About the volatility of boron in aqueous solutions of borates with vapour in relevance to BWR-Reactors

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Abstract

In BWR-reactors a boron injection system is installed to control a total or partial ATWS accident. The injected boron will be spread in the fluid and some of the boron will leave the reactor with the exhausted vapour. To analyse the lost of boron with the vapour is the great aim of this thesis. The volatility of the boron solution was measured by experiments in a little autoclave vessel up to 330 °C and 13 MPa and in a circulation loop called BORAN up to 225 °C and 2.5 MPa.

In the two test facilities different boron compounds in solution were analysed. Mostly, solutions of Disodium-Pentaborat are used because only this compound will be injected in BWR-reactors as a high concentrated solution. The boron concentration in the vapour depends mainly on temperature and void fraction of the two-phase-flow. The volatility can take values about some percent. As well the reason of the volatility of the analysed solutions will be discussed within a chemical background.

1. Introduction

Since boron is a very good captor for thermal neutrons, it is used to shut down the BWR-reactor, if the control rods fail. To investigate the boron injection system of a BWR, detailed knowledge about the boron compound that is used in the case of transient conditions is necessary. The compound, which will be injected into the reactor pressure vessel (RPV), is a solution of Disodium-Pentaborate-Decahydrate with a concentration not less than 135 g/L. For quantitative analysis of the boron content in the RPV during and after injection it is necessary to investigate the boron compound and the boron transport with steam.

This boron injection system is installed at every BWR all over the world and is only used in state of emergency. Because of the very good facility management in the power plants the control rods never failed and so this injection system was never used up to now. That is why it is very important, especially for probabilistic analyses, to know the effectiveness of this system.
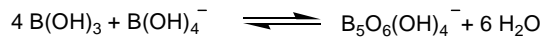
2. Theoretical background

Theoretically, all borate ions can be constructed out of boric acid and meta borate ions and also divided into these parts in aqueous solution. This is demonstrated in equations (1) to (3). In equation (1)
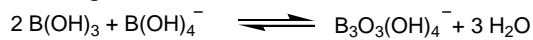
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the penta, in equation (2) the tri and in equation (3) the tetra borate is originated. The compound Disodium-Tetraborate-Decahydrate is also called Borax.
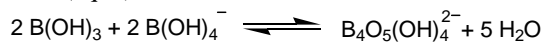
(eq. 1)
$$4\ B(OH)_3 + B(OH)_4^- \rightleftharpoons B_5O_6(OH)_4^- + 6\ H_2O$$

(eq. 2)
$$2\ B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3\ H_2O$$

(eq. 3)
$$2\ B(OH)_3 + 2\ B(OH)_4^- \rightleftharpoons B_4O_5(OH)_4^{2-} + 5\ H_2O$$

If the solid borates dissociate in water, they are forming lower borates and boric acid. How much of each borate will be created, depends on the pH-value of the solution. The region of interest starts for pH-values below 5 at approximately 100 % boric acid and ends with nearly 95 % meta borate for pH-values higher than 11. For pH-values in-between these borders, all other borates are detectable, for example using Raman spectroscopy (Anderson, 1964, Attinà, 2000) or other methods, like high-field-NMR (nuclear magnetic resonance) (Momii, 1967, Salentine 1983). The frequency scale of the borates is called "Borate-Vector" (Maya, 1976, Maeda, 1979) (see Fig. 1).
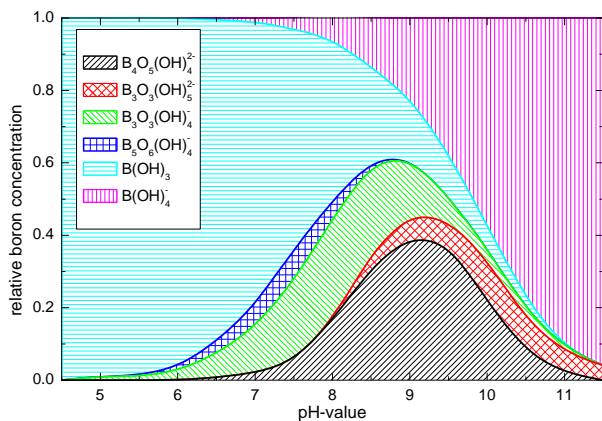

Fig. 1. pH-dependence of the "Borate-Vector" of solutions of borates.

