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

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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 coolant during power operation of the reactor unit (Subbotin et al. 1970, GOST 24693-81 1981, Avdeyev et al. 1992, Roschehtayev 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,
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 composition without the 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).

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 H₂O 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 1×10⁻⁴ 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...
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 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).

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.

Influence of boric acid

Table 2 presents the results of investigating the accumulation of hydrogen in hydroheterogeneous compositions (1 g of Al, 10 g of H₂O) 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-

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).
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.

Phase 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:

\[
\text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} = 2\text{Na}[\text{Al(OH)}_3] \tag{1}
\]

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, Al₉₈ (without the surface passivating layer of aluminum oxide):

\[
(\text{Al} + \text{Al}_2\text{O}_3) + 2\text{NaOH} + 3\text{H}_2\text{O} = \text{Al}_{16} + 2\text{Na}[\text{Al(OH)}_3] \tag{2}
\]

Stage 2 of the process is the interaction of activated aluminum, Al₁₆, 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:

\[
2\text{Al} + 3/2\text{O}_2 \rightarrow \text{Al}_2\text{O}_3 + 1676 \text{kJ} \tag{3}
\]

Activated aluminum, Al₁₆, also reacts with water vigorously (in an exothermal mode) with the hydrogen formation by one of the following reactions:

\[
\text{Al}_1\text{₆} + 6\text{H}_2\text{O} = 2\text{Al(OH)}_3 + 3\text{H}_2\text{g} \tag{4}
\]

\[
2\text{Al}_1\text{₆} + 2\text{NaOH} + 6\text{H}_2\text{O} = 2\text{Na}[\text{Al(OH)}_3] + 3\text{H}_2\text{g} \tag{5}
\]

\[
2\text{Al}_1\text{₆} + 6\text{NaOH} + 6\text{H}_2\text{O} = 2\text{Na}_3[\text{Al(OH)}_3] + 3\text{H}_2\text{g} \tag{6}
\]

\[
2\text{Al}_1\text{₆} + 2(\text{NaOH} \cdot \text{H}_2\text{O}) = 2\text{NaAlO}_2 + 3\text{H}_2\text{g} \tag{7}
\]

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/dm³, 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).

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