



# Uranium and fluorine cycles in the nuclear industry

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## ABSTRACT

In the nuclear fuel cycle, fluorine is currently not recycled. In this paper, we have examined the possible routes to implement such a cycle. Because UF<sub>6</sub> deconversion requires an excess of water, aqueous HF is produced. Two alternatives are then possible: either separate HF from H<sub>2</sub>O or recycle the HF–H<sub>2</sub>O in the deconversion process. Alternative UF<sub>6</sub> deconversion could also be implemented to resorb the high UF<sub>6</sub> inventory.

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## 1. Introduction

The development of the nuclear industry based on limited natural uranium resources has led the way to an optimization of the use of uranium in the nuclear fuel. Major nuclear companies, such as AREVA, have long promoted the idea of a cycle for the uranium in the LWR (light water reactor). Uranium can be recovered after irradiation in the power plant for further conversion and enrichment in <sup>235</sup>U in order to make new fuel. Also the <sup>235</sup>U depleted uranium coming out from the enrichment plants can be used to prepare MOX (mixed oxyde) fuel, since plutonium can also be recycled from the irradiated fuel. Fig. 1 shows the sequential steps of the U cycle together with the theoretical quantities that can be used.

On the long term, the energetic value of <sup>238</sup>U will be put in use in the fast breeder reactors, further limiting the need for natural resources. For these reasons, depleted or reprocessed oxides are temporarily also stored in the U<sub>3</sub>O<sub>8</sub> form.

In the conversion and enrichment steps of the fuel cycle, uranium and fluorine are intimately linked. However, contrary to uranium, fluorine is not currently recycled. In this paper, we have tried to outline the scientific and technical issues for implementing a “F” cycle in the nuclear industry. With increasing cost of raw materials, F recycling might become attractive for the nuclear industry.

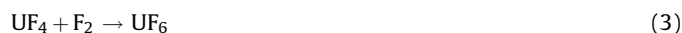
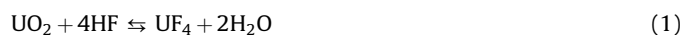
## 2. Principles for conversion and deconversion of UF<sub>6</sub>

The development of the “U” fuel cycle has prompted the rise of large-scale HF electrolysis and F<sub>2</sub>-based uranium chemistry. Indeed, <sup>235</sup>U enrichment technologies, such as centrifugation or gas diffusion, require a relatively low boiling point compound that UF<sub>6</sub>, uranium hexafluoride, readily provides. Also fluorine has only one isotope <sup>19</sup>F which is not the case for other halides. This is important because the centrifugation or diffusion processes are based on mass differentiation between <sup>235</sup>U and <sup>238</sup>U.

During the centrifugation, UF<sub>6</sub> molecules are introduced in very high speed rotating cylinders operating at low pressure. Depleted <sup>235</sup>UF<sub>6</sub> is recovered at the bottom of the cylinder and enriched UF<sub>6</sub> at the top. Thousands of cylinders are positioned in series.

In gaseous diffusion, UF<sub>6</sub> gas goes through ceramic membranes whose pores are smaller than the mean free path of the UF<sub>6</sub> molecules.

The main equations for fluorination currently used in the nuclear industry are the following:



Fluorine must be later separated from uranium in the following steps of the U cycle. Indeed, it must not be introduced in the UO<sub>2</sub> fuel. A specification as low as 20 ppm is internationally set (see for

