Shaderman F.I., Kremenetskii A.A. Kinetics of reactions of sublimation from fumarole gases of the Kudryavyi Volcano

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Fumarole processes of the Kudryavyi Volcano, situated in the northern part of the Iturup Island (Kuril Islands), are characterized by unique and stationary parameters during, at least, 100 years. Temperature of volcanic gases emitted by numerous fumarole fields of total area >3000 m^2 varies from 100 to >900^{O}C. Emitting of gases occurs with different rates, from 0.1 to 100 m/sec. The fumarole gases of the Kudryavyi Volcano show high concentrations (g/t) of Re – up to 1.5, Ge – up to 1, Se – up to 1, Bi – up to 3, Sb – up to 7, In – up to 5. That allow considering them as a new source of Re and other rare metals.

Authors have elaborated and patented (patent RF №2159296) a technology of extraction of Re from the gas, which applies a process of sublimation from the gas on some carriers. In order to choose an effective carrier, which provides a complete extraction and high rate of the process, we experimentally studied an interaction of the volcanic gas with diverse natural (basalt, andesite, and products of their decomposition by acid volcanic gases, clinoptilolite tuff) and synthetic (Al_2O_3, activated charcoal, glass wool) carriers differing in structural, sorption, and ion-exchange properties.

Sulfide and halogenide crystals forming from the gas are similar in morphology and composition to sublimates from the fumarole rocks. Figure 1 demonstrates a dependence of clarks of concentrations (K_k) of Re, Bi, In, Mo, Ge, Pb in altered rocks in fumaroles and in carriers on temperature. Experimental results show that dependence of accumulation of the elements on the carriers is practically identical to the temperature dependence of sublimation in fumaroles. There is an absence of selective sublimation on the carriers, despite some of them (natural zeolite, activated charcoal, Al_2O_3) have sorption and ion-exchange activity. No predominance of extraction of any metal on any specific carrier is observed in the interval 300-750^{O}C. Analogous pattern is observed also for Tl, As, Cu, Ag and other metals. Maximum of accumulation of Re and Bi on the carriers and the rocks are within 500-600^{O}C, for Mo, 700-800^{O}C, Pb, about 600^{O}C, Cu, 700^{O}C, etc. The results allow a conclusion that the rate of sublimation at other conditions being equal depends on the properties of the carrier surface only.

