Determination of the physicochemical properties of boric acid for VVER emergency modes

A V Morozov, A R Sahipgareev, A S Shlepkin and A S Soshkina

State Scientific Centre of the Russian Federation – Institute for Physics and Power Engineering named after A.I. Leypunsky, 1, Bondarenko Sq., Obninsk, 249033, Russia

E-mail: sas@ippe.ru

Abstract. The results of experimental research of physicochemical properties of water solutions of H_3BO_3 are presented in this article. The literature review about the influence of hydrogen ion exponent of H_3BO_3 solutions on its heat and mass transfer, and corrosiveness of an acid in the VVER reactor core in is given. It is found that the existing data does not cover the entire range of parameters (acid concentration, temperature and pressure) characteristic of a possible Loss-of-Coolant Accident (LOCA) at nuclear power plant with a VVER. The problem of the accumulation and crystallization of boric acid in case of LOCA and the operation of passive safety systems (such as hydro accumulators of the first, second and third stages, and a passive heat removal system) is formulated. Test equipment and techniques of research are described. The generalizing equations for the pH and acidity constant of hydrous solutions of H_3BO_3 in range of the concentration (5-100 gkg^{-1} H_2O) and temperature (25-50 °C) has been obtained.

1. Introduction

Within the concept of the safety of the VVER-TOI project, emphasis is paid to issues related to the accumulation and crystallization of H_3BO_3 in the core during Loss-of-Coolant Accident (LOCA) within 72 hours. As is known, the reactor autonomy during an emergency process is determined by the operation of the passive safety systems (PSS). PSS provide the core cooling by feed into the reactor of the water solution of boric acid from the hydro accumulators of the passive core flooding system (figure 1). As well as it is necessary to take into account the flow of condensate from the steam generators (SG) of three non-emergency loops, which operating into condensing mode due to the passive heat removal system [1-3].

Based on this, it is postulated that further mass transfer of boric acid in the core can be carried out in two ways. With a sufficient flow rate of the water solution of boric acid from the system of hydro accumulators of second and third stage (HA-2 and HA-3 systems), mixing of the flows occurs: the incoming solution, the condensate from the SG and the coolant remaining in the lower part of the core. Subsequently, a part of boric acid is carrying out into the break (figure 1, position 4). If the mixing of the condensate flows and the boric acid solution from HA-2 and HA-3 does not occur, then due to the higher density, the boric acid solution drops down to the lower part of the core. Above this layer, condensate accumulates with a low acid concentration. Further excess condensate from the steam generators carry away into the break. Thus, conditions are created for increasing the concentration of H_3BO_3 in the lower part of the core and for achieving the conditions for its crystallization.
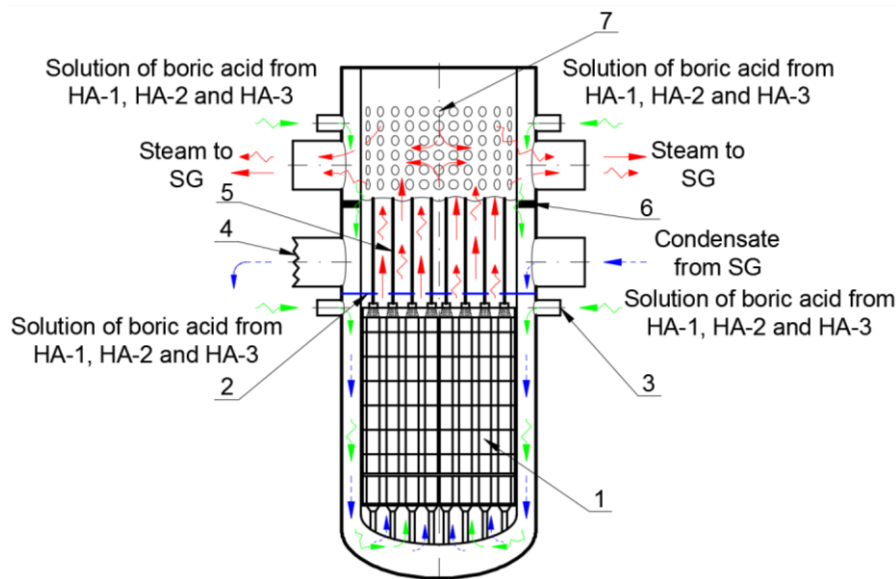
Figure 1. Mass transfer of H_3BO_3 solution in the VVER in LOCA. 1 – core; 2 – evaporation surface; 3 – nozzle of the emergency core cooling system; 4 – primary circuit break; 5 – protective tube unit; 6 – separation collar; 7 – the perforation of reactor barrel

