

Generation of hydrogen by hydroheterogeneous compositions based on aluminum and alkali metals*

Sergey R. Askhadullin¹, Viktor K. Milinchuk¹

¹ Obninsk Institute for Nuclear Power Engineering, NRNU MEPhI, 1 Studgorodok, 249040 Obninsk, Kaluga Reg., Russia

Corresponding author: Sergey R. Askhadullin (s.askhadullin@mail.ru)

Academic editor: Georgy Tikhomirov ♦ **Received** 20 October 2020 ♦ **Accepted** 27 March 2021 ♦ **Published** 23 June 2021

Citation: Askhadullin SR, Milinchuk VK (2021) Generation of hydrogen by hydroheterogeneous compositions based on aluminum and alkali metals. Nuclear Energy and Technology 7(2): 133–138. <https://doi.org/10.3897/nucet.7.69178>

Abstract

The process of hydrogen formation and the associated risk of combustion and explosion is a complex problem concerned with the hydrogen and radiation safety of nuclear reactors. Lithium, potassium and sodium hydroxides are used in VVER reactors as corrective additives for keeping the hydrogen potential of the water coolant with boric acid at a controlled level of 5.8 to 10.3. In the process of investigating the interaction of aqueous solutions of the above hydroxides with aluminum, the most chemically active of these is lithium hydroxide; this reaction proceeds with hydrogen formed at a high rate at room temperature (in an exothermic mode). The processes of hydrogen generation in hydroheterogeneous compositions with potassium and sodium hydroxides proceed at an acceptable rate with heating to ~ 60 °C. The kinetics of hydrogen generation depends in a complex way on the content of boric acid, namely, the hydrogen yield is at a level of ~ 1000 ml at a low concentration of 0.01 to 0.05 g/l, and there is no hydrogen formation at a concentration of 0.6 g/l. According to the coolant quality standards, in the hot state of a VVER-1000 unit or in the reactor state at the minimum controlled power level, the total concentration of alkali metals is about 1 mg/dm³, i.e. two to three orders of magnitude as less as in the investigated compositions. The discovery of the influence of alkali metal hydroxides on the formation of hydrogen with the participation of structural materials based on the example of aluminum makes it possible to suggest that the hydroxides of these metals contained in the coolant in a small amount can also take part in the hydroheterogeneous process of formation of minor hydrogen amounts. The potential for hydrogen formation in such a way needs to be taken into account during long-term operation of nuclear reactors, and during accidents and incidents at NPPs

Keywords

Water, hydrogen, aluminum, model metal, aluminum oxide, boric acid, lithium hydroxide, potassium hydroxide, sodium hydroxide, hydroheterogeneous composition, hydrogen and radiation safety of nuclear reactors

Introduction

Primary circuits of nuclear power plants (NPP) with VVER reactors use corrective water chemistry. Weakly alkaline reducing coordinated potassium-ammonia-hydrazine water chemistry with boron control is used for water cool-

ant during power operation of the reactor unit (Subbotin et al. 1970, GOST 24693-81 1981, Avdeyev et al. 1992, Roshchektayev 2010, Technical Justification 2016). Boric acid has a number of advantages in the reactor operation conditions: it is chemically stable in the primary circuit's radiation and temperature fields, is highly soluble in water,

* Russian text published: Izvestiya vuzov. Yadernaya Energetika (ISSN 0204-3327), 2021, n. 1, pp. 49–59.

and do not form sludge and scale. However, boric acid reduces the coolant's hydrogen potential (pH) value which leads to more intensive corrosion of the structural materials of the circuit components. Corrective additives are introduced into the coolant in the form of alkali metals (lithium, potassium, sodium), ammonia and hydrazine hydrate ($N_2H_4 \cdot 2H_2O$) to make up for the acidic qualities of boric acid and to maintain the optimum water chemistry parameters.

