Deactivation of Molybdenum Scrap from Uranium Dioxide Production and Developing a Fluoride Technology for Its Processing

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Abstract

Deactivation and processing of the man-caused wastes of molybdenum from the production of uranium dioxide by means of fluorination with elemental fluorine were studied. The level and depth of molybdenum contamination with radioactive substances were established, the major physicochemical parameters of molybdenum fluorination were determined: the equilibrium composition, duration and conditions of reaction. The apparent activation energies were determined, and kinetic equations were deduced.

Key words: molybdenum, uranium dioxide, waste, fluorination, kinetics, deactivation

INTRODUCTION

All the known methods for processing molybdenum metal waste are based on the dissolution of the metal in acid and alkali and the subsequent production of artificial powellite ($CaMoO_4$), sodium molybdate (Na_2MoO_4) or ammonium paramolybdate ($3(NH_4)_2O \cdot 7MoO_3 \cdot 4H_2O$). Further, these compounds are processed by means of a usual flowchart together with the ore concentrates to produce molybdenum trioxide or molybdenum metal [1, 2]. It should be noted that the man-caused raw material is characterized by high purity metals, since it is used in such high-tech fields as electrical, chemical, nuclear, *etc.* industries. In this context, processing it with ore concentrates is inappropriate. But if the molybdenum production wastes can be processed by means of the traditional technology, the wastes of molybdenum contaminated with radioactive substances should be disposed or recycled at radiochemical plants. The processing of molybdenum wastes is caused by its scarcity and very high cost.

So, in the case of producing fuel uranium dioxide pellets, at the final stages of sintering in a hydrogen atmosphere producers use molybdenum boats (containers) those after the loss of the mechanical strength are removed from the production process. Because the molybdenum surface is contaminated with uranium, the wastes are not processed, but stored at the enterprises of the nuclear industry. The amount of molybdenum waste for the entire period of the production of uranium dioxide in Russia is more than 300 t.

The fluoride technology proposed for processing molybdenum waste formed in the course of the production of uranium dioxide comprising the following steps: chemical removal of molybdenum surface layer contaminated by uranium oxide, molybdenum waste fluorination by elemental fluorine, purifying molybdenum hexafluoride, reducing molybdenum hexafluoride with hydrogen in the gas phase to yield metal molybdenum. Such a flow chart is compatible with the basic technology implemented in the nuclear industry, and it exhibits

TABLE 1

Thermodynamic parameters for the reactions of Mo and U_3O_8 fluorination by fluorine (*1*) and (2)

Temperature, K	ΔH_T^o, kJ/mol	ΔS_T^o, J/(mol · K)	ΔG_T^o, kJ/mol
25	−1550.0/−2980.0	−43.9/−872.1	−1536.9/−2720.1
300	−1703.2/−2989.2	−651.3/−618.7	−1312.4/−2618.0
700	−1879.0/−3004.6	−875.2/−638.2	−1003.8/−2366.4
1100	−2060.5/−	−1027.8/−	−621.6/−

Note. The first value stands for reaction (1), the second value stands for reaction (2).

incontestable advantages with respect to the traditional methods of refractory metal waste processing, in particular, a small number of stages and the absence of liquid waste.

In order to develop the technology it is necessary to determine the depth and the level of contamination for the molybdenum surface with radioactive substances, the thermodynamic and kinetic process parameters for the fluorination of lumpy molybdenum metal wastes from the production of uranium dioxide.

THERMODYNAMICS OF URANIUM OXIDE
AND MOLYBDENUM FLUORINATION BY FLUORINE

The overall reaction for the process of the fluorination of molybdenum waste contaminated with uranium oxides could be presented as it follows:

$$Mo + 3F_2 = MoF_6 \tag{1}$$
$$U_3O_8 + 9F_2 = 3UF_6 + 4O_2 \tag{2}$$
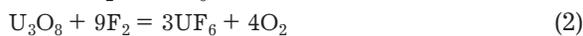
The thermodynamic modelling of the equilibrium composition for Mo−U−F−O system within the temperature range of 25−1200 °C was performed using TERRA automatic thermodynamic calculation system. The initial composition of the mixture was chosen basing on the results of radiometric and spectrophotometric analysis of molybdenum waste. The mass fraction of uranium in molybdenum after the use amounts to $2 \cdot 10^{-3}$ %, and only the inner surface of the boat is predominantly contaminated, that was in a direct contact with uranium oxides in the course of the operation [3−5].

