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A spectrofotometric study of pressure-temperature induced changes in the structure and stability of Ni and Co chloride complexes to 450 °C, 1 kbar

 $\begin{array}{c} \text{B.R. TAGIROV}^1, \text{A.V. ZOTOV}^1, \text{YU.V. SHVAROV}^2 \\ \text{AND L.A. KOROLEVA}^1 \end{array}$

¹IGEM RAS, Moscow, Russia (tagir@igem.ru) ²Moscow State University, Russia, (yshvarov@geol.msu.ru)

In chloride-bearing aqueous solutions Ni and Co exist in the form of hydrated octahedral species $Me(H_2O)_6^{2+}$, or Me-Cl complexes that can have both tetrahehedral or octahedral geometries. The aim of the present study is to investigate the effect of *PT* conditions and Cl⁻ activity upon the composition and structure of these species.

Spectroscopic experiments are performed using a home made flow-through spectroscopic cell. The cell is constructed from VT-8 titanium alloy and has sapphire windows. The volume of the cell is ~ 1 ml, aperture is 5 mm, and path length ~ 10 mm. Pressure inside the cell can be set up to 350 bar in the flow-through mode with the aid of the standard HPLC pump, and raised to 1 kbar with high pressure hydraulic pump in the stop-flow mode. The cell is connected to the Cary 4000 UV-VIS spectrofotometer with the aid of the quartz glass fibre optic.

We have recorded spectra of Ni-Cl solutions with HCl concentration of 0.15 - 0.25 mol, and m(NaCl) to 2 mol. In agreement with previous studies, the optical absorption spectra of Ni can be divided into 2 regions: 350 - 500 nm where the peaks of octahedral Ni are located, and 500 – 800 nm with tetrahedral Ni peaks. For 2m NaCl solution at 2m peaks. For 450 °C, 500 bar the absorbance maximum at 604 nm, arising from a tetrahedral complex, is ~ 2 units higher than the absorbance at ~ 450 nm which corresponds to Ni in octahedral coordination. Increase of pressure from 400 to 1000 bar at 350 – 450 °C results in decrease of the intensity of transitions at $\lambda > 500$ nm (tetrahedral complexes) and increase of absorbance at higher energies (octahedral species) with isobestic point at ~ 500 nm (350 °C) and ~ 530 nm (400 °C). For NaCl-free solution the most intense peaks are located at 500 \pm 50 nm, and the isobestic point at ~ 460 nm. The pressure effect on the spectra of this solution at 450 °C is more complex: with increase of pressure new peak arises in 450-500 nm region, that masks the isobestic point.

Experiments with Co-Cl solutions as well as the calculation of the stability constants of Ni-Cl and Co-Cl complexes are underway.