In the research of the accumulation and crystallization of boric acid in the VVER 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_3BO_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 H_3BO_3 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 H_3BO_3 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 VVER, the acidity of the medium due to the presence of an orthoboric acid solution with a concentration of 4-8 gl^{-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 alkalizing 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 VVER 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 and physicochemical properties of H_3BO_3. 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 VVER [11, 12]. In this regard, there was a need for additional experimental research.

2. Experimental equipment and techniques

At Joint Stock Company «State Scientific Centre of the Russian Federation – Institute for Physics and Power Engineering named after A.I. Leypunsky» (IPPE) the experimental research of physicochemical properties of water solutions orthoboric acid with the parameters characteristic of the first circuit of VVER 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 gkg^{-1} H_2O 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 gkg^{-1} H_2O) 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 – m_{max}=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 2). 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 gkg^{-1} H_2O was prepared. For this purpose, 5 g of dry orthoboric acid, pre-weighted on laboratory scales Adventurer Pro AV412C (maximum weight – m_{max}=410±0.01 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_3BO_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.
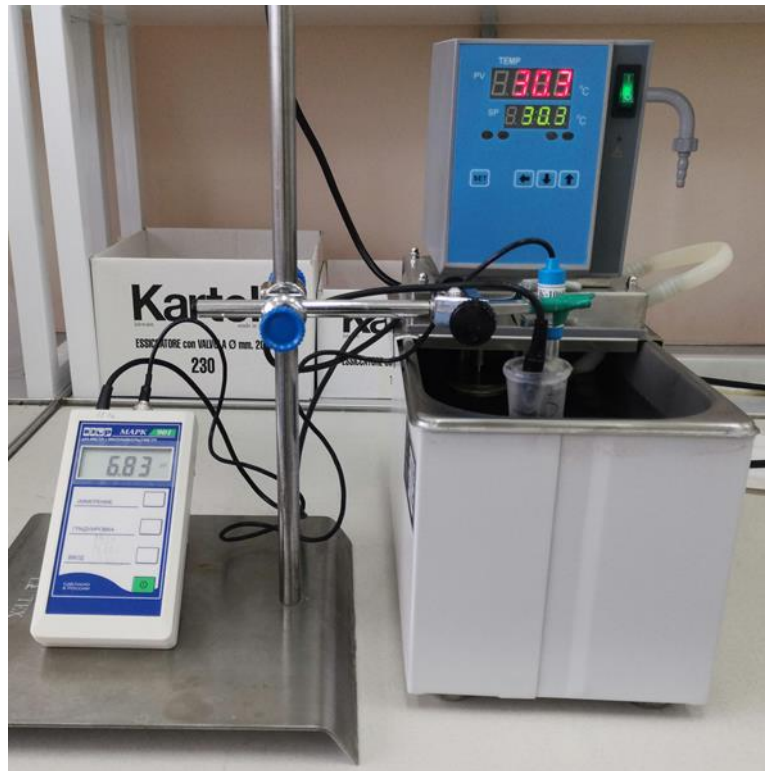
Figure 2. Test facility for hydrogen ion exponent measurement of water solutions of H_3BO_3.

3. Results of experimental research

On the test facility twenty one series of experiments was carried out, each of which included 4 measurements by the method described above. The obtained experimental data on temperature and *pH* were averaged and presented in table 1. Dependences of *pH* of boric acid water solution on temperature at various concentrations are shown in figures 3 and 4.

Table 1. The experimental data.

