Studying the thermophysical and physicochemical properties of solutions of boric acid for emergency core cooling of WWER

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Abstract. The results of experimental research of physicochemical (degree of acidity - pH) properties of aqueous solutions of boric acid are presented in this paper. A review of available literature data about the influence of properties of boric acid solutions on heat removal from the reactor core is given. It has been established that the available information is very general in nature and does not cover the entire range of parameters (temperature, pressure, acid concentration) characteristic of a possible emergency situation at NPPs with a WWER reactor. Experimental techniques and test facilities for research are described. The experimental data of the pH of aqueous solutions of boric acid in range of the concentration (5-100 g kg\(^{-1}\) H\(_2\)O) and temperature (25-50 °C) are received. The approximating dependence for the degree of acidity of aqueous solutions of boric acid has been obtained.

1. Introduction
The necessity for research processes of mass transfer of highly concentrated solutions of boric acid arose in the analysis of the operation of WWER-TOI passive core flooding systems. In case of the large break Loss-of-Coolant Accident (LB LOCA), passive safety systems provide long-term (up to 72 hours) cooling of the reactor core. The cooling occurs by supplying a boric acid solution with a concentration of 16 g kg\(^{-1}\) H\(_2\)O from the hydraulic accumulators of the first, second (HA-2) and third (HA-3) stages, as well as condensate from steam generators operating in condensation mode [1-3]. Considering the duration of the process, the boiling of the coolant and the low content of boric acid in the vapor phase, its crystallization in the reactor is possible. The limiting concentration of the boric acid solution corresponding to the start of precipitation process depends on the temperature. With the parameters corresponding to the emergency process with the large break LOCA, the maximum concentration of H\(_3\)BO\(_3\) in the core is about 450 g kg\(^{-1}\) H\(_2\)O [4].

In the research of the accumulation and crystallization of boric acid in the WWER core in the event of an accident conducted by the authors of this paper, it has been found that exceeding the maximum concentration of boric acid starts after 45 hours of the emergency process [5]. It should be noted that in the framework of these studies it was supposed that the only form of the existence of boric acid is orthoboric acid. However, in inorganic chemistry [6–8] there is a known tendency for the formation of polyboric acids with increasing concentration of orthoboric acid (H\(_3\)BO\(_3\)).
Orthoboric acid has very weak acidic properties, due to addition of a hydroxyl anion rather than to removal of a proton of hydrogen. The structure and composition of polyboric acids resulting from this process depend on the initial concentration of orthoboric acid and temperature.

The effect of polyborate complexes on the boric acid crystallization process has not been studied yet. The solubility of these particles may be higher than the solubility of orthoboric acid. In this case, their formation will favorably affect the processes of heat removal from the reactor core in case of an accident, because it will reduce the risk of sludge formation on the reactor internal surfaces. But, we can't exclude the possibility that the solubility of the formed polymer boron-containing particles will be lower than the solubility of orthoboric acid. This, in turn, can complicate the process of heat removal from the core. The intensity of the formation of polymer particles depends on the temperature and pH of the solution.

At the present, data on the effect of boric acid concentration on the pH of the solution are very limited due to the lack of experimental results of the studying of highly concentrated H₃BO₃ solutions. Boric acid in this form has very weak acidic properties and does not act as a proton donor, accordingly, its corrosion activity is extremely small. At the same time, in [9] the information is given that with increasing concentration of H₃BO₃ acidity of the environment increases and the formation of polymer particles, the structure of which is described above, occurs. In addition, as the degree of acidity increases, the corrosivity of the solution also increases. Under normal operating conditions of WWER, the acidity of the medium due to the presence of an orthoboric acid solution with a concentration of 4-8 g l⁻¹ in the reactor primary circuit is compensated by the addition of potassium hydroxide. In the event of LB LOCA, the entire mass of coolant that is in the reactor at the time of the accident is taken out to the containment. Thus, subsequently, in the reactor core there is only a solution of boric acid with a gradually increasing concentration (due to the operation of HA-2 and HA-3 systems) without any alkalinizing reagents.

As noted above, currently there are only theoretical studies of the properties of polyboric acids in assessing their effect on the water chemistry at NPPs with WWER reactors [9]. In addition, in the calculations, only the normal operation of the NPP is considered without regard to a significant increase in the concentration of boric acid in the reactor core in the event of an accident [10].

