

## On-demand hydrogen production from borohydride alkaline solution

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Extended application of hydrogen as energy carrier in transportation and on-demand production requires an economical and reliable technologies for storing and production of H<sub>2</sub>. Present and recent technologies for storing hydrogen in its various chemical states are reviewed. In particular chemical hydrides look promising as capable to overcome issues related to hydrogen safety and handling.

In ENEA Casaccia labs production of hydrogen from the sodium borohydride salt (NaBH<sub>4</sub>) reaction has been studied by experimental bench tests. Effective results on the catalyzed NaBH<sub>4</sub> hydrolysis and catalyst stability have allowed the application of such a technology in a new brand commercial device for the small production of hydrogen gas. In this work various schemes of NaBH<sub>4</sub> production system are modelled and the experimentally checked by a commercial hydrogen generator.

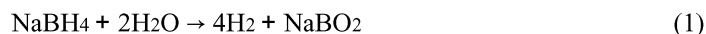
### Introduction

Although there is a significant amount of research and development being focused on fuel cells, significant issues remain with respect to the fuel source and fuel storage<sup>1</sup>.

A stabilized aqueous solution of sodium borohydride looks as a safe, simple and compact source of high-purity humidified hydrogen<sup>1</sup>. For its chemical properties, sodium borohydride is presently used as a reducing agent in the synthesis of organic chemical compounds and as a bleaching agent in the manufacture of paper.

By the way it could be an interesting alternative for hydrogen storage in portable fuel cell applications<sup>1</sup> for its hydrogen content: for example, aqueous solutions of 20 and 30 wt% of NaBH<sub>4</sub> have a hydrogen storage density of 4.2 and 6.5 wt%, respectively<sup>2</sup>.

The hydrolysis reaction is exothermic and proceeds according to:



As at ambient conditions a NaBH<sub>4</sub> solution spontaneously generates significant amount of hydrogen, it is stabilized increasing its pH (e.g. adding NaOH), requiring a catalyst to produce hydrogen in a controlled way<sup>2</sup>. Furthermore a hydrogen catalytic generator can have a safe and fast response to hydrogen demand<sup>2</sup>.

As the nature of studied hydrogen production from NaBH<sub>4</sub> is discontinuous, four different schemes of processes were studied and simulated. Theoretical trends were then compared with experimental data obtained from two processes tested. The experimental results were obtained by testing a commercial hydrogen generator, manufactured by Erredue srl (Italy).

### Batch Processes for Hydrogen production by NaBH<sub>4</sub> solution

A stabilized NaBH<sub>4</sub> solution, in presence of metal catalysts, hydrolyse to produce H<sub>2</sub> gas and water-soluble sodium metaborate, accordingly the (1).

The system operates in a batch mode, with a fixed circulating volume of NaBH<sub>4</sub> solution. As soon as the solution is exhausted fresh water or solution are refilled in the system.

In previous work<sup>3</sup>, the experimental data showed a decreasing linear profile of the concentration of circulating NaBH<sub>4</sub> solution vs time, showing a zero-order hydrolysis reaction, with the reaction rate not to depend on the NaBH<sub>4</sub> concentration but only from the kinetic constant K (calculated  $K = 0.0002 \text{ s}^{-1}$ ).

As reaction proceeds water is consumed and the soluble metaborate can precipitate in the system (tank, piping, reactor and catalyst surface), clogging system and limiting active catalytic surface, decreasing hydrogen production and system operability.

In order to decrease the borate precipitation, four different processes of batch catalytic sodium borohydride hydrolysis reaction of solution were theoretically studied. Table 1 reports starting and operating conditions and performance limits of simulation.

For every process mass balance were calculated, according to reaction stoichiometry and specific control strategy.

#### Process 1: All NaBH<sub>4</sub> solution recycled

In the first scheme the whole NaBH<sub>4</sub> solution is charged in the S tank and then supplied to the R reactor by the P pump (fig. 1). NaBH<sub>4</sub> concentration decreases according to the hydrogen production while borate concentrates in the recycled solution.

