# EXPERIMENTAL AND THERMODYNAMIC EVALUATION OF THE CONGRUENT AND INCONGRUENT DISSOLUTION OF FERBERITE IN THE CHLORIDE SOLUTIONS AT 500°C, 1 Kbar UNDER *KFSP-MS-QTZ-NI-NIO* BUFFER ASSEMBLAGE

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According to [1-4], ferberite solubility depends both from *m*KCl and *m*HCl. Thus, we carried out the experimental investigations in the Kfsp-Ms-Qtz buffered system to support a constant activity ratio of *m*KCl/*m*HCl. Taking in account that Fe and W are the elements of variable valence we used Ni-NiO buffer to keep a constant value of $fO_2$ in the system. The runs duration was 14-28 days.

The experiments were performed in Pt capsules in 5.15, 25 and 40 wt. % KCl in 0.1-0.01 *m*HCl. The pure synthetic ferberite prepared by hydrothermal procedure from $WO_3$ and FeO was used in the runs. The solid (microcline+muscovite+quartz+ferberite): solution (KCl+(0.01-0.1)*m*HCl = 1:8. The results of quenched solution analyses were taken into account to make a decision about a mechanism of the dissolution and the concentrations of dissolved compounds. It has been found that the concentrations of W and Fe after runs were different (*m*KCl/*m*W/*m*Fe:
0.706/0.0058/0.011, 0.706/0.011/0.0022,
2.367/0.016/0.053, 2.367/0.020/0.033,
4.471/0.021/0.10, 4.471/0.042/0.076,
8.942/0.021/0.15, 8.942/0.055/0.090),
i.e. the incongruent dissolution of ferberite took place in the runs.

To estimate ferberite solubility and the degree of polymerization of aqueous tungsten species (it is known only monomer species of Fe(II)) in brines, we used $S_{\mathrm{FeWO_4}} = \sqrt[\alpha+1]{m\mathrm{W}_\mathrm{T}^{\alpha} \cdot m\mathrm{Fe}_\mathrm{T}}$ equation in analysis of the results of the similar of the runs. This equation involves the total molal concentrations of dissolved compounds $m\mathrm{W}_\mathrm{T}$ and $m\mathrm{Fe}_\mathrm{T}$ with molar fraction $\alpha_i$ of the species of different nucleation $i$ ($\alpha = \sum_i \frac{\alpha_i}{i} = \sum_i \frac{m\mathrm{W}_i}{i \cdot m\mathrm{W}_\mathrm{T}}$). This equation gives precise solution in the case when the ratio of the monomers and polynuclear species changes a little. As a result, it was found that the monomer acidic species were predominant in 5 and 15 wt. % KCl solution whereas dimmer species producing neutralization of the quenched solutions were formed in 25 and 40 wt. % KCl.

The experimental results were used in analysis of the tungsten complexing in HCl-KCl solution. For the purpose of solving the reverse thermodynamic task we used a method of the numeric modeling by Gibbs [5] program. Except 4 known species of W(VI): $H_2WO_4°$, $HWO_4^-$, $KHWO_4°$, it 10 species of W(V): $WO_2^+$, $H_3WO_4°$, $WO_2Cl^o$, $WOCl_3°$, $W_2O_6^{-2}$, $HW_2O_6^-$, $KW_2O_6^-$, $H_2W_2O_6°$, $KHW_2O_6°$, $K_2W_2O_6°$ were considered. The thermodynamic analysis showed that the best coincidence between calculation and experiments at 500°C and 1 kbar can be reached when the species $H_3WO_4°$ and $K_2W_2O_6°$ were taken in consideration. The dominant iron specie was $FeCl_2°$ according to accepted thermodynamic properties. The results of ferberite solubility calculations based on experimental data and by the Gibbs program are shown in fig. 1. As we can see in fig. 1 the good fitting takes place between experimental and calculated estimations. The maximum divergence of solubility values does not exceed 20 %.