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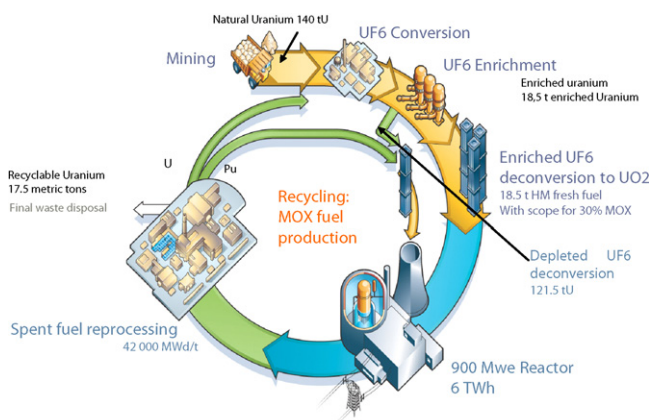
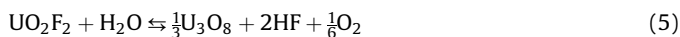


Fig. 1. Uranium cycle.

example the ASTM standard C26-753). Fluorine can be detrimental the Zircaloy cladding and also during the processing stages of the spent fuel. Fluorine is therefore removed during the deconversion stage of the  $UF_6$  to oxide powder before preparing the fuel. The general deconversion equations and process are shown below:



In Eq. (5), either  $U_3O_8$  or  $UO_2$  can be obtained depending if  $H_2$  is added or not.  $UO_2$  will be needed if the uranium is immediately used for the fuel (mostly enriched U) and  $U_3O_8$  if the uranium is meant for intermediate storage (mostly depleted U).

The only facility in the world that has accomplished for more than 20 years the depleted  $UF_6$  deconversion is AREVA's W plant, located in France (Fig. 2). Except in France, most of the depleted  $UF_6$  generated by enrichment plants has not been yet deconverted to  $U_3O_8$ , leading to a large accumulation of  $UF_6$  tails cylinders, limiting the possibility to recycle most of the "F". An inventory of more than  $500 \times 10^3$  tons of equivalent HF is currently in the  $UF_6$  form. However new deconversion units will start in the near future

in Russia and in the United States, opening the way to new considerations regarding the implementation of a "F" cycle.

F recycling would limit the transportation of large quantities of anhydrous HF used in the conversion and limit the need of fresh  $CaF_2$  ore, used for HF production. Also it would avoid the need to dispose of aqueous HF that has been in contact with U.

In Eq. (5) and to a lesser extent in Eq. (4), an excess of  $H_2O$  is needed to ensure complete pyrohydrolysis of the  $UO_2F_2$  or the  $UF_6$ . As a consequence, the resulting HF is in the low value aqueous form, typically 50–85 wt% HF. Since anhydrous HF is needed for the electrolysis to produce  $F_2$ , a  $H_2O$ –HF separation is necessary in order to fully recycle the F. However the HF– $H_2O$  system displays an azeotropic point at  $\approx 38\%$  HF. For example a simple distillation of 70 wt% HF will approximately yield half the F in the anhydrous form and half in the azeotropic composition. Because of this incomplete separation, HF recycling in the nuclear industry has not been implemented yet (Fig. 3).

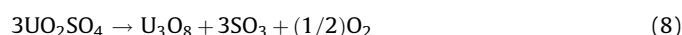
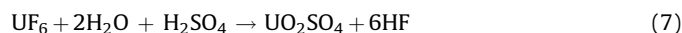
### 3. Alternative routes for $UF_6$ deconversion

As an alternative, the reaction of  $UF_6$  with  $H_2$  which produces anhydrous HF, has been considered