Table 1: starting and operating conditions and performance limits data for processes analysis

Produced Hydrogen Flow	100 mL/min
Initial Mass of NaBH <sub>4</sub>	80 g
Initial Mass of H <sub>2</sub> O	1000 g
Temperature	30°C
Limit Solubility of NaBO <sub>2</sub> (@ 30°C)	36.5 w/w
Initial NaBH <sub>4</sub> Concentration	0.08 w/v

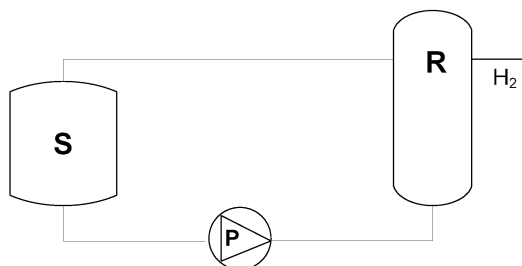


Figure 1: First scheme: all NaBH<sub>4</sub> solution recycled

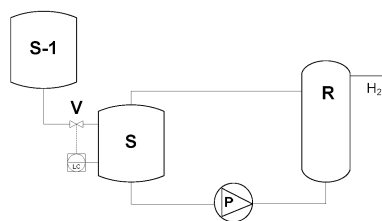


Figure 2: Second Scheme: all  $\text{NaBH}_4$  solution recycled with fresh water added

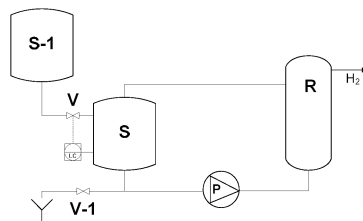


Figure 3: Scheme with solution discharge and refilling

#### Process 2: All $\text{NaBH}_4$ solution recycled with fresh water added

This configuration has the  $\text{NaBH}_4$  solution recycled between S tank and R reactor (as in first case) with fresh water supplied from S-1 reservoir as soon as S tank level decreases. (fig. 2). The fresh water added reduces the increasing of borate concentration, limiting risk of solid precipitation.

#### Process 3: $\text{NaBH}_4$ solution recycled with fresh $\text{NaBH}_4$ solution added

The third process scheme is alike the previous with the only difference that a fresh (e.g. 8% W/V)  $\text{NaBH}_4$  solution is added instead of fresh water to the S tank.

#### Process 4: $\text{NaBH}_4$ solution recycled with solution discharge and refilling

The last scheme is alike the third case but with a periodic discharge of exhausted solution (fig. 4). When the  $\text{NaBH}_4$  concentration is lower than set-point the valve V-1 is opened to discharge a fixed volume of exhausted solution, then replaced from a same amount of fresh solution. Against the previous schemes, here the recirculated  $\text{NaBH}_4$  solution has a reduced borate concentration with a limited precipitation issues.

As a disadvantage a part of  $\text{NaBH}_4$  is wasted with periodic discharge of the solution.

#### Analysis

These four processes were analysed and compared, with the results reported in table 2.

Table 2: data sheet of simulation result

	Process 1	Process 2	Process 3	Process 4
Operating Saturation Limit	30	30	30	30
$\text{NaBH}_4$ reacted (g)	67	80	80	88.6
Total $\text{NaBH}_4$ in solution (g)	80	80	96	104
Total water in solution (cc)	1000	1200	1200	1300
System Efficiency	83.2%	99.8%	83.2%	63.2%