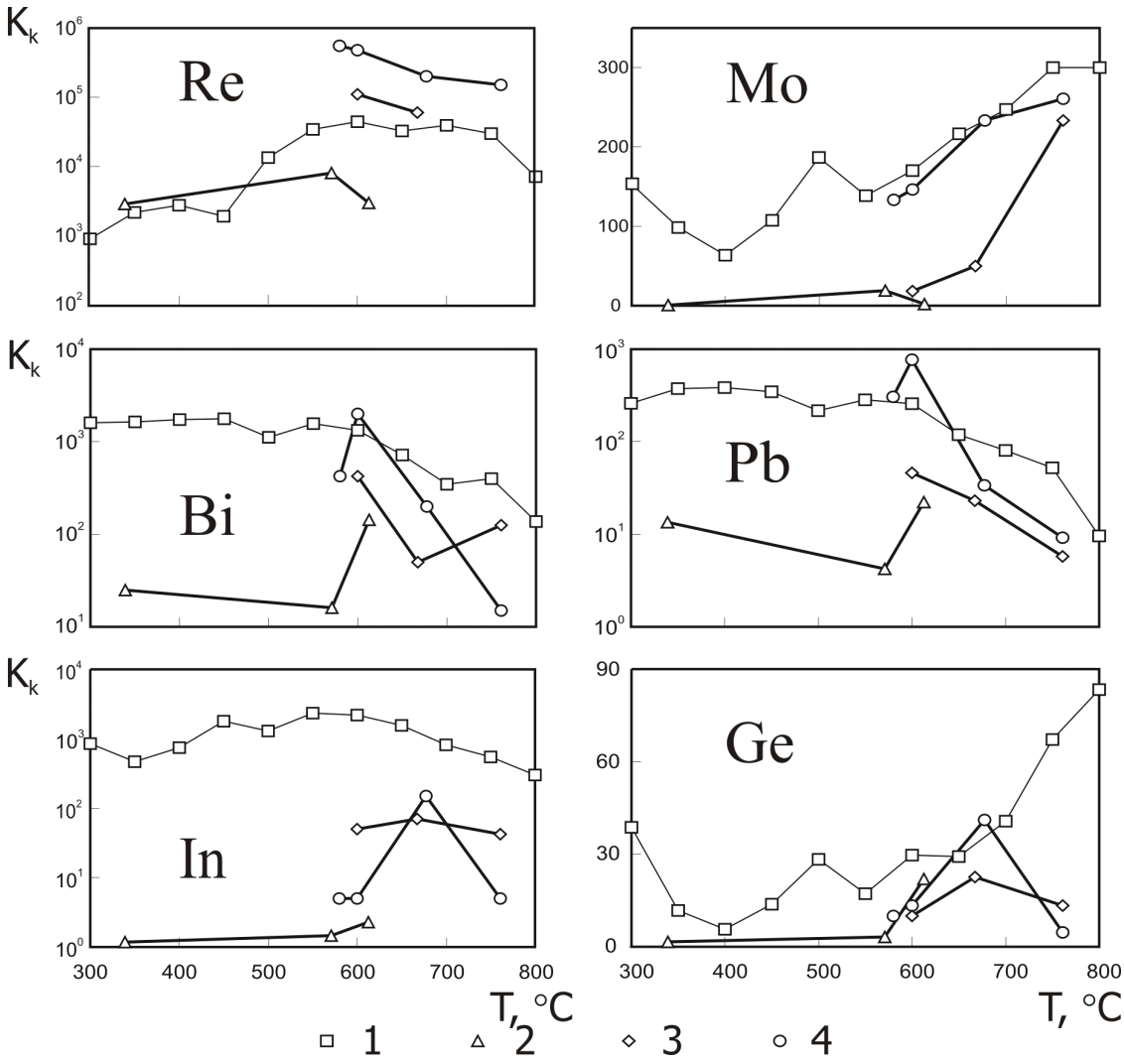

Fig. 1. Dependence of the clark of concentration (K_k) of ore elements on temperature of the volcanic gas: 1 – clarks of concentration in the unaltered rocks; 2-4 - clarks of concentration on carriers: 2 – Al_2O_3, 3 – activated charcoal, 4 – natural zeolite.

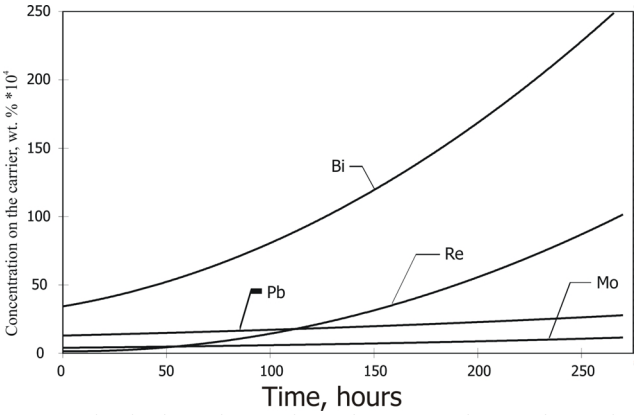

Fig. 2. Kinetic dependence of metal concentration on the carrier (clinoptilolite) at temperature of the gas and the carrier $500^{O}C$.

The following model of sublimation, based on the experimental results, is proposed. The model includes consequent stages operating in different media: 1) transfer and cluster formation (in gas), 2) primary adsorption with formation of activated centers (on the carrier surface), and 3) growth of crystal (on the active centers of newly formed phases). An effectiveness of the process is determined by kinetic factors, which influence on different stages: mechanisms of reactions of sulfide formation, time of contacting of the gas with the carrier surface, velocity of gas flux, and surface properties. In particular, the intensity of cluster formation is determined by temperature and gas composition, the kinetics of the primary adsorption is limited by surface properties and gas velocity, growth of crystals proceeds with constant kinetic parameters. Thus, an integral rate of sublimation is proportional to the amount of existing centers and increases in time (Fig. 2).

The best results were obtained for natural zeolites (klinoptilolite), which are characterized by developed surface with charged active centers.

Thus, the effectiveness of precipitation of Re, Mo, Ge, Bi, and other metal sulfides from the volcanic fumarole gases depends on properties of surfaces for accumulation, which influence on the stage of the primary adsorption.