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## **The significance of hydrogen concentration monitoring in primary coolant circuits**

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**Key words:** hydrogen determination; primary circuit; chemistry control; coolant radiolysis

To keep nuclear reactor's cooling loop as safe as possible, the production of corrosive species should be reduced during the coolant radiolysis. In the literature, several mathematical models exist to calculate the corrosive species concentration and to predict their decrease in dependence on hydrogen dosage into the primary coolant. None of the models, however, describes reliably the real situation and the calculated concentrations of individual species differ from the measured process values even by one order, as we show in the first part of this contribution. Therefore, the reliable way for primary circuit chemistry control is the process measurement of the concentration of as many species as possible. The most important species determining the primary circuit chemistry is hydrogen. Therefore, we deal with the hydrogen sensor development because there is a lack of really sensitive hydrogen sensors on the world market. This year, after reporting on the process tests in recent years, we report on the H-meter device optimization both from the viewpoint of the time span of its usage (service period) and from the viewpoint of its geometrical arrangement. The main results of the last period of H-meter development are the incorporation of recalibration system (HW and SW) and a consequent reduction of the device volume by 1/3.

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### **Abstract**

To keep nuclear reactor's cooling loop as safe as possible, the production of corrosive species should be reduced during the coolant radiolysis. In the literature, several mathematical models exist to calculate the corrosive species concentration and to predict their decrease in dependence on hydrogen dosage into the primary coolant. None of the models, however, describes reliably the real situation and the calculated concentrations of individual species differ from the measured process values even by one order, as we show in the first part of this contribution. Therefore, the reliable way for primary circuit chemistry control is the process measurement of the concentration of as many species as possible. The most important species determining the primary circuit chemistry is hydrogen. Therefore, we deal with the hydrogen sensor development because there is a lack of really sensitive hydrogen sensors on the world market. This year, after reporting on the process tests in recent years, we report on the H-meter device optimization both from the viewpoint of the time span of its usage (service period) and from the viewpoint of its geometrical arrangement. The main results of the last period of H-meter development are the incorporation of recalibration system (HW and SW) and a consequent reduction of the device volume by 1/3.

### **Introduction**

Primary coolant, usually water with additives, the most known of which the boric acid probably is, flows through the active zone of a nuclear reactor. The coolant undergoes massive irradiation (in the orders of 1020 photons per second, which corresponds with up to 10 000 kGy/h) in the active zone and large number of radicals are produced in it. Due to their strong reactivities, the

radicals, having very short lifetimes, intensively recombine to stable molecules producing also corrosion inducing species as hydrogen peroxide, nitric acid and oxygen are.

