Experimental modelling of mass transfer of boric acid with steam at parameters characteristic for VVER reactors in emergency mode

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Abstract. The paper presents experimental data obtained during the study of the mass transfer of boric acid with steam at a pressure of 0.1-0.3 MPa in the concentration range of 16-440 gkg⁻¹ H₂O. The volatility of boric acid in a range of parameters typical for a possible emergency at the VVER nuclear power plants (NPPs) was studied using the test facility. As a result, new experimental data on the change in the concentration of boric acid in steam during its boiling were obtained. The range of applicability of the dependence for determining the distribution coefficient of H₃BO₃ between the steam and the boiling coolant has been expanded.

1. Introduction

In the case of a possible loss-of-coolant accident (LOCA) at the NPPs with VVER reactor, the coolant will inevitably leak from the core. The fluid leak will cause a decrease in pressure in the primary circuit. Such circumstances pose a danger to the integrity of the shells of fuel rods. There is a danger of their melting and release of radioactive fission products into the environment since the heat sink will decrease.

A passive core flooding system contains hydraulic accumulators of the first (HA-1), second (HA-2), and third (HA-3) stages designed to compensate for the loss of coolant from the primary circuit in modern designs of NPPs with generation III+ VVER. All hydraulic accumulators were filled with a solution of boric acid with a concentration of 16 gkg⁻¹ H₂O [1]. A passive core flooding system is initiated if the pressure in the primary circuit drops below a certain level. The HA-1 system is designed to fill the core during the short time before the main emergency systems begin operating. The HA-2 system's tanks containing the solution of boric acid can be used to cool the reactor within 24 hours after the accident. The HA-3 system (provided as an option in some projects) is put into operation after the termination of the coolant flow from the tanks of the HA-2 system. It is capable of providing heat removal from the core over the next 48 hours. Thus, the coolant's combined volume in the passive core flooding system is sufficient for emergency cooling during three days after the start of the accident. It is taken into account that the generated steam will condense in the steam generators due to the operation of the passive heat removal system and return to the core [2].

However, taking into account steam generation due to the boiling of the coolant in the reactor, an increase in the concentration of boric acid in the core should be expected [3]. In this case, the solubility limit of H₃BO₃ at the accident parameters (~ 400 gkg⁻¹ H₂O) can be exceeded after 24 hours
of the accident. It may lead to deterioration in heat removal [4]. The possibility of crystallization of boric acid in the core of nuclear reactors in an emergency is confirmed by calculation and experimental studies [5, 6]. The removal of boric acid from the reactor with steam or due to droplet entrainment can significantly reduce the risk of its crystallization. Therefore the study of the processes of mass transfer of boric acid from the core is of practical importance for calculating processes during emergencies at NPPs with the new generation VVER equipped with passive safety systems.

It was found that the data available in the literature [7-12] do not cover the whole range of parameters (temperature and acid concentration) that is typical for an emergency at Russian NPPs with VVER [13].

For example, in [7, 8], the volatility of boric acid with steam in a test facility in the pressure range of 0.1-20 MPa was studied. The concentration of H3BO3 in water changed from 0.2 to 22 gkg-1. The condensation on the walls of the test section and droplet entrainment was minimized in the experiments. The authors of [7] founded a linear dependence of the concentration of boric acid in saturated steam on its concentration in the water when processing the experimental data. It was revealed that the volatility of H3BO3 with steam does not depend on the concentration of boric acid in boiling solution within the studied range of parameters. Based on the processing of experimental results, the volatility (distribution coefficient) of boric acid as the ratio of the densities of steam and liquid phases of the coolant is obtained. Besides, in [8], it is noted that with an increase of pH from 8 to 12, the distribution coefficient decreases. The dependences applicable at pressures above 3 MPa were obtained.

