

# Hydrozirconium reaction in heterogeneous compositions

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## Abstract

The research results presented in this article show the behavior of a hydrozirconium reaction for hydrogen generation at temperatures below 100 °C in heterogeneous compositions containing zirconium and chemical activators (e.g., hydrated sodium metasilicate, sodium water glass, or quicklime). The hydrogen yield increases with a temperature increase up to 95 °C and is about 0.1–0.21 per 1 g of zirconium. Zirconium processing with  $\gamma$ -radiation as well as exposure to acidic and neutral aqueous media increases the hydrogen yield by about 1.2 times. A hydrozirconium reaction is caused by the chemical activators removing the passivating protective zirconium oxide  $ZrO_2$  layer from the metal surface. The possibility of a hydrozirconium reaction occurrence should be considered in the organization of technical measures to ensure hydrogen explosion protection at NPPs.

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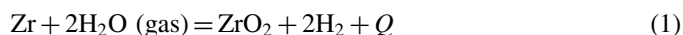
**Keywords:** Water; Zirconium; Hydrogen; Hydrozirconium reaction; Zirconium oxide; Hydroheterogeneous composition; Sodium water glass; Hydrated sodium metasilicate/quicklime.

## Introduction

It has previously been found that aluminum and aluminum alloys effectively decompose water into hydrogen at atmospheric pressure and temperatures up to 100 °C, if heterogeneous compositions contain chemicals which transform the metal in the active state relative to the water by removing the protective passivating layer of aluminum oxide ( $Al_2O_3$ ) [1–4]. To establish the general laws of interaction between the structural materials and aqueous media of nuclear power plants (NPPs), it is necessary to determine whether it is possible to decompose water into hydrogen under the same operational conditions using other structural materials.

In this regard, of particular interests are studies related to the behavior of zirconium and its alloys in aqueous media, since they are widely used as structural materials for

fuel assemblies containing nuclear fuel for reactors. Zirconium alloys are protected against the direct contact with water and water steam with the surface layer of zirconium dioxide ( $ZrO_2$ ). At temperatures above 860 °C, the zirconium–steam reaction proceeds in accordance with the equation



with the evolution of hydrogen ( $\sim 0.51$  per 1 g of reacted zirconium) and a large amount of heat  $Q = 6530$  kJ/kg [5–9]. At high temperatures, the surface protective zirconium oxide layer is destroyed and removed and activated “pure” zirconium (without the protective layer) is formed which efficiently interacts with water steam.

The paper presents the research results which indicate that, in heterogeneous compositions containing zirconium and chemical activators, at temperatures below 100 °C, a hydrozirconium reaction occurs resulting in hydrogen evolution due to the zirconium–water interaction.

## Experimental technique

For the study, the powder of calciothermal zirconium, PZrK1 (TU 48-4-234-84) grade, was taken with the con-

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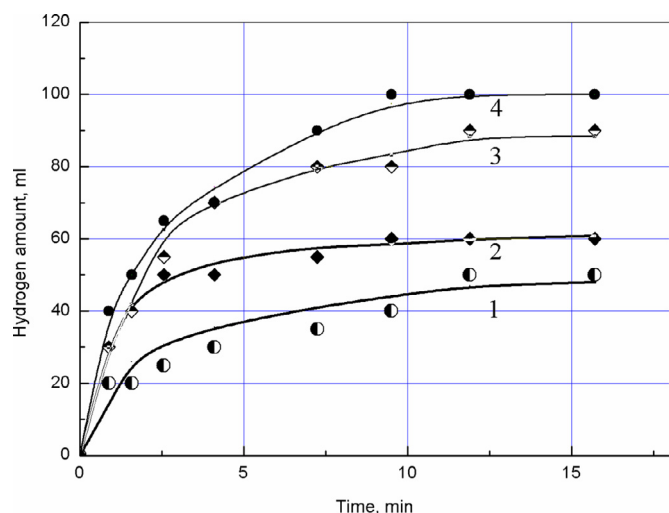


Fig. 1. Hydrogen accumulation curves in compositions containing 1 g of zirconium powder, 1 g of hydrated sodium metasilicate  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  and 10 g of distilled water depending on temperature ( $^{\circ}\text{C}$ ): 1–40 $^{\circ}\text{C}$ , 2–60 $^{\circ}\text{C}$ , 3–80 $^{\circ}\text{C}$ , 4–95 $^{\circ}\text{C}$ .

tent of active zirconium not less than 96%, hydrogen up to 0.15%, carbon up to 0.05%, iron up to 0.05%, calcium up to 0.05%, chlorine up to 0.003%, fractions with the particle size  $\sim 10\ \mu\text{m}$  at least 50% and specific surface  $\sim 2200\ \text{cm}^2/\text{g}$ . Sodium water glass and hydrated sodium metasilicate composed of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  with the melting point of 48 $^{\circ}\text{C}$  and quicklime were taken as aluminum activators.