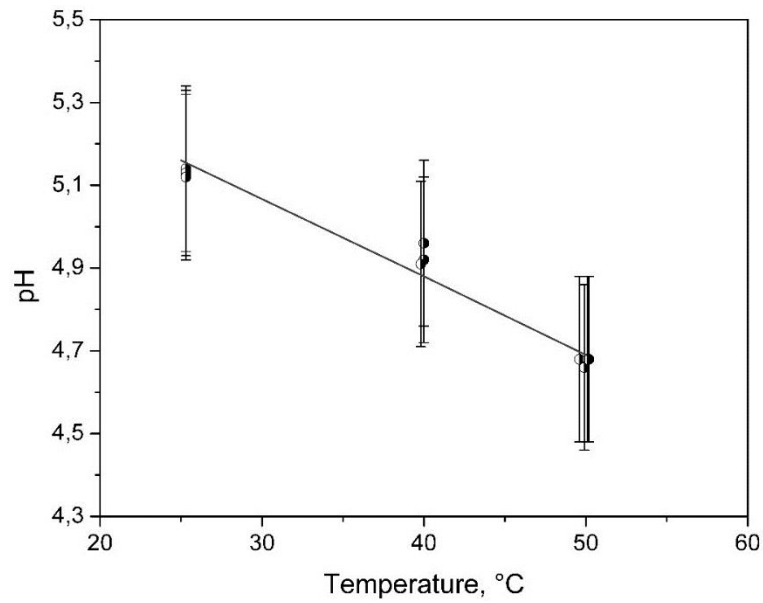| No. exp.	Concentration H_3BO_3 (gkg^{-1} H$_2$O)	Temperature (°C)	*pH*	No. exp.	Concentration H_3BO_3 (gkg^{-1} H$_2$O)	Temperature (°C)	*pH*
1	0	25.7	6.10	12	10	50.0	4.67
2	0	39.9	5.93	13	25	25.3	4.44
3	0	49.8	5.77	14	25	39.7	4.16
4	2.5	25.2	5.72	15	25	49.6	4.03
5	2.5	39.7	5.59	16	50	25.2	3.81
6	2.5	49.9	5.26	17	50	39.8	3.49
7	5	25.1	5.52	18	50	49.6	3.38
8	5	40.0	5.31	19	75	39.8	3.04
9	5	49.8	4.99	20	75	49.9	2.85
10	10	25.3	5.13	21	100	49.6	2.53
11	10	39.9	4.92				

Figure 3. The change of the hydrogen ion exponent of boric acid as a function of temperature at a concentration of 10 gkg^{-1} H$_2$O.

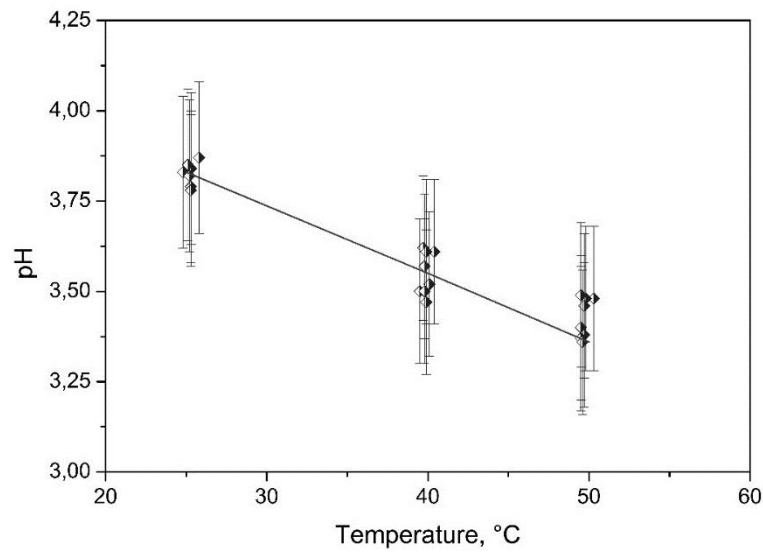**Figure 4.** The change of the hydrogen ion exponent of boric acid as a function of temperature at a concentration of 50 gkg^{-1} H$_2$O.