According to the coolant quality standards, the total concentration of alkali metal ions in the hot state of a VVER unit is $\sim 3.0 \text{ mg/dm}^3$ and is achieved by introducing alkali metal hydroxides into the primary circuit coolant in the amount depending on the concentration of boric acid and enabling the hydrogen potential to be kept at a level of $\text{pH} = 5.8\text{--}10.3$ (Yefimov et al. 1983, Shkolnikov et al. 2008, Klinshpont et al. 2012, Milinchuk et al. 2014, 2015). No influence of alkali metals on the hydrogen formation in the process of the water coolant interaction with the reactor structural materials has been investigated as part of this problem. The purpose of this study is therefore to determine the influence of lithium, potassium and sodium hydroxides on the process of hydrogen formation as a result of the coolant interaction with the reactor structural materials. For research, aluminum in the form of powder used in hydroheterogeneous compositions was chosen as the model metal (simulating the reactor structural materials). Aluminum was used in the form of powder to increase the contact area of the reagents (aluminum and aqueous solution with a corrective additive) and the hydrogen yield so that it would be possible to estimate the difference in the generation of hydrogen using aqueous solutions with different corrective additives of alkali metal hydroxides. Aqueous solutions with corrective additives of alkali metal hydroxides simulate the VVER reactor primary circuit water chemistry (Legasov 1978, Dmitriyev and Prokhorov 2003, Sheyndlin and Zhuk 2006, Tarasov and Lototsky 2006, Milinchuk et al. 2012, 2013, 2016, Milinchuk and Roshchektayev 2014, Aminov and Bayramov 2016, Salakhova et al. 2018).

Experimental procedures

Fig. 1 presents a laboratory setup of the Department of General and Special Chemistry at the OINPE for investigating the formation of hydrogen by chemical decomposition of water in hydroheterogeneous compositions. The facility makes it possible to study the generation of hydrogen by compositions in a temperature range from indoor temperature to 100°C . The hydrogen formation reaction is controlled by measuring the quantity of the liberated hydrogen in cylinder 7. The investigation target was a reaction mixture consisting of aluminum powder with a specific surface area of $1.6 \text{ m}^2/\text{g}$ in the form of flakes of 25 to $50 \mu\text{m}$ with a thickness of 0.25 to $0.50 \mu\text{m}$ (PAP-2 grade, GOST 5494-95) and lithium hydroxide (MRTU 6-09-4597-57 grade, GOST 8595-83), potassium hydroxide (ChDA grade, GOST 24363-80), and sodium hydroxide (ChDA grade, GOST 4328-77). Boric acid was also used as the additive (B grade, GOST 18704-78).

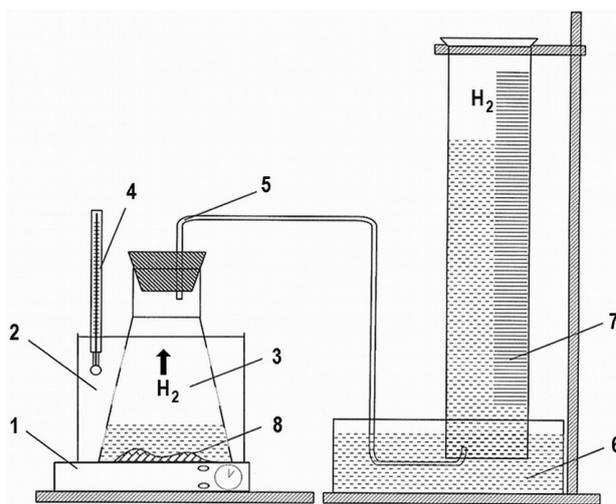


Figure 1. A laboratory setup for hydrogen production by chemical decomposition of water in hydroheterogeneous compositions (the components are described in the paper).

