Testing of electrochemical hydrogen meter in a sodium facility in Cadarache

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Abstract : An electrochemical hydrogen meter (ECHM) developed in Indira Gandhi Centre for Atomic Research (IGCAR), India has been tested in a sodium facility in French Alternative Energies and Atomic Energy Commission (CEA), Cadarache Center, France as part of IGCAR-CEA collaboration of fast reactor safety. ECHM which works in equilibrium mode provides an alternate technology to the conventional diffusion based hydrogen sensor (SPHYNX) that works in dynamic mode for detecting steam leaks into sodium. Tests involved introducing ~25 mg to 150 mg of NaH in liquid sodium to change the H concentration in sodium by ~25 ppb to 150 ppb, respectively. The signals of both ECHM and SPHYNX were monitored as a function of hydrogen concentration and temperature. The test results showed good agreement between the output of both types of sensors in detecting the change in hydrogen concentration in sodium and the response time of ECHM is found to be higher than SPHYNX.

Keywords: Fast breeder reactor, sensor, in-sodium, hydrogen, steam-leak

1. Introduction

Liquid sodium is the coolant of choice in fast breeder nuclear reactors due to its favourable physical, chemical and nuclear properties [1]. It is used as coolant both in the primary and secondary circuits to transfer the heat produced in a fast reactor core into steam generator. At the steam generator a single ferritic steel wall separates liquid sodium from high pressure water/steam. Any defect or micro crack in the structural material will cause the high pressure and high temperature steam to come into contact with sodium. The resulting sodium-water reaction is exothermic and the reaction products are sodium hydroxide and hydrogen. Under these conditions the caustic nature of sodium hydroxide can propagate the leak, resulting in catastrophic accident conditions [2]. As the hydrogen gas dissolves as NaH in liquid sodium at high temperature, the occurrence of steam leaks can be detected by continuous monitoring of hydrogen concentration in liquid sodium.

ECHM, offers an attractive alternate technology to the SPHYNX diffusion based hydrogen meter due to its simplicity and compactness and is used for steam leak detection into secondary sodium circuit in PFBR, Kalpakkam, India. ECHM was already tested and compared to SPHYNX at Phenix, France in 2009 [3] as part of Indo-French collaboration on fast reactor safety. It was found that the obtained results needed an additional test program which could be undertaken in a more flexible sodium facility than an operating reactor. The SUPERFENNEC sodium loop in the CEA, Cadarache has been chosen to host the SPHYNX and ECHM with the aim to compare the sensitivity and response time to hydrogen influx at different rates and at different operating temperatures. The results of the studies are discussed in this paper.

2. Description of SUPERFENNEC Sodium Loop

Figure 1 shows the schematics of the SUPERFENNEC sodium loop. It has various typical sections such as testing tank, storage tank, electromagnetic pump, cold trap, sodium air cooler, plugging indicator, etc. The section for hydrogen detection (HD) is introduced in a by-pass line. Table 1 gives the characteristics of the loop.