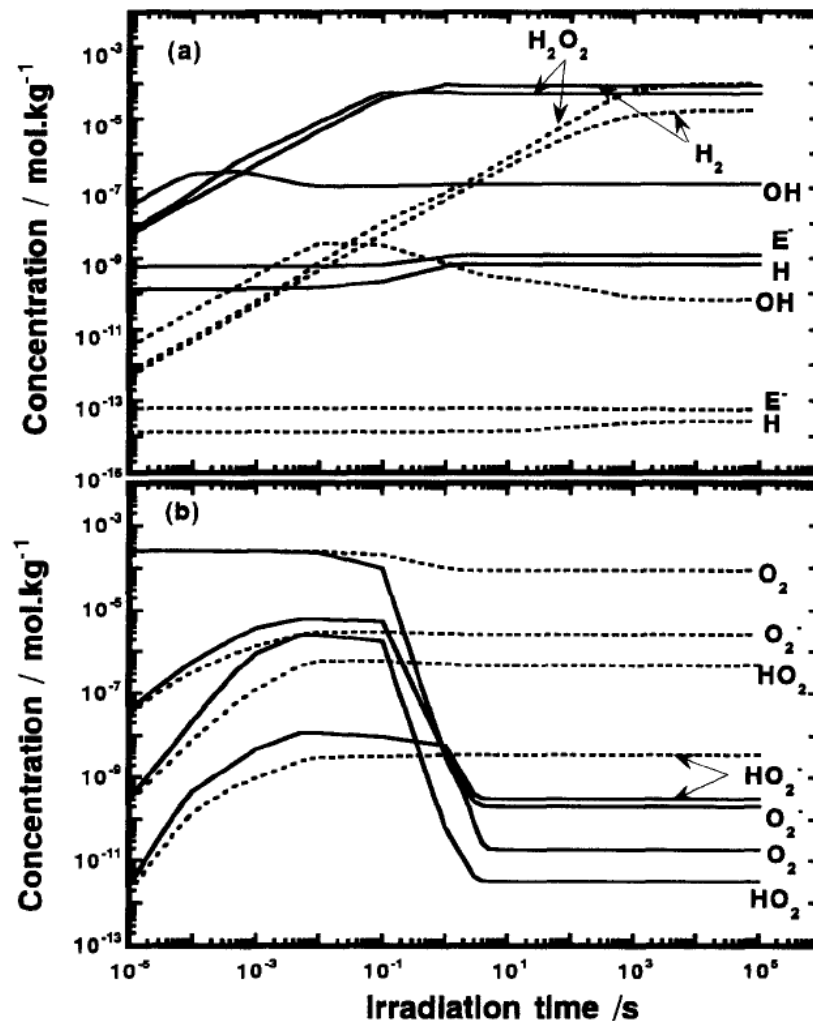
### **Mathematical modelling**

In the effort to reduce the corrosion risks, the recombination reactions have been studied for several decades. Christensen (1995), Sunaryo (1995b) and Katsumura (1998), e.g., studied the radiolysis of water containing boric acid. Later, Grachev and Sazonov (2021) described the details of ammonia radiolysis, which also occurs in the primary coolant, being dosed as the hydrogen source. An example of recombination reactions series (simplified, just for the illustration) follows, see Table 1

**Table 1:** recombination reactions of radicals produced by water molecules radiolysis as described by Butarbutar et al. (2018)