The hydrogen production process includes a number of procedures. Portions of aluminum powder 8, alkali metal hydroxides and boric acid are weighed on an OHAUS Adventurer analytical balance (accuracy, $\pm 0.0002 \text{ g}$). Distilled water is measured off using volumetric cylinders of 10 and 50 ml (GOST 1770-74, accuracy, $\pm 0.2 \text{ ml}$). The portions of aluminum powder, metal hydroxides, boric acid and distilled water taken in a particular proportion are loaded into glass reaction flask 3 with a volume of $100 \pm 0.2 \text{ ml}$ (GOST 1770-74) and mixed in a careful manner. The flask is placed in boiling water bath 2 fitted with thermometer 4 and heated to the required temperature on electric hot plate 1 which makes it possible to run the hydrogen generation process in a controlled mode at an acceptable rate. Reaction flask 3 is fitted with tube 5 to remove the hydrogen formed through water 6 into volumetric cylinder 7 with a volume of $1000 \pm 10 \text{ ml}$ (Lavoisier method). A pH-150 MA pH meter was used to measure the hydrogen potentials of the hydroheterogeneous compositions.

Results and discussion

Influence of lithium hydroxide

Fig. 2 presents curves for the accumulation of hydrogen in hydroheterogeneous compositions (1 g of Al powder, 10 g of H_2O distillate) depending on the content of lithium hydroxide (LiOH).

No hydrogen is formed in the composition without the addition of lithium hydroxide. With even a minor amount of lithium hydroxide (about $1 \times 10^{-4} \text{ g}$) added to the composition, hydrogen forms intensively already at indoor temperature. The reaction taking place at indoor temperature shows that this reaction proceeds exothermally in such hydroheterogeneous compositions. The hydrogen accumulation kinetics depends on the content of lithium hydroxide in these compositions. With the LiOH content

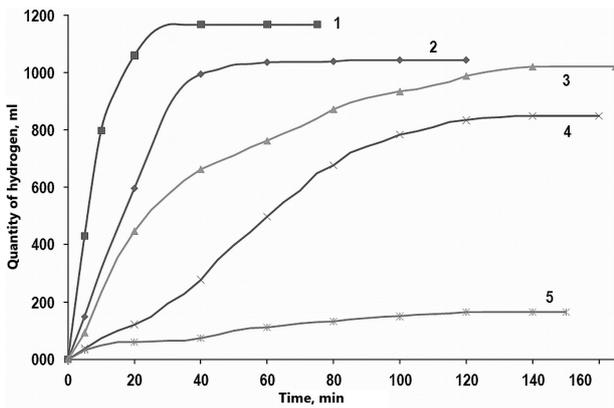


Figure 2. Curves of the hydrogen accumulation at room temperature in hydroheterogeneous compositions (1 g of Al, 10 g of H₂O) depending on the content of lithium hydroxide in them: 1 – 0.28 g; 2 – 0.05 g; 3 – 0.01 g; 4 – 0.003 g; 5 – 0.0007 g.

of ~ 1 g, hydrogen is generated at a high rate in an uncontrolled exothermal mode and violently which makes it impossible to measure carefully the hydrogen accumulation kinetics. With the lithium hydroxide contents of 0.0007 to 0.3 g, the process of the hydrogen accumulation at indoor temperature, which proceeds steadily, ends in 25 to 120 min with the threshold hydrogen yield being ~ 800 to 1100 ml per 1 g of the reacted aluminum. With the lithium hydroxide contents smaller by an order of magnitude (~ 0.0001 g), hydrogen forms at a low rate such that the hydrogen generation process proceeds for a very long time (tens of hours).

Influence of potassium hydroxide

No hydrogen formation is observed in the absence of potassium hydroxide in the composition. Adding KOH to the composition leads to the formation of hydrogen the accumulation of which takes place at an acceptable rate at temperatures of ~ 60 °C and higher (Fig. 3).

