Experimental study of solubility of boric acid in steam at boiling

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Abstract. The paper presents the results of experimental studies of the solubility of boric acid in steam, in a concentration range of 16-245 g H$_3$BO$_3$/ kg H$_2$O at atmospheric pressure. An overview of available literature data on the solubility of boric acid in steam, depending on the initial concentration in the water solution is presented. It has been established that the available in literature results do not cover the entire range of parameters (temperature, acid concentration) which typical for a possible emergency situation at NPPs with WWER. The experimental facility and the research procedure are described. The data obtained as a result of the experiments can be used to calculate the accident processes in the WWER reactor facility during the operation of the passive safety systems such as the passive core flooding system, the passive heat removal system from the steam generator and the system of the hydraulic accumulators of the third stage.

1. Introduction

At the moment, nuclear energy faces a number of problems, without the solution of which the successful continuation of its development is not possible. One of the most important of them is ensuring that serious accidents are avoided. In the Russian project AES-2006 with the WWER-1200 reactor facility, this task is being solved by using advanced safety systems that provide a significant advantage over previous generations of nuclear power plants [1, 2]. The project implements new passive safety systems, such as passive core flooding systems from the hydraulic accumulators of the first and second stages (HA-1 and HA-2 systems), the passive heat removal system, and the passive filtration system [3]. Within 24 hours, they ensure a continuous removal of residual heat from the core in case of the event than active safety systems for some reason cannot start their operation [4].

During the operation of passive safety systems, a solution of boric acid with a concentration of 16 g H$_3$BO$_3$/ kg H$_2$O comes into the core from the hydraulic accumulators of each stage [5]. Due to the duration of the process, given the low acid concentration in the vapor phase, it is possible to increase the amount of boric acid in the core coolant and to achieve crystallization conditions in the reactor volume, which may lead to a deterioration of the heat transfer [6, 7]. According to calculations carried out at IPPE [8, 9], after 24 hours of the emergency process, the boric acid concentration in the core is approximately 311 g H$_3$BO$_3$/ kg H$_2$O and does not reach the solubility limit.
However, according to EUR requirements for nuclear power plants of new generation, in case of accidents, the system of heat removal from the core should be designed for 72 hours of autonomous operation. In the WWER-TOI project, this task is being achieved by introducing an additional system of hydro accumulators of third stage (HA-3), which consists of 12 tanks with a total volume of 720 m³ filled with boric acid solution.

Thus, because of coming into the core the additional mass of boric acid, its solubility limit (~ 400 g H₃BO₃/ kg H₂O) in the core could be exceeded after 24 hours of the accident. Removal of boric acid from the reactor due to the solubility at steam or as a result of droplet entrainment can significantly reduce the risk of its crystallization in the core. Consequently, the experimental study of the processes of removal of boric acid from the core is of great practical importance for calculating emergency modes at nuclear power plants with WWER reactors equipped with passive safety systems.

In the literature, there are a number of studies of the solubility of boric acid in saturated water steam [10-13]. Thus, in [10], the solubility of boric acid in a vapor was studied by evaporation of a small part of a solution of a given concentration using a special test facility. The droplet entrainment was reduced to a minimum. To prevent condensation of steam on the walls, the facility had a steam jacket. The calorimetric method using carmine and the volumetric method by means of mannitol were used to determine the content of boric acid in samples of steam condensate. The tests were carried out in the pressure range from 0.1 to 20 MPa. The concentration of boric acid in water varied from 0.2 to 22 g H₃BO₃/ kg H₂O. As a result of the studies, a linear dependence of the concentration of boric acid in saturated steam on its concentration in water was discovered. It was also found that the distribution coefficient of boric acid

\[ K_D = C_s \left( \frac{\rho_s}{\rho_w} \right)^{0.9}, \]

where \( C_s \) and \( C_w \) are concentrations of H₃BO₃ in vapor and liquid phases correspondingly, \( \rho_s \) and \( \rho_w \) are densities of steam and water, kg/cub. m.

In [11], the authors considered experiments on the distribution of borates and boric acid between steam and water. The pressure range of 0.2-20 MPa was investigated. The concentration of boric acid in water and pH of boiling water changed in a wide range in the tests. In [13] the values of the distribution coefficients of borates and boric acid are presented as a function of the ratio of the solvent phase densities. It is noted that as the pH is increased, the distribution coefficient \( K_D \) is decreased.