The results of thermodynamic calculations demonstrate that the reactions (1), (2) occur with the release of heat, whereas within temperature range under consideration (25−1100 °C) the equilibrium is irreversibly shifted toward the formation of molybdenum hexafluoride and

uranium hexafluoride. Table 1 demonstrates the results of the thermodynamic calculation for the process of fluorination according to reactions (1) and (2).

Table 2 presents the values of the equilibrium composition for the Mo−U−F−O system depending on the temperature.

It can be seen that the main components of the equilibrium mixture at the temperature values lower than 700 °C are presented by MoF_6 and UF_6. Appearing the lower molybdenum and uranium fluorides at the temperature values higher than 950 °C among the products of fluorination could be caused by a thermal decomposition of the mentioned hexafluorides. The presence of oxygen in the system results in the formation of molybdenum and uranium oxyfluorides, and with increasing the temperature the equilibrium content of oxyfluorides and intermediate molybdenum and uranium fluorides exhibits an increase.

In the industry, owing to a severe corrosion of equipment the fluorination process is carried out at the temperature values lower than 600 °C. However, when the fluorination of large amounts of molybdenum and uranium oxides is performed, owing to a high exothermicity of the process in the layer of the initial materials there could develop a temperature higher than 1200 °C.

Data presented in [6] can be considered an experimental confirmation of the presence of molybdenum fluoride in different oxidation states in the gas phase. The authors of this work with the help of infrared spectrometric analysis determined the composition of the gas phase resulting from molybdenum fluorination with elemental fluorine. Depending on the initial temperature of fluorination, in the spectra there were detected molybdenum fluorides of vari-

TABLE 2

Equilibrium composition of Mo−U−O−F system depending on temperature. System pressure equal to 0.1 MPa; the composition of the initial mixture, mass %: Mo 45.57, U_3O_8 0.13, F_2 54.3; excess F_2 0 % with respect to the stoichiometry according to reactions (1), (2)

Compounds	Equilibrium composition, mol					
	Reaction temperature, °C					
	25	200	450	700	950	1200
$MoOF_2$	0	0	0	0	$7.26 \cdot 10^{-20}$	$5.83 \cdot 10^{-13}$
$MoOF_3$	0	0	0	$2.65 \cdot 10^{-18}$	$6.59 \cdot 10^{-11}$	$7.60 \cdot 10^{-7}$
$MoOF_4$	0	0	$1.15 \cdot 10^{-16}$	$2.86 \cdot 10^{-11}$	$4.17 \cdot 10^{-7}$	$3.41 \cdot 10^{-5}$
MoO_2F	0	0	0	0	0	$2.02 \cdot 10^{-17}$
MoO_2F_2	0	0	$4.18 \cdot 10^{-21}$	$4.74 \cdot 10^{-13}$	$2.34 \cdot 10^{-6}$	$1.26 \cdot 10^{-3}$
MoF_3	0	0	0	0	0	$5.01 \cdot 10^{-15}$
MoF_4	0	0	0	$1.14 \cdot 10^{-19}$	$2.74 \cdot 10^{-12}$	$2.25 \cdot 10^{-7}$
MoF_5	0	0	$8.52 \cdot 10^{-16}$	$3.12 \cdot 10^{-10}$	$1.99 \cdot 10^{-6}$	$6.84 \cdot 10^{-4}$
MoF_6	1.00	1.00	1.00	1.00	1.00	$9.98 \cdot 10^{-1}$
UF_4	0	0	0	$9.73 \cdot 10^{-20}$	$4.51 \cdot 10^{-13}$	$1.71 \cdot 10^{-9}$
UF_5	0	$1.32 \cdot 10^{-17}$	$1.02 \cdot 10^{-10}$	$3.71 \cdot 10^{-7}$	$1.29 \cdot 10^{-4}$	$8.70 \cdot 10^{-4}$
UF_6	$1.04 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$	$8.46 \cdot 10^{-4}$	$1.05 \cdot 10^{-4}$
UOF_2	0	0	0	0	0	$6.72 \cdot 10^{-21}$
UOF_3	0	0	0	0	$1.80 \cdot 10^{-17}$	$9.66 \cdot 10^{-14}$
UOF_4	0	0	0	$3.15 \cdot 10^{-17}$	$1.95 \cdot 10^{-12}$	$5.66 \cdot 10^{-11}$
UO_2F_2	0	0	0	0	0	$5.52 \cdot 10^{-20}$

ous compositions. So, MoF_6 prevailed at 150−400 °C, MoF_5 presented both in the form of trimer at 300−400 °C, and as a monomer within the range of 500−1100 °C. The molecules of MoF_4 were also detected (at 600−1200 °C), whereas MoF_3 molecules were observed at 1000 °C. At 250−500 °C there were MoF_4 molecules observed in the spectra [6].

