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Depleted uranium hexafluoride—The fluorine source for production of the inorganic and organic compounds

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ABSTRACT

The methods of the transfer of depleted uranium hexafluoride into the safer chemical forms have been analyzed. The depleted uranium hexafluoride is the very valuable source of the high-purity fluorine that it may be used for the production of the pure fluorine-containing compounds. The need for processing of hydrogen fluoride obtained as a result of depleted uranium hexafluoride (DUF_6) conversion, as a result of its high chemical and toxicological hazard. The methods and ways of fluorine application in different fields of science and technology are contained in DUF_6. Basic direction of fluorine application, contained in DUF_6, is nuclear fuel cycle.

1. Introduction

The process of enriched uranium production suitable for fabrication of nuclear fuel for power plants consists in separation of two uranium isotopes with the help of gaseous chemical compound – uranium hexafluoride. Isotope separation is carried out by different methods (diffusion, centrifuge and others) obtaining two fractions. In one fraction the content of $^{235}UF_6$ increases and in the other – the content of $^{235}UF_6$ decreases. The process of isotope separation is aimed to get the fraction with increased content of $^{235}UF_6$, this fraction is called enriched uranium hexafluoride. Another fraction is called depleted uranium hexafluoride (DUF_6). The content of ^{235}U in natural uranium is only 0.71% (mass) that is why the main part of uranium processed at separation plants is DUF_6 [1–4].

Within the period of enrichment plants operation about 1.7 million tons of DUF_6 have been accumulated and its stocks continue to increase by about 50 thousand tons annually [3]. At present one part of DUF_6 produced by diffusion separation with the content of $^{235}UF_6$ 0.2–0.5% goes to additional recovery of desired isotope by centrifuge technology where the content of $^{235}UF_6$ may be reduced up to 0.1% and even lower. The main part of DUF_6 is stored in special guarded open-air yards in steel 2.5–4 m^3 containers. Each container holds 10–15 tons of DUF_6 [3–5].

The main danger of long-term storage of DUF_6 in open-air is the possibility of uranium compounds to get out of container in environment (atmosphere, water resources, soil) in case of containers damage. Uranium hexafluoride is easily hydrolyzed by moisture (including atmospheric) and forms radiological hazardous uranyl fluoride and very toxic gaseous hydrogen fluoride. As a result of civilization development and negative factors connected with this development (the main of them is international terrorism and political adventurism) the need to reduce the risk of man-caused cataclysms (plane crash, missile attack, etc.) connected with DUF_6 storage appears. One of the most promising way to reduce the risk is DUF_6 conversion into safer forms of uranium – mixed oxide, uranium tetrafluoride, dioxide – U_3O_8, UF_4, UO_2 correspondingly. Moreover while conversion of UF_6 into these compounds fluorine releases. The estimation shows that the total quantity of fluorine in the world's supply of DUF_6 is 550 thousand tons or 580 thousand tons if convert from anhydrous HF (AHF).

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DUF_6 may be qualified as nuclear-pure compound that is its main advantage. That is why fluorine contained in DUF_6 will be chemically pure. Thus the main problem of developed DUF_6 conversion technologies is to use this pure fluorine in production of other fluorine-containing compounds.

2. Results and discussion

Different technologies of DUF_6 processing are worked out in the world [3–13]. Each of them has its advantages and disadvantages. Currently one of the main factors of expediency of application of one or another technology is economic indicator.

Now there are five promising methods of DUF_6 conversion into safe chemical forms (Fig. 1).

1. Reduction by alkenes and production of ozone safe khladons

$$UF_6 + R_{Cl} \rightarrow UF_4 + R_{Cl,F} \qquad (1)$$

2. Chemical conversion in water plasma

$$UF_6 + 3(H^+ + OH^-) = 1/3U_3O_8 + 6HF + 1/6O_2 \qquad (2)$$

3. Pyrohydrolysis

$$UF_6 + 3H_2O = 1/3U_3O_8 + 6HF + 1/6O_2 \qquad (3)$$

4. Reduction by hydrogen in fluorine–hydrogen flame

$$UF_6 + H_2 = UF_4 + 2HF \qquad (4)$$

5. Chemical reduction in hydrogen plasma

$$UF_6 + 2H^{\bullet} = UF_4 + 2HF \qquad (5)$$

Let us analyze every method.