Consequently, it is possible to create the higher borate ions with boric acid and hydroxide ions in various constitutions. The equilibrium concentrations of the boric acid and the hydroxide ions define the created borates, according to the mass action law. For pH-values below 10 a defined content of boric acid is always a present component in any solution of borates. This knowledge is very important to perform the analysis of the experiments about the volatility of borates in boiling aqueous solutions into steam.

3. Experimental investigation

3.1. Autoclave

To analyse the volatility of boron out of a solution of Sodium-Pentaborate an autoclave with a volume of 2 litres and the maximum experimental conditions of 330 °C in temperature and 13 MPa in pressure was used. The vessel was filled with a known solution (compound, concentration and pH-value). In the cap of the vessel a steam pipe with valve and condenser is attached. With this valve steam samples can be taken out of the vessel and condense at all temperatures.

3.2. BORAN – circulation loop

The autoclave has with the exception of the pressure and temperature no similarities with the RPV of a BWR. To have a better opportunity to compare the collected measurement data with a real BWR, a circulation loop called BORAN (BOR ANalysis) was constructed at the Technische Universität Dresden (see Fig. 2). In this facility the lost of Boron out of boiling solutions can also be analysed in dependence of the void fraction in the two-phase-flow, as one of the most important thermodynamic parameter in the BWR.

This facility is a model of the primary circuit of a RPV in volumetric scale 1:6000 and axial scale 1:1. The inner volume of the facility is 70 litres. At a normal fill level of 5500 mm are 45 litres for fluid and 25 litres for steam and gas, similarly scaled like in a real BWR. In five 3710 mm long electrical heater rods an installed power of 50 kW simulates 10 % of the scaled reactor power. A Wire-Mesh-Sensor from Forschungszentrum Dresden-Rossendorf measures the void fraction above the heater. To enlarge the spectrum of experiments an additional steam generator was connected to the loop to increase the pressure at constant coolant temperatures.

In BORAN it is possible to simulate the boron injection with a dosing pump and to investigate the lost of boron with the steam out of the facility. As well the transport of boron in the compound borate can be shown in fluid flow path by integrated measurement system of conductivity sensors. To simulate a LOCA (lost of coolant accident) in the upper part a valve connects the BORAN with the atmosphere with an 8 mm pipe.
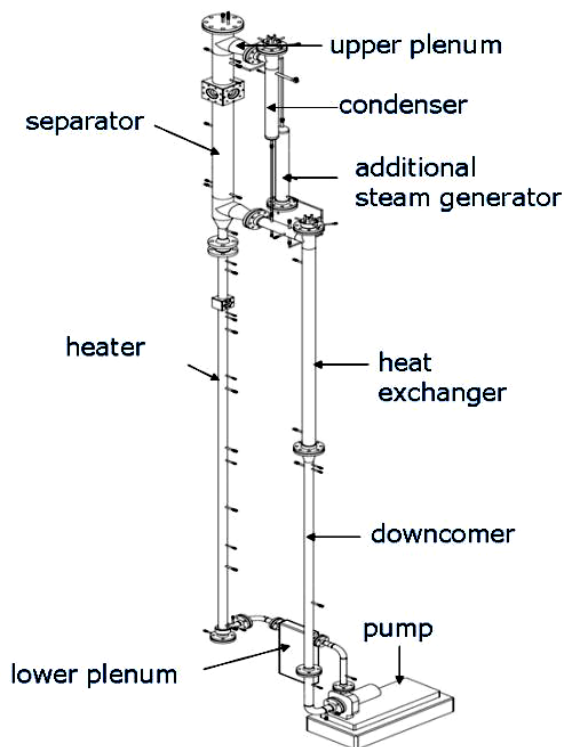

Fig. 2. Scheme of the BORAN facility to simulate a boron injection transient in a BWR-RPV
(technical data: max. pressure **2.5 MPa**, max. temperature **225 °C**, max. heater power **50 kW**, heater height **3.71 m**, total height **8.17 m**).

