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Hydrogen Generation in CSP Plants and Maintenance of DPO/BP Heat Transfer Fluids – A Simulation Approach

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Abstract. The ageing of diphenyl oxide/ biphenyl (DPO/BP) Heat Transfer Fluids (HTFs) implies challenging tasks for operators of parabolic trough power plants in order to find the economic optimum between plant performance and O&M costs. Focusing on the generation of hydrogen, which is effecting from the HTF ageing process, the balance of hydrogen pressure in the HTF is simulated for different operation scenarios. Accelerated build-up of hydrogen pressure in the HTF is causing increased permeation into the annular vacuum space of the installed receivers and must be avoided in order to maintain the performance of these components. Therefore, the effective hydrogen partial pressure in the HTF has to be controlled and limited according to the specified values so that the vacuum lifetime of the receivers and the overall plant performance can be ensured. In order to simulate and visualize the hydrogen balance of a typical parabolic trough plant, initially a simple model is used to calculate the balance of hydrogen in the system and this is described. As input data for the simulation, extrapolated hydrogen generation rates have been used, which were calculated from results of lab tests performed by DLR in Cologne, Germany. Hourly weather data, surface temperatures of the tubing system calculated by using the simulation tool from NREL, and hydrogen permeation rates for stainless steel and carbon steel grades taken from literature have been added to the model. In a first step the effect of HTF ageing, build-up of hydrogen pressure in the HTF and hydrogen loss rates through piping and receiver components have been modeled. In a second step a selective hydrogen removal process has been added to the model. The simulation results are confirming the need of active monitoring and controlling the effective hydrogen partial pressure in parabolic trough solar thermal power plants with DPO/BP HTF. Following the results of the simulation, the expected plant performance can only be achieved over lifetime, if the hydrogen partial pressure is actively controlled and limited.

INTRODUCTION

Since the 1980s, heat transfer fluids (HTFs) based on an eutectic mixture of biphenyl (BP) and diphenyl oxide (DPO) are commonly used in concentrating solar power plants with parabolic trough (PT) collector technology. Today more than 60 plants all around the world are operated with this type of HTF, summing up to a grid capacity of approximately 4,5 GW. The operating temperature of these plants is limited to 393°C or 739° F. This limitation is mainly caused by the highly temperature dependent thermal ageing process of the HTF, which is leading to an increasing fraction of degradation products. The accumulation rate of these products is mainly dependent on operating temperature, operating time and the condition of the HTF. As these products should not exceed the limits given by the HTF suppliers (typically in the range of 10% for high boilers and 1% for low boilers), they have to be separated periodically through ullage systems or they have to be reduced by exchanging a significant fraction of the aged HTF with new HTF. The following considerations are focusing on the hydrogen generation resulting from the

degradation process. While all carbon based degradation products are accumulating in the HTF until they are cleaned off by an ullage system, different assumptions have to be made for hydrogen due to its ability to permeate through iron based metals. The general aspects of hydrogen generation and permeation and the risks for the operation of the plant are well known [1], [2], [3], [4] and will be only briefly described at this point.

In parabolic trough plants the hydrogen will not only leave the system through the piping system into the atmosphere, but it will also permeate through the absorber tubes of the receivers into the evacuated annular space between absorber tube and glass cover tube. As the hydrogen would immediately destroy the vacuum conditions and cause high thermal losses due to its excellent heat conductivity, free hydrogen has to be avoided in the annular space of the receiver. Therefore special getter materials are mounted in the annular space in order to absorb the permeated hydrogen and maintain the vacuum conditions. In general, permeation rates are dependent on steel grades, geometric factors (e.g. wall thickness of pipes), hydrogen pressure and temperature. Hydrogen permeation rates of stainless steel grades such as 316L or 321H, which are commonly used for absorber tubes of parabolic trough receivers, can be assumed to be by a factor of 10 to 20 lower than hydrogen permeation rates of carbon steel grades. Anyhow, it is good industry practice that in order to ensure good vacuum performance over the full lifetime of the receiver, a maximum hydrogen pressure in the HTF system has to be defined by the suppliers and strictly controlled by the plant operators in order to avoid performance losses during the operation of the plant.