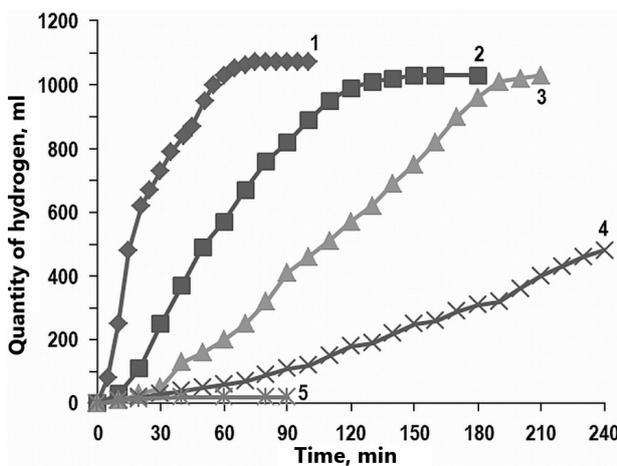


Figure 3. Curves of the hydrogen accumulation at 60 °C in hydroheterogeneous compositions (1 g of Al, 10 g of H₂O) depending on the content of potassium hydroxide in them: 1 – 0.06 g; 2 – 0.03 g; 3 – 0.01 g; 4 – 0.003 g; 5 – 0.001 g.

The hydrogen accumulation kinetics depends on the quantity of the alkali added. With a high content of potassium hydroxide (0.1 to 1.0 g), the process of accumulation is violent and high-rate. The maximum threshold yield of hydrogen (~ 1000 to 1200 ml per 1 g of the reacted aluminum) is reached at the potassium hydroxide concentration of 0.01 to 0.06 g for 75 to 210 min. Hydrogen forms also in compositions which contain small quantities of potassium hydroxide, up to the rated value of ~ 3 mg/dm³. As in compositions with sodium hydroxide, hydrogen is generated at room temperature at a high rate for a very long time (tens of hours).

Influence of sodium hydroxide

Table 1 presents the hydrogen accumulation rate, the threshold hydrogen yield, and the time for which the threshold hydrogen yield is reached in hydroheterogeneous compositions of 1 g of aluminum powder and 10 g of distilled water depending on the sodium hydroxide content of 0.0008 to 0.1 g at indoor temperature. With a large content of sodium hydroxide (0.2 to 1 g), the hydrogen formation is highly violent and involves much deposited heat, this indicating the exothermal nature of the hydrogen formation process. Such uncontrolled mode of the process does not make it possible to determine correctly the kinetic parameters of the reaction. Therefore, the kinetics of the hydrogen accumulation process was investigated for compositions with the content of sodium hydroxide being less than 0.1 g. With a small quantity of sodium hydroxide (~ 0.0008 g and less), a notable quantity of hydrogen (about 150 ml) forms only for the recording time of not less than 60 min.

Table 1. Hydrogen accumulation rate, threshold hydrogen yield, and time to the threshold hydrogen yield in hydroheterogeneous compositions depending on the content of sodium hydroxide in them at indoor temperature

Content of sodium hydroxide, g	Hydrogen accumulation rate, ml/min	Threshold yield of hydrogen, ml	Time to threshold hydrogen yield, min
0.0008	13.2	150	60
0.005	11.2	1000	40
0.009	8.3	1000	40
0.05	1.9	1040	40
0.1	0.6	1050	40

Influence of boric acid

Table 2 presents the results of investigating the accumulation of hydrogen in hydroheterogeneous compositions (1 g of Al powder, 0.05 g of NaOH, 10 g of H₂O distillate) depending on the content of boric acid in them at 60 °C. With the boric acid concentrations of 0.03 to 0.1 g, the threshold hydrogen yield for the recorded time of 100 to 200 min reaches a maximum value of ~ 1000 to 1270 ml.

