

Liquid Immiscibility in the System NaF–H₂O at 1073 K and 170–230 MPa and Its Effect on the Microlite Solubility

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Water-salt system, where sodium fluoride is a salt, refers to P-Q type. The phase diagram of this system is discussed in detail in [1, 2, 3] (Figs. 1-4). At temperatures below the critical point P a vapor phase contained a very small amount of salt (practically pure water) is in equilibrium with the salt solution. Above the critical point Q a liquid immiscibility appears in which coexist two fluid phases of different density: $L_1 - a$ fluid phase of moderate density and $L_2 - a$ dense fluid. Fluid phase is a supercritical state hydrothermal solution. The content of NaF in the L_1 and L_2 phases depends on total pressure. In the field of immiscibility the change of total NaF concentration produces the change of L_1 and L_2 phases remain constant for given T_2 narmeters. Obviously, fluids containing varies salt concentrations will have different ρ parameters. Obviously, fluids containing varies salt concentrations will have different solvency in relation to ore and rock-forming minerals. Many researchers believe that the decomposition of the homogeneous solution into two immiscible fluid phases can provoke multiple enhancement of ore minerals solubility and lead to mobilization, recrystallization or concentrated ore components in a fluid phase.

In spite of particular attention to the system NaF– H_2O , liquid immiscibility data is not enough. It is known that the second immiscibility field of fluid phases is located above the point Q at T > 973 K and p > 200 MPa [1]. According to forecasts [3], NaF concentration in the critical point Q can be very high. There is an opinion that the separation of the salt solution into the two fluids of different densities containing of salt different concentrations, is also accompanied by redistribution of the volatile components, the hydrolysis products of salt. This phenomenon in the system has not been studied. Therefore, the experimental data for the field of immiscibility in the system NaF-H₂O above the point Q are of interest to the solution of the problem of hydrothermal and magmatic ore formation.

Method and Experimental technique

A solubility method is proposed to be used for the study of fluid immiscibility. Method is based on analysis of the behavior of ore element (component, mineral) content, depending on the total concentration of NaF. At the transition from the homogeneous field of solution (HS-I and HS-II) in the field of immiscibility $(L_1 + L_2)$, due to changes in the phase composition of the solution is observed, there is an increase in the solubility of a solid mineral phase. As an investigated material was selected poorly soluble mineral microlite $(CaNa)Ta_0c_F$, which under dissolving in the hydrothermal solution cannot change the acid-base properties of the system NaF-H₂O. Microlite contains NaF as minal, which makes it a highly promising for research in this system.

The experiments were performed on a hydrothermal high pressure apparatus and the gas pressure vessel at 1073 K and p = 170 - 230 MPa. The obtained solution was analyzed using ICP-AES and ICP-MS methods.

Results and Discusion

The analysis results of solutions after experiments at 800°C and 170, 200, and 230 MPa are shown in Fig. 5 – 7. In homogeneous fields of HS-I and HS-II the curves are built on the results of thermodynamic calculations involving these particles in the solution of Ta⁵⁺: HTaO₃°, TaO₂F°, TaOOHF₂°, NaTaO₃°, Na₆H₂Ta₆O₁₉°. Thus, the reactions of microlite dissolution are:

$Mic + 2HF^{\circ} = FI + 2HTaO_3^{\circ} + NaF^{\circ}$	(1),
$Mic + 4HF^{\circ} = FI + 2TaO_{2}F^{\circ} + NaF^{\circ} + 2H_{2}O$	(2),
$Mic + 6HF^{\circ} = FI + 2TaOOHF_{2}^{\circ} + NaF^{\circ} + 2H_{2}O$	(3),
$Mic + NaF^{\circ} = FI + 2NaTaO_3^{\circ}$	(4),
	(F)

 $\label{eq:3} \begin{array}{l} 3 \mbox{Mic} + 3 \mbox{NaF}^\circ + \mbox{H}_2 \mbox{O} = 3 \mbox{FI} + \mbox{Na}_6 \mbox{N}_1 \mbox{A}_6 \mbox{O}_1 \mbox{O} \mbox$ solving the inverse thermodynamic task using software package HCh [4] and the program Optima A [5].

Thermodynamic properties of the species of sodium, calcium, and fluorine (Na NaCH⁹, NaF⁹, Ca₂⁺, CaOH⁺, CaF⁺, F, HF₂, HF⁹) were taken from [6, 7]. Calculation of the ion activity coefficients was carried out on the extended Debye-Hückel's equation.