DEGRADATION OF DPO/BP AND HYDROGEN GENERATION

In the recent years extensive ageing tests for DPO/BP Heat Transfer Fluids have been performed and published by DLR Cologne [5] and Dow [6]. The thermal stability of fresh and pre-aged HTF samples has been investigated on the basis of the methods described in DIN 51528.

The formation of hydrogen in DPO/BP fluids is part of a general degradation process generating a mixture of degradation products such as low boilers, high boilers and gases. This degradation process is mainly driven by the bulk temperature of the fluid. The increase of hydrogen concentration in fresh and pre-aged HTF samples has been determined by DLR in lab tests over a period of 1000 h for temperatures of 400°C -450°C. For 400°C the average hydrogen generation rate of fresh HTF over 1000h has been determined to 5,7 µmol/kg/h, for 420°C to 55 µmol/kg/h, which means an acceleration factor of approximately 10. The value for pre-aged HTF at 400°C is in the range of 20 µmol/kg/h, which is approximately four times higher than fresh HTF.

As no data is available for temperatures below 400°C, hydrogen generation rates have been extrapolated for lower temperatures with an exponential approach, using the calculated activation energies of 278 kJ/mol for fresh HTF and 256 kJ/mol for pre-aged HTF. From 350°C to 390°C an acceleration factor of 38 is calculated by using the described method, leading to the conclusion, that nearly all hydrogen generation is obviously taking place at the hot end of the loops and in the header pipes from the solar field to the power block.

For the temperature level of 390°C, the average hydrogen generation rate has been determined to 3,0 µmol/kg/h. The hydrogen generation rate of pre-aged HTF at 390°C was determined in the range of 9,3 µmol/kg/h, which is approximately three times higher than fresh HTF.

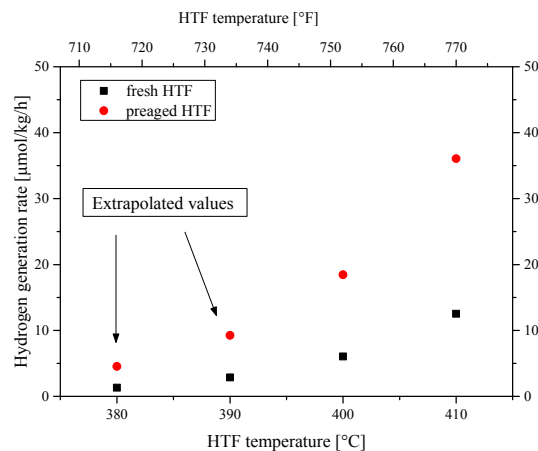


FIGURE 1. Hydrogen generation rate of fresh and pre-aged HTF for different ageing temperatures

Assuming that the pre-aged HTF sample corresponds to the “final state” condition after 10 years of lifetime, the data was used as the start and end point of an interpolated curve, which describes the development of hydrogen generation rates over the lifetime of the plant.

The hydrogen generation rate $\dot{c}_{H_2,i}$ is calculated using the interpolation:

$$\dot{c}_{H_2,i}(t, T_i) = \dot{c}_{H_2,0} \cdot \exp\{-(\tau \cdot t)\} \cdot \frac{\exp\{-H_a(t)/R/T_0\}}{\exp\{-H_a(t)/R/T_i\}} \quad (1)$$

$$H_a(t) = 278 - t \cdot 8,1 \cdot 10^{-4} \text{ kJ / mol} \quad (2)$$

Another method to estimate hydrogen concentration in liquid DPO/BP is based on stoichiometric balancing of liquid phase degradation products. The method requires the knowledge of the chemical structure and the quantification of all major degradation products. High purity DPO/BP was sealed in a glass ampoule and heated to 426,7°C (800°F) for one week or 168 h. Analysis by GC-MS was used to identify and quantify the liquid phase decomposition products. Numerous components were found, quantified and identified in the degraded DPO/BP. They were categorized in TABLE 1 based on their hydrogen forming potential. The low boilers phenol and benzene require hydrogen to be formed while hydrogen is released when high boilers are formed. Tetra-aryls form twice more hydrogen than Tri-aryls. The formation of furans releases even more hydrogen.

