Hydrogen sensor's testing in primary circuit of nuclear reactor

Tomáš Moucha[1], Václav Linek[1], Adam Bouřa[2]

[1]University of Chemistry and Technology, Prague, Chemical Engineering Dept., Technická 5, 166 28 Praha 6, Czech Republic; tel: +420220443297, e-mail: mouchat@vscht.cz

[2]Czech Technical University in Prague, Faculty of Electrical Engineering, Department of Microelectronics, Technicka 2, 166 27 Prague 6, Czech Republic

ABSTRACT

The usage of hydrogen in many industrial branches also necessitates its concentration measurement. In the development of the measurement technique, really selective to hydrogen, we focus on the H_2 concentration determination in the primary coolant of a nuclear reactor. To keep optimal process conditions in the primary cooling circuit of nuclear power plants, various chemical species are dosed in and monitored. Hydrogen, together with oxygen, belongs to the key components in the primary circuit chemistry. While a plenty of companies offer oxygen sensors suitable for the measurement in primary coolant, the hydrogen sensor, really selective to H_2 concentration, is offered by only one producer. It is worth, therefore, accomplishing the development of hydrogen sensor, which begun at UCT Prague more than two decades ago and was soon interrupted due to fateful events in the research team. Several successful measurements were, however, managed in this millennium beginning in Dukovany nuclear power plant thus promising results were left. We introduce here the results of the contemporary Hmeter development conducted in the Mass Transfer Laboratory. The connection of modern technologies, including electronics, with the experience from 1990's allowed us to develop a functional samples showing good long-term stability. Recently, we verified the usability of our Hmeter at industrial conditions, when our sensor reported primary circuit hydrogen concentrations for 64 days of its installation. Having both long-term stability and the industrial conditions endurance of our sensors confirmed, we are ready to develop a prototype and find the industrial partner to start the production of monitoring units.

Key words:
Hydrogen sensor
Amperometry
Primary circuit
Process measurement

1. Introduction

The need for hydrogen concentration measurement is associated with the hydrogen dosing into the primary circuit in new nuclear power plants (NPP) (as an alternative to the dosing of ammonia and hydrazine). This way is used in some contemporary NPPs of the former "western" countries, while in the NPPs of the former Soviet bloc, ammonia and hydrazine were only dosed. Now, for instance, in The Czech Republic the hydrogen dosage is also planned for new blocks which are to be built. It is, therefore, desirable to have measuring device that is available to provide a feedback in the regulation of hydrogen dosing without any time delay. According to the statement of potential users in energy industry, there is currently no choice on the market in sensors for monitoring the concentration of hydrogen in liquids. In connection with stricter standards for the reduction of corrosion risks in power generation technologies, it is increasingly important to accurately measure in the primary coolant not only the low concentrations of oxygen (fractions of thousandths of air oxygen solubility) but also hydrogen concentrations (of the partial pressure up to 3 bars).

Having long-term experience on the development of the measurement device for oxygen concentration [1] in NPP primary coolant, we focus now on the hydrogen concentration measurement. Our workplace will thus be able to offer the device for the measurement both oxygen and hydrogen concentrations in gases and liquids. In addition, wider range of applications is considered. For instance, oxygen saturation of blood or in the area of geological research of groundwater and in the case of hydrogen, its concentartion determination in petrochemical industry including monitoring of hydrogen leaks, thaks to the fast response of the new sensor.

There are two goals of our contemporary work. First, we aim at the development of electronics with very low noise level in order to obtain accurate data even when measuring values corresponding with the fractions of per mille of the measuring range. Second, we aim at the improvement of the long-term stability and industrial conditions endurance of hydrogen sensor.

2. The principle of the sensor

The hydrogen, amperometric, sensor connected to constant polarization voltage provides a current signal proportional to the concentration of hydrogen in front of the membrane covering the electrode. Hydrogen diffuses to the electrode through the membrane and a thin electrolyte layer, with zero hydrogen concentration maintained at the surface of the electrode in the optimum operating mode, which is illustrated by **Figure 1.** The probe operating at the limiting diffusion current provides a linear response to the hydrogen concentration in front of the membrane.