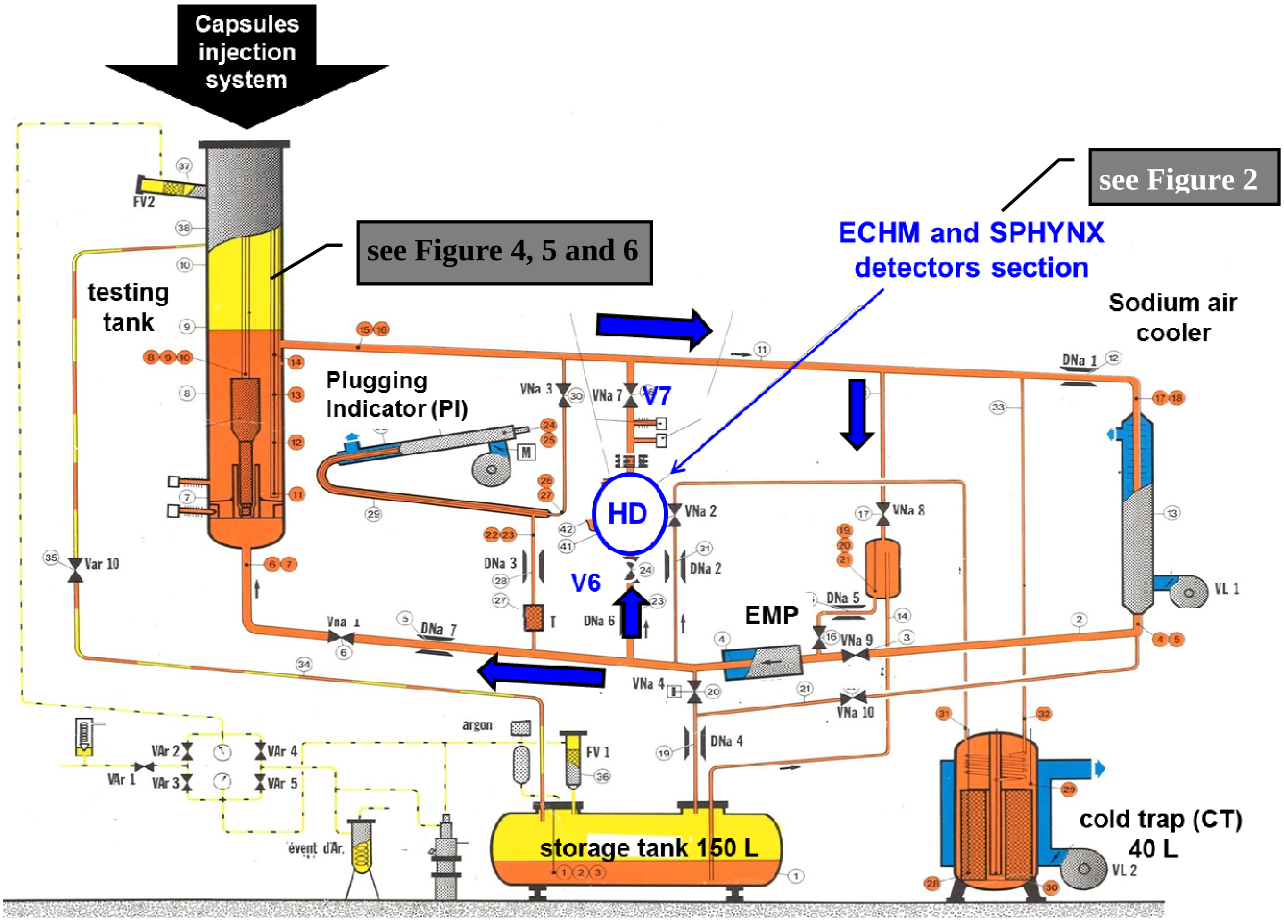


Figure 1: Schematics of the SUPERFENNEC Na loop

Table 1 Characteristics of sodium loop

Maximum Na temperature	550°C
Electromagnetic pump	P (Pressure) = 1 bar, Q (Flow rate) = 2 m^3/h
Total Na storage tank volume	150 L
Sodium flux volume	48L
Cold trap	Q = 40 +/- 5 L/h, V = 40 L
Plugging indicator	Q = 180 L/h

2.1 Sensor Section

In this section, both ECHM and SPHYNX are installed in series. Thus they are subjected to the same temperature (T_{Na}) and flow rate (Q_{Na}) parameters and the hydrogen concentration [H] measurements are related to the same Na flow sampling. The schematics of this section is shown in Figure 2. This section has isolation valves, vacuum circuit and detectors for SPHYNX, heaters, temperature controllers, etc.