The experimental data shown in figures 3 and 4 are well approximated by the following dependence:

$$pH_{sol} = pH_{dist}(T_{sol}) - (12.72 C_{H_3BO_3}^{0.59} + 0.49 \times 10^{-2} T_{sol}), \tag{1}$$

where the hydrogen ion concentration of distilled water is:

$$pH_{dist}(T_{sol}) = 6.46 - 1.36 \times 10^{-2} T_{sol}, \tag{2}$$

where T_{sol} is the temperature of the H_3BO_3 solution, °C; and $C_{H_3BO_3}$ is the concentration of boric acid in mixture, gg^{-1}. The discrepancy between the experimental points and the approximating curves is less than 10%.

The obtained experimental data on the hydrogen ion concentration of boric acid were compared with the known literature data. It has been established that, for example, in chemistry manuals [15], the pH of H_3BO_3 is given at a temperature of 20 °C and a concentration of less than 2 gkg^{-1} H_2O. The data obtained in experiments conducted by Westinghouse lie outside the range under study [17]. Also, in [16], an equation for the estimated calculation of the hydrogen ion exponent of weak acids is presented:

$$pH = \frac{1}{2}pK_a - \frac{1}{2}\lg(C_M), \qquad (3)$$

where pK_a is acidity constant; and C_M is the molar concentration of the water solution of H_3BO_3, moll^{-1}.

The molar concentration can be determined taking into account the known empirical dependency for calculating the solution density of boric acid [4] according to the following equation:

$$C_M = \frac{m_{H_3BO_3}\rho_{sol}}{M_{sol}(1000 + m_{H_3BO_3})}, \qquad (4)$$

where $m_{H_3BO_3}$ is the mass of H_3BO_3, g; M_{sol} is the molar mass of the solution, gmol^{-1}; and

$$\rho_{sol} = 1141 - 0.48(T_{sol} + 273.15) + 39217(T_{sol} + 273.15)^{-0.843}C_{H_3BO_3}, \qquad (5)$$

is the density of the boric acid in solution, gl^{-1}; and $C_{H_3BO_3}$ is the concentration of boric acid in solution, gg^{-1}.

In addition, to calculate the concentration of hydrogen ions according to equation (3), it is required to know the acid constant pK_a. Known literature data on the acidity constant are limited [15], and in the formulas for its determination the influence exerted by the concentration of H_3BO_3 is not taken into account [12].

In this regard, it is required to determine the dependence of the acidity constant of boric acid on its concentration in solution. The equation for calculating of acidity constant of H_3BO_3 using empirical dependency hydrogen ion exponent (1) and molar concentration of boric acid (4) was obtained and the following form:

$$pK_a = 2(pH_{dist}(T_{sol}) - (12.72C_{H_3BO_3}^{0.59} + 0.49 \times 10^{-2}T_{sol})) + \lg(C_M), \qquad (6)$$

the terms of the equation are described above.

Figure 5 presents a dependence of pH of boric acid aqueous solutions on various concentrations.

As shown in figure 5, not only temperature, but also concentration affects the change in pH of boric acid.

Equations (1) and (6) for calculating the hydrogen ion concentration and acidity constants presented in this paper can be used in the following parameter interval of boric acid solution:

- temperature of solution T_{sol} =25-50 °C;
- boric acid concentration in water solution – $C_{H_3BO_3}$ = 0-100 gkg^{-1} H_2O.
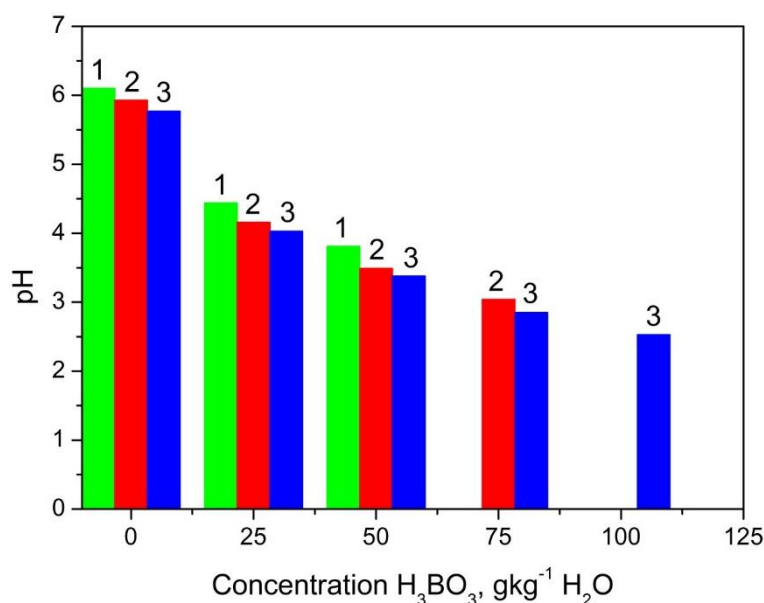
Figure 5. Comparison of the hydrogen ion exponent of boric acid at the change its concentration in the range of 0-100 gkg^{-1} H$_2$O: 1 – 25 °C; 2 – 40 °C; 3 – 50 °C.

