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Study of Hydrogen Generation of Aluminum-Containing Compositions with Boric Acid

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Abstract

The results of investigations of the kinetics of hydrogen generation compositions with aluminum, chemical activators (hydrated sodium metasilicate, oxide and calcium hydroxide) boric acid. Aluminium and its alloys used for the manufacture of protective sheaths of fuel elements and control rod protection system management, pipelines, tanks, and various support structures in the active zone of atomic reactors RBMK, research water-cooled reactors. The aluminum is protected from direct contact with water and steam surface layer of metal oxide having a high corrosion resistance at high temperatures in powerful radiation fields. However, after removal or when the discontinuity of the oxide layer of activated metal efficiently decompose water to hydrogen. It is established that the hydrogen aluminum-containing compositions is dependent on the concentration of boric acid. The discovery of the involvement of boric acid in these reactions expands the ideas about regularities of chemical processes of formation of hydrogen flowing in the water coolant of VVER reactors with the participation of the corrective additives and impurities.

Keywords: hydrogen, aluminum, boric acid, the oxide layer, hydrated sodium metasilicate, oxide and calcium hydroxide.

1. Introduction

The study of production of hydrogen by reaction of water with reactor coolant the materials is an important stage in the development of scientific and technical measures for ensuring hydrogen explosion protection of nuclear power plants [1, 2]. This problem is insufficiently investigated regularities of formation of hydrogen in the interaction of reactor materials with corrective additives and impurity molecules of water coolant. First of all, this applies to the elucidation of the impact of such fundamental importance for water chemistry of VVER reactors as boric acid, which is used for soft regulation of the reactivity of the reactor [3–5].

It is established that in aqueous medium in the presence of chemical compounds, giving the aqueous medium of the alkaline nature of the aluminum efficiently decompose water to hydrogen [6–16]. The process of decomposition of water into hydrogen proceeds with a high rate at temperatures up to 100 °C. For example, in a composition of 1 g of aluminum, 1 g of hydrated sodium metasilicate $Na_2SiO_3{\cdot}5H_2O$ and 10 ml of distilled water at 60 °C hydrogen is formed with maximum output of 1200 ml per 1 g of the reacted aluminum. This is because if in the aquatic environment are chemical substances, for example, silicon–, or calcium-containing compounds that give the water environment is alkaline in nature, in such a system flow physico – chemical processes with the formation of hydrogen, which can be divided into three stages [8–13]. Thus, in compositions containing as a chemical activator of salt of sodium metasilicate, in the first stage by hydrolysis with sodium metasilicate are formed chemically active compounds: $Na_2SiO_3 + H_2O = NaHSiO_3 + NaOH$, $NaHSiO_3 + H_2O = H_2SiO_3 + NaOH$ (1). The hydrolysis product sodium hydroxide NaOH interacts with the oxide coating Al_2O_3 by reactions $(Al + Al_2O_3) + 2NaOH = Al + 2NaAlO_2 + H_2O$ (2), $(Al + Al_2O_3) + 2NaOH + 3H_2O = Al + 2Na[Al(OH)_4]$ (3). As a result, the surface of aluminum is removed, the oxide film, and formed aluminium in an enabled state (without the oxide coating). The resulting activated aluminium decomposes water into hydrogen, for example, by the reaction $2Al + 6H_2O = 2Al(OH)_3 + 3H_2$ или $2Al + 3H_2O$ (ж) $= Al_2O_3 + 3H_2$ ($\Delta H = -272.8$ kJ/mol, $\Delta G = -287.8$ kJ/mol) (4).

2. The experiment

The accumulation of hydrogen was studied on heterogeneous hidroregjioni compositions the following compositions: aluminum powder – 1.0 g (GOST 5494 – 95, mark PAP – 2, the surface of 1.6 m^2/g); chemical activators – hydrated sodium metasilicate of composition $Na_2SiO_3{\cdot}\,5H_2O$, calcium oxide CaO, calcium dioxide, $Ca(OH)_2$ in an amount of from 0.2 to 1.0 g; boric acid in the amount of 0.16 – 0.48 g; distilled water – 10 g.

Process for producing hydrogen includes the following procedures: aluminum powder, chemical activator, and water taken in certain proportions, was charged into a glass flask with a volume of 250 ml and stirred. The reaction flask is placed in a thermostat equipped with a thermometer, heated to the required temperature at which the process goes in a controlled manner and with satisfactory speed, and further maintained at this temperature until the end of the process of hydrogen evolution.

