

flow rate at large  $H_2$  concentrations in Ar and the rate of moisture condensation in off-gas coolers were measured.

The paper presents the isotherms of technetium dioxide reduction over a wide temperature range from 673 to 1118 K. Over this entire temperature range, the isotherms have a clearly defined sigmoid character, and the inflexion (the point of the maximum reaction rate) correspond to the reduction degree of about 0.4.

The experimental results are well approximated by the Erofeev reaction:

$$\alpha = 1 - (1 - \alpha_0) \cdot \exp(-k^2 t^2) \quad (1),$$

from which the rate constants for the reduction reaction were calculated. The study of the rate constants for the reduction at a fixed temperature showed that, in a first approximation, it depended on the hydrogen flow rate at the reactor inlet and on the amount of  $TcO_2$  placed into the reactor. If a "dimensionless" time parameter is introduced:

$$\tau = t \cdot V_H / M_{Tc} \quad (2)$$

(where  $\tau$  is "dimensionless" time,  $V_H$  is the hydrogen flow rate (mol/h),  $M_{Tc}$  is  $TcO_2$  mass, and  $t$  is the current time); "dimensionless" rate constant for reduction depends only on the ratio between the reduction rate to the  $TcO_2$  mass, and after the introduction of  $V_H/2M_{Tc}$  parameter, remains constant at fixed temperature of the process. The study of the reduction at any temperature reveals the independence of the "dimensionless" constant ( $K_r$ ) on the reductant concentration and the flow rate of the reaction gas at the inlet to the reactor. This, in turn, means that neither external nor adsorption-desorption events can be limiting, slow stages of the reduction process.

The plot of  $K_r$  on temperature showed that the constant passes through a maximum at  $\sim 1000$  K then declines. According to the generally accepted concept of kinetics and mechanism of nucleation of a new phase, if the reduction rate is determined by the rate of formation and growth crystallization centres, the maximum of the reduction constant should be between  $1/3 T$  and  $1/2 T$  (where  $T$  in our case is melting temperature of metal technetium); i.e., between 824 and 1236 K, which is actually the case.

In order to prove or reject the above-made assumption about the limiting stage, we estimated the virtual activation energy of the process on the ascending branch of the plot of  $K_r$  as a function of temperature according to the Arrhenius equation:

$$\ln K_r = \ln K_0 - E_a / R t \quad (3).$$

The activation energy is  $22.6 + 4.8$  kJ/mol. Because the activation energy is virtually equal with the melting heat of metal technetium ( $\Delta H = 24$  kJ/mol), this definitely indicates that the limiting stage is crystallization of metal technetium from pseudoamorphous metal-technetium phase formed on the  $TcO_2$  surface as a result of its reaction with the reductant.

The investigations described made it possible to obtain kilogram quantities of powder metal technetium of high radiochemical and chemical purity (total radionuclides impurities were not more than 100 Bq/g  $Tc^{99}$  and chemical impurities were not more than 0.1 %).