Appearing the lower fluorides in the reaction mixture could be connected with the kinetics of fluorination because the fluorination process for multivalent metals proceeds *via* the successive addition of fluorine atoms according to the scheme as it follows

$Mo + 3F_2 > MoF_2 > MoF_3 > MoF_4 > MoF_5 > MoF_6$
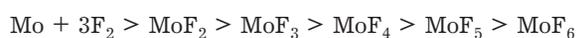
The boiling point of MoF_5 is equal to 214 °C [7], so it is evaporated, whereas the interaction in the gas−gas system is less likely than in the gas−solid system.

Thus, under the joint fluorination of molybdenum and triuranium octoxide at the temperature values lower than 700 °C, the main compounds are presented by molybdenum and uranium hexafluorides. In order to process the molybdenum waste by means of the fluoride method it is necessary to remove uranium oxides from the surface of the boat, since to separate molybdenum hexafluoride from uranium hexafluoride impurities *via* rectification is rather problematic due to the close values of the gas phase transition temperature for these compounds ($T_{boil}(MoF_6) = 33.9$ °C, $T_{subl}(UF_6) = 54.6$ °C) [1]. For this purpose, one should determine the level and depth of molybdenum contamination by uranium oxide and by uranium radioactive decay products.

STUDYING THE DEPTH OF MOLYBDENUM CONTAMINATION AND THE KINETICS OF MOLYBDENUM SCRAP FLUORINATION BY FLUORINE

As a parent material, we used the fragments of molybdenum boats before and after using $10 \times 10 \times 5$ mm in size with the mass of 5 g, the anode gas from a medium-temperature electrolyzer (about 92−95 vol. % F_2 and 5−8 vol. % HF), and ch.d.a. grade argon.

The depth of molybdenum contamination and the kinetics of fluorination were investigated by means of a gravimetric method widely used for studying the reactions of a gas + solid a gas type [8, 9]. Just this type of the reactions comprises the molybdenum and triuranium octoxide fluorination reaction. The reaction products such as MoF_6, UF_6 readily pass into the gas phase, so in the course of molybdenum fluorination, a continuous change in the mass of the sample occurs.

In preliminary experiments, it was found that the reaction occurs in the isothermal mode when the volume fraction of fluorine is less than 15 %. In this regard, the study was performed within the temperature range of 200−600 °C, with the volume fraction of fluorine amounting to 13 %.

Studying the kinetics of compact molybdenum fluorination was performed using an experimental set-up (Fig. 1), with a periodic measurement of α and β activity, the thickness and the mass of the sample. The main part of the experimental setup is presented by a horizontal reactor (*10*) which represents a heat-insulated nickel pipe of with an inner diameter of 30 mm and length of 500 mm, equipped with an electric heater.