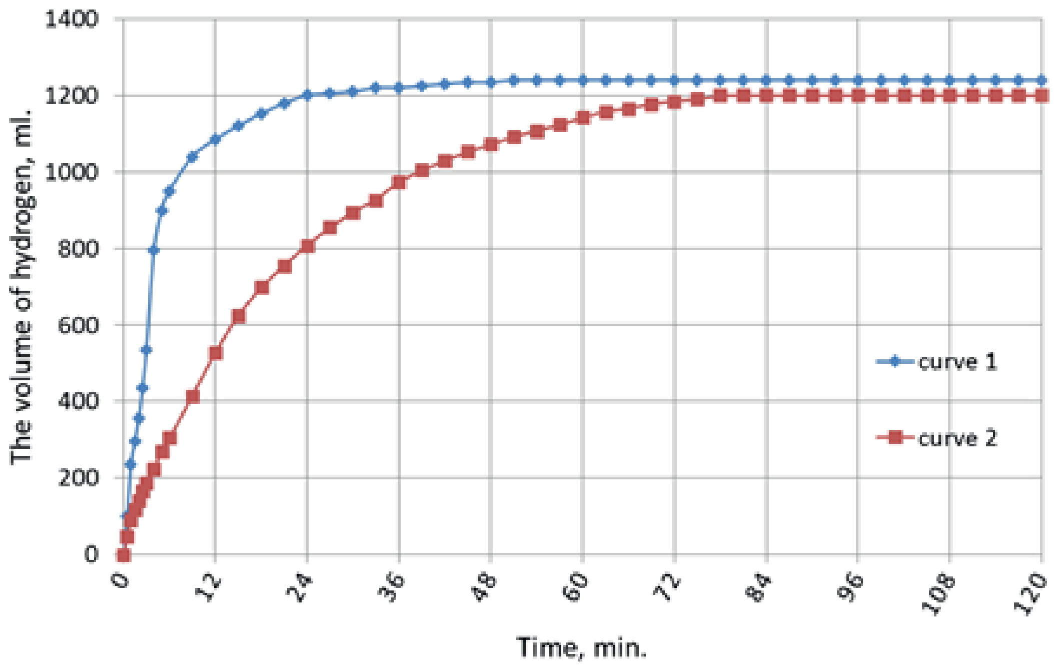

Figure 1: Curves of hydrogen accumulation in the compositions containing: 1 g of aluminum, 1 g of hydrated sodium metasilicate $Na_2SiO_3\cdot 5H_2O$ and 10 ml of distilled water (curve 1); 1 g aluminum, 1 g of hydrated sodium metasilicate $Na_2SiO_3\cdot 5H_2O$ and 10 ml (0.16 g) boric acid (curve 2), t = 60 °C.

Glass reaction flask equipped with a glass tube to drain the water in the measuring vessel generated hydrogen.

3. Results and discussion

3.1. The effect of boric acid on generation of hydrogen aluminization compositions with crystalline sodium metasilicate

All the studied compositions have an alkaline character, and, as seen in Fig. 1, the curves of hydrogen accumulation are similar in the shape of kinetic curves of hydrogen accumulation, characterized by the close initial velocities of formation of hydrogen and limits the amount of hydrogen. In the compositions without chemical activator of the formation of hydrogen occurs. Thus, a prerequisite for the generation of hydrogen hidroregjioni compositions is alkaline nature of the water environment of composition, which is consistent with the ideas about the mechanism of formation of hydrogen involving chemical activators proposed in earlier articles [5 – 7]: a) the dissolution of aluminium oxide $Al_2O_3 + 2NaOH + 3H_2O = 2Na[Al(OH)_4]$; b) the interaction of aluminum