The results of an experimental study of the volatility of boron with steam during boiling of aqueous solutions of borates (boric acid, sodium penta- and tetraborates) as applied to boiling reactors (BWR) are presented in the paper [9]. The experiments were carried out using two test facilities. The first was an autoclave with a volume of 2 liters, in which the authors managed to achieve the following parameters: temperature up to 330 °C, and pressure up to 13 MPa. The volatility of boron from boiling aqueous solutions depending on the temperature (100-330 °C), boron concentration (0.1-20 gL-1), pH (3.5-10.2), and the type of chemical compound were investigated in an autoclave. The second test facility was BORAN. It is a model of the first circuit of a boiling reactor in volumetric and high-altitude scaling ratios of 1:6000 and 1:1. In experiments, the reactor model was filled with two-thirds of its volume with the test solution, similar to the real BWR. The maximum power of the test facility was 50 kW. The vapor content above the boiling solution was measured using special sensors [9]. The working parameters on the test facility were limited to a temperature of 225°C at a pressure of 2.5 MPa. In BORAN, only aqueous sodium pentaborate solution with a maximum concentration of 8 gL-1 with a void fraction content in a two-phase flow up to 70% was studied.

The authors of [9] have found the dependence of boron volatility on the following parameters: concentration, temperature, pH of the solution, the composition of the medium (boric acid or sodium borates), and the void fraction in two-phase flow. Also, it was found that the concentration of boron dissolved in steam does not exceed several percents of the boron concentration in boiling borate solutions. Parallel with measuring of volatility, the authors of [9] determined the physicochemical reasons for the transfer of boron from liquid to the steam phase. It was found that only boric acid was carried away with the steam flow during the boiling of sodium borates. The main reason for this process is the nature of boric acid, namely, weak acidity, resulted from very weak dissociation. This conclusion was drawn based on the borate frequency scale called the "Borate Vector" [10, 11], according to which solid borates dissociate in water to form lower borates and boric acid. The amount of H3BO3 formed in the sodium borate solution depends on the pH value.

The results of determining the solubility of boric acid in steam at a limited concentration range at atmospheric pressure are presented in paper [12].

An analysis of the literature data performed showed that experimental data on the solubility of boric acid in steam were obtained for low concentrations in a boiling solution. In this regard, it became necessary to carry out additional experiments within an extended range of concentrations and pressures to use the obtained data in the calculation of the emergency at NPPs with VVER.
2. Test facility and procedures
Experiments to determine the volatility of boric acid with the steam at the parameters typical for a possible accident at the NPPs with VVER were carried out in IPPE JSC. The facility designed for this research is shown in figure 1.

![Test facility diagram](image)

Figure 1. Test facility to determine volatility of boric acid in steam: 1 – solution preparation tank; 2 – test section (TS); 3 – condenser; 4 – sampling; 5 – line of H$_3$BO$_3$ solution supply; 6 – a cylinder of the gas supply system; 7 – steam extraction lines; 8, 9 – pressure sensors; 10 – mixing device.

The test facility includes a solution preparation tank; test section - evaporator (TS), made of a two-piece stainless steel cylindrical pipe with a height of 2.8 m and an inner diameter of 0.027 m; separation device inside TS designed to eliminate droplet entrainment; condenser and auxiliary systems to maintain pressure, temperature, supplying a solution and controlling the power of the condenser. The heating of the test section is carried out by an adjustable nichrome heater. The altitude mark of steam extraction in the TS is equal to the distance between the evaporation surface and the axis of the cold nozzle of the reactor. The main elements of the test facility are connected by the technological lines equipped with shut-off valves.

The following parameters were recorded using the sensors: pressure and temperature in the solution preparation tank and the test section; steam flow rate and fluid level into TS. The stability of the level of boric acid solution in the evaporation zone of the test facility is an essential condition for obtaining reliable experimental data. The monitoring of the level of boric acid solution in TS is carried out using a liquid-level gauge. The temperature is measured with the K type cable thermocouples with the accuracy of ±1 °C. The pressure in the system is recorded using METRAN transducers (measurement error ± 0.1%). The data is recorded with a frequency of 1 Hz.