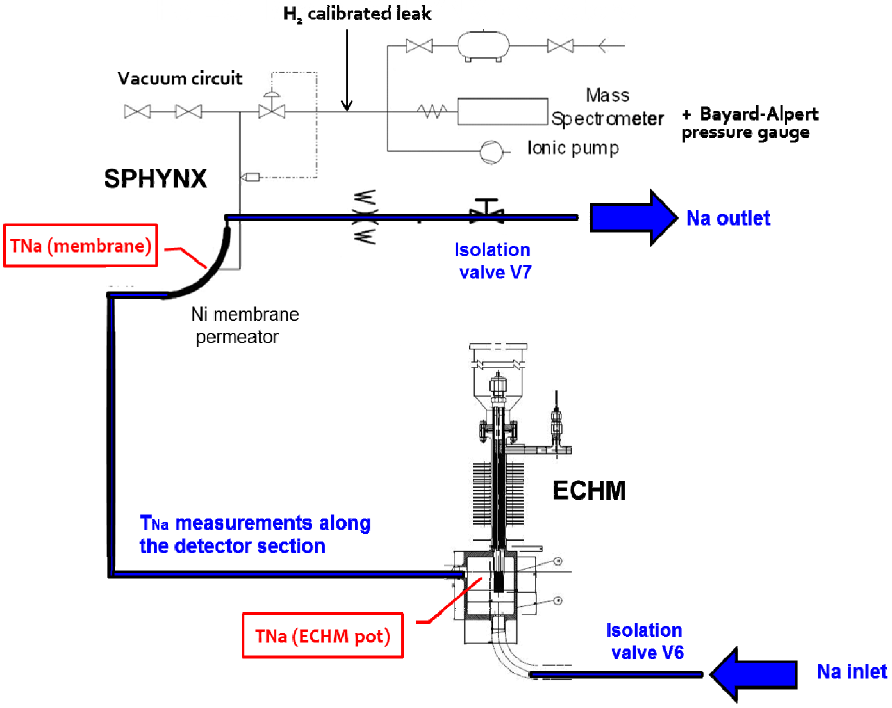
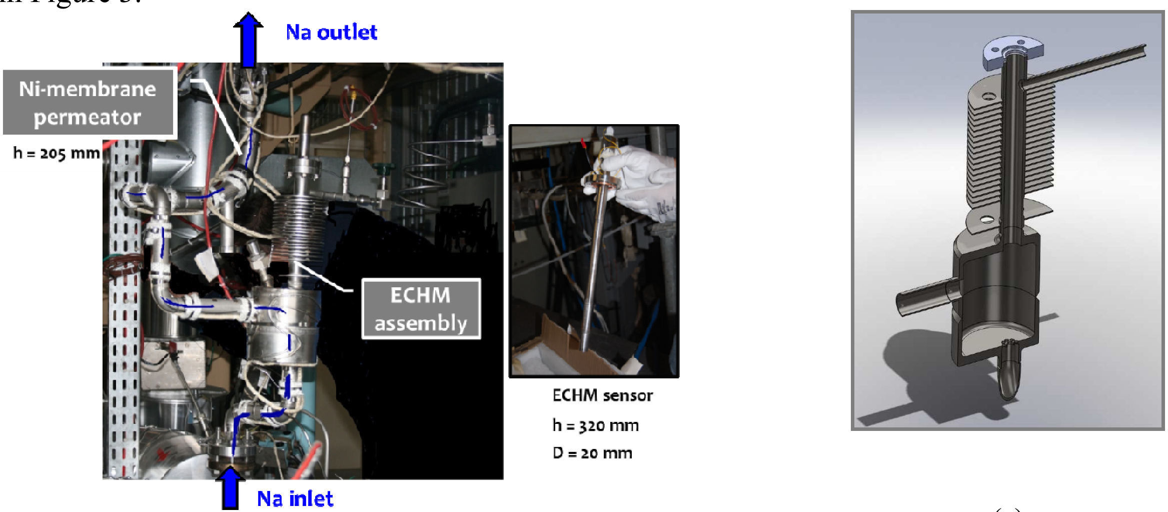


Figure 2: Details of the sensors section of the SUPERFENNEC loop

The sodium temperature in this section can be varied by means of a temperature controller. Photographs of (a) sensor section, (b) ECHM and (c) schematics of ECHM assembly are shown in Figure 3.



(a) (b) (c)

Figure 3: Photograph of (a) sensor section with the Ni-membrane permeator and the ECHM assembly, (b) ECHM and (c) cut view of the relevant ECHM assembly.

2.2 Hydrogen Injection System

Hydrogen is introduced in the sodium circuit by means of sodium hydride, NaH (95% purity, dry, Sigma Aldrich). The NaH powder is inserted in the specially designed capsule and enveloped with sodium, assembled inside an argon atmosphere glove box. Photographs of the capsule are shown in Figure 4.

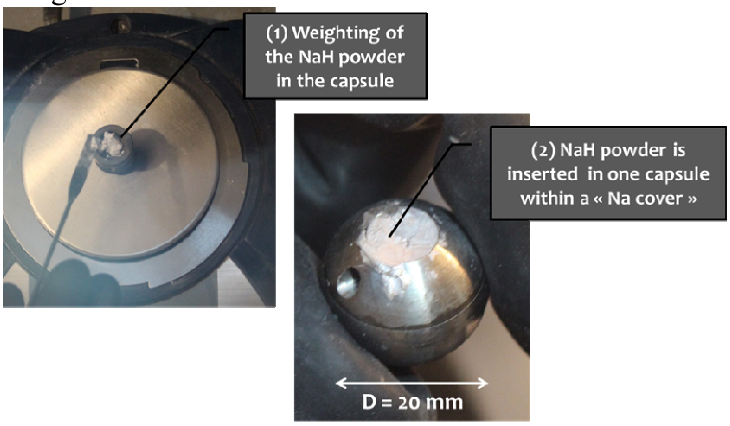


Figure 4: Photograph of NaH capsule

These capsules can be introduced into sodium through the injection system installed on the plug of the SUPERFENNEC testing tank shown in Figure 5. This system has provision to introduce the NaH capsules inside the testing tank in a safe and leak-tight manner.

