FIRST RESULTS OF EXPERIMENTAL STUDY OF MIGRATIONAL PROPERTIES OF ZEROVALENT FORMS OF MERCURY

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The problem of anthropogenic mercury pollution needs to be named actual. The big attention is paid to it all over the world in connection with growing emission of man-caused mercury, essentially influencing on global environmental balance. Now mercury is one of few elements for whom anthropogenic sources can be comparable to natural sources in a geochemical cycle of this element. Very frequently increasing general anthropogenic loading on natural complexes leads to transition of already available in our midst mercury to more mobile and much more toxic forms. It is important to take into account, that the processes of mutual transition of three forms of mercury (elementary (Hg^o) and cationic (Hg_2^{2+}), (Hg^{2+}), strong complexes) are spread in nature. They contrast differ with the solubility and volatility, and consequently migration mobility.

To the reasons of an enhanced attention to mercury it is possible to attribute the fact, that it is among the elements (Cd, Zn, Pb, Cu, As, Sb, Sn, Bi, Hg, Au, Ag, Se, I), for which there are significant divergences between rated concentration and observed natural data on aerosol compositions by evaluation of the general balance (taking into account all known sources of elements: oceanic, continental and anthropogenic components). This fact specifies their receipt from any not taken into consideration sources. It allows to assume the existence of the certain global process dispersed on a surface of the Earth, with small density of a stream - so-called cold endogenous gas emission - emanation by rocks mainly not lythophyle elements. This version is most probable for mercury, however, feasible forms and rates of gas migration, and also speeds and mechanisms of oxidation are investigated insufficiently.

Two series of methodically various experiments with research of migrational properties mercury vapour and its hydration were carried out. The first series is devoted to studying of mercury vapour hydration in a gaseous phase in $Hg\text{-}H_2O$ system at 180^0C. For this purpose micro containers with liquid mercury were balanced in titanic autoclaves at variable pressure of water vapour. There was 2 series differing on time of counterpoising - 48 and 72 hours. It is determined, that mercury vapour are not hydrated because of evaporated quantities of mercury (determined by the losses of weight method) enough precisely corresponds with mercury vapour pressure in pure system (fig.1), that perhaps allows to extend this conclusion to other temperatures.

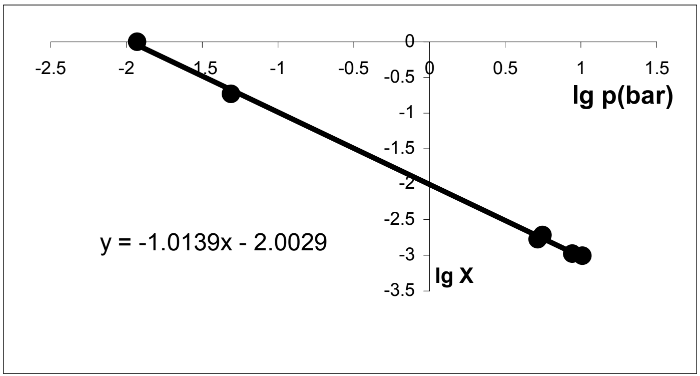

Fig.1. Mole part of mercury in gaseous phase at 180 ^{0}C in system $Hg\text{-}H_2O$.

Slope coefficient of regression equation (–1) corresponds non-hydrated mode of Hg^0. Extrapolated pressure of mercury vapour when lgX=0 (lgp=-1,98) differs insignificantly from known vapour pressure (lgp=-1,93) in pure system.

Diffusional vapour migration from liquid mercury was investigated in the second series of experiments with columns from Jurassic age loams with the start contents of mercury 0,024 ppm and natural humidity at a variation boundary conditions (fig. 2). Emission of mercury vapour was set to its evaporation from a sample of the same loam with the contents of liquid mercury (780 ppm). In all three cases it was developed close to linear diffusional profile of mercury adsorption on loam. It has allowed to define formed gradient of concentration, density of mercury stream and value of full adsorptional saturation of loams on contact with liquid-drop mercury in the bases of columns. In all cases between loam as medium of diffusional transport and the polluted sample in the basis of columns great concentration leap (on contact of two mediums - 780 ppm and 38,6 - 43,4 ppm.) was kept - such there are neither diffusional, nor filtrational profiles in a homogeneous medium. Such profile is feasible only in case of full adsorptional saturation of loams on contact to the dirty sample containing abundance of liquid-drop mercury in the bases of columns, i.e. where there is an achievement of adsorptional balance with the saturated mercury vapour.

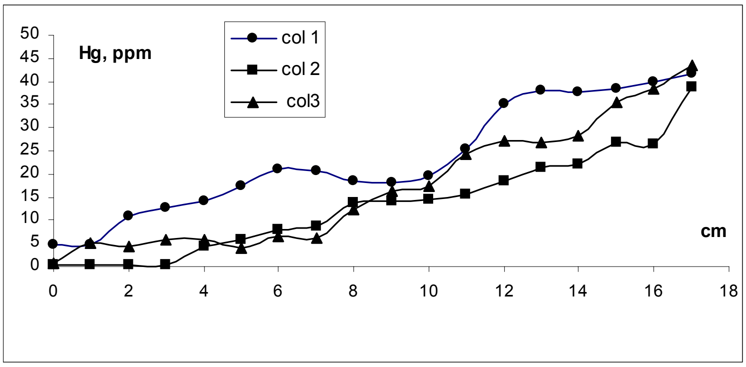

Fig2. Diffusional profiles of mercury concentration in loams.

Column 1 – is open on air. Columns 2,3 – are isolated. The loam in column 3 is covered with zeolite to determine lower pressure of mercury vapour as a boundary condition. Experiment duration is 100 days. $T=20^0C$. The analysis was made level-by-level in 1 centimeter.

After the level-by-level analysis for each sample it is simple to make material balances, and for columns 2-3 these balances of emission from a dirty sample are complete. In all three cases total emission from dirty samples are comparable, i.e. for 100 days

$$\Sigma_{emiss} = C_{med} * m_{clay} = ½ C_{max} * m_{clay} = 20*10^{-3} \text{ mg } * 150 \text{ g} = 3 \text{ mg for 100 days.}$$

It is simple to calculate density of molar mercury stream J for linear diffusional profiles (taking into account the atomic weight), equal $2*10^{-8}$ mol/cm ^{2} day. Using the equations

$$J = D_{\text{эф}}*\text{grad}C_{Hg}\text{, and grad}C_{Hg} = \Delta C/l = \Delta C/(\xi*h)$$

(where *l* –length of a way taking into account the factor of pore tortuosity ξ and height of the column *h*),

we calculate $D_{\text{эф}}$ ~1cm^2/day или $1.16*10^{-5}$ cm^2/sec. This value of diffusion coefficient allows affirm, that processes of adsorption and migration are limited by not gaseous diffusion but the most slow process – diffusion in liquid phase of moist sample. Most likely the limit of saturation (about 40 ppm in all columns) and the presence of great concentration leap in the base of columns are depend on the maximal absorption capacity at a balance with the saturated vapour of elementary mercury at inevitable occurrence of other valent forms as a result of oxidation on a moist mineral surface. Stability of value of mercury concentration in the basis of columns opens interesting prospects for an estimation of a emission of mercury stream from lithosphere by comparison of clarke values of mercury in various types of rocks and experimental data on their absorption capacity with saturated vapour of elementary mercury.