To the reactor was placed a nickel boat with a sample of molybdenum. Preliminary heating the reaction gas mixture was performed at the left side of the reactor (*10*) filled with nickel chips, with the temperature of 200−600 °C. The flow rate of argon fed into the reaction zone was measured by means of rotameter (*6*), whereas the consumption of fluorine was constant with maintaining by supplying the electric current density of 0.4 A/cm^2 at the anode of the electrolytic cell (*1*).
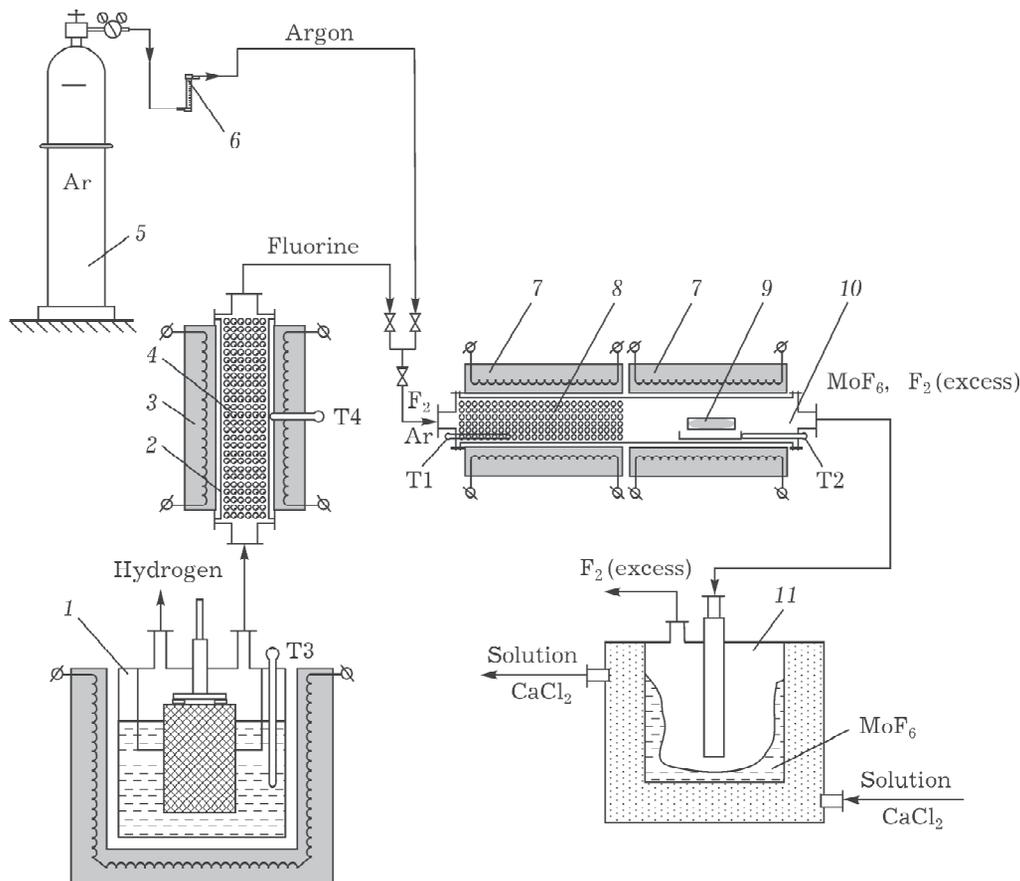
Fig. 1. Experimental set-up for studying the kinetics of lumpy molybdenum fluorination: *1* − electrolytic cell for the production of fluorine; *2* − column with NaF sorbent; *3, 7* − electric resistance furnace; *4* − NaF sorbent; *5* − cylinder with argon; *6* − argon flow-rate rotameter; *8* − nickel filler; *9* − molybdenum sample; *10* − fluorination reactor; *11* − condenser; T1−T4 − thermocouples.

The temperature in the reactor (*10*) was measured by means of a chromel-alumel type thermocouples (T1, T2), and it was recorded by a KSP-2 type potentiometer. For trapping the products of fluorination, a condenser (*11*) was attached in series to the reactor. The gases those passed through a condensation unit were supplied to an additional trapping column which represented a nickel tube filled with marble chips. After removing fluorine, the gases were dumped into a ventilation system. The fluorination process was carried out in a periodical manner. When fluorination finished, the supply of fluorine was stopped. In order to reduce the effect of the reaction heat on the process, fluorine was diluted with argon. Fluorine concentration was equal to 13 vol. %, whereas the fluorine flow rate amounted to 4.8−4.9 L/h.

Figure 2 demonstrates the reaction level depending on time and on temperature for the molybdenum samples before and after use. It can be seen that the rate of fluorination for the samples after use is lower than that for non-

used samples. This fact could be associated with a difference in the microstructure, chemical composition of the surface and inner layers of the samples [3−5].

The time of complete reaction for the samples does not exceed 480−800 min being not limited by the amount of fluorine, since the excess of the reagent in experiments is great enough.

The kinetic data were processed according to the Gray−Viddington shrinking sphere equation [9, 10].

According to the results of experimental data, we determined the values apparent activation energy and derived kinetic equations for the fluorination of non-used and used molybdenum samples (before and after operation).