The study of the hydrogen storage kinetics includes the following procedures. The reaction mixture was prepared by thoroughly mixing the zirconium powder with the activator in a certain ratio with addition of distilled water [4]. The mixture sample weight was loaded into a glass bulb of 500 ml with a tube for removing hydrogen through the water into the measure cell. The reaction vessel was placed into a thermostat and heated to a specified temperature. Hydrogen generation was monitored by measuring the amount of hydrogen evolved in the measure cell. The experiments were carried out using compositions of 1 g of zirconium powder, 1 (2) g of chemical activator and 10 g of distilled water within the temperature range from ambient to 95 $^{\circ}\text{C}$ .

For the radiation processing, the aluminum powder was placed in thick-walled glass vessels of 500 ml and irradiated by  $\gamma$ -rays at room temperature in air using a  $\gamma$ -source  $^{60}\text{Co}$ , with 1.0 and 2.0 mGy doses at a specific absorption rate of 1.5 Gy/s. [4]. The zirconium samples were kept at room temperature in an aqueous boric acid solution (concentration 16 g/l) and in distilled water for 170 h.

## Results and discussion

Fig. 1 shows hydrogen accumulation curves in compositions containing hydrated sodium metasilicate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) as a zirconium activator. It can be seen that the hydrogen accumulation rate increases as the temperature rises. The amount of the evolved hydrogen reaches a predetermined limit of 50 ml at 40 $^{\circ}\text{C}$  and 100 ml at 95 $^{\circ}\text{C}$ ,

Table 1

Hydrogen yield (ml) depending on the chemical activator temperature and amount.

Chemical activator	Component ratio	40 $^{\circ}\text{C}$	60 $^{\circ}\text{C}$	80 $^{\circ}\text{C}$	95 $^{\circ}\text{C}$
Hydrated sodium metasilicate	1:1:10	50	60	90	100
	1:2:10	50	65	100	140
Sodium water glass	1:1:10	20	60	110	130
	1:2:10	25	80	120	150
Quicklime	1:1:10	25	80	110	150
	1:2:10	35	85	130	160

Table 2

Hydrogen yield (ml) in compositions with zirconium  $\gamma$ -irradiated in air at room temperature with a dose of 2 mGy depending on temperature and type of chemical activator.

Chemical activator	Component ratio	V (ml) 40 $^{\circ}\text{C}$	V (ml) 60 $^{\circ}\text{C}$	V (ml) 80 $^{\circ}\text{C}$	V (ml) 95 $^{\circ}\text{C}$
Hydrated sodium metasilicate	1:1:10	60	100	125	185
	1:2:10	60	105	135	195
Sodium water glass	1:1:10	30	60	110	180
	1:2:10	35	70	120	180
Quicklime	1:1:10	60	80	120	190
	1:2:10	60	90	140	190

respectively. At these temperatures, the hydrogen generation reaction involves only a part of the metal.

The maximum hydrogen yields in compositions containing hydrated sodium metasilicate, sodium water glass and quicklime as zirconium activators depending on the activator amount and temperature are presented in Table 1. It is seen that the chemicals used are zirconium activators in the presence of which the compositions generate hydrogen. A hydrogen yield increase resulting from the temperature rise depends on the activator type: the limit yield at 95 $^{\circ}\text{C}$  increases by about 2–3 times with hydrated sodium metasilicate involved, by about 6 times with sodium water glass, and by 5–6 times with slacked lime, respectively. By increasing the activator amount in the composition by two times, the hydrogen yield is increased by approximately 40%. The ratio of components in the composition, 1:1 (2):10, is optimal for the maximum hydrogen yield which, during the hydrozirconium reaction in the temperature range studied, was 20–30% of the maximum hydrogen yield in the zirconium–steam reaction at high temperatures (0.51 per 1 g of zirconium).

For determining the hydrozirconium reaction kinetics and mechanism, it is necessary to study the effects of the factors simulating the NPP conditions. For this purpose, zirconium was exposed to  $\gamma$ -radiation  $^{60}\text{Co}$  and held in neutral and acidic aqueous solutions. As Fig. 2 shows, both the hydrogen evolution rate and its limit yield are increased in a composition containing zirconium  $\gamma$ -irradiated with a dose of 1 mGy. This is indicative of a decrease in the zirconium oxide chemical resistance to a chemical activator after irradiation. Based on the results presented in Table 2, we can judge on the effects of temperature and activator types on the hydrogen yield in compositions with zirconium  $\gamma$ -irradiated with a dose of 2 mGy in air at room temperature. Hydrogen yields in compositions with  $\gamma$ -irradiated zirconium are similar at different

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