3.3. *Measurement matrix and analysis*

In the autoclave the volatility of boron out of boiling solutions was analysed in dependence of temperature (100 °C to 330 °C), boron concentration (0.1 g/L to 20 g/L), pH-Value (3.5 to 10.2) and also the compound (penta borate, tetra borate and boric acid). Three times the pH-value of the solution was changed with hydrochloric acid or sodium hydroxide. The temperature of the BWR at normal operation is 270 °C. Because of an estimated cool down of the reactor before boron injection, the temperature area between 100 °C and 200 °C is for the boron injection transients the most important. To have a complete data set of the volatility of boron also experiments until 330 °C and 13 MPa and with different compounds were performed.

In BORAN the temperature is limited to 225 °C at a pressure of 2.5 MPa. Because of the bigger volume of 50 litres only analysis with penta borate solution at a maximum concentration of 8 g/L was done, but this at different void fractions in the two-phase-flow from 0 up to 70 %.

The condensed steam samples had been analysed with ICP-MS (inductively coupled plasma - mass spectrometry) at the VKTA (Verein für Kernverfahrenstechnik und Analytik Rossendorf e.V.).

4. Results and discussion

The measurement data in figure 3 was generated with the autoclave, the data in figure 4 with the BORAN facility. Indicated concentrations are pure boron concentrations.

All the measurement data are used to calculate analytic coefficients (5 – 10). Out of these coefficients an equation (4) was constructed. With this equation the volatility (v) for all boron compounds can be calculated very easily at defined conditions. The volatility is described as the quotient of c_{BK} and c_{BA} (4) without any unit.

$$v = \frac{c_{BK}}{c_{BA}} = \frac{a_c \cdot a_{pH} \cdot a_t \cdot a_{void} \cdot a_{BC}}{c_{BA} / \frac{g}{L}} \qquad (4)$$

c_{BK} =   boron concentration in the condensate
c_{BA} =   boron concentration in primary coolant
c_{NaPBO} = concentration of Sodium-Pentaborate

To describe the influence of the boron concentration the coefficient a_c is used. The analytic description is divided into two parts.

for $c_{BA} < 1.5$ g/L:
$$a_c = 0.0036 \cdot \frac{c_{BA}}{g/L}$$

else:
$$a_c = 0.0038 \cdot \left(\frac{c_{BA}}{g/L}\right)^{0.7} \quad (5)$$

as information:
$$c_{BA} = c_{NaPBO} \cdot K_{Mol} \quad (6)$$

Table 1
Calculation of K_{Mol} for equation (6)

Boron comp.	$n_{Bor} \cdot M_{Bor}$ / g/mol	$M_{Comp.}$ / g/mol	K_{Mol}
boric acid	10.8	61.8	0.175
penta borate	108	590	0.183
tetra borate	43.2	424.2	0.102

The dependence of the pH-value, the temperature and the void fraction can be calculated with the following equations (7 – 9). The linear influence of the void fraction is exponentially weighted by the temperature (9).

$$a_{pH} = \left(8.906 + \left(\frac{-7.874}{1 + e^{\frac{pH - 9.54}{0.327}}}\right)\right)^{-1} \quad (7)$$

$$a_t = -0.08 + 0.0091 \cdot \frac{t}{^\circ C} \quad (8)$$

$$a_{void} = 1 + 0.2 \cdot void \cdot e^{\frac{t}{60 ^\circ C}} \quad (9)$$

Because boron acid has a higher volatility a fifth coefficient has to be constructed. The coefficient a_{BC} is 1.35 in the case of boron acid. For all the other compounds it is 1. (10)

By this method it is possible to predict the volatility of different borates with steam in the range of the experimental data and therefore also in the range of BWR- and PWR-reactors. It should be noted that the volatility of boron out of a boric acid solution was verified nearly 100 years ago by Gmelin (1922), but there are no quantitative data for temperature above 100 °C available in the literature.