The solid phase investigation showed that among initial phases the potassium tungsten bronzes (PTB) $K_xWO_3$ were observed in the run products. Using experimental data and thermodynamic properties of $WO_3$ we calculated the free energies of the PTB row from 0 to 0.5 mol of potassium.

Figs. 2 a, b show the effect of PTB of different composition and magnetite (Mag) on equilibrium $m\mathrm{W}_\mathrm{T}$ and $m\mathrm{Fe}_\mathrm{T}$ in ferberite-bearing systems. One can see from fig. 2a that concentration of W becomes stable and few depends on *m*KCl when ferberite together with PTB are subjected to dissolution. In such systems the concentration of W depends on the composition of PTB and varies from 0.06-0.05 mole/kg $H_2O$ for $K_{0.2}WO_3$ to $5{\cdot}10^{-4}$ for $K_{0.5}WO_3$. In our runs $m\mathrm{W}_\mathrm{T}$ was in a range from 0.005 to 0.05 mole/kg $H_2O$ that corresponds to x =0.21–0.31 in PTB. The iron concentration, on the contrary, has a strong dependence on *m*KCl (fig. 2b).

The conducted investigation shows that the dominant aqueous species for transportation of tungsten in reduced conditions on the ferberite (wolframite) ore deposits could be the compounds of W(V) such as $H_3WO_4°$, $K_2W_2O_6°$, and their concentrations in the hydrothermal solutions depended on the total iron in them.

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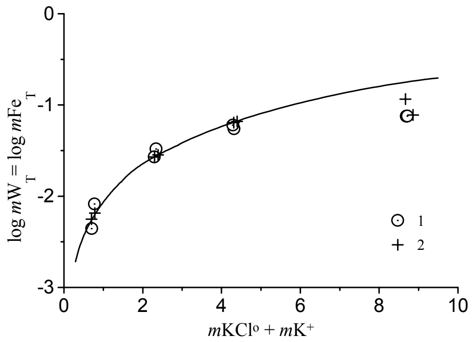


Fig. 1. Dependence of ferberite solubility on total $m$KCl in Kfsp-Ms-Qtz buffered system (solid line) at 500$^o$C, 1 kb, $fO_2$=$fO_2$(Ni-NiO): 1-from authors experimental data, 2 - calculated for the conditions of the runs

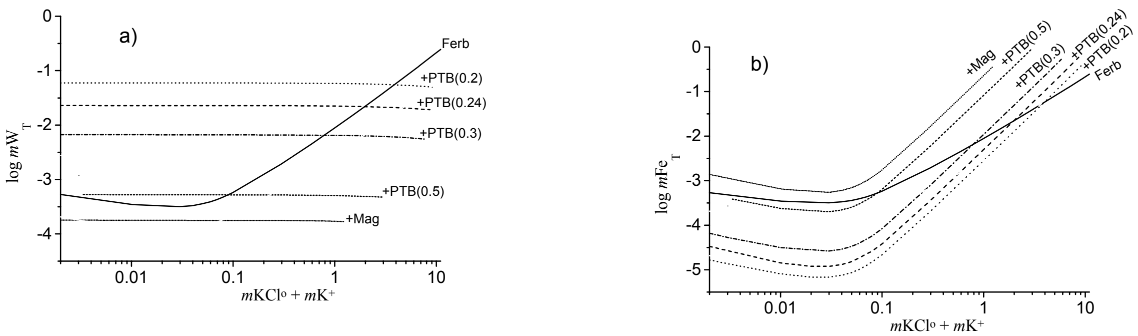


Fig. 2. The effect of $m$KCl on ferberite solubility and values of log $m$W$_T$ (fig. a) and log $m$Fe$_T$ (fig. b) of ferberite-bearing assemblages (with PTB, $K_xWO_3$, of different composition (x=0.2-0.5) and with magnetite, Mag) in Kfsp-Ms-Qtz buffered system at 500°C, 1 kb and $fO_2$=$fO_2$(Ni-NiO)