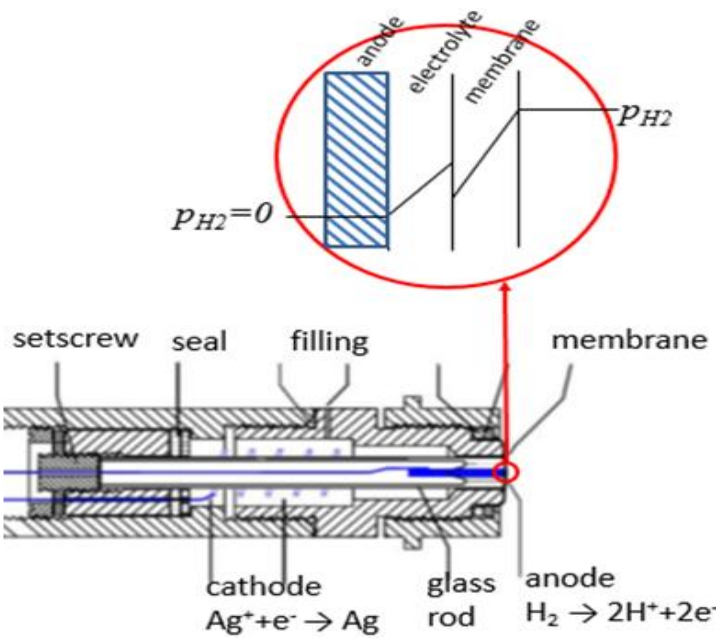

Figure 1: The scheme of amperometric Hydrogen sensor with the detail of the membrane and electrolyte diffusion layers.

The sensor is characterized by a quick response to a step change in hydrogen concentration in front of the membrane (with a first-order response time constant of about 0.2 s^{-1}). The sensor electrodes are located in the common electrolyte-filled compartment. When the electrolyte compartment is thoroughly filled and closed, the probe signal is insensitive to the changes in total pressure in the measured environment, when a constant value of hydrogen partial pressure is maintained.

3. State-of-the-art

The first version of our dissolved hydrogen measurement device, H-meter, was developed in 1990's. The development was conducted in Mass Transfer Laboratory at Prague Institute of Chemical Technology (today University of Chemistry and Technology Prague). Several pieces were tested in the Czech nuclear power plant Dukovany. The tests in 1990's brought the results showing two months stability of the signal at laboratory conditions (see Figure 2) and almost stable signal (the sensitivity decay about 25%) under process conditions for one week in the NPP Dukovany (see **Figure 3**).