Thus, to improve the accuracy of calculations of accumulation and crystallization of boric acid and taking into account their impact on the efficiency of heat removal from the core in case of emergency, it is necessary to know the thermophysical and physicochemical properties of H₃BO₃. The existing data on the degree of acidity (pH) and density of boric acid solutions cover a limited range of parameters (temperature, pressure, acid concentration), which is not typical for an accident at a nuclear power plant with WWER [11, 12]. In this regard, there was a need for additional experimental research.

2. Experimental equipment and techniques
At JSC «SSC RF – IPPE» the experimental research of thermophysical and physicochemical properties of boric acid solutions with the parameters characteristic of the first circuit of WWER reactor facility in 24 hours after the start of an accident has been made [13]. The experiments were conducted in two stages. At the first stage, the density of boric acid solutions with a concentration of 2.5-400 g kg⁻¹ H₂O at a temperature of 25-130 °C in the pressure range of 0.1-0.4 MPa were measured in a specially designed test facility [14].

At the second stage of research, the experiments for determining the degree of acidity of aqueous solutions of boric acid depending on the concentration (5-100 g kg⁻¹ H₂O) and temperature (25-50 °C) were conducted. pH-meter MARK-901 – a universal device designed to measure the activity of hydrogen ions (pH) was used for measurements. The measurement error of the activity of hydrogen ions for this gauge is ±0.1 pH.

The experiments were carried out according to the following technique. Before starting the measurements, the pH meter was calibrated in a special buffer solution with a pH of 7.0. Further, in accordance with the given program of experiments, the degrees of acidity of distilled water and boric acid solutions with different concentrations were measured. On laboratory scales BP2100 (maximum weight – mₘₐₓ=2100±0.1 g) the required mass of distilled water (1 kg) is weighed at room temperature.
Then this volume of water is poured into four conical flasks of 250 ml each. These vessels are then sequentially placed in a thermostat filled with distillate and equipped with a heating device for warming up the liquid up to the required temperature (25, 40 and 50 °C). When the specified temperature is reached, the heater is switched off and a pH meter and an electronic thermometer are placed inside the bulb (figure 1). Readings from both devices are recorded within 10 minutes. Then the flask with distilled water is removed from the thermostat. The next vessel with the test liquid is placed inside the device and the procedure is repeated according to the technique described above.

After determining the degree of acidity of distilled water, a solution with a concentration of 5 g kg\(^{-1}\) H\(_2\)O was prepared. For this purpose, 5 g of dry orthoboric acid, pre-weighted on laboratory scales Adventurer Pro AV412C (maximum weight – \(m_{\text{max}}=410\pm0.01\) g), is added to 1 kg of distillate placed in a beaker. Then, with the help of magnetic stirrer MSH-300 a complete dissolution of H\(_3\)BO\(_3\) crystals is achieved. For the preparation of the solutions with concentrations exceeding the limit of solubility of boric acid at room temperature, a heater is switched at the stirring device. Further procedures are performed according to the method described above.

Figure 1. Scheme of test facility for pH measurement of aqueous solutions of orthoboric acid:
1 – test medium, 2 – water vessel, 3 – thermostat, 4 – glass combined electrode, 5 – temperature sensor, 6 – measuring converter.

3. Results of experimental research
The experimental data obtained in [14] are described by the following dependence:

\[
\rho_{\text{sol}} = A + BC_{\text{H},\text{BO}} ,
\]

the coefficients of which are as follows:

\[
A = 1141 - 0.48(T + 273.15);
\]
\[
B = 39217(T + 273.15)^{-0.841},
\]

where \(T\) is the temperature of the solution, °C; \(C_{\text{H},\text{BO}}\) is the concentration of boric acid in the solution, g g\(^{-1}\) H\(_2\)O; and \(\rho_{\text{sol}}\) is the density of the boric acid solution, kg m\(^{-3}\). The maximum error between the calculated and experimental data is 2%. A further ratio (1) is applied in determining the physicochemical properties of boric acid.

In accordance with the developed technique, experiments to determine the pH of aqueous solutions of boric acid were carried out four times for each concentration. The results of experiments on the study of physicochemical properties of boric acid are shown in figures 2 and 3.
Figure 2. Dependence of pH of boric acid aqueous solution on temperature and its concentration: 1 – distilled water, 2-6 – boric acid with concentrations 5, 10, 25, 50 and 75 g kg⁻¹ H₂O, respectively.