TABLE 1. Degradation of fresh DPO/BP after one week at 426,7°C (800°F) in a glass ampoule and hydrogen generation determined by Dow via a stoichiometric balance of the degradation products

	wt%	Mol%	H ₂ factor	H ₂ mol%
Benzene	1,04	2,198	-0,5	-1,10
Phenol	1,473	2,581	-0,5	-1,29
Tri-aryl	1,03	0,70	0,5	0,35
Tetra-aryl	3,21	1,61	1,0	1,61
DBF	0,42	0,415	1,0	0,41
Higher- DBFs	0,26	0,163	1,67	0,27
Total degradation products	7,47	7,95		0,26
			→ H ₂ wt%	0,0032

For modeling the hydrogen generation in parabolic trough CSP plants, it is assumed that the distribution of degradation products in DPO/BP shown in TABLE 1 is the same in parabolic trough CSP plants. The proportion of hydrogen generation versus degradation products can also be assumed to be kept constant. The hydrogen /degradation product proportion from TABLE 1 is as follows:

$$\text{Hydrogen formation at 1\% wt. HTF degradation:} \quad \frac{1\% \text{ wt}}{\text{Total degr. proportion}} \cdot \text{H}_2 \text{ conc.} = 4239 \text{ ppb} = 2103 \text{ } \mu\text{mol/kg}$$

Using the information above, it is possible to model the hydrogen generation rate for a return header from the PT collector field as a function of operating time and HTF degradation product concentration (low boilers + high boilers). It will be assumed that the return header maintains a constant temperature of 390°C (734°F) during operating hours. The initial purity of the DPO/BP is 99,9 wt%. After start-up, the system will not be vented until the low boiler concentration reaches 1 wt%, which will take approximately three years. The system will be vented at a rate that maintains the level of low boilers at 1 wt% once the level of low boilers reaches 1 wt% in the fluid. High boilers will continue to accumulate in the system at this approach. This will result in a steady accumulation of degradation products in the fluid over time. High purity DPO/BP will be added to replace mass lost due to venting of low boilers. FIGURE 2 (left) shows hydrogen generation rate as a function of HTF degradation product concentration. In general the higher the level of HTF degradation product concentration, the higher the hydrogen generation rate. Likewise, FIGURE 2 (left) shows that as HTF degradation product concentration increases the rate at which the

DPO/BP degrades also increases. Combining the data in FIGURE 2 (left) with the system operating assumptions (TABLE 2) applied for a maximum header temperature of 390°C (734°F) at 3400 operation hours per year, the HTF degradation product concentration and hydrogen generation rate for the header can be estimated (FIGURE 2 right). Note that at year 3, when low boiler venting begins, there is an inflection in both the HTF degradation product concentration and hydrogen generation rate curves. Nevertheless the HTF degradation product concentration and the hydrogen generation rate curves further increase after low boiler venting is started due to the fact that high boiling degradation compounds comprise the majority of the degradation products.