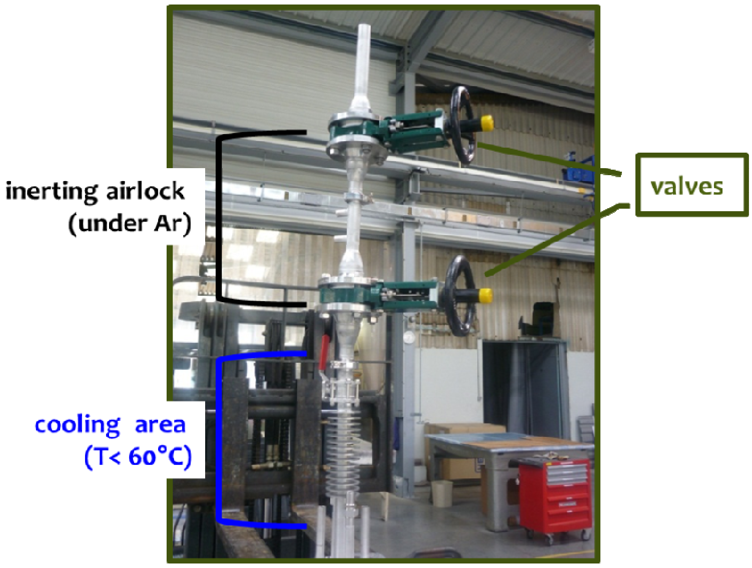


Figure 5: Details of the upper part of the capsules injection system settled on the testing tank

The design of the basket which contains the capsules (shaped as spherical pebbles) can be immersed in sodium within the testing tank as shown in Figure 6.

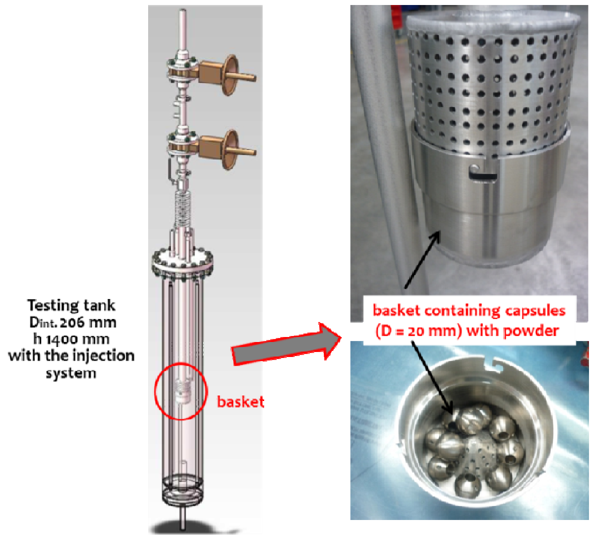


Figure 6: Cut view and photograph of the capsules injection system

3. Description of the ECHM

A detailed description of ECHM is given in ref.[4]. ECHM is a concentration cell and can be used to measure the hydrogen pressure. The cell is represented as

$$p_{H_2}(\text{sample})|\text{electrolyte}|p_{H_2}(\text{ref}) \quad (2)$$

The electromotive force that develops across the electrolyte is given by the Nernst relation:

$$E = \frac{RT_M}{2F}\ln\left(\frac{p_{H_2}(\text{ref})}{p_{H_2}(\text{sample})}\right) \quad (3)$$

where, the reference hydrogen partial pressure, $p_{H_2}(\text{ref})$ is known and fixed at the sensor operating temperature, $p_{H_2}(\text{sample})$ is the hydrogen partial pressure in sodium, R is the universal gas constant, F is the Faraday constant and T_M is the temperature of meter operation. Hydrogen detection in sodium involves measurement of the hydrogen partial pressure in equilibrium with the dissolved hydrogen in sodium. Hydrogen partial pressure (pH_2) is correlated to hydrogen concentration in sodium (C_H) by Sievert's law [5]:

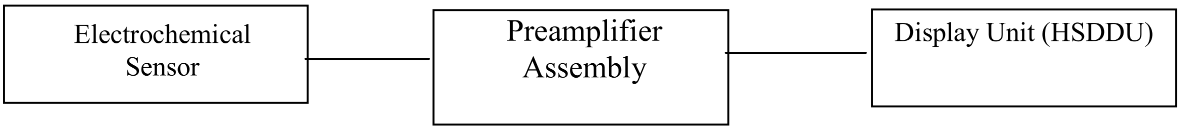
$$\left(p_{H_2}\right)^{1/2} = \frac{C_H}{k} \quad (4)$$

where, k is the Sievert's constant for this system, which is found to be almost independent of temperature [5, 6].