Reaction	$k (M^{-1} s^{-1})$	Reaction	$k (M^{-1} s^{-1})$
$H^+ + H^+ \rightarrow H_2$	$5.2 \times 10^9$	$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2 OH^-$	$7.3 \times 10^9$
$H^+ + ^\bullet OH \rightarrow H_2O$	$1.6 \times 10^{10}$	$e^-_{aq} + H^+ \rightarrow H^\bullet$	$2.1 \times 10^{10}$
$H^+ + H_2O_2 \rightarrow H_2O + ^\bullet OH$	$3.6 \times 10^7$	$e^-_{aq} + O_2^\bullet \rightarrow H_2O_2 + 2 OH^-$	$1.3 \times 10^{10}$
$H^+ + e^-_{aq} \rightarrow H_2 + OH^-$	$2.8 \times 10^{10}$	$e^-_{aq} + HO_2^\bullet \rightarrow O^{\bullet -} + OH^-$	$3.51 \times 10^9$
$H^+ + OH^- \rightarrow H_2O + e^-_{aq}$	$2.4 \times 10^7$	$e^-_{aq} + O^{\bullet -} \rightarrow 2 OH^-$	$2.31 \times 10^{10}$
$H^+ + O_2 \rightarrow HO_2^\bullet$	$1.3 \times 10^{10}$	$e^-_{aq} + H_2O \rightarrow H^\bullet + OH^-$	15.8
$H^+ + HO_2^\bullet \rightarrow H_2O_2$	$1.1 \times 10^{10}$	$e^-_{aq} + O_2 \rightarrow O_2^{\bullet -}$	$2.3 \times 10^{10}$
$H^+ + O_2^{\bullet -} \rightarrow HO_2^-$	$1.1 \times 10^{10}$	$e^-_{aq} + HO_2^\bullet \rightarrow HO_2^-$	$1.3 \times 10^{10}$
$H^+ + HO_2^- \rightarrow ^\bullet OH + OH^-$	$1.5 \times 10^8$	$e^-_{aq} + O(^3P) \rightarrow O^{\bullet -}$	$2.0 \times 10^{10}$
$H^+ + O(^3P) \rightarrow ^\bullet OH$	$2.0 \times 10^{10}$	$e^-_{aq} + O_3 \rightarrow O_3^{\bullet -}$	$3.6 \times 10^{10}$
$H^+ + O^{\bullet -} \rightarrow OH^-$	$2.0 \times 10^{10}$	$H^\bullet + O^{\bullet -} \rightarrow ^\bullet OH$	$5.0 \times 10^{10}$
$H^+ + O_3 \rightarrow O_2 + ^\bullet OH$	$3.7 \times 10^{10}$	$H^\bullet + O_2^{\bullet -} \rightarrow HO_2^\bullet$	$5.0 \times 10^{10}$
$H^+ + O_3^{\bullet -} \rightarrow OH^- + O_2$	$1.0 \times 10^{10}$	$H^\bullet + OH^- \rightarrow H_2O$	$1.2 \times 10^{11}$
$^\bullet OH + ^\bullet OH \rightarrow H_2O_2$	$6.3 \times 10^8$	$H^\bullet + O_3^{\bullet -} \rightarrow ^\bullet OH + O_2$	$9.0 \times 10^{10}$
$^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O$	$2.9 \times 10^7$	$H^\bullet + HO_2^\bullet \rightarrow H_2O_2$	$5.0 \times 10^{10}$
$^\bullet OH + H_2 \rightarrow H^\bullet + H_2O$	$4.0 \times 10^7$	$OH^- + O(^3P) \rightarrow HO_2^-$	$4.2 \times 10^8$
$^\bullet OH + e^-_{aq} \rightarrow OH^-$	$3.6 \times 10^{10}$	$OH^- + HO_2^\bullet \rightarrow O_2^{\bullet -} + H_2O$	$1.3 \times 10^{10}$
$^\bullet OH + OH^- \rightarrow O^{\bullet -} + H_2O$	$1.3 \times 10^{10}$	$O_2 + O^{\bullet -} \rightarrow O_2^{\bullet -}$	$3.7 \times 10^9$
$^\bullet OH + HO_2^\bullet \rightarrow O_2 + H_2O$	$9.0 \times 10^8$	$O_2 + O(^3P) \rightarrow O_3$	$4.0 \times 10^9$
$^\bullet OH + O_2^{\bullet -} \rightarrow O_2 + OH^-$	$1.1 \times 10^{10}$	$HO_2^\bullet + O_2^{\bullet -} \rightarrow HO_2^- + O_2$	$9.7 \times 10^7$
$^\bullet OH + HO_2^- \rightarrow HO_2^\bullet + OH^-$	$8.3 \times 10^8$	$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$	$1.94 \times 10^8$
$^\bullet OH + O(^3P) \rightarrow HO_2^\bullet$	$2.02 \times 10^{10}$	$HO_2^\bullet + O(^3P) \rightarrow O_2 + ^\bullet OH$	$2.02 \times 10^{10}$
$^\bullet OH + O^{\bullet -} \rightarrow HO_2^-$	$1.0 \times 10^9$	$HO_2^\bullet + H_2O \rightarrow H^\bullet + O_2^{\bullet -}$	$1.4 \times 10^4$
$^\bullet OH + O_3^{\bullet -} \rightarrow O_2^{\bullet -} + HO_2^\bullet$	$8.5 \times 10^8$	$O_2^{\bullet -} + O^{\bullet -} \rightarrow O_2 + 2 OH^-$	$6.0 \times 10^8$
$^\bullet OH + O_3 \rightarrow O_2 + HO_2^\bullet$	$1.11 \times 10^8$	$O_2^{\bullet -} + H_2O \rightarrow HO_2^\bullet + OH^-$	0.155
$H_2O_2 + e^-_{aq} \rightarrow OH^- + ^\bullet OH$	$1.1 \times 10^{10}$	$O_2^{\bullet -} + O_3 \rightarrow O_3^{\bullet -} + O_2$	$1.5 \times 10^9$
$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$	$1.33 \times 10^{10}$	$HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$	$1.27 \times 10^6$
$H_2O_2 + O(^3P) \rightarrow HO_2^\bullet + ^\bullet OH$	$1.6 \times 10^9$	$HO_2^- + O^{\bullet -} \rightarrow O_2^{\bullet -} + OH^-$	$8.02 \times 10^8$
$H_2O_2 + O^{\bullet -} \rightarrow HO_2^\bullet + OH^-$	$5.55 \times 10^8$	$HO_2^- + O(^3P) \rightarrow O_2^{\bullet -} + ^\bullet OH$	$5.3 \times 10^9$
$H_2 + O(^3P) \rightarrow H^\bullet + ^\bullet OH$	$4.77 \times 10^3$	$O^{\bullet -} + O^{\bullet -} \rightarrow H_2O_2 + 2 OH^-$	$1.0 \times 10^8$
$H_2 + O^{\bullet -} \rightarrow H^\bullet + OH^-$	$1.3 \times 10^8$	$O^{\bullet -} + O_3^{\bullet -} \rightarrow 2 O_2^{\bullet -}$	$7.0 \times 10^8$
$O(^3P) + O(^3P) \rightarrow O_2$	$2.2 \times 10^{10}$	$O^{\bullet -} + H_2O \rightarrow ^\bullet OH + OH^-$	$1.3 \times 10^6$
$O(^3P) + H_2O \rightarrow 2 ^\bullet OH$	$1.9 \times 10^3$	$O_3^{\bullet -} + H_2O \rightarrow O^{\bullet -} + O_2$	46.5