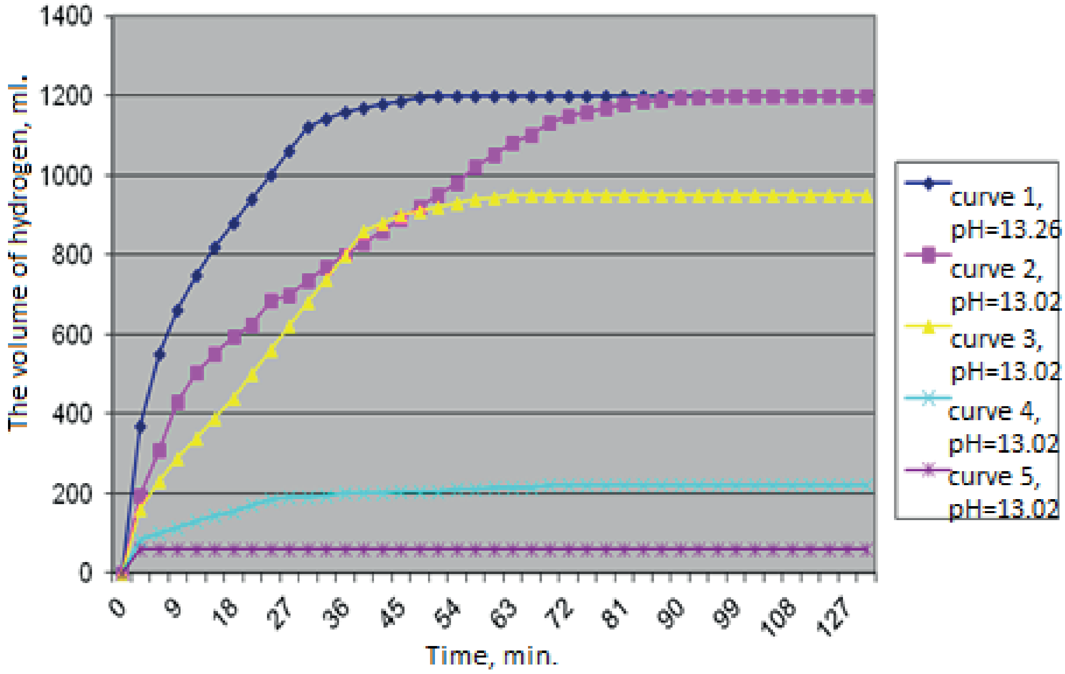

Figure 2: Curves of hydrogen accumulation in the compositions containing: 1 g of aluminum, 1 g of hydrated sodium metasilicate $Na_2SiO_3 \cdot 5H_2O$, 10 ml of distilled water (curve 1); 1 g aluminum, 1 g of hydrated sodium metasilicate $Na_2SiO_3 \cdot 5H_2O$ and an aqueous solution with a content of boric acid 0.16 g (curve 2), 0.24 g (curve 3), 0.32 g (curve 4) and 0.48 g (curve 5), when t = 60 °C.

with water: $2Al + 6H_2O = 2Al(OH)_3 + 3H_2$; c) the interaction of $Al(OH)_3$ with an excess of NaOH: $Al(OH)_3 + 3NaOH = Na_3[Al(OH)_6]$.

In the compositions with boric acid significantly changes the process of accumulation of hydrogen. In more detail the influence of boric acid on the generation of hydrogen in such compositions described in the following sections.

3.2. The formation of hydrogen aluminum-containing compositions with crystalline sodium metasilicate and a different amount of boric acid

In Fig. 2 shows curves of the accumulation of hydrogen at a temperature of 60 °C in the composition containing 1 g of aluminum, 1 g of hydrated sodium metasilicate $Na_2SiO_3 \cdot 5H_2O$, 10 g of distilled water (curve 1) and an aqueous solution with a content of boric acid 0.16 g (curve 2), 0.24 g (curve 3), 0.32 g (curve 4) and 0.48 g (curve 5). It is seen that the maximum concentration of hydrogen depend on the amount of boric acid in the composition. At low boric acid concentration the maximum hydrogen concentration is the same as in the composition of distilled water is about 1.2 l/ 1 g Al. When boric acid

