STUDYING OF THE U(IV) COMPLEXATION IN CHLORIDE SOLUTIONS AT 300-600°C AND 1000 BAR

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The main goal was to methodize the data on UO_2 solubility in chloride solutions (H_2O-HCl, KCl-HCl), to settle with predominant complexes of U(IV) species, to estimate thermodynamic properties of the predominant species, and to consider an influence of T, *m*HCl, and *m*KCl on UO_2 solubility in hydrothermal solutions.

Most reliable data on UO_2 solubility in water (fig. 1) presented by Parks & Pohl (1988), Redkin et al. (1989, 1990), has been served as a basis in an estimation of the thermodynamic properties of $U(OH)_4^o$ (Shock et al., 1997, and this work).

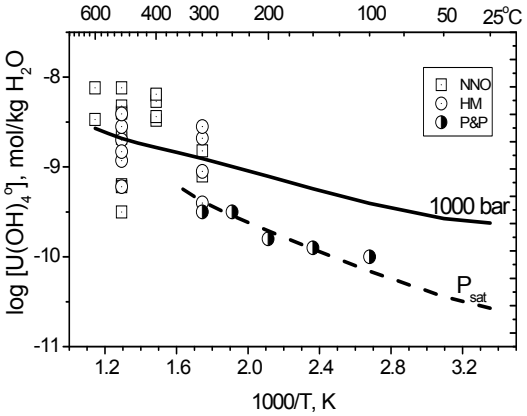

Fig.1. Solubility of UO_2cr in water by experimental data of Parks & Pohl (1988) (P&P) at $P(H_2)$=500 bar и Redkin et al. (1997) (NNO = Ni-NiO, HM = Fe_2O_3-Fe_3O_4). Dash and solid lines were calculated at P= $P(H_2O)_{sat}$, and P = 1000 bar, respectively

Our experimental data on UO_2 solubility in chloride solutions (H_2O-HCl, KCl-HCl) at 300-700°C (fig. 2) were analyzed and we found that these data can be fair accuracy describe by presence in the solution of three U(IV) species: $U(OH)_4^o$, $U(OH)_3Cl^o$ (or $UOOHCl^o$) и $U(OH)_2Cl^+$ (or $UOCl^+$). We calculated the Gibbs free energies and HKF parameters of the listed species (tab. 1). The software HCh (Shvarov & Bastrakov, 1999) 4.2 and subprogram Optima were used in calculation. Relying on these model calculations, the influence of *m*HCl, ionic strength and temperature on UO_2 solubility in chloride solutions as the possible factors for migration and precipitation of ore compound was considered (fig. 3). It was found that KCl concentration does not effect greatly on uraninite solubility.

Table 1

Standard thermodynamic properties (298.15 K, 1 bar) and HKF parameters of aqueous U(IV) species (our data)

HKF	$U(OH)_4^o$	$UOCl^+$	$UOOHCl^o$
$\Delta_f G^o_{298}$, cal/mol	-345547	-201882	-251649
S^o_{298}, cal/(mol K)	9.56	67.48	75.15
a_1, cal/(mol bar)	27.1930	1.5823	1.9544
$a_2 \times 10^{-2}$, cal/mol	-77.4475	-4.7751	-3.0093
a_3, cal K/(mol bar)	-6.0222	-8.5593	6.9329
$a_4 \times 10^{-4}$, cal K/mol	0.4227	-0.4193	-2.6546
c_1, cal/(mol K)	46.5688	-24.0424	-14.4603
$c_2 \times 10^{-4}$, cal K/mol bar	26.3128	2.1783	6.7430
$\omega \times 10^{-5}$, cal/mol	-0.0990	-0.7214	-0.7300

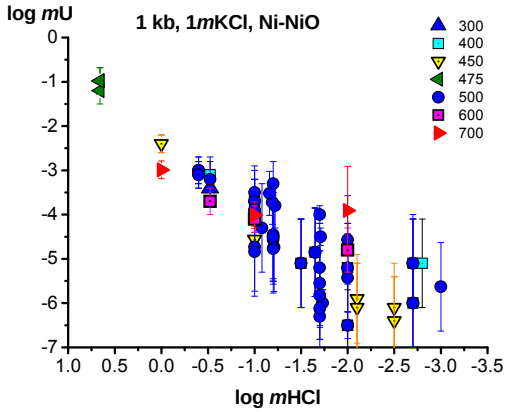

Fig.2. UO_2cr solubility in chloride solutions by experimental data (Redkin, 1987, Yudintsev et al., 1988)

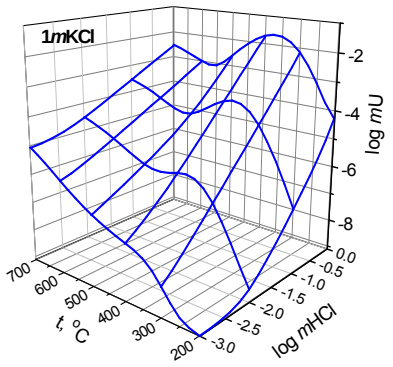

Fig.3. Influence of the temperature and HCl concentration on solubility UO_2cr in 1*m*KCl at P=1000 bar, Ni-NiO buffer by thermodynamic simulation

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