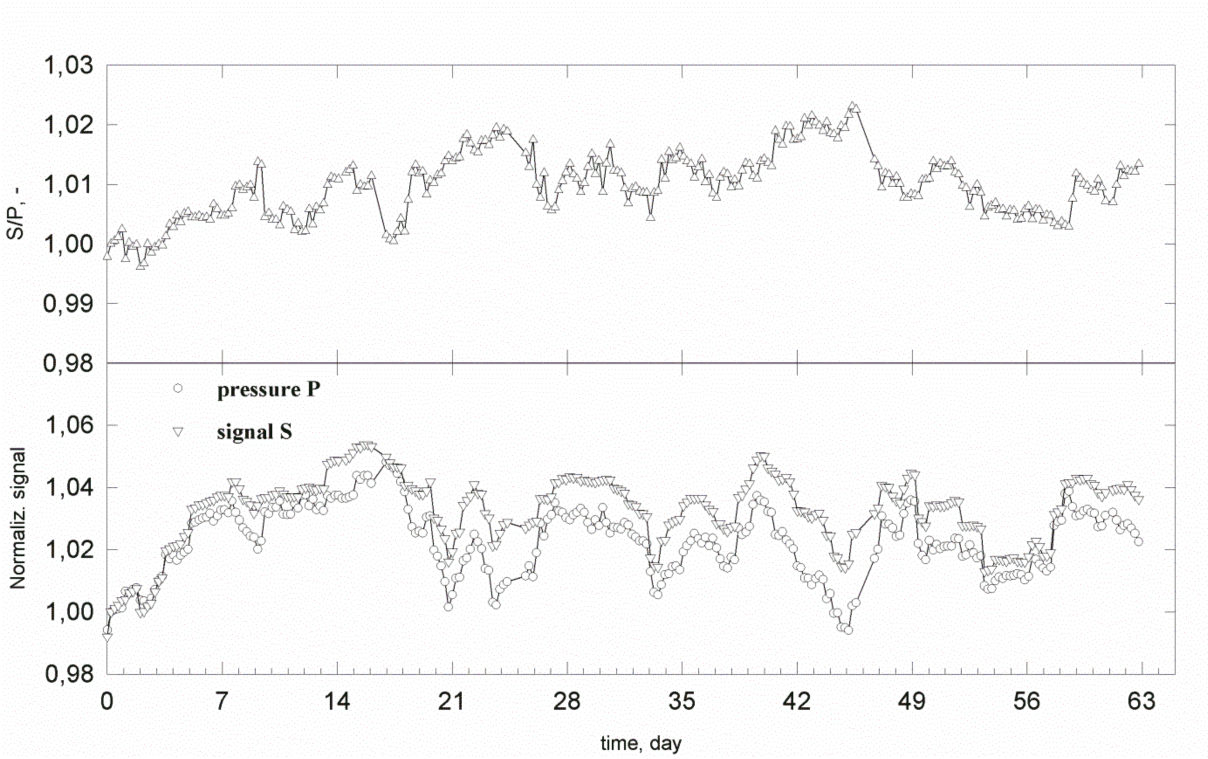

Figure 2**:** H-meter signal during the measurement in gas phase at laboratory conditions. Relative H-meter signal **S** when pure hydrogen flows through a measuring cell with the output open to the atmosphere. The fluctuations of the signal correspond with barometric pressure changes (relative values **P**). The pressure-normalized signal **S**/**P** makes the observed quantity.