ECHM uses $CaBr_2$-CaHBr biphasic mixture as the electrolyte. It is a solid electrolyte and conducts H^- ions. A mixture consisting of calcium and magnesium along with calcium hydride is used as the reference electrode that fixes the reference hydrogen pressure at the meter operating temperature. Hydrogen concentration in sodium fixes the sample hydrogen pressure. The meter operating temperature (T_M) has been optimized and chosen as 450°C. When the operating temperature of the meter is varying, the reference hydrogen pressure would also vary and so the meter output would also vary accordingly. Hence, it is essential that the meter operating temperature must be controlled within an accuracy of ±1°C.

3.1 Configuration of the ECHM System

ECHM unit consists of three main parts as shown in the block diagram below [7]:



The sensor produces an EMF output in volts which is logarithmically related to hydrogen concentration and the instrumentation which consists of the preamplifier assembly and the Hydrogen in Sodium Detector Display Unit (HSDDU), processes the sensor signal suitably and makes it available for recording. A schematic diagram of the electrochemical hydrogen sensor along with its preamplifier assembly is shown in Figure.7(a). The meter consists of a pure iron thimble for housing the electrolyte and another pure iron thimble for holding the reference electrode materials. The electrolyte thimble is then welded to a stainless steel pipe which in turn is welded to a knife-edged flange. The reference electrode mixture is hermetically weld closed inside the other iron thimble and welded to a stainless steel rod of 3 mm diameter through a connecting sleeve. The electrolyte cast from its molten state fills up the annular gap between the two iron thimbles. The space between electrolyte compartment and the electrode compartment is filled with few numbers of small cut tubes of alumina. Fig.7(b) shows the photograph of the sensor. At the top of the sensor flange the preamplifier assembly is housed. Fig.7(c) shows the photograph of the pre-amplifier assembly. It consists of a pre-amplifier, a connector and a stainless steel cylinder surrounding the pre-amplifier. The pre-amplifier is fixed to a stainless steel flange and is connected to a connector that is provided on the flange. A stainless steel cylinder covering the pre-amplifier is connected to the flange by bolts and nuts. The output from the preamplifier assembly as well as its power supply is carried through a couple of shielded cables that connect the preamplifier assembly and display unit (Fig.7(d)).

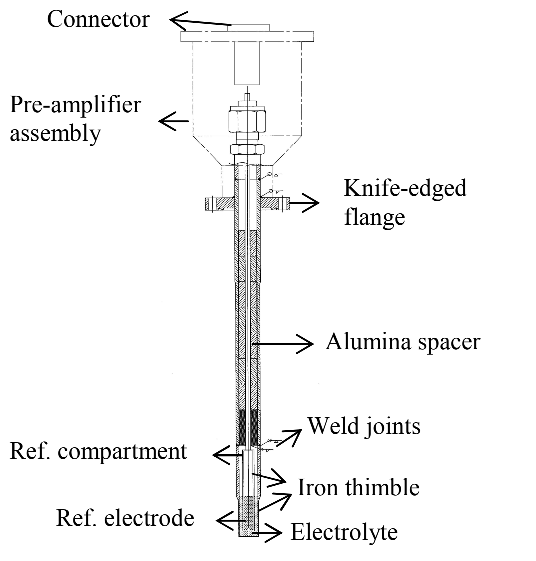


Fig. 7(a) Schematics of electrochemical hydrogen sensor cum preamplifier.

Fig.7(b) Photograph of electrochemical sensor.

Fig.7(c) Photograph of pre-amplifier assembly.

Fig.7(d) Photograph of display unit.

The meter has been calibrated as a function of hydrogen concentration in sodium in a bench top sodium loop at IGCAR. The output of the meter is in the millivolts range. Amplified output from the preamplifier unit is converted into pulses so as to enable the transfer of the signal without any interference over long distances to the power supply cum display unit. In the display unit, the signal is converted back to analog output, digitized, displayed in volts. The signal is transmitted by transreceiver components. The calibration constants are entered into the display unit and the output is displayed by a digital potentiometer in concentration units of ppb (parts per billion) of hydrogen in sodium. The same output is available for recording from the rear panel of the display unit. This output has a range of 0 to 10 V which corresponds linearly to hydrogen concentration from 0 ppb to 2000 ppb.