Fig. 4 shows that the curves for the hydrogen accumulation in hydroheterogeneous compositions have a com-

Table 2. Influence of the boric acid content on the hydrogen potential of hydroheterogeneous compositions, the hydrogen accumulation rate, the hydrogen yield, and the time to the threshold hydrogen yield at 60 °C

Content of boric acid, g	Hydrogen potential of composition, pH	Hydrogen accumulation rate, ml/min	Yield of hydrogen, ml	Time to threshold hydrogen yield, min
0.03	13.8	13.2	1270	100
0.05	13.4	11.2	1020	100
0.07	11.0	8.3	1080	200
0.1	10.8	1.9	920	160
0.5	8.0	0.6	100	100
0.7	7.1	0.1	~25	100

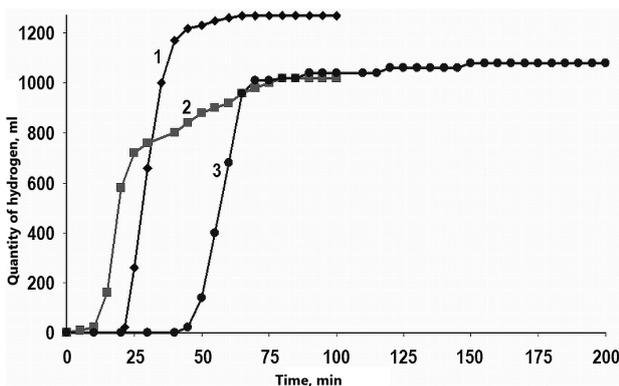
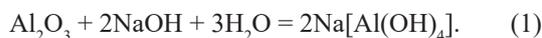


Figure 4. Curves of the hydrogen accumulation in hydroheterogeneous compositions (1 g of Al, 0.05 g of NaOH, 10 g of H₂O) depending on the content of boric acid in them: 1 – 0.03 g; 2 – 0.05 g; 3 – 0.07 g. Temperature 60 °C.

plex dependence on the concentration of boric acid (0.03 to 0.07 g) and the exposure time (up to about 200 min).

All of the above accumulation curves have an induction segment of 10 to 50 min for which no hydrogen formation is recorded. The length of this segment depends on the content of boric acid and the exposure time. Acid in this length seems to be neutralized in full by the NaOH alkali. The second curve segment shows a rapid accumulation of hydrogen which is caused by an increase in the composition's alkalinity and the high rate of the hydrogen formation thanks to the chemical decomposition of water by activated aluminum. More complex is the nature of the accumulation curves for compositions with a high content of boric acid: some 100 ml of hydrogen accumulates with the acid content being ~ 0.5 g, and there is no hydrogen accumulation altogether with 0.7 g.

The process of hydrogen formation in hydroheterogeneous compositions, involving hydroxides of alkali metals, can be presented in the form of two stages. Stage 1 is the interaction of alkali metal hydroxides with a thin surface layer of aluminum oxide (5 to 10 μm), Al₂O₃. Aluminum oxide, Al₂O₃, being an amphoteric compound, can react not only with acids but also with alkali; let us take sodium hydroxide as an example:

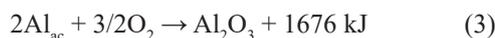


This leads to the removal of the surface layer of aluminum oxide and to the formation of aluminum metal which

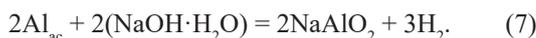
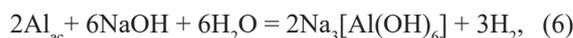
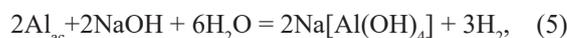
stays for a short time in air in an activated state, Al_{ac} (without the surface passivating layer of aluminum oxide):



Stage 2 of the process is the interaction of activated aluminum, Al_{ac}, with the oxygen contained in air and water. Aluminum in the form of powder or chips (with a high specific surface area) flares in air with the formation of aluminum oxide, while liberating much heat:



Activated aluminum, Al_{ac}, also reacts with water vigorously (in an exothermal mode) with the hydrogen formation by one of the following reactions:



The threshold yield of hydrogen in hydroheterogeneous compositions, involving hydroxides of alkali metals, is defined by the weight of aluminum, the quantity of alkali metal hydroxides, and the process time.