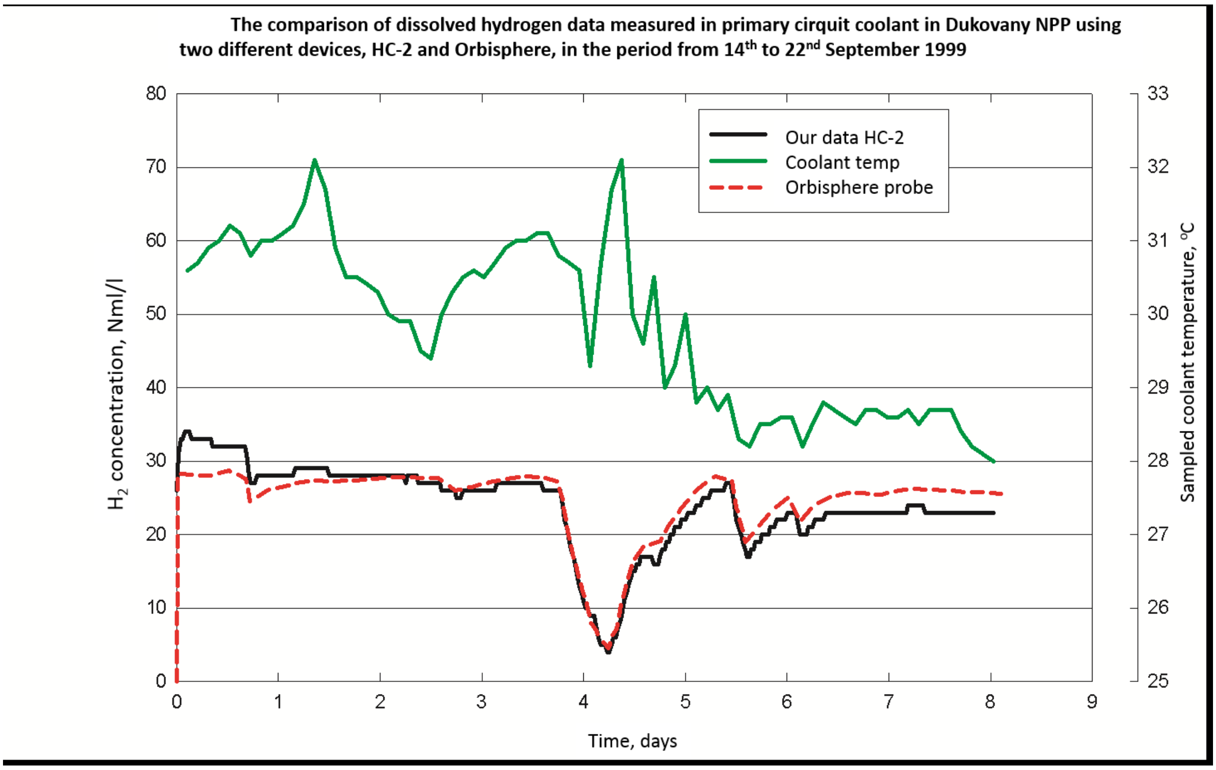

Figure 3: primary coolant hydrogen concentration measured in NPP Dukovany (the legend HC-2 refers to H-meter produced at UCT Prague, while "Orbisphere probe" means the standard termal conductivity sensor). Good temperature compensation is seen. H-meter's probe is of significantly faster response (time constant about 4.3 s).

4. Contemporary experimental set-up

The sensor has a cylindrical shape with a diameter of 19 mm and a length of 220 mm, with the outer part made of plexiglass. The sensor's geometry is illustrated by **Figure 1** above. The probe anode is made of a glass stem with a sealed platinum gold-plated contact covered by a polymeric membrane. A silver cathode is placed inside the probe, and the space between the anode and the cathode is filled with a potassium chloride solution. The probe connected to constant polarization voltage provides a current signal proportional to the concentration of hydrogen in front of the membrane. The sensor usually provides a very low current signal (units of nanoampers; nA), and it is therefore the task of the development of electronics to prevent signal noise in the analog section. Proper shielding and signal processing was implemented through the last year, so the electronics ensures an accurate and reliable signal.

The electronics consists of several sub-circuit blocks that are centrally controlled by an ARM processor from the STM32 family. The electronics contains a block for setting the DC polarization voltage for the sensor in the range of 0 to 2 V, with accuracy better than 1 mV. A low-noise operating amplifier with sufficient current capacity is used to supply the sensor with a current up to 10 mA. The current from the sensor is sensed by the block with a current-to-voltage converter. Due to the magnitude of currents in the nA lines, great emphasis is placed on the converter. The converter is designed with high gain, but it must also be unconditionally stable, i.e. resistant to self-oscilations. It must also be resistant to external interference, which is ensured by sufficient shielding of the circuit and the sensor itself. For further treatment of the sensor signal, the electronics is prepared to include temperature and pressure sensor inputs. It also operates the display unit, keyboard and the data transfer to a PC using USB interface (UART FT232 converter). **Figure 3** shows the functional sample of new control unit.