4. Conclusion

As a result of research at JSC «SSC RF – IPPE», experimental data on the physicochemical properties of highly concentrated H$_3$BO$_3$ solutions at the parameters typical for LOCA on NPPs with VVER 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 profound interest for NPPs with VVER 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 VVER 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.

Acknowledgments

References
[1]   Berkovich V M, Korshunov A S, Taranov G S, Kalyakin S G, Morozov A V and Remizov O V 2006 *Atomic Energy* **100(1)** 14-9
[2]   Morozov A V and Remizov O V 2012 *Thermal Eng.* **59(5)** 365-70
[3]   Morozov A V, Remizov O V and Tsyganok A A 2010 *Trans. American Nuclear Society 2010 ANS Annual Meeting* (San Diego) 676-7
[4]   Morozov A V, Pityk A V, Ragulin S V, Sahipgareev A R and Shlepkin A S 2017 *Proc. Int. Cong. on Advances in NPP (Fukui and Kyoto)* 186-92
[5]   Morozov A V, Pityk A V, Ragulin S V, Sahipgareev A R, Soskina A S and Shepkin A S 2017 *Journal of Physics: Conference Series* **899(9)** 092010
[6]   Bates R G 1973 *Determination of pH. Theory and practice* (NY: John Wiley & Sons)
[7]   Karapet'yants M Kh and Drakin S I 1981 *Obshchaya i neorganicheskaya khimiya* [General and inorganic chemistry] *(*Moscow: Khimiya) [In Russian]
[8]   Cotton F, Wilkinson G and Gaus P 1987 *Basic inorganic chemistry* (NY: John Wiley & Sons)

[9]   Gavrilov A V, Kritsky V G, Rodionov Yu A and Berezina I G 2012 *Thermal Eng.* **60(7)** 482-6

[10]   Morozov A V, Sorokin A P, Ragulin S V, Pityk A V, Sahipgareev A R, Soshkina A S and Shlepkin A S 2017 *Thermal Eng.* **64(7)** 490–5

[11]   Azizov N D and Akhundov T S 1996 *High temperature* **34(5)** 788-91

[12]   Manov G G, DeLollis N J, Lindvall Ph W and Acree S F 1946 *J. of Research of the National Bureau of Standards* **36** 543-58

[13]   Morozov A V, Sorokin A P, Pityk A V, Sahipgareev A R, Soshkina A S and Shlepkin A S 2018 *Atomic Energy* **125(3)** 178-84

[14]   Morozov A V, Pityk A V, Sahipgareev A R and Shepkin A S 2018 *J. of Physics: Con. Series* **1128** 012103

[15]   Simanova S A 2004 *Novyi spravochnik khimika i tekhnologa* [New Handbook of chemist and technologist] (St. Petersburg: ANO NPO "Professional") [In Russian]

[16]   Glinka N L 1981 *Obshhaya ximiya* [*General chemistry*] (Moscow: Mir publishing) [In Russian]

[17]   Byers W A, Brown W L, Kellerman B E, Shearer K S and Fink D J 2010 Summary of Tests to Determine the Physical Properties of Buffered and Un-buffered Boric Acid Solutions *WCAP-17021-NP Revision 1*