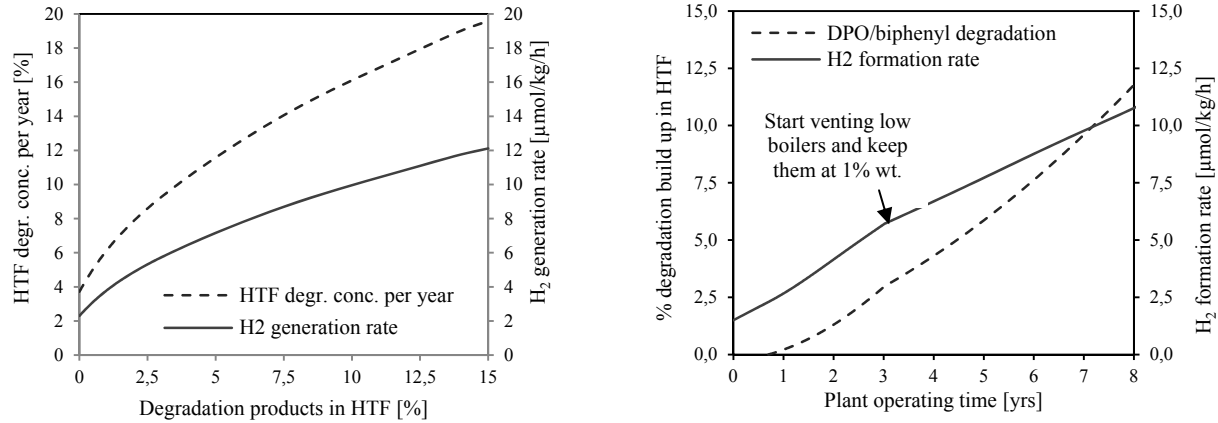


FIGURE 2. Degradation model of DPO/BP and hydrogen in parabolic trough CSP plants [6] for the header pipe at 390°C depending on degradation level of DPO/BP (left); over time with the removal of low boiling degradation products only (right)

As shown in FIGURE 2 (right) the hydrogen generation rate is at a level of 2,5 $\mu\text{mol}/\text{kg}/\text{h}$ after 1 year of operation. After 8 years of operation the calculation is predicting an increase by a factor of 4 (10 $\mu\text{mol}/\text{kg}/\text{h}$). These values are in good agreement with the values of 3 $\mu\text{mol}/\text{kg}/\text{h}$ for fresh HTF and 9,3 $\mu\text{mol}/\text{kg}/\text{h}$ for pre-aged HTF from DLR. Two different definitions of hydrogen pressure are used to describe the balance of the system. The partial pressure of hydrogen that builds up in an inert gas atmosphere over the HTF according to Henry's Law is the value that could be directly measured in the expansion tank:

$$p_{H2, Henry, i} = H(T) \cdot \frac{n_{H2, i}}{n_{H2, i} + n_{HTF}} \quad (3)$$

The material constant $H(T)$ has been measured by DLR[5] and can be approximated with $\ln H = 267/T + 7,3$ for pure hydrogen or $\ln H = 452/T + 6,5$ for 1% hydrogen in nitrogen. The comparative pressure is a calculated value corresponding directly to the hydrogen concentration in the HTF:

$$p_{H2, comp, i} = \frac{n_{H2, i}}{V_{HTF}} \cdot R \cdot T_i \quad (4)$$

Since hydrogen permeation is primarily driven by the concentration gradient, the comparative pressure is used for the calculation of the hydrogen permeation. The increase/decrease of hydrogen content in the HTF due to permeation is determined using

$$\dot{n}_{H2, perm, i} = \phi(T_i) \cdot \frac{A}{s} \cdot (p_1^b - p_2^b) \quad (5)$$

with

$$\phi(T_i) = \phi_0 \cdot \exp\{-H_0 / R / T_i\} \quad (6)$$

Given the prevailing pressures it is assumed that the permeation rises with $p^{0,5}$ [9], although there is no information as to how the permeation is influenced by the fluid medium on the inner tube surface as opposed to the commonly used purely gaseous media [11]. For every time step dt the hydrogen generation $\dot{n}_{H2, gen, i}$ and the hydrogen permeation $\dot{n}_{H2, perm, i}$ are determined and summed up according to

$$n_i = n_i + \dot{n}_{H_2,gen,i} \cdot dt + \dot{n}_{H_2,perm,i} \cdot dt \quad (7)$$

for every part i of the field, and according to

$$n = n + \dot{n}_{H_2} \cdot dt + \dot{n}_{H_2} \cdot dt \quad (8)$$

for the total field, with

$$\dot{n}_{H_2} = \sum_i \dot{n}_{H_2,i}(dt) \quad (9)$$

Since the HTF ages exponentially with temperature each part of the field i is assigned an effective age according to

$$dt_i = dt_i \cdot \frac{\exp\{-H_a / R / T_0\}}{\exp\{-H_a / R / T_i\}} \quad (10)$$