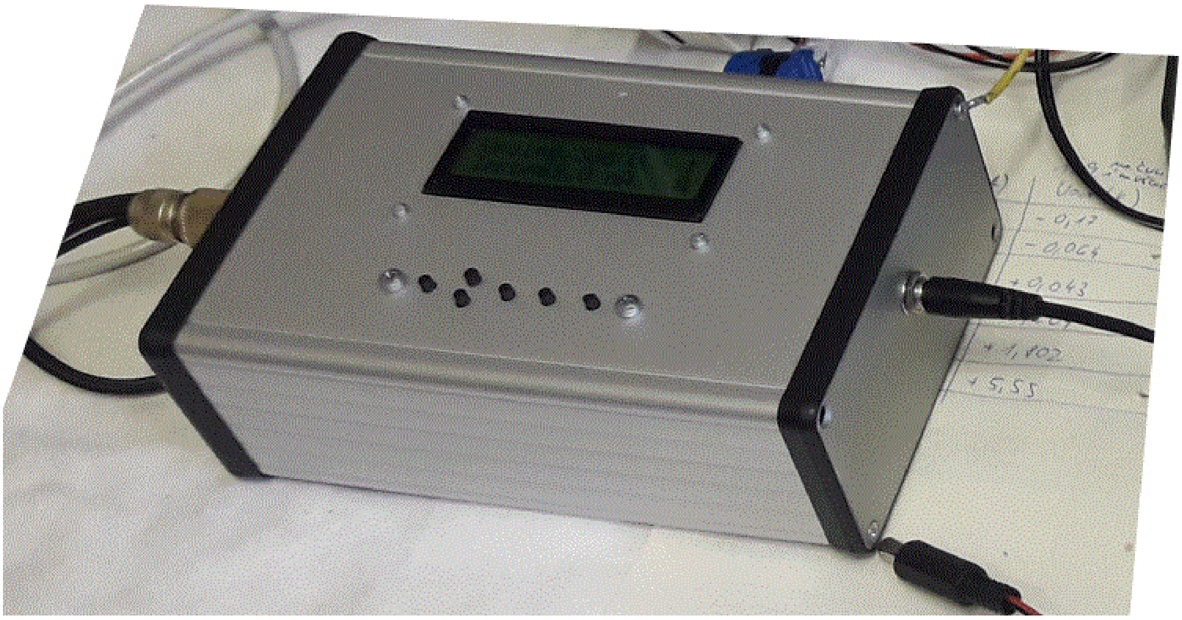

Figure 3: Control unit developed for H-meter

5. Results of recent tests

5.1. Long-term stability and temperature dependency

The long-term stability of the hydrogen sensor is permanently tested and improved because, contrary to oxygen sensor, this is the limiting parameter in the way to a prototype development. The sensors are usually tested for the periods of 200 days to verify their stability for a quarterly period including a safety overlap.

During the long-term stability tests, together with H-sensor's signal, we also recorded the measuring cells temperature and obtained the data enabling to quantify the temperature dependency of hydrogen concentration signal. An example of such data shows **Figure 4**.

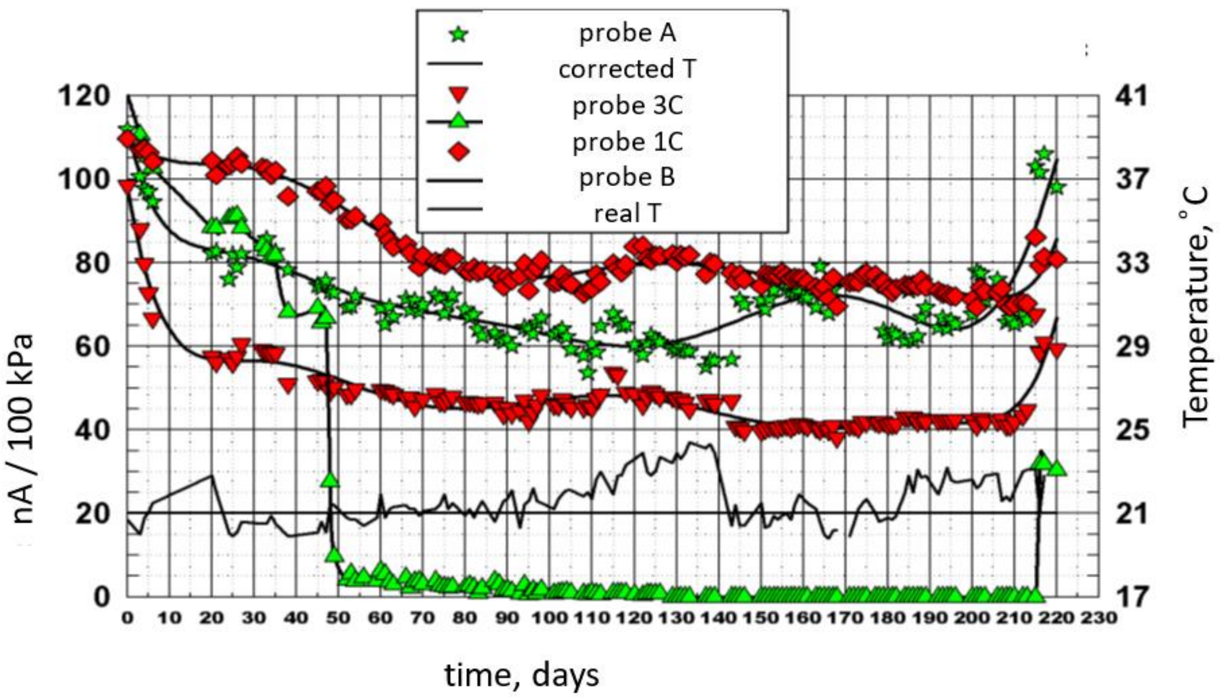

Figure 4: H-sensors' signal record illustrating their long-term stability after the initial maturing period, which also include the signal corrections to temperature fluctuation (see black line between 19 and 24 °C). Usually, uncorrected signal changes by 4% of the signal range per one °C.