2.1. Khladons production

According to this technology DUF_6 is converted to UF_4, it may be stored for a long time and may be applied in further treatment. Uranium tetrafluoride practically does not react with moisture and if under the circumstances it gets to natural objects it will not be widespread. The other product of DUF_6 conversion according this technology is ozone-safe khladons being required in industry. The main disadvantages of this technology are:

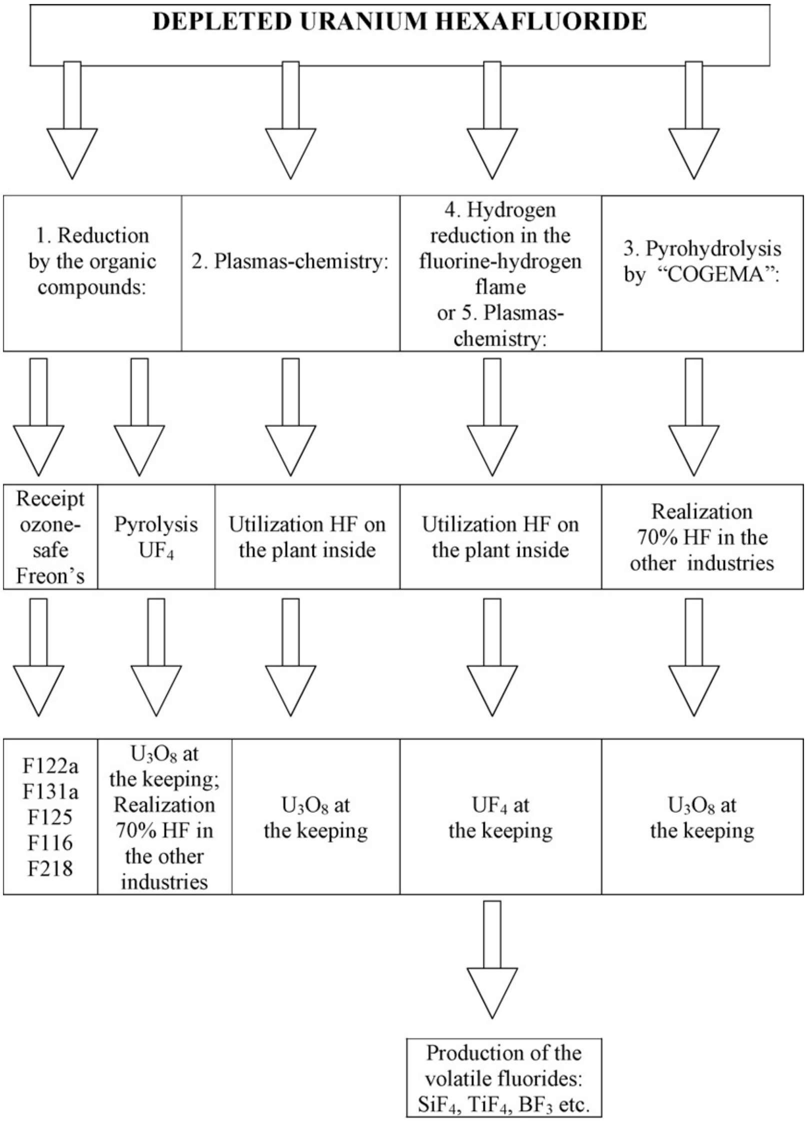

Fig. 1. Conversion methods of DUF_6.

1. Production of only one conditioned product – either khladons or tetrafluoride;
2. Formation of by-products – fluorine- and chlorine-containing that are to be dehydrated.