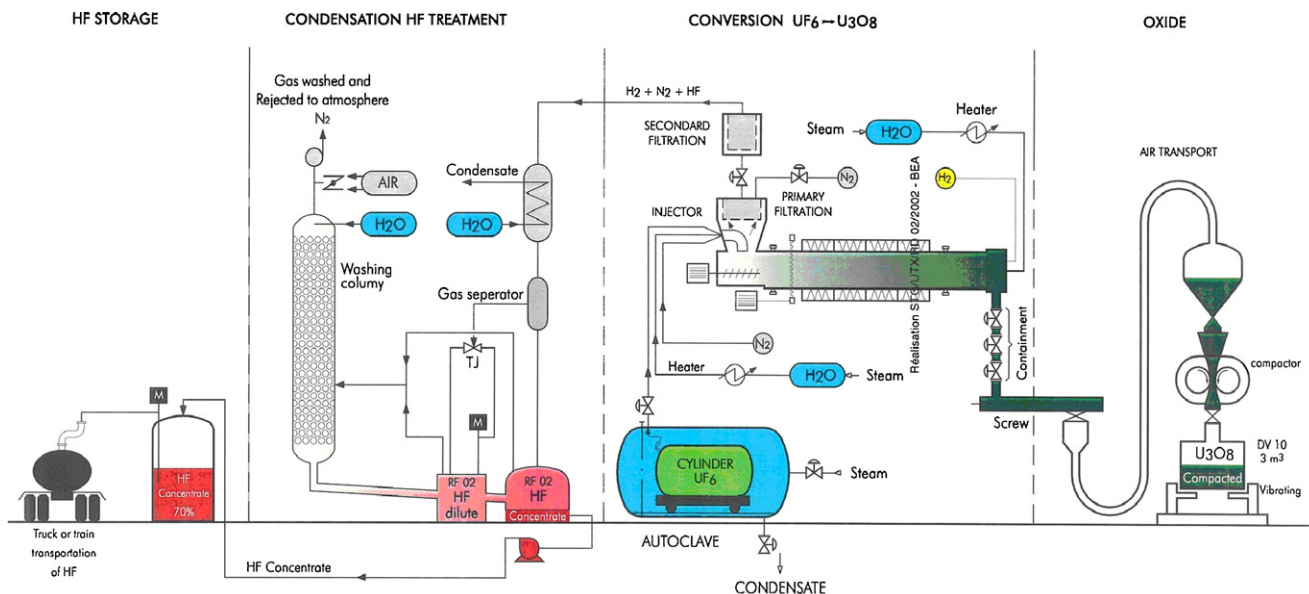


But then the  $UF_4$  must be hydrolysed to the oxide. In some publications [1], the  $UF_4$  was reacted with  $SiO_2$ ,  $B_2O_3$  or  $GeO_2$  to produce an uranium oxide together with  $SiF_4$ ,  $BF_3$  or  $GeF_4$ . However only 1/3 of the F is then recycled and the metal fluorides are always slightly contaminated with U. The  $UF_4$  can also be pyrohydrolysed at  $700^\circ C$  to  $UO_2$  or  $U_3O_8$  according to Eq. (1) but an excess of water is necessary therefore leading to aqueous HF.

Another route consists of hydrolysing the  $UF_6$  with sulphuric acid [2], producing  $UO_2SO_4$  which can then be thermally decomposed to  $U_3O_8$  and  $SO_3$  (later recovered as sulphuric acid).



The same applies when sulphuric acid is replaced by phosphoric acid. However with such processes, entrained traces of sulphur or

Fig. 2.  $UF_6$  French deconversion process.

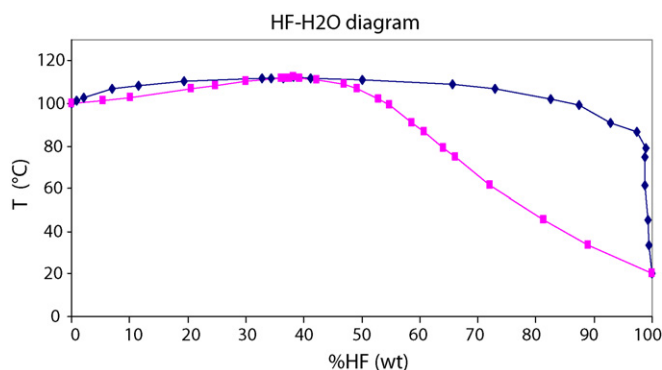


Fig. 3. HF–H<sub>2</sub>O diagram.

phosphor compounds (such as SO<sub>3</sub> or HSO<sub>3</sub>F) might be a problem when the HF is recycled in the F<sub>2</sub> electrolytic cells [17]. Also the corrosive properties of HF–H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O must be considered.