The authors established the dependence of the distribution coefficient of boric acid on the degree of dissociation determined by the pH value:

\[ K_D = \beta \cdot K_D^{und} + (1-\beta) \cdot K_D^d, \]

where is \( K_D^{und} \) is the distribution coefficient of undissociated boric acid molecules; \( K_D^d \) is the distribution coefficient of dissociated ions; \( \beta \) is the degree of hydrolysis of the given salt. However, this relationship is valid only at pressures above 3 MPa.

The results of experiments carried out at a temperature of 155 °C in the pressure range from 0.02 to 0.55 MPa are presented in [12]. The authors found that at 155 °C at low water pressures, a decrease in the concentration of boric acid in samples is observed, but then, when the water pressure exceeds 0.2 MPa, the sharp increase of concentration occurs.

In the book [13] some physical and chemical properties of dry boric acid are presented and the values of the molar volume concentration of boric acid in the distillates obtained by distilling it with steam in the temperature range from 90 to 140 °C are given.
In addition to the direct study of the solubility of boric acid, studies have also been carried out earlier in which the solubility value was set for carrying out a calculated or experimental analysis of the processes occurring during an accident in the reactor [14, 15]. Thus, based on the analysis of the publications on the solubility of boric acid in a steam, it can be concluded that the studies of this process were carried out at H$_3$BO$_3$ concentrations, which are not typical for the emergency operation of passive safety systems of NPPs with WWER. It follows from this that it is necessary to carry out an experimental study of the solubility of boric acid in a steam on conditions that equal to those ones for emergency situations at reactor unit.

2. Test facility

To study the processes of mass transfer of boric acid the test facility was constructed in IPPE. An arrangement of main equipment of the test facility is shown in figure 1 and the process flowsheet of the facility is presented in figure 2.

The test facility includes: a solution preparation tank with a volume of ~ 14 l; test section made of stainless steel with an internal diameter of 27 mm and a height of 2800 mm; steam separator; steam condenser. The lower (evaporative) part of the test facility is heated with an adjustable heater. The main equipment of the facility is connected between each other by insulated and heated technological lines and equipped with shut-off valves. The height from the level of the boiling liquid to the line of steam extraction in the test section corresponds to the distance from the evaporation surface in the WWER reactor vessel to the lower generatrix of the cold branch of the main circulation pipeline. The auxiliary equipment of test facility includes: a pressure maintenance system, H$_3$BO$_3$ solution supply system, a temperature maintenance system, and a condenser power control system. The experiments were carried out at a test section power of approximately 350 W.

The instrumentation installed on the test facility allows the following parameters to be recorded during the experiments: the pressure and temperature of the medium in the solution preparation tank and test section, level of the boric acid solution in the test section.
The pressure is registered with the METRAN-150 gauge (measurement error ± 0.1% of the pressure range). Monitoring of the boric acid solution level in the test section is carried out using a glass level gauge. To measure temperature, cable thermocouples of K type with a diameter of 1 mm (measurement error of 1 °C) are used. The sampling frequency of measuring channels of the data acquisition system is equal to 1 Hz. The main measured value in the experiments is the concentration of H$_3$BO$_3$ in the condensate samples obtained by condensing the steam generated in the test section by boiling of boric acid solution.

3. Test procedure
At the beginning of the test, solution preparation tank was filled with necessary amounts of distilled water and dry powder of H$_3$BO$_3$ to make a solution of boric acid with a given concentration. Then the solution was mixed by a mechanical device up to achieving the complete dissolution of the dry H$_3$BO$_3$, which was monitored by means of portholes on the tank. After that nitrogen was supplied to the upper volume of the solution preparation tank from gas cylinder through the gas reducer. Thus a gas cushion was created with a pressure exceeding the saturation pressure at a given temperature in order to prevent the boiling of boric acid in the tank. Further, the solution preparation tank, the test section and the H$_3$BO$_3$ solution supply line were successively heated to the required temperatures. The set temperature is maintained with an accuracy of ± 1 °C throughout the entire experiment using a relay controller.

After the preheating is completed, the valves in the H$_3$BO$_3$ solution supply line are opened in series, and the lower part of the test section is filled to a necessary level with a solution of boric acid with concentration equal to the concentration in the preparation tank. Further, the power of the main electric heater on the test section is increased to a predetermined level, recorded from the voltmeter and ammeter readings, which leads to the start of the H$_3$BO$_3$ solution boiling and a decrease in the liquid level in the test section.