The equation for the calculation of the void influence (9) is currently only valid for the BORAN facility. The value of the void was measured by the Wire-Mesh-Sensor for many working points before the experiments with borates has been started. At a known working point the void can be estimated at this position only. For a transmission on a plant it is necessary to have more information about the geometry of the fluid channel.
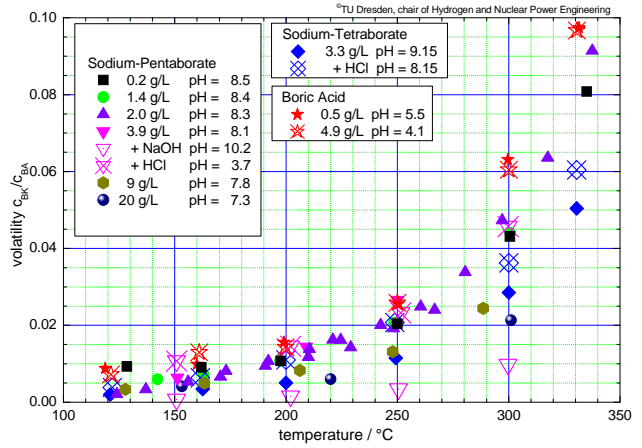

Fig. 3. Volatility of boron out of boiling solution with defined boron contents from different boron compounds – measurements with autoclave.

Another possibility to get the void fraction in the facility is a calculation with a thermal hydraulic code like the ATHLET-Code from the Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH. A second possibility to measure the local void fraction in the heating duct with conductivity sensors is now under way.
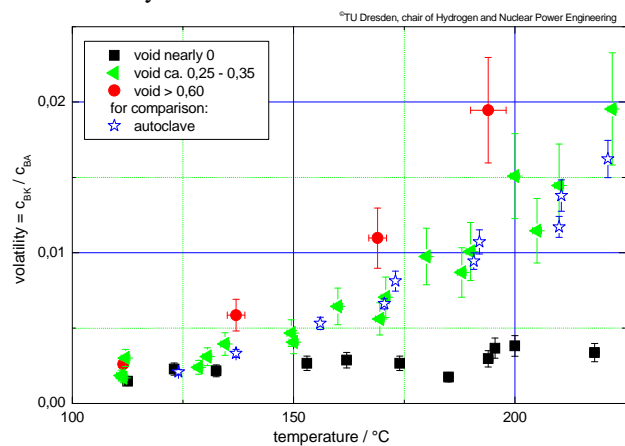

Fig. 4. Volatility of boron out of boiling pentaborate solution with a defined boron content ($c_{boron} = 1.3$ g/L) at various void fractions– measurements with BORAN.

4

Following influences and dependences can be extracted out of the measurement data in figure 3 and 4:

- Exponential temperature dependence for all temperatures
- Saturation effect in volatility by increasing the boron concentration over 5 g/L
- A decreasing pH-value increases the volatility and inverted
- Different boron compounds create nearly the same volatilities at the same concentration and pH-value
- Boric acid is 35 % more volatile than penta borates
- A increasing void fraction increases the volatility of the boron up to a factor 5 in comparison to a vapour-free fluid-flow

5. The influence of the void fraction

The result of the measurements of the volatility with the BORAN facility is a very important dependence on the void fraction in the two-phase-flow (see fig. 4). The higher the void fraction the higher the interfacial area between fluid and vapour.

At a bigger surface the probability is higher for a boric acid molecule to change from the fluid into the vapour. Prasser et al. (2007) have done some measurements about the interfacial area density in dependence on the volumetric gas content of a water-air-flow. They measured a nearly linear relation between air-content and interfacial area density. In this work this method was transferred to a flow of water and vapour.

To have a better possibility to compare measurement data between various facilities, it will be the best to use only the interfacial area and not the void fraction because of different geometries. At this time it is not possible to measure the interfacial area density of a vapour-water flow; only data of a gas-water flow are available.