Finally, since UF<sub>6</sub> is both an oxidative and fluorinating agent, direct reaction with organic compounds have also been envisioned in order to prepare for example R134a [3] or other C2 to C8 fluorinated compounds [4,5].



A review on the use of this very pure UF<sub>6</sub> in the organic industry has been recently published [6]. However, with such an approach, the F is not recycled and the obtained fluorinated product may contain traces of U which may not be appropriate for the non-nuclear industry. None of these alternatives have been put into very large-scale industrial use. However they might be needed in the future to resorb the large UF<sub>6</sub> inventory.

#### 4. HF–H<sub>2</sub>O separation techniques

The separation of HF from H<sub>2</sub>O has been extensively studied in the last 6 decades due to the development of fluorination processes. However not all technologies may be adapted for the treatment of large quantities of HF. The reference process is still considered the distillation with sufficient plates to reach less than 200 ppm water.

In order to break the azeotrope, one of the most promising addition compound is sulphuric acid. In a very similar way to the HNO<sub>3</sub>–H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O system, the addition of concentrated H<sub>2</sub>SO<sub>4</sub> tends to lower the vapor pressure of water and stimulates the transition of HF in the vapor phase [7]. A second distillation column is necessary to separate H<sub>2</sub>SO<sub>4</sub> from H<sub>2</sub>O in order to recycle the sulphuric acid and dispose of the water [8]. The same reserves than in [2] may apply: corrosion issues, purity of HF and H<sub>2</sub>O, build-up of impurities such as UO<sub>2</sub>F<sub>2</sub> in the recycled H<sub>2</sub>SO<sub>4</sub>.

Other third body compounds have been reported [9], such as ethylene glycol. This is a multi-stage distillation and the long-term stability of the glycol with HF has to be addressed. Other distillation processes have been patented [10], but resulting in even more distillation columns.

As an alternative to the high energy cost multi-distillation, liquid/liquid extraction has been considered to break the azeotrope resulting from the standard distillation. The most promising compounds are ternary amines [11], following the idea of the strong complex formed between F<sup>−</sup> and NH<sub>4</sub><sup>+</sup>. However the HF-amine re-extraction must be performed at elevated temperature (such as 260°C) which may cause some decomposition of the amine. Also water is also extracted with the amine, leading to an additional step where water is removed.

Another process which has been considered in conjunction with distillation is the absorption on high surface area fluoride pellets such as NaF, KF or LiF [12,13]. HF is absorbed at a temperature where water is not absorbed, typically 80–120°C and the pellets are then heated to 260–500°C to recover HF. Aging of the pellets must be considered due to dust formation in the repeated temperature cycles. The capacity of absorption depends on the solid but also on the temperature and pressure, typically HF/NaF = 0.5 can be obtained at 100°C [14]. This process is often considered for small HF streams containing little H<sub>2</sub>O content.

Finally, other techniques such as ionic exchange, membrane electro dialysis, high temperature reduction of water with carbon, have been published but are not considered adapted to the multi-thousand tons scale. The precipitation of HF with Ca(OH)<sub>2</sub> and the introduction of dried CaF<sub>2</sub> to prepare anhydrous HF and CaSO<sub>4</sub> in the chemical industry (as with fluorspar) is not considered economically attractive and leaves unresolved the potential problem of trace U in the CaF<sub>2</sub>.

#### 5. Recycling azeotropic HF–H<sub>2</sub>O

Since alternative routes for deconversion do not seem promising and that the separation of the azeotrope does not seem industrially attractive, a third option remains to directly recycle the azeotrope in the conversion or deconversion process. This means either using the water present in the azeotrope to further hydrolyse UF<sub>6</sub> in Eq. (4) or the HF present to react with UO<sub>2</sub> in Eq. (1).