2.2. Chemical conversion in water plasma

According to this technology of conversion practically insoluble in water uranium compound U_3O_8 is formed as well as HF. The advantage of the method – the process has only one stage and cheap reagent –water. Uranium oxide is formed, it has high bulk density – up to 5 g/cm^3. Moreover HF is formed as 95–97% hydrofluoric acid suitable as fluorinating agent in different fields of industry including the production of AHF. The essential disadvantage of the method is large power inputs. Besides desired product U_3O_8 needs additional stage of residual fluorine removal (to 0.1%) by high-temperature glowing.

2.3. Pyrohydrolysis by water vapor

In industrial scale French firm «COGEMA» realizes this method. By now this method allowed processing about 190 thousand tons of DUF_6. Practically all advantages and disadvantages of this method are the same as of DUF_6 conversion in water plasma. As a rule end product U_3O_8 contains up to 0.5% (mass) of fluorine, that causes additional troubles during its storage.

2.4. Reduction by hydrogen in fluorine–hydrogen flame

Obtained UF_4 has practically no impurities besides minimum of non-reduced uranium. This is the advantage of the method. Formed AHF has only the traces of uranium. In comparison with other methods of DUF_6 the quantity of produced AHF is not large and this product does not need further purification. Besides obtained uranium tetrafluoride has moderate bulk density (1.5–2.7 g/cm^3). The main disadvantage of the method is the necessity to apply deficit molecular fluorine. Now investigations are held to minimize the consumption of fluorine and hydrogen. The process of DUF_6 conversion at installation "Kedr" is presented in Fig. 2.

2.5. Chemical reduction in hydrogen plasma

This method has the same advantages and disadvantages as the previous method but in this technology molecule fluorine is not used and significant energy consumption is required. It is significant that UF_4 may be produced by UF_6 reduction in gaseous hydrogen obtained as a result of ammonia dissociation.

This method was applied in experimental-industrial scale in the middle of the 1990's in the Republic of Korea [3]. The main difficulty was connected with the formation of ammonium hydrofluoride.

Thus HF production (either anhydrous or in the form of aqueous solutions) is typical for all the methods of DUF_6 conversion. Moreover uranium tetrafluoride obtained by methods 1 and 4 contains sufficient mach fluorine (2/3 of its content in DUF_6). Fluorine recovery will require additional costs and this process will be rational only in case of need for fluorine in the concrete process.

AHF may be applied as work material to get elementary high-clean fluorine that will be reused in the technology of natural uranium hexafluoride.

Hydrogen fluoride is possible to use not only in different fields of industry but also in the production of cryolite applied in electrochemical production of metallic aluminum, in synthetic fluor-spar production and in quartz production and many others [14]. It is possible to produce about one million tons of cryolite Na_3AlF_6 from the world's reserves of fluorine concentrated in DUF_6. The technology of quartz production includes flotation to separate quartz from brood. The solutions of hydrofluoric acid are used as floating agents. In Russia there are eight plants of quartz production, their annual need in hydrofluoric acid is about 10 thousand tons (4 thousand tons of AHF).