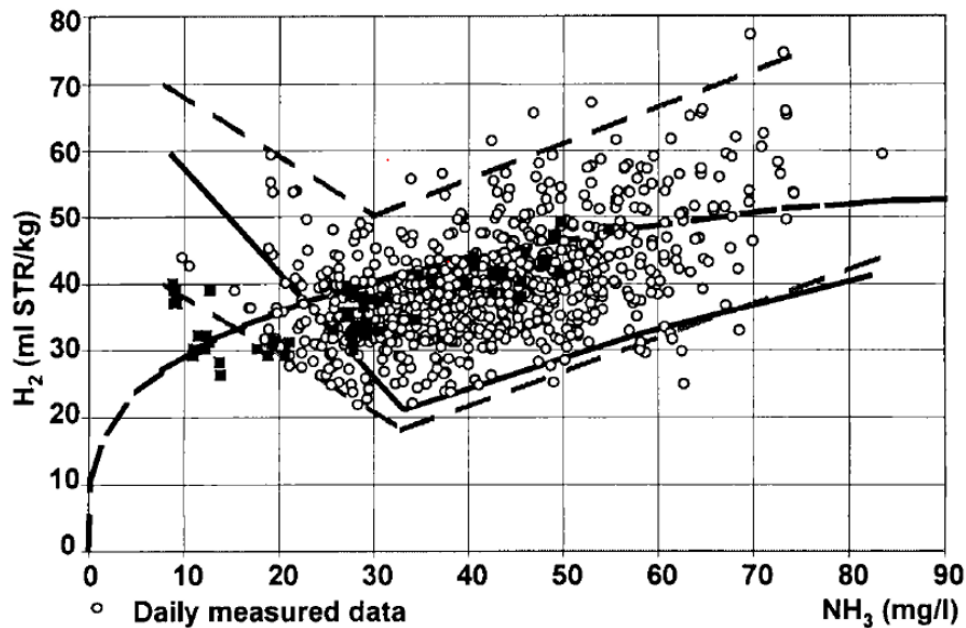
By several other studies it was found and confirmed that the dosing of hydrogen into the primary coolant can shift the recombination reaction rates so that the corrosive products are significantly reduced (Kritski et al., 2001 and Grachev et al., 2021). There are two steps of water radiolysis simulation in literature: i) pure water radiolysis and ii) complete primary coolant radiolysis including also nitrogen+hydrogen species, e.g., ammonia and hydrazine. While various mathematical models of pure water radiolysis gave the same results, the simulations of complete primary coolant radiolysis brought a variety of quantitatively different results. For the illustration, see Figure 1 describing the pure water radiolysis.



**Figure 1:** Water radiolysis time development for various irradiation rates (3600 Gy/h for dotted line and 36 000 kGy/h for full line). Taken from Sunaryo et al. (1995)