4. Description of the SPHYNXHD System

The SPHYNX hydrogen detection (SPHYNX HD) system comprises of the following components: (i) an ultra-high vacuum circuit just downstream of the Ni-membrane which is composed of a primary pump, a ionic pump and a "Bayard-Alpert Pirani combination gauge ". This gauge measures the total pressure in the vacuum circuit down to ultrahigh vacuum pressures and is used to corroborate and / or to help to calibrate the mass spectrometer, (ii) a quadripolar mass spectrometer (QMS) which has its own total pressure gauge and gives access to the hydrogen partial pressure as well as to the partial pressures of the first 100 masses of gases in the vacuum circuit, (iii) a calibrated hydrogen leak used to perform an accurate calibration of the QMS regarding the hydrogen partial pressure. The overall SPHYNX HD system implemented on the SUPERFENNEC loop is described in Figure 8.

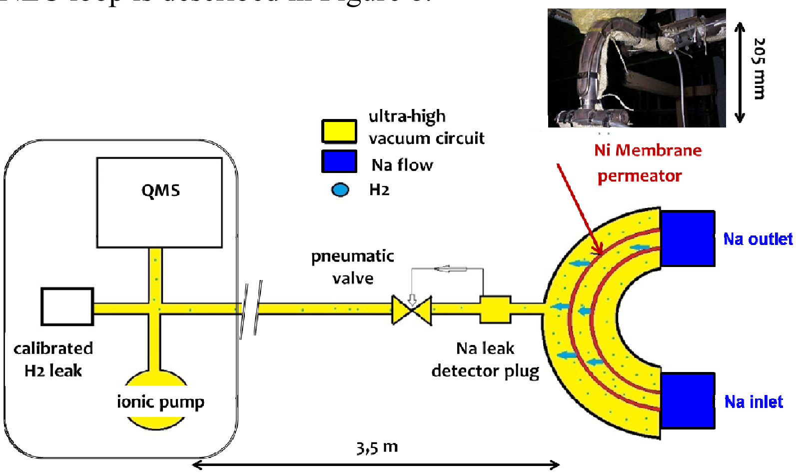


Figure 8: The overall components of the SPHYNX HD system

The entire vacuum circuit (L ~3.5 m) is equipped with heating cables and is insulated for degassing. The tubes are connected by UHV flanges with copper gaskets. The pumping as well as the analysis devices are placed in a regulated and controlled cabinet at 25°C. The ultra-vacuum and measurement components supplied by the VEGATEC Company, France were integrated in the dedicated cabinet.

5. NaH injection Studies

5.1 NaH injection Process

Figure 9 shows the schematics of the SUPERFENNEC Na circuit involving NaH addition through the testing tank.

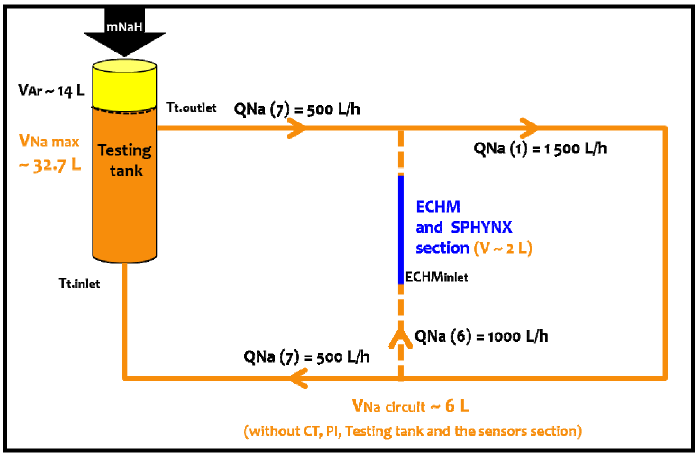


Figure 9: Outlines of the SUPERFENNEC Na circuit and NaH addition at the testing tank

As an example, for a 1000 L/h-Na flow rate applied in the sensors section, the order of magnitude of the hydraulic travel times should be as follows:

- from $Tt._{outlet}$ up to $ECHM_{inlet}$→t_{TH} = 15.5 s, that corresponds to the most direct transfer from the testing tank up to the ECHM sensor;
- from $Tt._{outlet}$ up to SPHYNX $_{inlet}$→t_{TH} = 16.5 s, that corresponds to the most direct transfer from the testing tank up to the SPHYNX sensor. The hydraulic travel time of Na between the ECHM sensor and the permeator sensor is around 1 second;
- from $Tt._{outlet}$ up to $Tt._{outlet}$ through the circuit and testing tank (i.e., a complete cycle)→t_{TH}~ 24 + 235 ≈260 s.

Prior to the injection the purification of sodium is carried out via cold trap. The purity of the sodium is checked by plugging indicator which indicates background hydrogen concentration in liquid sodium. The signals for both the sensors were continuously recorded and monitored for their stability and background value (BV) for 24 h. After isolating the cold trap and plugging indicator, NaH has been injected into sodium at 450°C in order to achieve a target hydrogen concentration of BV + 100 ppb in the sodium flow. The time of injection is noted and the performance of both the sensors was monitored for 60-90 min. Subsequently, purification of sodium has been resumed via the cold trap.