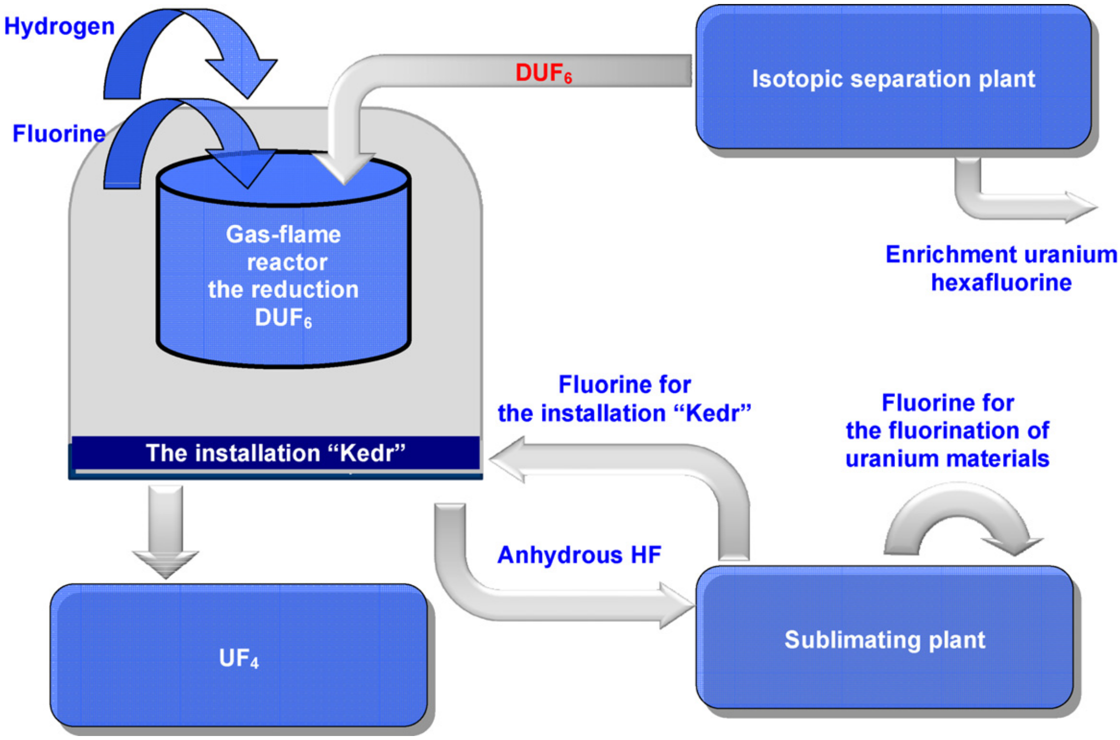

Fig. 2. The processing of DUF_6 at the conversion installation "Kedr".

Let us examine some directions of DUF_6 use and the products of its conversion too. We consider that the most productive process relative to application of fluorine from DUF_6 will be the process that uses UF_6 as fluorinating agent. It is significant that UF_6 is the fluorinating agent of middle power because of its chemical activity. It is stronger than the highest fluorides of the elements of IV, V, and VI transition groups except the highest fluorides of chromium and ruthenium CrF_5, CrF_6 and RuF_6 but it is less active than the highest fluorides of transuranium elements, in particular PuF_6 and NpF_6. However at high temperature UF_6 will be sufficiently powerful oxidizing agent. Taking into consideration the oxidizing power UF_6 may be compared with such fluorinating agents as JF_6, HgF_2 except CoF_3, F_2 and ClF_3 [15–17].

The only method of UF_6 conversion from examined above and offering the advantage is the process of ozone-safe khladons production. Khladons -122a, -132c, -134a, -218 and their mixtures are recovered by this method [6,12,13].

Besides the production of ozone-safe khladons, UF_6 is possible to be used for the production of fluoroelastomers and fluorocarbon polymers. Technology consists in the fluorination of perchlorethylene by depleted uranium hexafluoride with khladon-12 production that may be converted into khladon-113 by the method of catalytic fluorination. Khladon-113 may be dechlorinated to obtain the monomer $CF_2 = CFCl$. This compound is the basis of fluoroelastomers and fluorocarbon polymers production and after oligomerization for the production of different fluorinechlorinecarbon liquid with good dielectric properties. These compounds are recommended to use in power transformers instead of flammable hydrocarbon oils and highly toxic polychlorinebiphenyl.

Nevertheless uranium hexafluoride as fluorinating agent can also be used in the production of secondary fluorine-agents and mother compounds for subsequent production high-purity metals, for example by precipitation from gas phase. These processes are illustrated by the following chemical reactions [3,4,18,19]:

$$CO + UF_6 = COF_2 + UF_4 \tag{6}$$

$$WF_4 + UF_6 = WF_6 + UF_4 \tag{7}$$

$$MoF_4 + UF_6 = MoF_6 + UF_4 \tag{8}$$

$$PF_3 + UF_6 = PF_5 + UF_4 \tag{9}$$

$$H_2S + 3UF_6 = SF_4 + 2HF + 3UF_4 \tag{10}$$

$$SiO_2 + 2UF_6 = SiF_4 + 2UF_4 + O_2 \tag{11}$$

$$CS_2 + UF_6 \rightarrow SF_6 + (CF_3)_2S_n + UF_4 \tag{12}$$

In spite of advantages of direct use of UF_6 in organic and inorganic synthesis the quantity of accumulated DUF_6 requires efficient conversion into safe chemical forms.