Conclusion

It follows from the obtained results that the nature of the hydroxides of alkali metals (Li, K, Na) has a major influence of the process of hydrogen formation in hydroheterogeneous compositions with aluminum, since these metals are strong activators of the hydrogen formation process. Lithium hydroxide is the most chemically active activator in this process. Hydrogen forms at a high rate at indoor temperature in an exothermal mode in compositions with lithium hydroxide. In compositions with potassium and sodium hydroxides, hydrogen accumulates at a rate acceptable for recording when heated to 60 °C. The accumulation rate and the hydrogen yield in these compositions depend on the content of boric acid, e.g. the hydrogen yield is ~ 1000 ml per 1 g of the reacted aluminum with the boric acid content of ~ 0.03 g/l, and there is no hydrogen formation at 0.6 g/l due to the potassium hydroxide neutralization by boric acid. In these compositions, therefore, alkali metals are efficient activators of the hydrogen formation process and boric acid is the inhibitor of this process.

According to the coolant quality standards, in the hot state of a VVER-1000 unit and in the reactor state at the

minimum controlled power level, the total concentration of alkali metals is about 1 mg/dm^3 , i.e. two to three orders of magnitude as small as in the compositions under investigation (Roshchektayev 2010). However, the discovered influence of alkali metal hydroxides on the formation of hydrogen, involving structural materials, as considered on the example of aluminum that simulates the reactor structural material, allows one to suggest that hydroxides

of these metals, which are present in the coolant in small amounts, may take part in the hydroheterogeneous process of formation of small quantities of hydrogen. The potential for the hydrogen formation in such a way needs to be taken into account, specifically during continuous long-term periods of the nuclear reactor operation, as well as in conditions of incidents and accidents at NPPs (GOST 24693-81 1981, Avdeyev et al. 1992, Technical Justification 2016).