5.2 Response of Sensors

Typical response behavior of the sensors is shown in Figure 10. The results of NaH injection at 450°C is given in Table 2. Injection No.1 was used to check the qualitative response of the sensors and hence not shown in Table 2. For the remaining injections, both the sensors measured closely comparable quantitative response for various amounts of NaH injections. However, the targeted increase in H concentration in sodium was not measured by both the sensors in any injection. The reasons for not attaining the target concentration could be due to the possible evolution of hydrogen gas bubbles into the cover gas space over the sodium surface, caused by the faster thermal decomposition kinetics of NaH than its solubility. This possibility has been reported earlier in the literature [8].

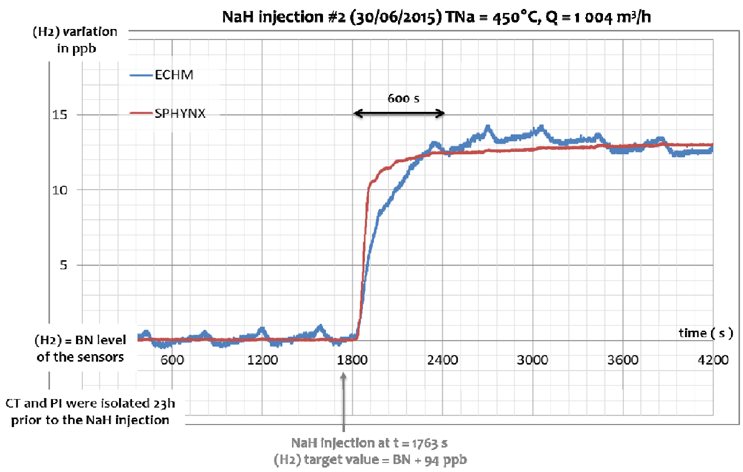


Figure 10: Typical response the sensors at 450°C.

5.3 Response time analysis

Calculation of response times of the sensors for each injection is obtained from the sensor signals as shown in Figure 11 as described below:

-t_0, represents the NaH injection onset ;

-t_{RD}, represents the take-off time of the signal: the point at which the ramp signal begins to grow;

-$t_{R\ equilibrium}$: represents the point at which the (H_2) variation has reached 90% of its steady state value.