Let us examine the possible directions of uranium tetrafluoride processing. UF_4 obtained in the process of reduction by metallic calcium or magnesium may be converted into metallic uranium suitable for subsequent storage or application in magnets, semiconductors and catalysts production [1–4]. Produced CaF_2 may be used for hydrofluoride production according to the classical technology [14]. The other methods of uranium tetrafluoride conversion are the conversion into oxides by interaction with the oxides of p- and d-elements of III, IV and VI groups of Mendeleev's periodic table and volatile fluorides formation according to general reaction [6,21–23]:

$$UF_4 + MO_n = UO_2 + MF_m, \tag{13}$$

where M = B, Si, Ge, Ti, W; n, m = 1, 2, 3, ...

In report [24] it has been proved that mechanochemistry plays a large role in solid-phase processes according the reaction (13). High-purity volatile fluorides of boron, silicon, germanium, titanium and others with minimum impurities content are formed as a result of such processes.

Obtained oxide uranium compounds are ecologically safer than DUF_6. They can be stored for practically unlimited period of time in waterproof containers in open-air yards. In future depleted uranium dioxide can be applied in the fast-breeder reactors or as protective material from neutron- and gamma-emissions [2–5].

As mentioned above practically in all cases of DUF_6 conversion hydrogen fluoride, anhydrous or in the form of hydrofluoric acid solutions are formed. HF storage especially in the presence of moisture possesses strong corrosiveness. HF is more toxic than UF_6 and many other fluoride compounds. Fluorine ion is universal cell poison and strong dehydrating compound and has affect upon all sell structures of plant and animal organisms [25–27]. That is why HF obtained as a result of DUF_6 conversion is to be immediately directed to the adjoining technological processes.

Conversion of 70% hydrofluoric acid by DUF_6 Pyrohydrolysis into calcium fluoride makes it possible to produce end product – synthetic fluorite concentrate that is much in demand at the enterprises of atomic industry and other fields of industry. The advantage of fluorine conversion into CaF_2 is easy transportation to the consumer owing to chemical inactivity and low toxicity. Besides it is possible to obtain anhydrous hydrogen fluoride without impurities from 70% hydrofluoric acid by treatment with oleum. Hydrofluoric acid and AHF are produced as a result of rectification. It is necessary to note that rectification easily joints the functioning production of anhydrous hydrogen fluoride.

The processes of hydrofluorination of the oxides of different metals make up one of the way of AHF application. Taking into account the potential presence of uranium impurities in AHF it is advisable to use oxides of natural or regenerated uranium with subsequent fluorination to UF_6 and isotope separation. In this very case fluorine gets into the cycle and it is very valuable because the need for AHF production from mineral resources decreases.

One more direction of AHF application is the production of molecular fluorine and halogens fluorides is the production of uranium fluorides and fluoride adsorbent for the processing of gas mixtures and its recovery from process and exhaust gases of sublimation–separation cycle of the uranium plants [28–32].

To solve the problem of application of AHF obtained from DUF_6 in the other fields of industry it is necessary to develop the methods for deep purification of AHF from uranium admixture to 1–2 ppm right up to its natural content in the most part of natural objects.

3. Conclusion

1. DUF_6 is valuable source of high-purity fluorine that may be applied in the production of pure fluorine-containing compounds.
2. The methods of DUF_6 conversion into safer chemical forms for long-term storage in the open-air yards were examined.
3. The need for hydrogen fluoride processing from DUF_6 conversion because of its high chemical and toxicological danger was well founded.
4. The methods and ways of fluorine application in different fields of science and technology were proposed. The main direction of fluorine application from DUF_6 is nuclear fuel cycle.

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