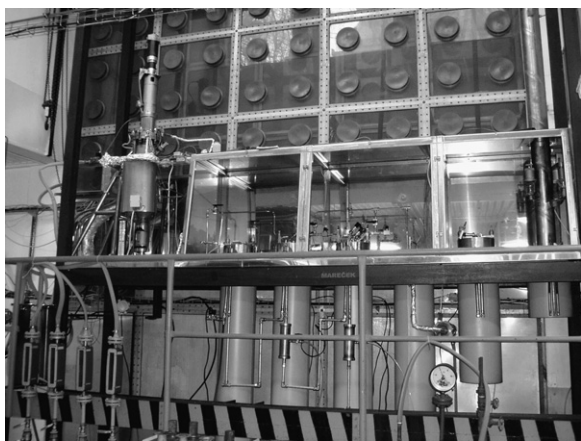


Fig. 2. Experimental line FERDA for R&D of fluoride volatility method (from the left: flame fluorination reactor, series of three condensers, sorption columns and distillation column).

Table 2

Achieved separation efficiencies of selected spent fuel components by using of fluoride volatility method

Chemical elements	Separation efficiency (%)
U	95–99.5
Pu	~98–99.5
Np	~60–70
Nb, Ru	~95–99
Am, Cm	Individually inseparable (in non-volatile fluoride stream)
FP forming solid fluorides	Individually inseparable (in non-volatile fluoride stream)

and material research and to the process control [12,13]. The experimental semi-technological line called FERDA, shown in Fig. 2, was manufactured and placed in the alpha-radiochemical laboratory of the NRI Řež plc. The technology consists of flame fluorinator, series of condensers, sorption columns and from distillation column. The short-run capacity of flame fluorination reactor is 1–3 kg of fuel per hour, but the process has a batch character and the maximum quantity of material processed during the experiment is about 7 kg. The pressure of pure fluorine gas taking from the cylinder is reduced by a regulator to about 1 atmosphere before entering the fluorination reactor, the flow of process gasses through the line is controlled by the vacuum system.

The main present experimental effort is focused to the mastering of the fluorination process and to the elimination of some bottlenecks of the technology. After the tests done with the uranium fuel (pure UO_2 or U_3O_8), the present program is aimed to the verification of the main unit operations with the simulated spent oxide fuel constituted from a mixture of uranium oxides and non-radioactive oxides representing selected fission products (lanthanides, Cs, Sr, etc.). The objective of the experiments with simulated spent fuel is the verification of the partitioning of volatile from non-volatile products of fluorination reaction. The next planned experiments should verify the suitability of the technology also for reprocessing of advanced types of oxide fuels, especially those containing selected inert matrixes (ZrO_2 and MgO). The achieved separation efficiencies of the FVM are discussed in Table 2. The anticipated difference in separation efficiency of uranium is dependent on the allowable content of neptunium in the uranium product.

4. Conclusions

Fluoride volatility method has a good potential to be used within the fuel cycles of several current or advanced reactor types for reprocessing of current or future advanced 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 high radiation resistance of the used chemical agents (fluorine gas and inorganic fluorides), which allows to reprocess the spent fuels after the cooling time of about 6 months only. Also the attractiveness to use FVM as the “Front-end” technology of Molten-Salt Transmutation Reactor is high due to the conversion of oxide form of original spent fuel into fluorides—the chemical form of Molten-Salt Reactors. Another attractiveness of the process comes out from the possibility to process those oxide fuel types, which are insufficiently soluble in nitric acid used in PUREX process, like oxide fuels with inert matrixes containing ZrO_2 or fuels with high content of plutonium. Further advantages of the technology come out from the achieved compactness of the whole process and from the exclusion of any moderating agent, which allows to handle higher amount of fissile material in smaller volume. However to reach the separation efficiencies similar those,

achieved by current industrial hydrometallurgical processes will require further intensive research and development.

Acknowledgements

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