6. About the reason of volatility

6.1. Chemistry and consideration

The dissociation of the borates in lower borates and boric acid is the basic fact for the description of the volatility of boron out of boiling solutions of borates. Gmelin (1922) implied that the boron in solutions of boric acid can left the boiling solution. The volatility by sublimation of solid boric acid in the glass industry is generally known while melting. The sublimation pressure of boric acid at room temperature is 280 Pa.

More investigation of the volatility of solid boric acid was done by Stackelberg et al. (1937). He predicted the volatility of solid boric acid without water. But if the temperature gets higher than 130 °C the ortho boric acid will lost its content of water and becomes meta boric acid and for temperatures about 400 °C boron oxide ($H_3BO_3 \rightarrow$ OBOH $\rightarrow B_2O_3$). The monomers of meta boric acid are connecting each other to a fibrous polymer chain. This effect stops the volatility.

Under pressure the solutions of boric acid are always in the liquid phase to have ortho boric acid for all temperatures and every time without any dry out. That is why the boric acid is available as ortho boric acid with huge water content at every temperature. It is volatile. The correlation between the vapour pressure of water and the sublimation pressure of boric acid is a result of the mass action law. The proportionality factor depends on the temperature.

Also Stackelberg et al. (1937) demonstrated a correlation between the boron concentration in the solution and in the condensate of the vapour. Therefore the influence of the concentration and temperature on the volatility can be established.

At the end Stackelberg et al. (1937) published volatility data of boiling solutions with boric acid at different concentrations at nearly 100 °C. He measured a volatility of about 30 %, 60 times bigger than the measured values of the current work of nearly 0.5 %. Stackelberg et al. (1937) used the titration against barium hydroxide, a very error-prone method in comparison to the analysis by ICP-MS of the current samples. Furthermore the experimental conditions in the 1930s are particularly not traceable and completely different from the conditions now. The measurement data of this work are from two facilities and they accord. Therefore

this data have a higher plausibility in comparison to the literature data.

6.2. *Physical Data of volatility*

Gmelin (1922) collected the data of sublimation pressure from different papers. Two temperature-pressure-points can be used for the calculation of the volatility for this analysis. At first for 100 °C results a pressure of 8 kPa, for 128 °C a pressure of 32.3 kPa. For water the saturation pressures are higher, 101 kPa for 100 °C and 254 kPa for 128 °C (Schmidt, 1989). Menzel et al. (1934) and Thiel et al. (1934) measured the sublimation pressure of boric acid, too. The data of Menzel et al. (1934) are only for temperatures until 75 °C. Thiel et al. (1934) describes at first the correlation between the saturation pressure of water and the sublimation pressure of boric acid in solution. The publicised sublimation pressures are smaller than in Gmelin (1922).

Another physical parameter, which influences the volatility, is the sublimation enthalpy of boric acid. Pankajavalli et al. (2007) reported a value of (174.1 ± 4.7) kJ mol^{-1} at a mean temperature of 72 °C. Stackelberg et al. (1937) measured a value of 105.6 kJ mol^{-1} over the temperature range 109 – 140 °C. The enthalpy of the evaporation of water is nearly 40 kJ mol^{-1} (20 kJ mol^{-1} for each hydrogen bridge bond) and depends, like every physically parameter, on the temperature.

The high molar enthalpy of sublimation of boric acid depends on the high number of the strong hydrogen bridge bonds between the three hydroxyl-groups of the boric acid. To crack each bond there are 20 kJ mol^{-1} necessary. The high enthalpy of evaporation of water has the same reason.

A third factor, which influences the volatility of a solution of borates, is the "Borate-Vector". It describes the distribution of the boron atoms on the ions and the boric acid in the solution in the dependence of the pH-value. The pH-value of the used solution is 8.3. The result is that only 30 % of all boron atoms are compounded in the boric acid and contribute to the volatility of the boiling solution (see Fig. 1). The boron acid molecules are un-dissociated because of their very week acidity, another assumption for the volatility. Dissociated acids cannot leave the fluid with the vapour. There will be a division of charge, which is physically forbidden.

