A Study of the Kinetics and Mechanism of Reduction of Technetium Dioxide to Metal

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Technetium-99 application is not developed up to day. Transmutation is generally recognized to be a radical method of liquidation of Tc^{99} and others radiologically harmful long-lived nuclides. Of these radionuclides only Tc^{99} yields a stable and valuable product: ruthenium, and the most likely form of a transmutation target being metal technetium.

The Production Association "Mayak" in collaboration with Khlopin Radium Institute and the Institute of Physical Chemistry of RAS have organized a large-scale separation and purification of technetium in the form of its pertechnetate from spent nuclear fuel. The amount produced depends on a customer order. The Production Association "Mayak" and the Institute of Physical Chemistry of RAS carried out a whole range of investigations to develop the technology of transformation of $KTcO_4$ to metal technetium. The scheme of the technological process was the next:

1. The saturated (at room temperature) solution of $KTcO_4$ in distilled water was diluted in two times and was passed through cationic exchange resin (KU-2) in H^+- form.
2. The obtained solution of $HTcO_4$ was neutralized by concentrated NH_4OH solution to pH~9 and then evaporated by heating on water bath approximately in 20 times and then slowly cooled to ~300 K.
3. The resulting crystals of NH_4TcO_4 were decanted and then three times recrystallized from water and then dried in atmosphere of air.
4. Dried crystals of NH_4TcO_4 were decomposed at 600 K in argon atmosphere and black powder of technetium dioxide was obtained.
5. Obtained technetium dioxide was reduced by molecular hydrogen to metal technetium.

This paper presents the results of the study of the transformation of the intermediate compound (technetium dioxide) to metal by reducing TcO_2 by hydrogen and kinetic peculiarities of this process.

The indirect reduction reaction that takes place during this process is a particular case of topochemical adsorption-catalytic reactions occurring in the interface between two solid phases. The great variety of possible slow stages does not allow the most suitable technological conditions to be selected *a priori*. Therefore, the kinetics and mechanism of the reduction process was studied by varying the reductant concentration, the amount of TcO_2, the feed rate of reaction gas, and the temperature of the process. The process was monitored using differential methods based on the gas phase potential measurements at the reactor outlet, carried out using "Zircon" or "Fluorite" gas analyzers. Changes in the gas