REMOVAL OF RuO₄ VAPORS ON NATURAL CLINOPTILOLITE

F. KEPÁK,* S. KOUTOVÁ,* M. KOČIŘÍK,** A. ZIKÁNOVÁ**

*Nuclear Research Institute, 250 68 Rež (ČSFR)
**J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 182 23 Praha 8, Dolejskova 3 (ČSFR)

(Received October 11, 1991)

Natural clinoptilolite has been used for the retention of RuO₄ vapors and its sorption properties were determined under a dynamic regime. In the course of retention, dissociation of RuO₄ to RuO₂ and O₂ proceeds, which is probably in the first phase catalyzed by Fe₂O₃ contained in clinoptilolite and in the second phase, after the formation of RuO₂, it is autocatalyzed by this oxide. The autocatalytic reaction, which is promoted by an increase of temperature, can theoretically proceed up to the complete clogging of the intergrain volume, which would give the RuO₄ retaining opacities by several orders of magnitude higher than in the case of mere physical sorption. However, the exploitation of this capacity is, prior to the onset of the autocatalytic reaction, limited by the transient breakthrough of RuO₄. Conditions were found under which this transient breakthrough is completely avoided.

Introduction

The removal of the radioactive vapors of ¹⁰⁶RuO₄ is a serious problem in the vitrification of high-activity wastes produced in the course of the spent nuclear fuel reprocessing. These vapors are usually sorbed on various inorganic sorbents.¹⁻⁶ Numerous natural materials, including also natural zeolites,¹⁻⁴ are frequently used for this purpose.

Previous studies in this respect have shown that the predominant mechanism of volatile ¹⁰⁶RuO₄ vapor retention is not physical sorption but rather the deposition of non-volatile ¹⁰⁶RuO₂.⁷⁻¹⁰ This deposition is connected with the dissociation of RuO₄ to RuO₂ and O₂, known to be catalyzed by certain metal oxides, e.g., Fe₂O₃. It is also well known that autocatalysis by the RuO₂ formed plays an important role in this process.⁸⁻¹¹ From the published literature it follows that in contrast to a number of other sorbents, e.g., silica gel, which must first be impregnated by a redox catalyst in order to be able to induce the dissociation reaction mentioned above,⁷,⁹ on some zeolites this process can be initiated without any pretreatment.⁵,⁶

In this work we have studied the RuO₄ vapor retention on the tuff of inland provenance that contains a large portion of clinoptilolite (henceforth we shall speak of clinoptilolite only). No relevant data have been found in the published literature available concerning the use of clinoptilolite for ¹⁰⁶RuO₄ retention.
Experimental

Apparatus

The apparatus used for the measurement of RuO$_4$ breakthrough curves on solid beds of clinoptilolite is schematically presented in Fig. 1. Its main parts are as follows: carrier gas (nitrogen) reservoir, RuO$_4$ generator, glass reactor containing crushed clinoptilolite, and the absorber of RuO$_4$ breaking through the reactor. The gas flow rate was measured in the gas supply inlet by a rotameter, located beyond the gas-flow stabilizer.

Carrier-gas supply: Nitrogen was taken from a pressure flask, its flow rate was controlled by a needle valve. It was dried by passing through a U-tube with molecular sieve DUSIMO S 3 A, then through an aerosol filter made of glass microfibers (AEROS-C); a gas flow rate stabilizer and a rotameter were mounted into the line.

RuO$_4$ generator: For RuO$_4$ generation (non-radioactive Ru was used in these experiments) a saturating unit was used, consisting of Stefan’s tube, in the lower part of which there was the liquid RuO$_4$ sample (melting point of solid RuO$_4$ is 25.4 °C). RuO$_4$ vapors diffused through the stagnant nitrogen layers in the tube into the nitrogen flow that passed over the Stefan’s tube orifice. After the steady concentration profile is established along Stefan’s tube, the RuO$_4$ concentration in the carrier gas achieves a stationary value which is assumed to be given by the equilibrium value, depending on the liquid phase level, on the temperature of the thermostat in which Stefan’s tube is kept (this temperature was 30 °C), and on the gas flow rate. All these parameters were therefore stabilized, except for the RuO$_4$ level in the tube, which was assumed to change.