5.2. Operational tests in nuclear power plant

After the long-term stability verification, the measurement under process conditions was realized in Dukovany NPP. It was possible to let our sensor installed for the period of 64 days. The data were compared with the standard Orbisphere thermal conductivity sensor. The results, illustrated by **Figure 5**, show good agreement of Hmeter data with those measured by standard Orbisphere device on average.

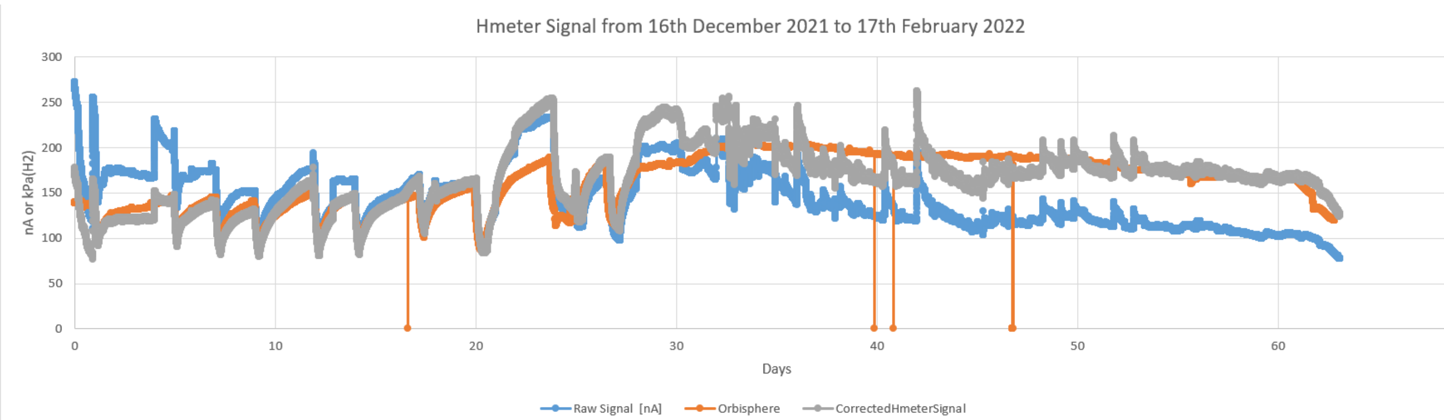

Figure 5: Hmeter and Orbisphere data comparison from the measurement in primary circuit sampling channel in the NPP Dukovany. The gray line represents the Hmeter signal compared to the Orbisphere's one (brown line). The blue line shows the original current signal of Hmeter, which was then recalculated using temperature compensation, hydrogen solubility and H-sensor calibration.

In addition, we can see more local peaks of the Hmeter signal, which we ascribe to faster response of the Hmeter compared to Orbisphere, which we observed already in the period of the measurement 20 years ago (**Figure 3**). There is, however, also the risk of the pressure dependence of our sensor (the membrane movement, which changes the electrolyte layer thickness), which also could produce the signal fluctuation. This might be the case of the second half of the measuring period in Figure 5 and will be verified. The elimination of pressure dependence is the nearest issue of our future work.

6. Conclusions

After successful realization of new electronics for the control unit and the long-term stability tests of new sensors the recent results on the measurement at process conditions in the NPP were acquired. These preliminary results promise that the prototype of modern hydrogen sensor can be successfully developed in the Mass Transfer Laboratory at UCT Prague, which will be suitable for hydrogen concentration monitoring in nuclear power plants. As the only one producer on the world market offers the similar, hydrogen selective amperometric device suitable for the measurement in NPP's, we will be able to offer the alternative.

7. Acknowledgements

Financial Support by Specific University Research (MSMT No. A1_FCHI_2022_005) and by European Regional development Fund-Project **ORGBAT** No.CZ.02.1.01/0.0/0.0/16_025/0007445 are gratefully acknowledged.

8. References

[1] V. Linek, V. Vacek, J. Sinkule, P. Benes, Measurement of Oxygen by Membrane-Covered Probes, *Ellis Horwood,* 1988