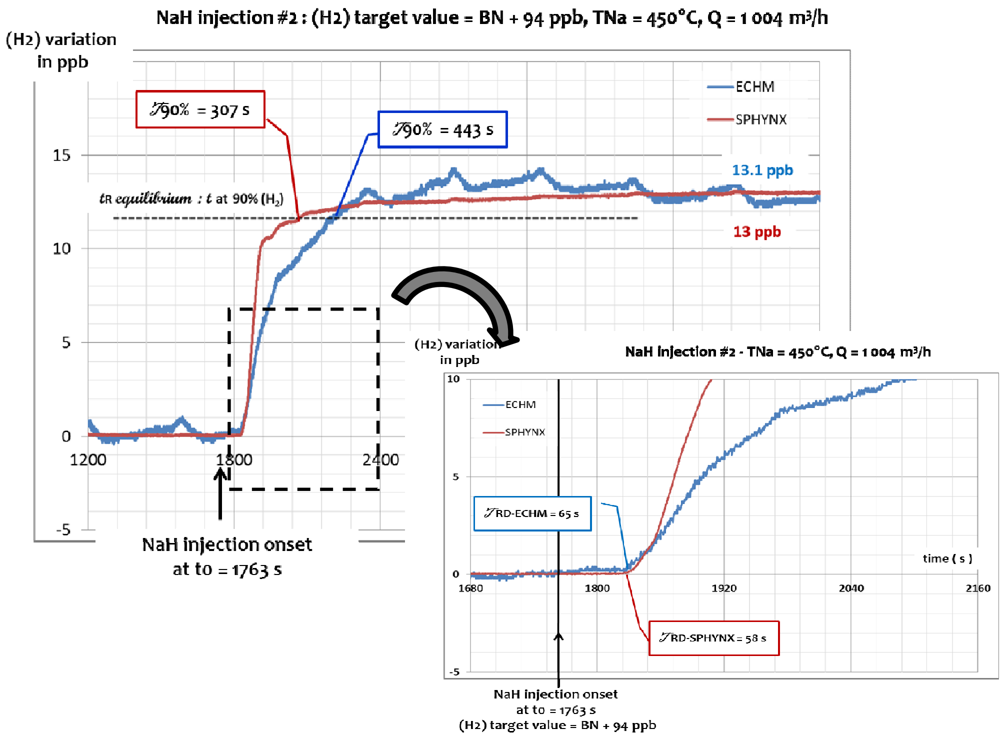


Figure 11: Time response analysis of the sensor signals for NaH injection

For injection 2, as indicated on the data curves, it can be noted that

- the signals take off within relatively similar periods of time,with t_{RD}=58 s for the SPHYNX HD system and 65 s for the ECHM HD system.
- $t_{Requilibrium}$ equals 307 s for the SPHYNX HD system in comparison with 443 s for the ECHM HD system.
- The response times for injections 2, 3 & 4 are given in Table 2.

Table 2 Response of sensors at 450°C

Injection Test No.	Target Value	Sensor Response			
		[H] / ppb (% Response)		Response Time /s (t_{rd})	
		ECHM	SPHYNX	ECHM	SPHYNX
2	+ 94 ppb	+13.1 (14%)	+13.0 (14%)	65	58
3	+ 145 ppb	+23.2 (16%)	+25.0 (17%)	76	42
4	+ 45 ppb	+12.0 (26%)	+9.5 (21%)	18	14

+ means over the background value; t_{rd}: take-off time, the point at which the ramp signal begins to grow

The response times of both types of the sensors for injections at different temperatures for a targeted amount of 25 ppb increase in H in sodium is summarised in Table 3.

Table 3 Response of sensors at different temperatures

Injection Test No.	Sensor type	Temperature /°C	Response time /s (t_{rd})	($t_{90\%}$)	[H] / ppb (% Response)
5	ECHM	449.2	54	240	4.4 (18%)
	SPHYNX	449.2	---	52	3.0 (12%)
6	ECHM	423.4	56	355	7.8 (31%)
	SPHYNX	423.4	31	251	4.6 (18%)
7	ECHM	453.1	87	416	7.0 (28%)
	SPHYNX	453.1	28	121	4.7 (19%)
8	ECHM	445.7	75	538	13.4 (54%)
	SPHYNX	445.7	44	105	6.9 (28%)

$t_{90\%}$: represents the point at which the (H_2) variation has reached 90% of its steady state value

As the ECHM was calibrated at 450°C, the signals obtained at other temperatures were normalized to the calibration temperature by incorporating meter temperature coefficient, namely 0.02 V/°C. This is to compensate for the change in the reference hydrogen potential of the reference electrode due to different operating temperature. Apart from this, instantaneous variation in the meter temperature of ±0.8°C creates asymmetric potentials across the electrolyte that results in the noise of ± 0.5 ppb in the signal.

The response times (t_{rd}) of ECHM is found to vary generally between 55 to 75 seconds for injections 2 to 8 except for inj.4 and 7 (where it is 18 s and 87 s). This includes a direct transport time of 15 seconds, from the test vessel to the location of ECHM. Thus, the instrument response time of ECHM is determined to vary between 40 s and 60 s. The response times (t_{rd}) of SPHYNX is faster and varies between 28 s to 44 s except injections 2 and 4 (where it is 58 s and 14 s). Subtracting the transport time of 16 s, it is determined to vary between 12s and 28 s. There is no direct correlation between the observed response times of the sensors and the experimental parameters, such as sodium temperature, amount of H injected.

Conclusions

Different amounts of hydrogen additions into pure cold-trapped sodium were made in the form of NaH powder under inert atmospheric conditions and the response both ECHM and the SPHYNX sensors were recorded. Both the sensors detected a fractional increase of 13 to 26% of hydrogen injected in tests made at 450^{o}C. The incomplete mass balance during injections is attributed to the evolution of gas bubbles into the cover gas above sodium in the injection test chamber, which is in commune with storage tank cover gas space. Such a possibility of H2 gas transport by bubble mechanism into the cover gas is reported in literature. As the kinetics of dissolution of evolved hydrogen gas into liquid sodium is slow and depends on the hydrogen pressure over sodium and the [H] in sodium, only a fraction (13 to 26%) of injected hydrogen increment is probably observed. The response times ($_{trd)}$ of ECHM is found to be higher than SPHYNX. There is no direct correlation between the observed response times of the sensors and the experimental parameters, such as temperature, amount of H injected. Even with independent calibrations both types of sensors showed good agreement between their signal output in detecting the change in hydrogen concentration in sodium. The response times (t_{rd}) of ECHM and that of SPHYNX are found to be 60s and 28s, respectively as a conservative estimate from these experiments.

Acknowledgements
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