P3-4

NEW OXIDATION STATE OF PLUTONIUM: +8 AND THE FIRST OBSERVATION OF GASEOUS PuO_3 FORMATION

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The presented subject-matter was briefly discussed earlier. The results of the experiments on oxidation of plutonium to the octovalent state and on PuO_3 preparation are considered. The behaviour of volatile compounds formed under heating of trace quantities of ^{238}Pu and ^{239}Pu in a stream of He and O_2 mixture was studied by using the thermochromatographic (TC) methods and quartz TC columns. The concentration of the reagent c_{O_2} was changed between 50 and $\leq 10^{-7}$%. The deposition zones were measured with an α-spectrometer. It was found that under certain conditions plutonium forms four adsorption zones with the centers at 450±25°C, 250±25°C, 130±50°C and −105±25°C.

For the interpretation of the results a series of model experiments with carrier-free radioisotopes of Os, Re, Ru and Tc was performed. It was shown that in the stream of He with a negligible touch of O_2 they were adsorbed at 450-500°C and at 250-300°C in the forms of dioxides and trioxides, respectively. The results of the TC separation of volatile products of ^{nat}U and ^{249}Cf oxidation are also presented. Based on the data obtained we assume that the first adsorption zone (450±25°C) is due to PuO_2 formation, the second one is due to PuO_3 formation and the third one is, probably, due to formation of a plutonium acid. Comparison of OsO_4 and RuO_4 adsorption zones with the last deposition zone indicates their similarity. It is shown that at low concentration of O_2 only lower plutonium oxides form, which is also characteristic of Ru and Os. We can conclude that octovalent plutonium was produced which in a form of very volatile PuO_4 deposited at negative temperature. The distribution of PuO_2, PuO_3, a possible plutonium acid and PuO_4 is shown in the figure. One can note that mass-spectrometric measurements of vapour over PuO_2 [2] confirm our conclusion about formation of volatile PuO_3 as well as well as existence of volatile UO_2, UO_3 and PuO_2. Theoretical verification of the PuO_4 formation has already been obtained [3]. Experimental verification can be done, probably, by negative ion mass spectrometry of $(PuO_4)^-$ formed by electron capture.

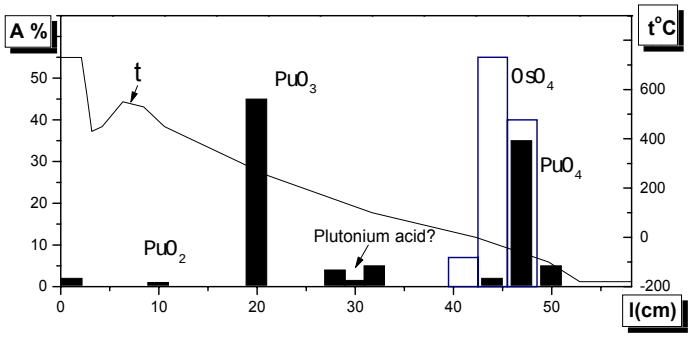

Figure. Thermochromatogram of volatile plutonium compounds at c_{O_2} = 50%.

[1] V.P. Domanov, G.V. Buklanov, Yu.V. Lobanov. In: C.E.A. Palmer (Ed.) Abstract Book of the Seventh International Conference on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, Lake Tahoe, CA, 1999, p.164.
[2] C.Ronchi. F.Capone, J.Y.Colle, J.P.Hiernaut. J. Nucl. Mater. 280(2000)11.