The experiments started with the making of a solution of the required concentration. To this, the necessary quantity of dry boric acid and two-thirds of the required volume of distilled water is poured into the solution preparation tank. Then the remainder of the water is added, and the mixing device is turned on. The solution is stirred until complete dissolution of boric acid. After then, nitrogen is
pumped into the upper part of the solution preparation tank to create necessary pressure. Next, the test facility is heated to the required temperature with accuracy 1 °C.

Then, a heated solution of boric acid is delivered to the test section through a series of valves on the supply line. Control over the filling of the test section is carried out according to the glass liquid-level gauge. Then the power of electric heaters increases, which causes the liquid to boil inside the TS and accordingly to decrease in its level. The compensation of evaporated acid is carried out from the solution preparation tank through the line equipped by a needle valve. The flow of generated steam is directed to a condenser. Condenser power is adjusted by changing the airflow from the fans. The sampling of condensate is carried out periodically into measured containers with a volume of 50 ml.

The principal measured value in the study was the concentration of boric acid in the condensate samples received from the test section. It was determined by the method of quantitative analysis (titration).

3. Experiment Results

The experiments on the test facility were carried out at three steam pressures: 0.1; 0.2, and 0.3 MPa, and with concentrations of boric acid in a solution ranged from 16 to 440 gkg\(^{-1}\) H\(_2\)O. The initial acid concentration in all experiments was assumed to be the same, equal to 16 gkg\(^{-1}\) H\(_2\)O. This concentration corresponds to the acid content in the hydraulic accumulators of the passive core flooding system of the VVER reactors.

Figure 2 shows the dependencies of the concentration of boric acid in saturated steam on its content in water in the studied pressure range. It can be seen from the figure that at all the pressures studied, a linear character of the change in the concentration of acid in the steam is observed. The maximum concentration of boric acid in the steam is 1.6 gkg\(^{-1}\) when boiling a solution of boric acid with a concentration of 440 gkg\(^{-1}\) H\(_2\)O.

![Figure 2: The dependence of the solubility of boric acid in saturated steam on its content in the water at various pressures](image)

![Figure 3: The dependence of the volatility of boric acid on the concentration in the test section at various pressures](image)

The obtained experimental data with an error not exceeding 20% can be described by the following dependence:

\[ C_{\text{steam}} = K_D \cdot C_{\text{sect}} \] (1)
where \( C_{\text{steam}} \) is the concentration of boric acid dissolved in steam, g kg\(^{-1}\) H\(_2\)O; \( C_{\text{sect}} \) is the concentration of acid in the test section, g kg\(^{-1}\) H\(_2\)O; and \( K_D \) is the distribution coefficient (volatility) of boric acid between the phases of the coolant, equal:

\[
K_D = 105.4 \cdot 10^{-4} \cdot P_{\text{sect}}
\]

where \( P_{\text{sect}} \) is the pressure in the test section, MPa. Dependences (1) and (2) are valid in the pressure range of 0.1-0.3 MPa and \( \text{H}_3\text{BO}_3 \) concentration in the liquid phase of 16-440 g kg\(^{-1}\) H\(_2\)O.

The change in the calculated distribution coefficient \( K_D \) at various pressures is shown in Figure 3. Figure 3 shows that the distribution coefficient (volatility) of boric acid between the phases in the studied range of parameters remains constant, almost to the limit of solubility at a fixed pressure. An increase in steam pressure leads to a significant increase of \( K_D \). The mean value of the distribution coefficient at a steam pressure of 0.3 MPa is 0.0035.

**Conclusions**

The experimental studies of the volatility of boric acid at the parameters characteristic for emergency operation of NPPs with VVER were provided in IPPE JSC using the test facility at a pressure of 0.1-0.3 MPa and a concentration range of boric acid of 16-440 g kg\(^{-1}\) H\(_2\)O. The results of the experiments made it possible to obtain the dependence for calculating the concentration of boric acid in the steam. The dependence validity range was extended to the maximum solubility limit of \( \text{H}_3\text{BO}_3 \) in the coolant during the LOCA. The data obtained from the experiments can be used to simulate emergency processes in the NPPs with VVER reactor during operation of passive safety systems complex designed to cool the core for 72 hours.

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