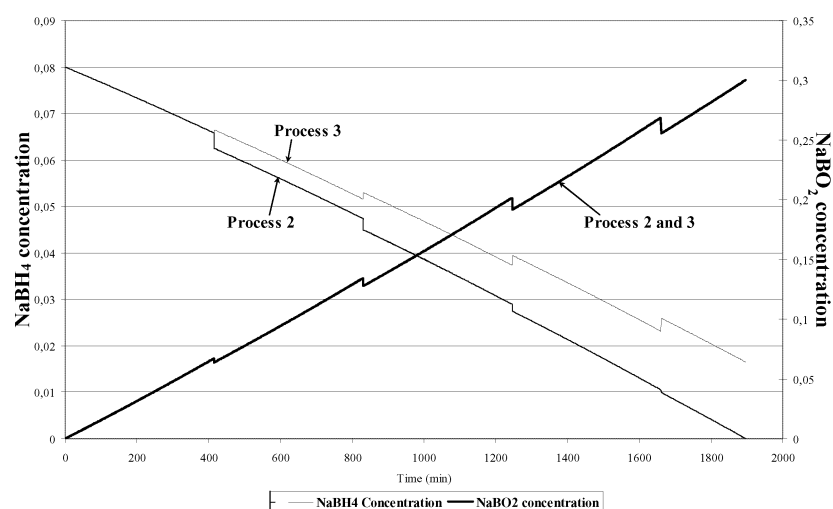


Figure 4: NaBH<sub>4</sub> and NaBO<sub>2</sub> trends

Every process was simulated for a constant production of hydrogen (100 ml/min), up to reach the borate operating saturation limit (30 w/w). Process efficiency is defined as the ratio of hydrogen produced to hydrogen in the NaBH<sub>4</sub> solution actively present in the process. For every process the amount of reacted NaBH<sub>4</sub>, the total amount of NaBH<sub>4</sub> and water in solution, and finally the system efficiency were calculated during production.

From the table 2, the second process has the highest efficiency as the solution at the end of the process (determined from reaching the borate solubility limit) has a less amount of unreacted NaBH<sub>4</sub>. In fact the NaBH<sub>4</sub> concentration in process 2 is always less than in other ones (in fig. 4 NaBH<sub>4</sub> trends in process 2 and 3 are compared).

On the other end the reduced NaBH<sub>4</sub> concentration has a lower mass transfer gradient with increased contact times between solution and catalyst and increased pump work.

## Experimental

To validate models two different versions of a commercial hydrogen generator, manufactured by ErreDue (Livorno), were tested. Both apparatuses produce a maximum flow rate of 150 mL/min of hydrogen at a maximum pressure of 5 bar.

The two generators operate according to the previously scheme 2 and 4 respectively. In fig. 5 the diagram of the process with recycling of solution with no discharge is depicted.

An 8% (w/V) NaBH<sub>4</sub> solution is loaded into a tank (S-2). During running the fuel pump (P-1) moves the solution from the S-2 tank to the catalytic reactor (R-1) and recycles it back to S-2. This phase is running until the system pressure reaches the fixed set-point value.

The reactor consists of two concentric cylinders, with the borohydride solution flowing upwards inside annulus. On the surface of internal tube the supported catalyst is magnetically maintained, and eases the reaction and generation of H<sub>2</sub>, that rises along

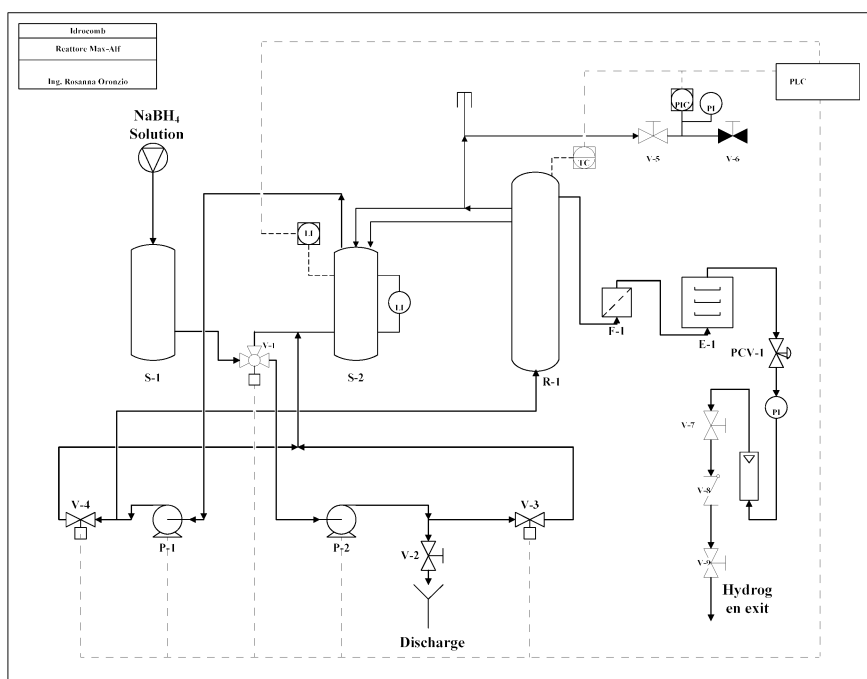


Figure 5: Scheme of the Erredue commercial hydrogen generator

the reactor mixed with solution. At the top of the column the two-phase mixture separates and hydrogen stream, before delivery, is dried in a silica drier (E-1).