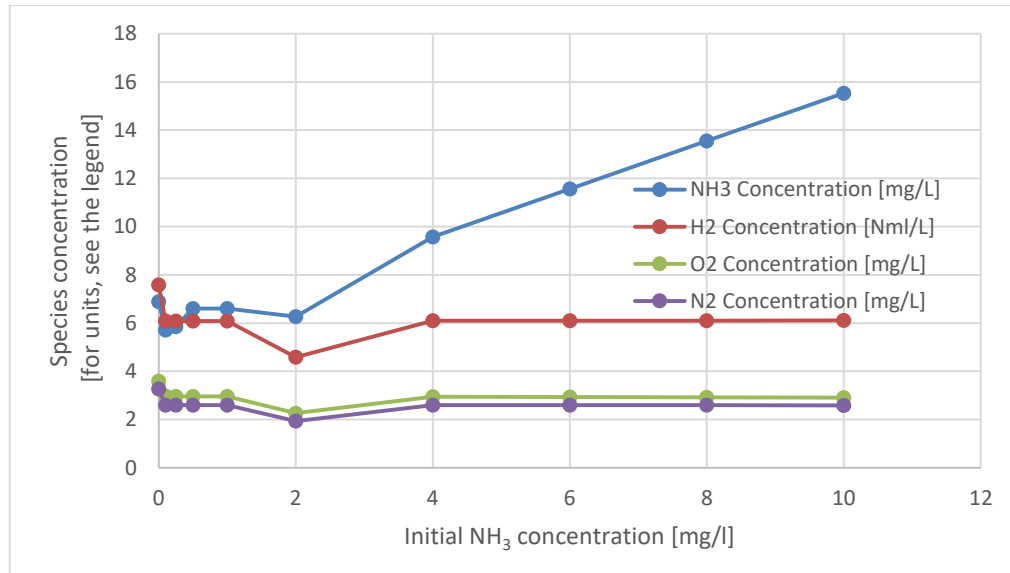
It is worth noticing that these concentration profiles were successfully obtained also by the computational module we developed in Fortran at our workplace - UCT Prague (Linek et al., 2000), and what is interesting on that: we used the chemical equation series published by Christensen et al. (1995) and obtained exactly the same concentration profiles of water radicals like those shown in Figure 1. This meant that the pure water radiolysis was described well in literature, when two independent sources gave the same simulation results.

As already mentioned above, different situation governs in the radiolysis simulation of complete primary coolant. As the ammonia dosage aims to an increase in hydrogen concentration to hinder corrosion products concentration, resulting quantities are given in terms of hydrogen concentration dependent on the ammonia dosage. Note the hydrogen concentration minimum when about 30 mg/L of ammonia dosed.



**Figure 2:** Hydrogen concentration in primary coolant in dependency on the ammonia concentration. Calculated by Kritski et al. (2001) using several mathematical models - all the lines (dashed and full) and compared with several NPP's measured data - all the symbols (circles and squares).

Let's compare the results in Figure 2 with those we obtained by simulation using complete equation series, i.e., not only pure water radiolysis description but also the equations describing nitrogen species taken from Grachev (2021). The results of our simulation are given in Figure 3.



**Figure 3:** Concentrations of several species in dependency on the ammonia concentration in primary coolant. Calculated for this work using our radiolysis simulation software developed at UCT Prague.

The results of our computation show the minimum in hydrogen concentration at ammonia dosage around 2 mg/L (corresponding with H<sub>2</sub> concentration about 4,5 Nml/L). Compare it with the results by Kritski et al. (2001) in Figure 2, where the minimum in hydrogen concentration occurs at by one order higher ammonia dosage as well as the hydrogen concentration itself.

Process measurement – H-meter development

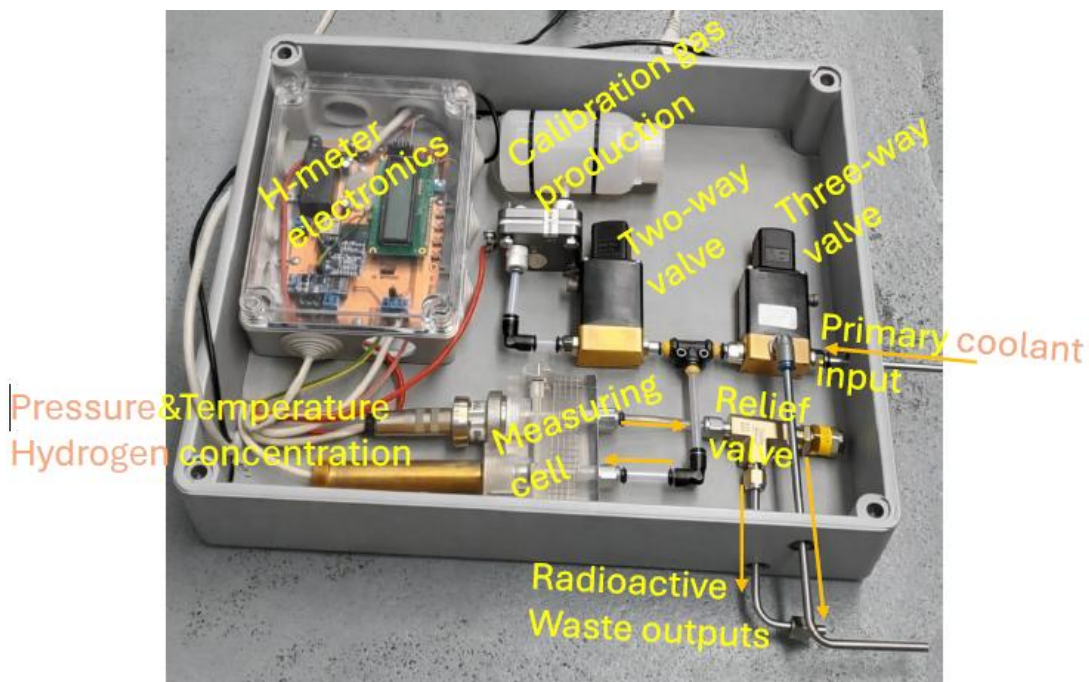
Even if there exist some agreements in mathematical modelling about the trends in primary coolant chemistry, the quantification data show, however, significant differences. It is, therefore, of significant importance to directly determine the concentrations of key components by process measurement using precise devices.