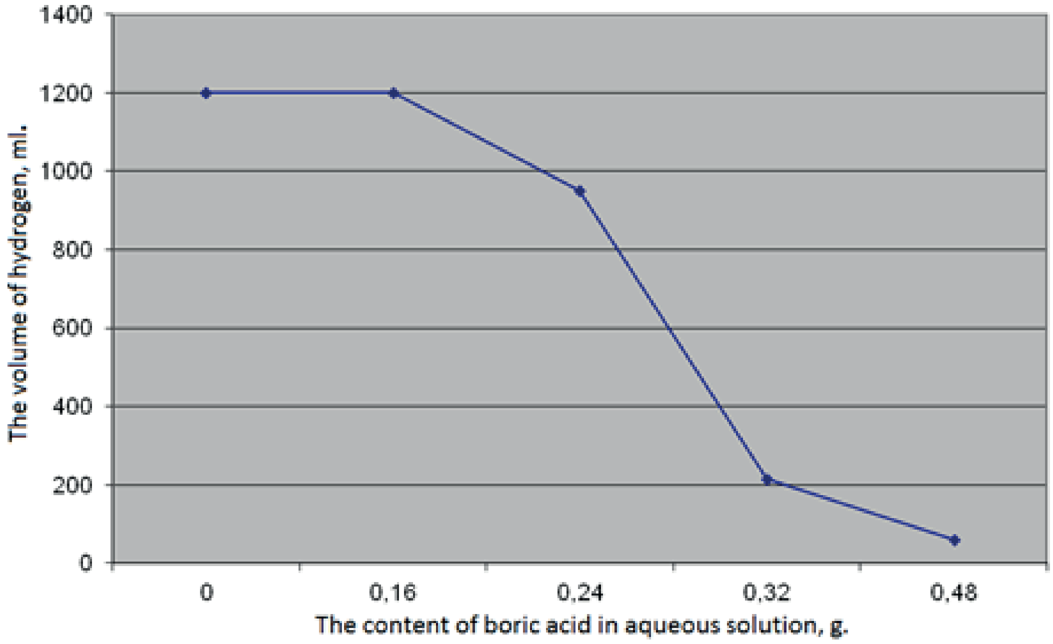

Figure 3: The dependence of the limiting the release of hydrogen from the content of boric acid (g) aluminization compositions with hydrated sodium metasilicate.

concentration of about 0.2 g limit hydrogen concentration is reduced by about 30%. When the concentration of boric acid up to 0.3 g and higher concentration of hydrogen is reduced 5 times or more. When the concentration of boric acid of more than 1.0 g of hydrogen generation in the song completely stops.

In Fig. 3 it can be seen that the maximum hydrogen yield nonlinearly depends on the concentration of boric acid in the composition. When the concentration of boric acid of about 20% occurs cachoerinha minimized to the maximum concentration of hydrogen. This result indicates that boric acid in the heterogeneous compositions is actively involved in the processes that ultimately lead to suppression of the formation of hydrogen due to the interaction of aluminum with water.

The acidic properties of boric acid is not due to the elimination of a proton H^+, and attach the hydroxyl anion $B(OH)_3 + H_2O \rightarrow H[B(OH)_4]$. Formed in the hydrolysis of sodium metasilicate, the sodium hydroxide NaOH reacts with boric acid $2NaOH + 4H_3BO_3 \rightarrow Na_2B_4O_7 + 7H_2O$ with the formation of tetraborate. An excess of alkali tetraborate is transferred to the metaborate $2NaOH + Na_2B_4O_7 \rightarrow 4NaBO_2 + H_2O$. Meta – and tetraborate are hydrolyzed, but to a lesser degree. It should be noted that boric acid may interact with aluminum, zirconium, iron with the formation of hydrogen, for example, $Al + H_3BO_3 \rightarrow AlBO_3 + 1.5\ H_2$.