However Eq. (1) is an equilibrated reaction whose constant depend on the temperature (see Fig. 4). Therefore injection of large quantities of the azeotrope at this stage may displace the equilibrium and produce detrimental UO<sub>2</sub>/UF<sub>4</sub> mixtures.

Contrary to Eq. (1), Eq. (4) is not reversible and the hydrolysis of UF<sub>6</sub> is possible with mixture of HF–H<sub>2</sub>O. In 1994, a patent from Sequoyah Fuels [15] described the method for recovering U<sub>3</sub>O<sub>8</sub> and a commercial grade anhydrous hydrogen fluoride using this

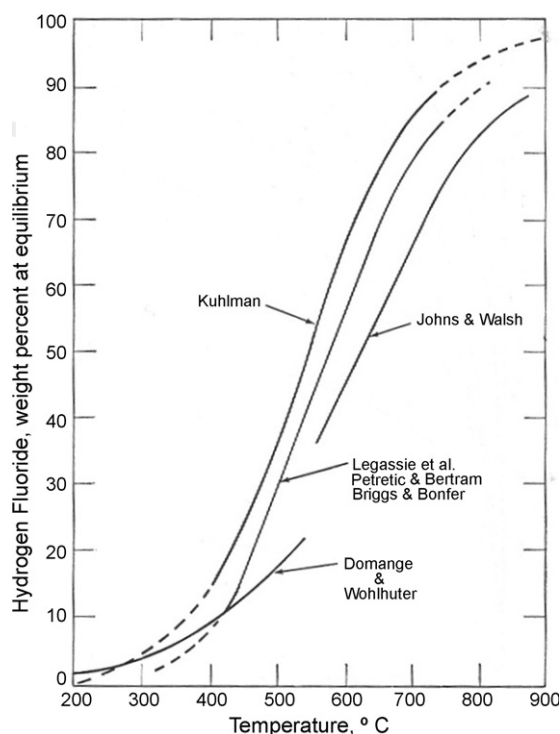


Fig. 4. Equilibrium composition of HF–H<sub>2</sub>O in Eq. (1).

reaction. The method still considers the distillation as the first step of the process. Aqueous HF coming from a deconversion kiln is directed to the distillation column. HF azeotrope is collected at the bottom of the distillation column when anhydrous HF is recovered as the top. HF azeotrope is reinjected in the kiln, used in place of steam water for the hydrolysis of  $\text{UF}_6$  into  $\text{UO}_2\text{F}_2$ .

The mass balance of all the reactants is equilibrated in such a way that the steam water from azeotrope HF need for the hydrolysis reaction ( $\text{UF}_6$  to  $\text{UO}_2\text{F}_2$ ) is equal to the water in excess for the endothermic pyrohydrolysis reaction ( $\text{UO}_2\text{F}_2$  to  $\text{U}_3\text{O}_8$ ).

A pilot plant operated up to 1998 in Metropolis [16] to demonstrate the feasibility of this process producing 600 kg anhydrous HF.

Anyway at that time this process appeared the most promising way for the complete beneficial reuse of HF coming from the deconversion process.

The pilot faced problems of corrosion and difficulties to exactly equilibrate the mass balance of the reactants.

## 6. Conclusion

With the worldwide “renaissance” of the nuclear industry and increasing demand on raw materials, the introduction of a F cycle seems probable in the future. Considering the very large depleted  $\text{UF}_6$  inventory plus the future production, total quantities of potential anhydrous HF (HFa) coming from the deconversion will be higher than the HFa conversion demand, even this demand is

expected to increase in the near future. Both reuse of this HFa in and out the nuclear fuel cycle need to be considered. However the reuse of a maximum of this HFa inside the nuclear cycle is more than an opportunity. It will be a major beneficial discriminator. Nuclear companies programming implementation of both conversion and deconversion units on a same site will be favored.

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