DEVELOPMENT OF THE TECHNIQUE AND MONITORING MEANS FOR CONVERSION OF AMMONIA PERTECHNETATE INTO TECHNETIUM DIOXIDE

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Among different methods of radioactive waste treatment special attention is paid to transmutation of the long-lived radionuclides into stable or short-lived isotopes by nuclear reactions. One of the elements with large half-life period accumulated in nuclear fuel is Tc^{99} Its transmutation produces stable ruthenium.

"Mayak" has a significant experience in technetium extraction from the nuclear fuel waste reprocessing in industrial scale, potassium pertechnetate salt, in particular. Experts of the "Mayak" Production Association and The Institute of Physical Chemistry of the Russian Academy of Science performed a large complex of studies with the purpose to develop and perform the technique for transformation of potassium pertechnetate into technetium metal. This form is a suitable one for further transmutation.

In the presentation the data from studies on one of the processes of the developed technique are given. This technique is transfer of the intermediate stage, ammonia pertechnetate into technetium dioxide. The need to single out this process into a separate stage in the pertechnetate recovery to metal with hydrogen is caused by strong exothermic effect of this transformation and possibility of uncontrolled process with probable loss of a valuable product. There is no data in the literature on kinetics and mechanism of NH4Tc04 decomposition that are required for selection of the optimum conditions for the process of technetium dioxide fabrication.

Therefore, the isotherms of ammonia pertechnetate was recorded for temperature range from 180°C to 250°C with derivatograph in argon. It was stated that isotherms are sigmoid shape and described with Erofeyev equation:

$$\alpha=l-(1-\alpha)\exp(-k^2t^2)$$

where α - decomposition share;

t - time;

k - decomposition rate.

In order to justify the mechanism of decomposition it was found proper to use the method of transition state, that is characterized with high (relatively period of crystalline cell relaxation) period of existence and free energy of formation could be determined for it. Therefore, regularity between the constant of reaction rate and temperature was studied. When Arrenius equation was applied to this regularity is became possible to derive activation energy that was 140 kJ/mol. Based on the reference data and suppose that NH_4TcO_4 and NH_4ReO_4 thermal capacity dependence from temperature is the same, change of thermodynamic parameters of decomposition reaction was calculated for the temperature range of interest. This, in the first turn, allowed to determine the constant of NH_4TcO_4 decomposition rate at any fixed temperature from the interval under study. The knowledge of the rate constant allows to calculate the thermal balance of decomposition reaction in the point of maximum rate and to evaluate the required rate of inert gas blow through in order to provide stable cooling and to exclude the danger of explosion.

For monitoring the completeness of the process of thermal decomposition of ammonia pertechnetate several methods were tested, that resulted from the knowledge of thermolysis products and probability of their measurement. However, the most applied one was the method for measuring the exposure dose rate (EDR) from bremstrahlung of technetium chemicals. Monitoring of TcO_2 accumulation in ammonia pertechnetate decomposition reaction is possible because technetium weight in reaction is constant, volumes of NH_4TcO_4 and TcO_2 within measurement error is the same and the exposure dose rate (equivalent dose) of the bremsstrahlung by the increase of the mean atomic number, increases. In the presentation the data on theoretical statement of the dose rate and ways of its realization are given. The use of a developed method and way of monitoring allowed to reprocess more than 2.2 kg of ammonia pertechnetate and to obtain about 1.6 kg TcO_2, at that mean yield was about 99%.