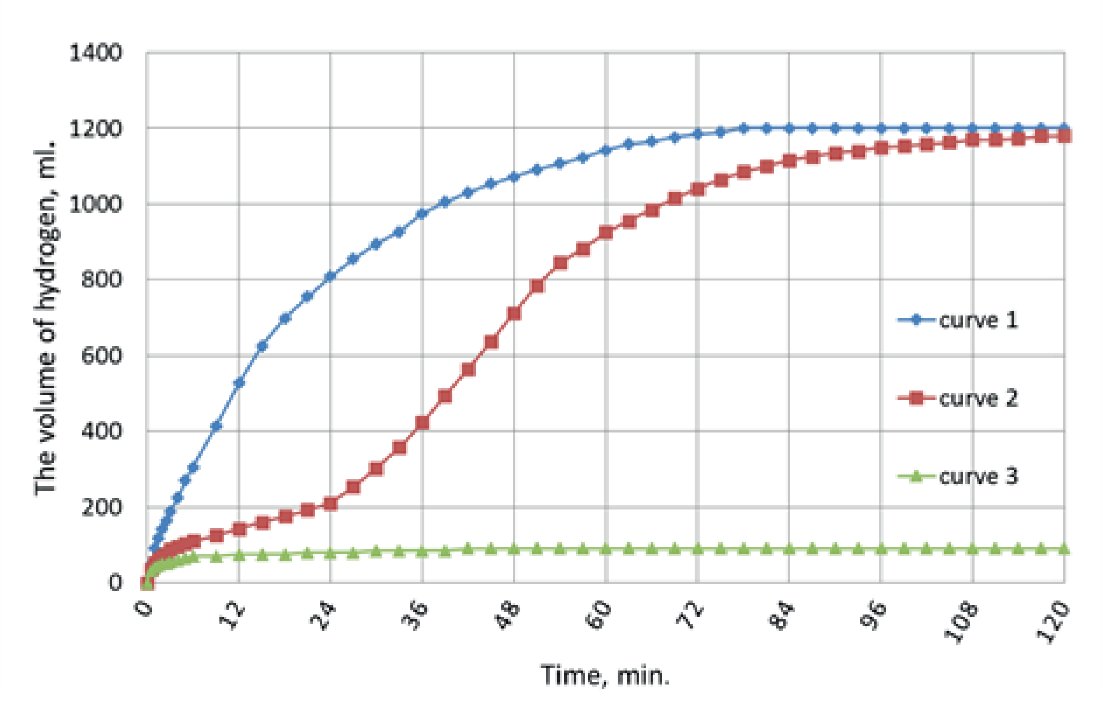

Figure 4: Curves of hydrogen accumulation in the compositions containing 1 g of aluminium and 10 ml (0.16 g) of boric acid and different amounts of crystalline sodium metasilicate $Na_2SiO_3 \cdot 5H_2O$: curve 1 – 1 g, curve 2 – 0.5 g, curve 3 – 0.2 g at t = 60 °C.

We can assume the following scheme of the mechanism of the influence of boric acid on hydrogen formation in compositions containing aluminium and aluminium activators. First, boric acid can decrease the rate of interaction of aluminum with activator by reducing the rate of hydrolysis of crystalline sodium metasilicate. Second, the boric acid reacts with the products of the hydrolysis activator, reduces the concentration of hydrolysis products, reduces the speed and efficiency of their interaction with the surface layer of aluminum oxide Al_2O_3, and thereby reduces the rate of formation and maximum concentration of hydrogen. In this composition, boric acid can be effectively neutralized one of the main products of hydrolysis with sodium hydroxide NaOH with the formation of poorly water soluble polyborates: $3H_3BO_3 + 3NaOH = (NaBO_2)_3 + 6H_2O$, $3H_3BO_3 + 2NaOH = Na_2B_4O_7 + 7H_2O$.

3.3. The formation of hydrogen aluminum-containing compositions with an aqueous solution of boric acid and different amounts of crystalline sodium metasilicate

In Fig. 4 shows the curves of hydrogen accumulation in the compositions containing: 1 g of aluminum, 1 g of hydrated sodium metasilicate $Na_2SiO_3 \cdot 5H_2O$, with 5 ml of distilled