In the circulating solution soluble sodium metaborate, produced from the  $\text{NaBH}_4$  hydrolysis reaction, increases its concentration and, in order to avoid its precipitation fresh water or solution is added.

Then from the second tank (S-1), filled with water or fresh  $\text{NaBH}_4$  solution, an amount is pumped by P-2, controlled by the S-2 solution level.

This operation resembles the previously analyzed second simulated scheme. When the volume of solution in the tank S-1 is lower than the sensor level set-point the system stopped and fresh water must be refilled.

The hydrogen dry flow rate is finally monitored by a mass flow meter (F-201C Bronkhorst Hi-TEC). All signals are acquired by an acquisition system (34970 A Agilent HP) and then logged on computer through the data-acquisition software HP VEE.

## Results

Both commercial hydrogen generators were tested, and experimental data compared with calculated ones. A better agreement in the overall mass balance was obtained from the second analyzed scheme due probably to the less disturbance induced by the not periodic discharges.

Fig. 6 shows the calculated trend of the  $\text{NaBH}_4$  concentration in the solution during operation vs the  $\text{H}_2$  produced.

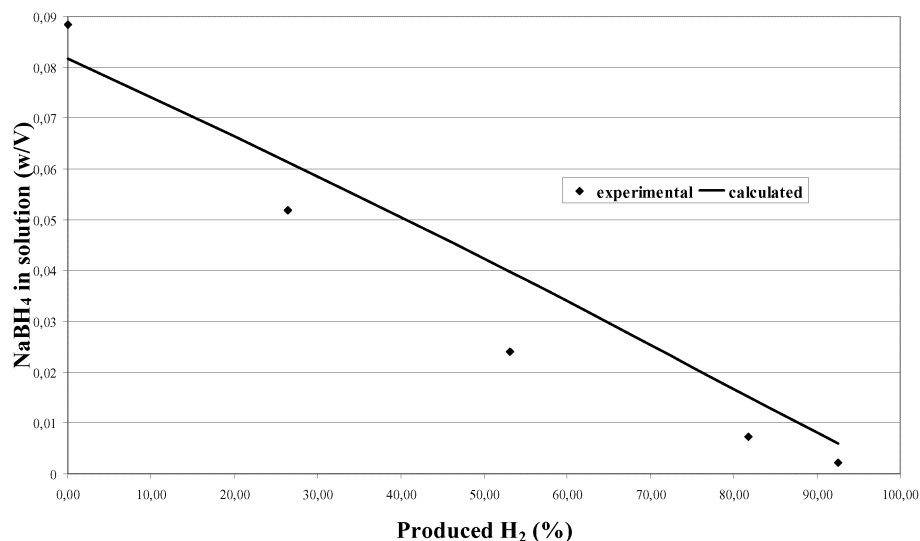


Figure 6: Comparison simulated and experimental data for Process 2

At the start the system contains a fresh solution of 8% (w/V), decreasing as soon as hydrogen is produced. The experimental data were obtained sampling, at a specific H<sub>2</sub> yield, a small amount of solution, by adding HCl and accounting the amount of degassed hydrogen and related NaBH<sub>4</sub> concentration..

The difference between data could be explained by not homogeneous distribution of solution in the circuit and changes in the solution density.

## Conclusions

The batch production of hydrogen from NaBH<sub>4</sub> was studied and various operating schemes were analyzed, focusing on higher hydrogen production and the borate saturation. From analysis of their mathematical models, efficiency of the process with a circulating NaBH<sub>4</sub> solution and periodic supplies of fresh water looks to be higher with a reduced issue of borate precipitation inside system.

This promising scheme was tested in a commercial hydrogen generator and calculated data verified, confirming a discrete agreement with experimental data.

By the way improvements in such a system are requested to reduce as much as possible borate precipitation when working at concentrated solution.

## References

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