As shown in figure 2, the experimental data obtained can be generalized by the following dependence:

\[ pH_{\text{sol}} = pH_{\text{dist}}(T) - (12.72 C_{\text{H₃BO₃}}^{0.59} + 0.49 \times 10^{-2} T), \]

where the degree of acidity of distilled water is:

\[ pH_{\text{dist}}(T) = 6.46 - 1.36 \times 10^{-2} T, \]

\( T \) is the temperature of the medium under study, °C; and \( C_{\text{H₃BO₃}} \) is the concentration of boric acid, g g⁻¹ H₂O. The deviation of the experimental points from the approximating curves does not exceed 10%.

After the experiments, a comparison of the obtained data on the acidity of aqueous solutions of boric acid with those available in the literature was carried out. The analysis has shown that only a fixed value of \( pH=5.2 \) at a temperature of 20 °C and an acid concentration of 0.1 moll⁻¹ (or 1.81 g kg⁻¹ H₂O) is given for \( \text{H₃BO₃} \) in the chemical reference books [15]. In addition, in [16] an expression for calculating the pH of weak acids, which include \( \text{H₃BO₃} \) is presented:

\[ \text{pH} = \frac{1}{2} pK_a - \frac{1}{2} \log(C_{\text{Msol}}), \]

where \( C_{\text{Msol}} \) is the molar concentration of the solution determined from the expression:

\[ C_{\text{Msol}} = \frac{C_{\text{H₃BO₃}} \rho_{\text{sol}}}{M_{\text{sol}}(1000 + C_{\text{H₃BO₃}})}, \]

where \( C_{\text{H₃BO₃}} \) is the concentration of boric acid, g g⁻¹ H₂O; \( \rho_{\text{sol}} \) is the density of the boric acid solution, g l⁻¹; and \( M_{\text{sol}} \) is the molar mass of the mixture, g mol⁻¹.

Also, to calculate the pH value according to the formula (6), it is necessary to substitute the acidity constant \( pK_a \). The analysis of literature data has shown that the information on this value is very limited. For example, reference tables [15] give the value \( pK_a = 9.24 \) only for temperature 25 °C. The paper [12] presents a formula for calculating the acidity constant of \( \text{H₃BO₃} \), but it does not take into account the influence of boron concentration.
Thus, it became necessary to obtain dependence for the calculation of the acidity constant of boric acid. It was obtained from expressions (6) and (7) using empirical dependencies (1) and (4) for calculating the solution density and pH, respectively. This formula has the following form:

$$pK_a = 2(pH_{\text{dist}}(T) - (12.72C_{H_3BO_3}^{0.59} + 0.49 \times 10^{-2} T)) + \log(C_{M_{\text{mol}}})$$  

(8)

where $pH_{\text{dist}}$ is the degree of acidity of distilled water; $C_{H_3BO_3}$ is the concentration of boric acid, g g$^{-1}$ H$_2$O; $T$ is the temperature of the medium, °C; and $M_{\text{mol}}$ is molar mass of the mixture, g mol$^{-1}$.

Figure 4 presents a comparison of the experimental and calculated by formula (6) values of pH of orthoboric acid, taking into account the values of the acidity constant.

![Figure 3](image3.png) **Figure 3.** Changes of the acidity of H$_3$BO$_3$ in the range of boric acid concentration 0-100 g kg$^{-1}$ H$_2$O at different solution temperatures.

![Figure 4](image4.png) **Figure 4.** Calculated and experimental pH values of aqueous solutions of boric acid.

As we can see from figure 4, the difference between values obtained by the calculated and experimental ways does not exceed 10%.

The obtained dependences (4) and (8) for the calculation of physicochemical properties of boric acid are applicable in the following range of parameters:

- boric acid temperature $T = 25-50$ °C;
- concentration of H$_3$BO$_3$ in water $- C_{H_3BO_3} = 0-100$ g kg$^{-1}$ H$_2$O.

**Conclusion**

As a result of research at JSC «SSC RF – IPPE», experimental data on the physicochemical properties of highly concentrated orthoboric acid solutions with parameters typical for the emergency conditions on nuclear power plant with WWER have been obtained. These results can significantly expand the range of known properties of H$_3$BO$_3$ solutions.

The results of experiment are of great importance for NPPs with WWER reactors equipped with passive safety systems. The obtained data can be used to assess the effect of boric acid on the water chemistry parameters of the WWER primary circuit, both in normal operation and in the case of an accident, and to clarify the results of calculations of emergency heat removal processes in the reactor, carried out using computer codes.

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