Search for solution of the inverse thermodynamic task is made for 1073 K and p = 200 MPa. Evidently, the effect of pressure in the range of 170 – 230 MPa on the results of the experiments is slightly. Therefore, curves of dependence of the equilibrium concentrations of tantalum (*m*Ta) on the concentration of sodium fluoride (*m*NaF) in homogeneous fields of H5-I and H5-II at 170, 200, and 230 MPa are similar. As a result of the non-linear paravirabilities decidentiate detailed in preserve constraints of microtic language. approximation of calculation data of microlite incongruent solubilities were suggested the following equations:

in the range of 0.001 to 1.0 mNaF: mTa = 2.555×10⁻⁷+2.284×10⁻⁶×(mNaF)^{0.5}-1.293×10⁻⁹×(mNaF)^{-0.5} (6); in the range of 1.0 to 26.5 mNaF:

mTa = 2.488×10⁻⁶+2.2367×10⁻⁶×mNaF+1.0757×10⁻⁷×(mNaF)² +2.439×10⁻⁹×

(*m*NaF)³ (7). In fact, the dependence of *m*Ta on *m*NaF is more complicated than the equations 2 and 3, as H₅ H₂O₂ and NaF participate in the reactions of microlite incongruent dissolution with the fluorite precipitation and formation of HTaO₃°, TaO₂F°, TaOOHF₂°. In the immiscibility field microlite apparent solubility and mass concentration of tantalum In the initiation of the weight concentration of NaF (C_{NaF}). Experimental data of C_{Ta} depending on C_{NaF} in immiscibility field of L₁ and L₂ fluid phases are presented on small boxes in Figures 1, 2 and 3. Accordingly, the linear equations for pressures of 230, 200, and 170 MPa have the forms:

and 170 MPa have the forms: $C_{17} \times 10^5$ (wt. %) = 5.782 - 0.223× C_{NaF} (wt. %) ± 1.5 (8), $C_{17} \times 10^5$ (wt. %) = 10.494 - 0.295× C_{NaF} (wt. %) ± 1.5 (9), $C_{17} \times 10^5$ (wt. %) = 13.459 - 0.457× C_{NaF} (wt. %) ± 1.5 (10). The data obtained let to outline the immiscibility field in the system NaF-H₂O at 1073 K. Compositions of the L₁ and L₂ phases at pressures of 230, 200 and 170 MPa are 12 and 25 wt. %, 5 and 26 wt. %, 1 and 11 wt. % NaF, respectively. The phase diagram, presented in Fig. 4, shows that the immiscibility field at 1073 K limited above by a pressure $P_{cr} \max = 236 \pm 5$ MPa and below by $P_{cr} \min = 165 \pm 5$ MPa. At these points L₁ and L₂ phases have the same composition (L₁ = L₂, 3 and 20 wt. % NaF). The stepwise change in mTa when appearance L₁ phase has place is denoted to mechanism of the NaF hydrolysis features in the L₁ and L₂ phases. As a result, L₁ phase shows acidic properties, as L₂ phase is characterized by an excess of alkali (NaOH). In spite of high concentration of NaF, microlite solubility was negligible. The

In spite of high concentration of NaF, microlite solubility was negligible. The homogeneous solutions HS-I, containing from 0.001 to 6.0 *m*NaF, total concentration of tantalum although grew with $10^{-6.5} \pm 0.5$ to 10^{-5} *m*Ta, but remained insufficient for the formation of commercially viable ore deposits . The increase in microlite solubility with increasing mNaF was associated with the accumulation of the tantalum fluorocomplexes in the solution – TaO₂F°. To mobilize tantalum in concentrations exceeding 10⁻⁴ mTa are necessary or brines containing \ge 32 mNaF, or acid solutions in which mHF \ge 0.2.

Both those and others solutions are theoretically possible, but the probability of their occurrence in the earth's crust is unlikely. By this, apparently, is explained by tantalum ore are confined to Li-F type granites and pegmatite in which tiny phenocrysts of ore minerals are formed at the end of the melt crystallization of the most recent differentiates of Li-F granites [8].



Fig. 1. Schematic T–X sections of the phase diagrams of water-salt systems of the (I) first and (II) second types by Kotelnikova & Kotelnikov, 2008GI.



Т Fig. 3. Fig.1 P-T projection of the phase diagram P-Q type system with unstable area of stratifying. E – eutectic point, T_{H2O} , T_{B} , C_{P} , C_{B} – triple, critical points of water and salt B. Βv Peretyazhko, 2008





Fig. 2. P-T section of the H₂O-NaF-SiO₂ system with schemes of inferred phase equilibria by Kotelnikova & Kotelnikov, 2010.



Fig. 4. High-temperature region of immiscibility in the system NaF-H₂O by Peretyazhko, 2008



P_{cr.max}

HS-II

P_{cr mir}

25 30



Fig. 5-7. Results of experiments on microlite incongruent solubility in solutions of NaF at 1073 K and $\rho = 170, 200$, and 230 MPa. The lines show the trends of change *m*Ta on *m*AlaF. Symbols: HS-I – homogeneous solution at low concentrations of NaF, HS-II – a homogeneous solution at high concentrations of NaF, L₁ + L₂ – immiscibility field of fluid phases L₁ and L₂ in the system NaF–H₂O.

Fig. 8. Immiscibility field $(L_1 + L_2)$ in the system NaF-H₂O at 1073 K on the experimental data.

Conclusion

- 1. By microlite solubility method, the immiscibility boundaries and compositions of fluid phases L_1 and L_2 are defined in the system NaF–H₂O at 1073 K.
- The model of L₁ phase "acidification" and L₂ phase "alkalizing" is supposed. It is based on NaF feature hydrolysis in the two liquid phases: hydrolysis products in vapor phase L₁ are HF and Na_2O , in liquid phase $L_2 - H_2F_2$ and NaOH.

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