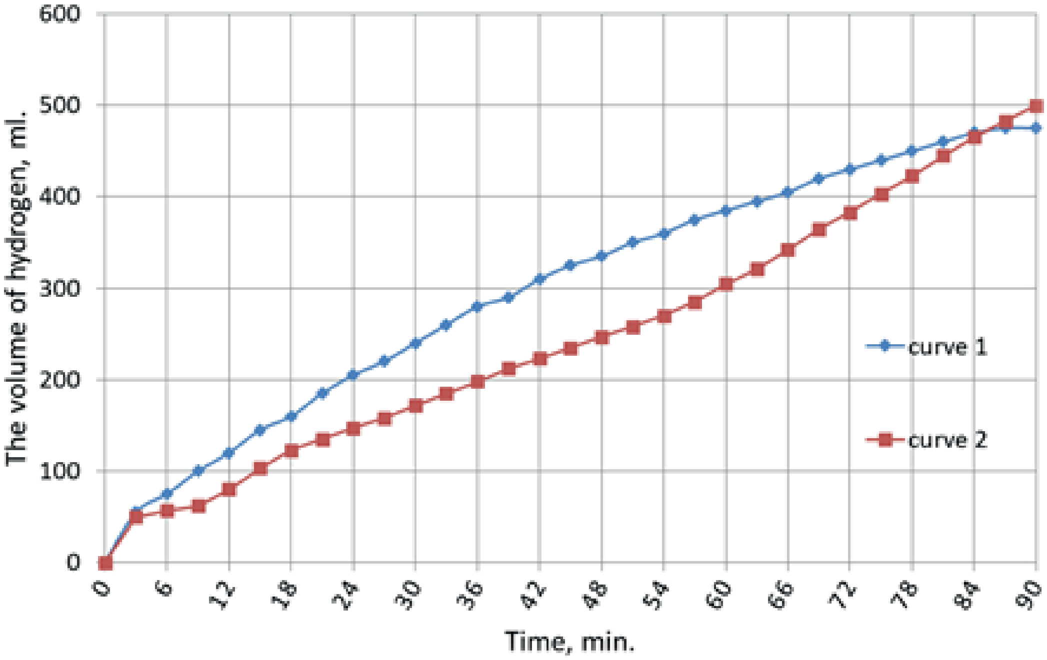

Figure 5: Curves of hydrogen accumulation in the compositions containing: 1 g of aluminum, 1 g $Ca(OH)_2$ 10 ml (0.16 g) boric acid (curve 1); 1 g aluminum, 1 g Cao and 10 ml (0.16 g) boric acid (curve 2), t = 60 ^{0}C.

water and 10 ml (0.16 g) boric acid (curve 1); 1 g of aluminium, 0.5 g of crystalline sodium metasilicate $Na_2SiO_3 \cdot 5H_2O$, with 5 ml of distilled water and 10 ml (0.16 g) boric acid; 1 g of aluminum, 0.2 g of hydrated sodium metasilicate $Na_2SiO_3 \cdot 5H_2O$, with 5 ml of distilled water and 10 ml (0.16 g) of boric acid. In the compositions with boric acid significantly changes the process of accumulation of hydrogen. It is seen that if the concentration of activator in the presence of the compositions of boric acid did not significantly affect the character of the curves of hydrogen accumulation. By reducing the concentration of the activator in the 2 times changes the shape of the curves of accumulation, namely, the clearly visible presence of the induction sites. By reducing the concentration of the activator in the composition to 0.2 g of hydrogen formation occurs.

3.4. The formation of hydrogen compositions with aluminum oxide, dioxide, of calcium and an aqueous solution of boric acid

In Fig. 5 shows the curves of hydrogen accumulation in the compositions containing 1 g of aluminum powder and 10 ml of boric acid, depending on the type of activator oxide and calcium hydroxide. It is seen that the hydrogen yield reaches ~ 480 ml per 1 g of aluminum within ~ 1.5 h. Thus, in Hydrotreating heterogeneous composition containing aluminum powder, oxide or hydroxide of calcium and boric acid, chemical reactions that result in hydrogen formation. The shape of the curves of accumulation is affected by the nature of the chemical activators - the rate of accumulation of hydrogen and calcium hydroxide are higher than with calcium oxide. This allows to conclude that the calcium-containing chemical activators in the interaction with boric acid do not affect the ultimate yield of hydrogen generation, but reduce the rate of accumulation of hydrogen.

4. Conclusion

The condition of generation of hydrogen hidroregjioni compositions with boric acid and a chemical activator is the alkaline nature of the aquatic environment, which confirms the put forward early ideas about the mechanism of formation of hydrogen by chemical decomposition of water with the participation of chemical activators. The speed and concentration of hydrogen generated by the compositions with chemical activators, nonlinear depends on the amount of boric acid, which indicates the interaction of boric acid with aluminum and chemical activators. Kinetics of hydrogen generation of aluminum-containing compositions is dependent on the concentration of hydrated sodium metasilicate, namely, the decreasing concentration of the activator increases the induction phase on the curves of hydrogen accumulation, indicating a decrease in the rate of removal of the oxide layer. Found that calcium chemical activators in the interaction with boric acid do not affect the ultimate yield of hydrogen generation, and only reduce the rate of accumulation of hydrogen. The results obtained indicate the complexity of the interaction of reactor materials with water coolant, in the presence of corrective additives and impurity molecules that must be considered when adjusting water chemistry water-cooled reactors of VVER type.

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