The kinetic equations can be presented as it follows:

for non-used molybdenum samples:

$$1 - (1 - \alpha)^{1/3} = 3.79 \cdot 10^{-3} e^{-(3900 \pm 500)/(RT)} \tau$$

for molybdenum samples after operation:

$$1 - (1 - \alpha)^{1/3} = 1.97 \cdot 10^{-3} e^{-(2500 \pm 500)/(RT)} \tau$$

The values of the apparent activation energy indirectly indicate that the molybdenum fluorination reaction rate is determined by the diffusion of fluorine through the layer of the reaction intermediates. One of the most probable reasons for this reaction regime is the formation of a film from lower fluoride molybdenum on the surface of the metal under fluorination. The fluorination of polyvalent elements occurs, as a rule, *via* a successive addition of fluorine and *via* the formation of a number of binary fluorides. In this case, the lower nonvolatile fluorides MoF_3, MoF_4, MoF_5 would be located on the surface of the metal under fluorination, whereas volatile MoF_6 should be in the gas phase [7]. The presence of a low-fluoride based film on the metal surface of molybdenum was determined visually, in the case of incomplete fluorination of the metal. The film colour changed from yellowish brown (MoF_3) to green (MoF_4).

In the course of the experiments it was found that despite a small surface area, the fluorination process proceeds with a sufficient reaction rate and processing the lumpy waste of molybdenum boats is fundamentally possible without grinding. Organizing this process one should take into account that the molybdenum hexafluoride in the gaseous state exhibits a
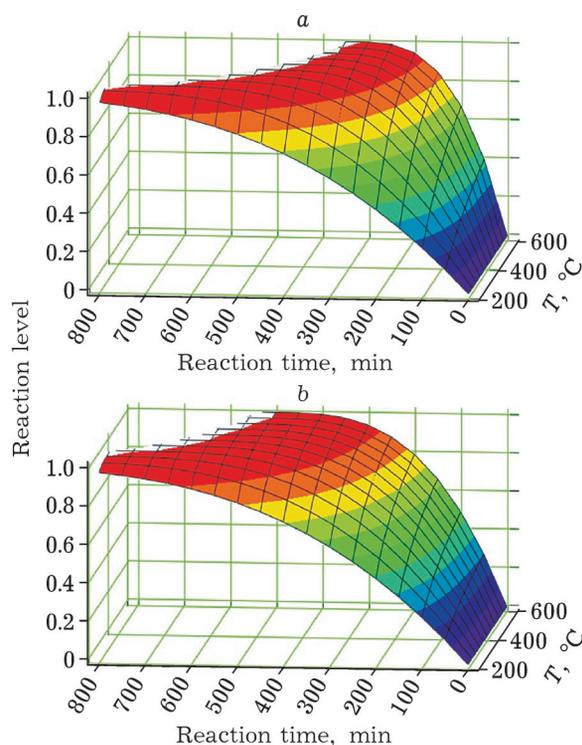
Fig. 2. Level of reaction for lumpy molybdenum fluorination by elemental fluorine depending on time and temperature samples before (*a*) and after (*b*) operation (used samples).

much higher density than the fluorine (8 and 1.693 kg/m^3, respectively), thus in the course of fluorination a screening of the reaction surface occurs [7]. Consequently, the fluorination reactor should be vertical, whereas in the case of a horizontal design the reactor should have a slope of at least 5° towards the outlet. In this case, the molybdenum hexafluoride would "drain", and the reaction surface could be renewed.

The determination of the depth and the level of molybdenum contamination was performed *via* layer-by-layer chemical etching the molybdenum sample $10 \times 10 \times 5$ mm in size (elemental fluorine, volume fraction of 13 %), after the complete lifetime operation in the furnace for sintering the fuel uranium dioxide. The process was carried out at the temperature of 500 °C in the experimental setup (see Fig. 1). The thickness of the remaining layer was determined using a micrometer, further using MKSRM1402M dosimeter-radiometer (engineering specifications TU RB 14804920.017−99) with detection unit BD-05 we measured the counting rate concerning α and β activity with a confidence probability equal to ±5 %. When measuring the flow density, the detection unit was located above the surface of the molybdenum sample in such a way that the entrance window of the detector was located as close as possible to the surface of the sample, but without touching it.

In order to eliminate the effect of low-energy α radiation on the measured data, in the course of measuring β radiation, the detection unit was shielded by a cover of plastic film according to the State Standard GOST 10354−82.

An average α and β activity of the molybdenum after the operation is equal to $A_\alpha = (190 \pm 10)$ decays/min, $A_\beta = (1005 \pm 50)$ decays/min.

The results of layer-by-layer chemical etching of molybdenum samples are demonstrated in Fig. 3.

