EXPERIMENTAL STUDY OF CALCIUM BORATE SOLUBILITY AT 250-350°C

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Boron is one of main components of hydrothermal fluid. New chemical data of fluid inclusions in minerals show that concentration of boron in ore-forming solution is to be grams per kg of water [1]. Thermodynamic properties of aqueous boric acid (the main specie of boron in nature conditions) are not studied in detail at high temperature. The main aim of this work is the experimental determination of takedaite ($Ca_3(BO_3)_2$) [2] solubility at 250-350oC and calculation Gibbs free energy of aqueous boric acid formation.

The synthesis of takedaite was carried out from system CaO-B_2O_3-H_2O, resulting phases were determined and concentration of boron and calcium in water solutions were studied.

Experiments were carried out in titanium-alloy autoclaves. The titanium container with calcium oxide was put on the autoclave with boric acid solution (100 mg/kg of boron).The placement of container and water loading coefficient were calculated for permission of reaction between calcium oxide and boric acid only at high temperature. So, saturation of calcium goes from above, and boron from below. The amount of calcium oxide was taken for portlandite formation. The duration of experiment was determined by kinetic investigation, that shows, that equilibrium is established at 7 days at 250°C. In the completion of experiment, container was taken and washed by distilled water free from carbonic acid. Calcium borate crystals insoluble with water were washed, dried and studied by microscope. Photos of crystals, synthesized at different temperatures, are showed at fig.1.

а *б* *в*

Fig.1. Photo of takedaite crystals, synthesized at 350 (*a*), 300 (*b*) и 250 (*c*) °C. Scale 20x

Crystals were identification was carried out by X-ray phase analyze at DRON-2. The result shows, that at all temperatures there are takedaite and portlandite. The X-ray data of takedaite has good agreement with $Ca_3(BO_3)_2$ phase from PCPDFWIN database and other article [3].

Boron concentrations were determined by colorimetric method with ash- resorcinol. Calcium concentrations were determined by AAS.

Results are showed at fig. 2. The solubility of takedaite in association with portlandite decreases with temperature. This data allow to determine the reaction of takedaite formation:

$3Ca(OH)_{2\,s} + 2H_3BO_{3\,aq} = Ca_3(BO_3)_{2\,s} + 6H_2O_L$

Gibbs free energy of aqueous boric acid formation were calculated with thermodynamic properties of H2O, Ca (OH)2 and $Ca_3(BO_3)_2$ from [4]. The average values of $\Delta G^o f(T)$ are -1087,81±0,33 kJ/mol, -1071,72±0,84 kJ/mol, -1057,84±1,35 kJ/mol at 350, 300, 250°C correspondingly. This data are close to recommended by G.Pokrovsky [1]. The thermodynamic calculation of experiment by this data shown at fig. 2 demonstrates good agreement with experimental points.

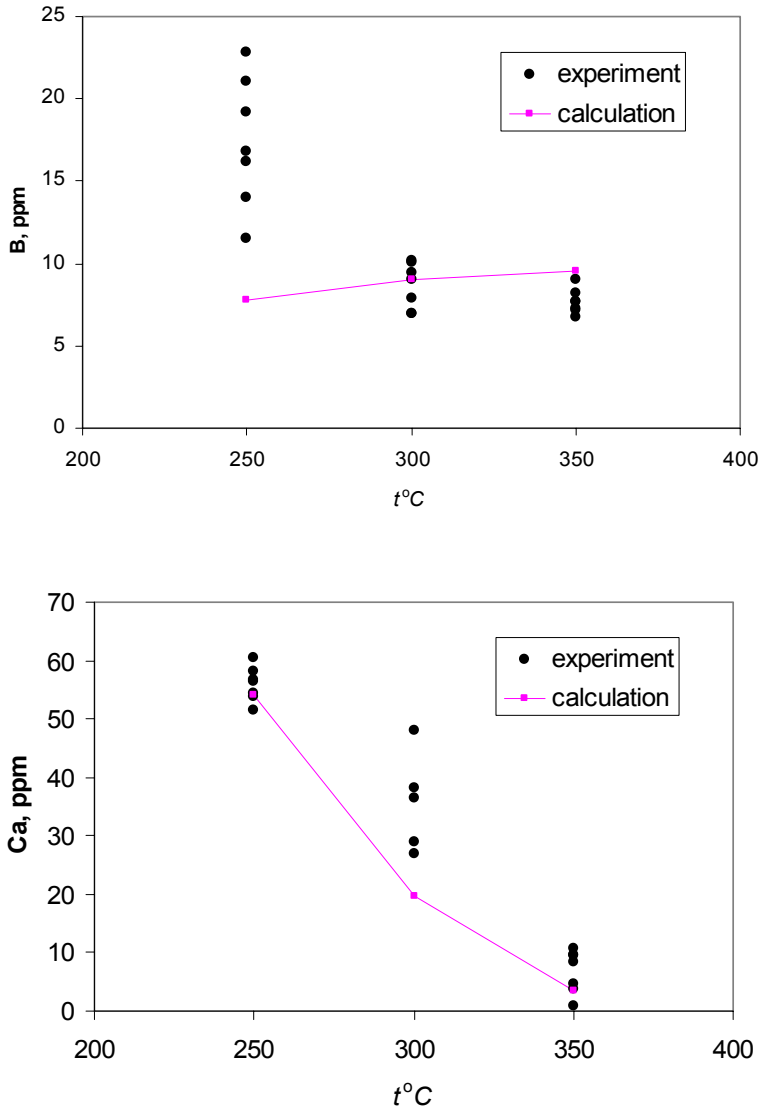

Fig.2. Boron (a) and calcium (b) concentrations in aqueous solution in equilibrium with takedaite and portlandite ad different temperatures

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References

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