References

- Aminov RZ, Bayramov AN (2016) Combining hydrogen energy cycles with nuclear power plants. Nauka Publ., Moscow, 14–30. [in Russian]
- Avdeyev YeF, Baklushin RP, Golba VS, Ivanenko IYu, Kuzevanov VS, Slobodchuk VI, Solovov SP, Ignatenko Yel (1992) Accidents and Incidents at Nuclear Power Plants: Training Guide. Prof. S.P. Solovyev (Ed.). IATE Publ., Obninsk, 300 pp. [in Russian]
- Dmitriyev AL, Prokhorov NS (2003) Prospects of using hydrogen as an energy carrier. *Khimicheskaya promyshlennost* 80(10): 27–29. [in Russian]
- GOST 24693-81 (1981) Pressurized Water Vessel-type Nuclear Power Reactors. General Requirements for the Boron Control System. Intr. 1982-07-01. Publishing House of Standards, Moscow, 5 pp. [in Russian]
- Klinshpont ER, Roshchektayev BM, Milinchuk VK (2012) Kinetics of hydrogen accumulation during chemical decomposition of water in heterogeneous compositions. *Alternativnaya energetika i ekologiya*. – ISJAE 9: 116–120. [in Russian]
- Legasov VA (1978) Methods of hydrogen production by decomposition of water. *Atomno-vodorodnaya energetika i tekhnologii*. Atomizdat Publ., Moscow, 1: 37–61. [in Russian]
- Milinchuk VK, Belozarov VI, Ananyeva OA, Laricheva TYe, Kunitsyna TYe (2014) Chemical decomposition of water into hydrogen in heterogeneous aluminum-containing compositions. *Izvestiya vysshikh uchebnykh zavedeniy. Yadernaya energetika* 4: 32–40. <https://doi.org/10.26583/npe.2014.4.04> [in Russian]
- Milinchuk VK, Belozarov VI, Shilina VI, Ananeva TYe, Kunitsyna TYe, Gordienko AB (2013) Investigation of hydrogen generation in interaction of aluminum with aqueous solutions. *Izvestiya vysshikh uchebnykh zavedeniy. Yadernaya energetika* 2: 39–47. <https://doi.org/10.26583/npe.2013.2.05> [in Russian]
- Milinchuk VK, Klinshpont ER, Belozarov VI (2015) Autonomous hydrogen generator based on chemical decomposition of water by aluminum. *Izvestiya vysshikh uchebnykh zavedeniy. Yadernaya energetika* 2: 49–59. <https://doi.org/10.26583/npe.2015.2.05> [in Russian]
- Milinchuk VK, Klinshpont ER, Belozarov VI, Khavroshina IS, Sadikov EI (2016) Transformation of aluminum oxide coatings during simulation of nuclear power plant factors. *Izvestiya vuzov. Yadernaya energetika* 2: 45–54. <https://doi.org/10.26583/npe.2016.2.05> [in Russian]
- Milinchuk VK, Roshchektayev BM (2014) An autonomous hydrogen generator. Patent for the invention RU 2510876 C2, 10.04.2014. Application No. 2012115818/05 of 19.04.2012. [in Russian]
- Milinchuk VK, Shilina AS, Ananyeva OA, Kunitsyna TYe, Pasevich OF, Laricheva TYe (2012) Investigation of environmentally safe and energy-saving methods for hydrogen production by chemical decomposition of water. *Alternativnaya energetika i ekologiya*. IS-JAE 4: 49–54. [in Russian]
- Roshchektayev BM (2010) Water Chemistry at NPPs with VVER-1000 and RBMK-1000 Reactors: Training Guide. M.: NIYaU MIFI Publ., 132 pp. [in Russian]
- Salakhova AA, Suvorov VA, Firsova AI, Belozarov VI, Milinchuk VK (2018) Influence of boric acid on generation of hydrogen by aluminum-containing compositions with chemical activators. *Izvestiya vuzov. Yadernaya energetika* 3: 171–179. <https://doi.org/10.26583/npe.2018.3.15> [in Russian]
- Sheyndlin AYe, Zhuk AZ (2006) Alumina-hydrogen power concept. *Rossiyskiy khimicheskiy zhurnal*, L (6): 105–108. [in Russian]
- Shkolnikov Yel, Yakushko SA, Tarasova SA, Parmuzina AV, Ilyukhin AS, Sheyndlin AYe (2008) A study into the operation of an aluminum-water hydrogen microgenerator for compact power sources. *Elektrokhimicheskaya energetika* 8(2): 86–91. [in Russian]
- Subbotin VI, Ivanovsky MN, Arnoldov MN (1970) Physicochemical Fundamentals of Using Liquid Metal Coolants. Atomizdat Publ., Moscow, 295 pp. [in Russian]
- Tarasov BP, Lototsky MV (2006) Hydrogen for energy generation: problems and prospects. *Alternativnaya energetika i ekologiya*. IS-JAE 8: 72–90. [in Russian]
- Technical Justification (2016) Amendments and Additions to the VVER-1000 NPP Unit Primary Circuit Water Chemistry Standard (with Regard for the Comments from Rostekhnadzor) Concerning the Revision of the Standard STP EO 0004 – 00 “Water Chemistry of the VVER-1000 Nuclear Power Plant Unit Primary Circuit. Coolant Quality Standards and Means to Ensure These”. 2011/4.1.1.1.1/46111 (Y025/2011//4600002685/00) Stage 29. Rostekhnadzor Publ., Moscow, 71 pp. [in Russian]
- Yefimov AI, Belorukova LP, Vasilkova IV, Chechev VP (1983) Properties of Inorganic Compounds. *Khimiya Publ.*, Leningrad, 392 pp. [in Russian]