It is seen that in the course of the chemical etching the activity monotonically decreases depending on the thickness and at a depth of 0.3 and 0.1 mm from the surface becomes comparable with the background activity concerning the α and β radiation, respectively. Increasing α radiation activity whose maximum is observed at a depth of 0.01−0.02 mm (see Fig. 3, *a*) could be attributed to the accumulation of α-active elements (U^{238}, U^{235}, U^{234}) in the process of fluorination. This is connected with the
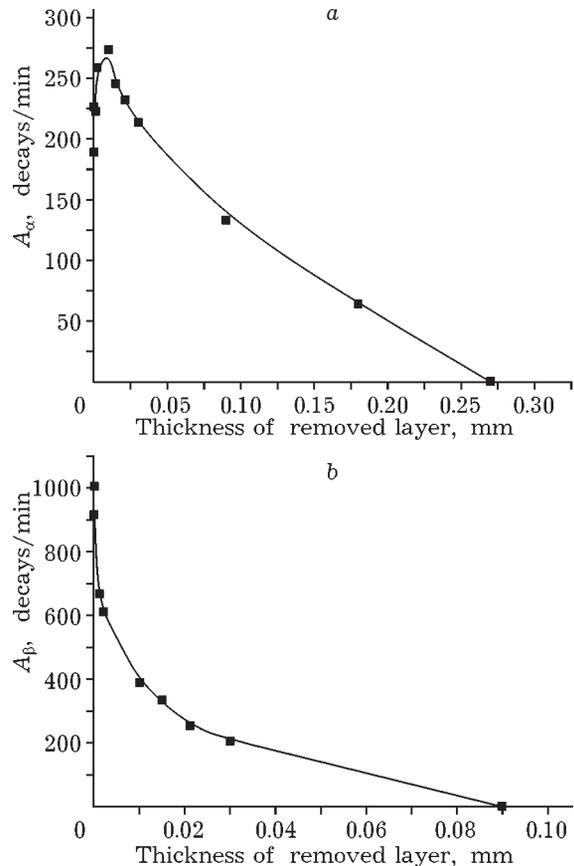
Fig. 3. Mean α activity (*a*) and β activity (*b*) for molybdenum boat samples depending on the thickness removed layer.

fact that the metal oxides, in particular, UO$_{2 \pm x}$, are more resistant with respect to the action of fluorine than molybdenum, both from thermodynamic, and from kinetic standpoint [1, 7−9].

Thus, by means of the X-ray fluorescence, spectrophotometric and radiometric analysis we established that in the course of the operation with molybdenum boats the surface layers are contaminated with uranium oxides and uranium radioactive decay products to a depth of 0.3 mm. In this case, their inner surface is mainly contaminated. The average uranium content in molybdenum after operation, determined by means of a spectrophotometric method is equal to 0.002−0.004 mass % [4, 5].

CONCLUSION

The thermodynamic analysis of the Mo−U−F−O system demonstrated that the maximum equilibrium yield of molybdenum hexafluoride is achieved at the temperature values lower than

1000 K. Owing to the close values of the vapour pressure for molybdenum and uranium hexafluorides, and their complicated separation *via* distillation it is necessary to remove uranium oxides from the surface of molybdenum boat by means of chemical etching procedure before the stage of fluorination.

The kinetic studies demonstrated that the process of fluorination molybdenum samples before and after operation exhibits the activation energy value equal to (3.9 ± 0.5) and (2.5 ± 0.5) kJ/mol, respectively. The rate determining stage is presented by the diffusion of fluoride through the layer of reaction intermediates. The difference in the intensity of the reaction could be explained by differences in the composition and microstructure of the samples.

The use of X-ray fluorescence, spectrophotometric and radiometric analytical techniques demonstrated that during the operation the surface layers of molybdenum oxide are contaminated by uranium and its radioactive decay products to a depth up to 0.3 mm. The average uranium content in molybdenum after operation is equal to 0.002-0.004 mass %. For the deactivation of molybdenum scrap, prior to the fluorination stage one must remove the surface layer contaminated with uranium oxides.

The fluoride method of molybdenum waste treatment has a high refining capacity and the absence of liquid wastes. The estimated cost of processing according to the scheme proposed does not exceed 30−40 USD per 1 kg whereas the market value of 1 kg of molybdenum is equal to 150−200 USD. This method can be used for the processing of man-caused wastes and concentrates containing niobium, tantalum, molybdenum, tungsten, and rhenium.

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