Then, using a gradual opening of the control needle valve (valve V6, figure 2) on the H$_3$BO$_3$ supply line, a flow rate from the solution preparation tank corresponding to the flow of steam from the test section is established, which leads to stabilization of the solution level in the evaporation part of the test section. At the same time, in order to prevent the presence of a steam-air mixture in the test section, by the opening of a blow-off valve, the steam-air mixture is blown out of the main equipment into the atmosphere. Then the steam condenser power is adjusted. Increasing of its power is provided by the switching on of the air fans. The criterion for the achievement of the required value of the condensation power is the constancy of the value of the pressure in the test section and the temperature of the condensate at the outlet of the condenser. Then periodically during the whole experiment a 50-ml samples of condensate is taken to the measuring containers. The actual evaporation power of the facility was determined by the duration of condensate gathering at the time of sampling. After the completion of the experiment, the titration method was used to determine the concentration of boric acid in the samples.

4. Results of experimental study
The experiments considered in this article were carried out at atmospheric pressure and steam mass flow from the test section, varying in the range of 0.154-0.162 g / s. The initial concentrations of boric acid in the solution preparation tank were 10, 16, 20, 30 and 80 g H$_3$BO$_3$/ kg H$_2$O - in order to study the solubility of H$_3$BO$_3$ in a steam at different rates of acid accumulation in the test section. Average steam flow rate in test was 0.157 g/s and average temperature at the outlet of the condenser was about 30 °C.

Six experiments were performed during this series. In figure 3 the accumulation of boric acid in the evaporative part of the test section is shown. It could be seen from figure 3 that the change in the concentration of boric acid has the character of linear dependence. The slope of the straight line depends on the initial concentration of boric acid coming into the evaporative part of the test section C(H$_3$BO$_3$)$_0$, and the power of the facility.
In Figure 4, the dependence of boric acid concentration in saturated water steam on its content in water at atmospheric pressure is presented. As can be seen from Figure 4, the experimental values of the solubility of boric acid in a steam with an error of 20% can be described by a linear relationship of the following form:

$$C(\text{H}_3\text{BO}_3)_{\text{s}} = 0.0014 \cdot C(\text{H}_3\text{BO}_3)_{\text{TS}},$$  \hspace{1cm} (3)

where $C(\text{H}_3\text{BO}_3)_{\text{s}}$ is the concentration of boric acid dissolved in the steam, g/kg H$_2$O; $C(\text{H}_3\text{BO}_3)_{\text{TS}}$ is concentration of boric acid solution in the test section, g/kg H$_2$O. This dependence is valid at a steam pressure of 0.1 MPa and in a H$_3$BO$_3$ concentration range of 16-245 g H$_3$BO$_3$/ kg H$_2$O.

In addition, it should be noted that the deviation of the solubility of boric acid in a steam in two experiments performed at the same concentration in a boiling solution equal to 30 g H$_3$BO$_3$/kg H$_2$O does not exceed 7%, which indicates a satisfactory repeatability of the results.

As can be seen from Figure 5, the distribution coefficient of boric acid $K_D$ at the entire range of the investigated concentrations of H$_3$BO$_3$ remains constant practically up to the solubility limit. The average value of the distribution coefficient from the results of processing all the experimental data is 0.0014, which coincides with an accuracy of 10% with the values given in the literature [11] for solutions with lower concentrations of boric acid.
5. Conclusion
To study the processes of solubility of boric acid at steam the test facility was constructed in IPPE. The experiments were carried out at atmospheric pressure and an average steam flow rate of 0.157 g/s. The initial concentration of boric acid ranged from 10 to 80 g H\textsubscript{3}BO\textsubscript{3}/kg H\textsubscript{2}O.

The results of the experiments confirm the data available in the literature that the rate of growth of the concentration of boric acid in water vapor is described by a linear law. The range of application of the known dependence, which makes it possible to calculate the solubility of H\textsubscript{3}BO\textsubscript{3} in steam, is extended to a concentration of boric acid in a solution of 245 g H\textsubscript{3}BO\textsubscript{3}/ kg H\textsubscript{2}O, close to the solubility limit of H\textsubscript{3}BO\textsubscript{3} in water at atmospheric pressure.

The data obtained as a result of the experiments can be used for the computational modeling of emergency processes in the WWER reactor facility during the operation of passive safety systems, including a passive core flooding system, a passive heat removal system from the steam generator and a system of the hydraulic accumulators of the third stage.

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