As there is a lack of selective hydrogen sensors on the world market, we started to develop such a device. In recent years we reported on our hydrogen sensor for primary coolant analysis (Moucha et al. 2024). After the functional verification in Dukovany nuclear power plant, we continued with

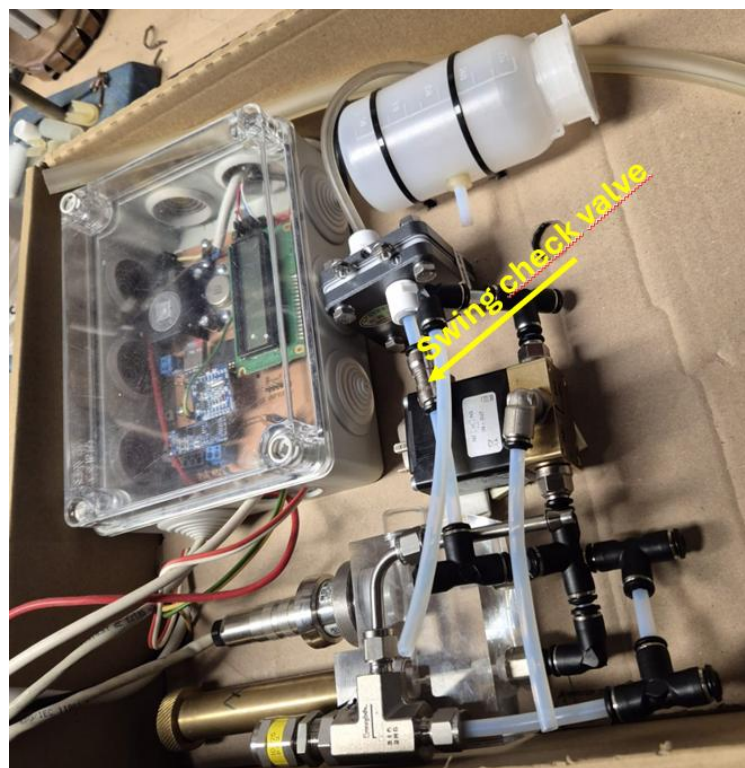
- i) the completion of the device by the inclusion of the SW and HW of a recalibration system and
  - ii) the spatial optimization of the device,
- as we report this year.

After the verification of our prototype of hydrogen sensor and its electronics at process conditions (the parts “H-meter electronics” and “Measuring cell” with sensors in Figure 4), we incorporated them into a spatial study of the whole device comprising recalibration part. This part means the valves declining the primary circuit sample to radioactive waste, bypassing the measurement cell (using “Three-way valve” in Figure 4), and introducing hydrogen for calibration from “Calibration gas production” (membrane electrolysis of water) using “Two-way valve”. The system of electrical valves with their controlling SW in “H-meter electronics” has been tested at laboratory conditions for one year and can be considered as a pilot prototype. After assembling the device using the prototype and pilot prototype (Figure 4) we reduced the device dimensions. After the series of rearrangements, we obtained the configuration of the size of almost 2/3 of the original one (approximately from 45x33x10 cm to 33x33x10 cm, see Figure 5).





**Figure 4:** Spatial study of H-meter device comprising measuring prototype („H-meter electronics“ + „Measuring cell“ with sensors) and pilot prototype of recalibration system („Calibration gas production“ with water electrolysis + valves)



**Figure 5:** Spatial study of H-meter device after dimensions reduction. The pilot prototype was reduced (the “Two-way valve” connecting „Calibration gass production“ with „Measuring cell“, shown in Figure 4, was replaced by „Swing check valve“)

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