To leave the fluid the boron has to go over the interfacial area between the fluid and the vapour. This is a barrier for the boron.

6.3. *Calculation*

With the combination of all these influences the concentration in the condensed vapour can be estimated. Because of the lower vapour pressure of boric acid in comparison to water the part of the lost water is higher than the part of boric acid. The quotient is described in equation (11).

$$ f_p = \frac{p_{V,water}}{p_{V,boricacid}} \qquad (11) $$

The quotient of the molar enthalpies in equation (12) describes the energy distribution of the molecules of the added energy for boiling. Because of the higher enthalpy of boric acid much more water will leave the boiling solution.

$$ f_h = \frac{h_{mol,boricacid}}{h_{mol,water}} \qquad (12) $$

The two quotients f_p and f_h depend on the temperature! If they will be multiplied with each other and with the ratio of boric acid (for pentaborate and a pH-value of 8.3 is the ratio nearly 0.3) in the solution the boron concentration in the vapour can be estimated. For an example temperature of 128 °C the volatility is estimated in the following equation 13.

$$ f(128°C) = \frac{32.3kPa}{254.3kPa} \cdot \frac{39.2kJ/mol}{174.1kJ/mol} \cdot 0.3 = 0.86\% \quad (13) $$

The measurement data at 128 °C for different void fractions are 0.3 % for a void at nearly 0 % and 0.6 % for a void of 60 %. This values are in the near of the calculate ones. If the interfacial area will be bigger, more boron can escape the solution and the calculated value can be achieved.

7.   Future work - connection to BWR

For a better quality of the extracted equations out of the measurement data it is necessary to have

more data points. At this way the model about the lost of boron will become better. It is fundamental that the model is conservative at every measurement or calculation point. That means the result of the calculation gives a bigger lost of boron than the measurement at every time.

For the ATHLET-Code from the GRS an input data for the BORAN facility was created. With this integral thermal hydraulic code nearly all parameters like temperature, pressure, mass flow and boron concentration in each node of the test facility can be calculated. The whole test facility is described in approximately 200 nodes. The calculation of the lost of boron with exhausted steam with the ATHLET-Code is not possible. The boron transport with the vapour cannot be calculated, only in the liquid phase. Some changes in the code are inescapable. But the code is suitable for the calculation of the thermo hydraulic parameter.

The next step is to simulate some transients with the test facility BORAN and the ATHLET-code. By the use of the valve, which connects the vapour-chamber of the facility with the atmosphere, a LOCA-experiment can be performed.

Based on the ATHLET-calculation of a real reactor the lost of boron with exhausted steam can be estimated. All parameter for calculation of the lost of boron can be get out of the main edit of ATHLET.

The great aim of this analysis is a new validation of the effectiveness of the boron injection system in a boiling water reactor to decrease the reactivity of the core. The higher the boron concentration the lower is the reactivity of the core. That is why the calculation has to be conservative!

8.   Summary

In this paper the lost of boron out of sodium borate and boric acid solutions was investigated. The volatility was studied with two facilities; an autoclave and the BORAN test facility. The result of the measurement data are correlations to the concentration, the temperature, the pH-value, the compound and the void fraction in the two-phase flow of BORAN. Out of these correlations some equations were derived. The boron concentration in the vapour can be about some percent of the boron concentration in the borate solution.

In addition to the measurement of the volatility the physical and chemical reasons of the transfer of boron from the liquid in the gaseous phase was shown. The built boric acid after solving the sodium borate sublimates. That is why the boron can leave the solution over the interfacial surface.

The aim of this project is to estimate the lost of boron out of a real BWR with boron-treated feed water. The volatility correlation will be implemented in the ATHLET-code and therefore applied for the calculation of boron injection transients at a real BWR. This work will be done at the Forschungszentrum Dresden-Rossendorf.

9.   Acknowledgement

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