MODEL DESCRIPTION

Structure of the Plant Model

For the calculation of the hydrogen balance, a simplified plant model has been used consisting of 4 modules: the cold header (module 1), the hot header (module 2), the loop (module 3) and the expansion tank (module 4) described in FIGURE 3. Other components of the HTF cycle system such as heat exchangers or additional piping have not been considered and can be added later in a more detailed model. The index i refers to the different parts of the field in the following descriptions. For the header and expansion tank module homogeneous temperature levels have been assumed. The temperature increase in the loops from 300°C to 400°C implies a separation into sub-modules

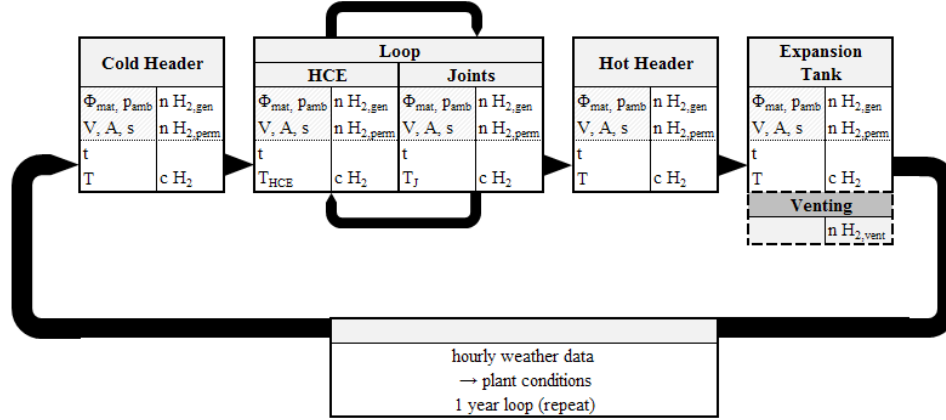


FIGURE 3. Simulation sequence with description of relevant parameters in the different modules

according to the linear temperature distribution. For each time step in the simulation, the hydrogen generation rate is calculated depending on the HTF temperature in each module T_i (e.g. cold or hot header) and the accumulated aging time of the HTF:

$$\dot{n}_{H_2,gen,i} = \dot{c}_{H_2,i}(t_i, T_i) \cdot m_{HTF,i} \quad (11)$$

The cold and hot headers: The cold header is assumed to be completely at inlet temperature, and the hot header is assumed to be at outlet temperature. Due to the high pumping speed during operation the temperature gradient over the header length during operation is neglected.

The loop: It is assumed that in the loop the HTF temperature rises linearly from inlet to loop outlet. For the receivers the properties of the SCHOTT PTR®70 were used.

The expansion tank: The expansion tank is assumed to be at inlet temperature. Hydrogen generation is considered, hydrogen permeation is neglected due to the relatively low temperature level. Optional venting of the expansion tank by flushing with nitrogen or separation in the gas phase is considered as an additional hydrogen loss mechanism. As a simplification of the model it is assumed that the hydrogen stream from the solved phase in the HTF into the gas phase is not limited and hydrogen can be completely removed by venting or separation in the expansion tank. Anyhow, for very low hydrogen concentrations in the HTF, outgassing of hydrogen from the HTF may become a limiting factor.

Input Parameters

Assuming that the pre-aged HTF sample corresponds to the “final state” condition after 8 years of lifetime, the data shown in chapter 2 were used as the start and end point of an interpolated curve, which describes the hydrogen generation rate of the HTF over the lifetime of the plant (FIGURE 5). The relation between lab ageing time in hours and simulated operation time in years has been calculated with:

$$t_{op} = 8760 h \times \frac{t_{aging} \times V_{HTF,total}}{t_{op,t,max} \times V_{HTF,hot}} \quad (12)$$

where t_{aging} is the lab ageing time in hours, $t_{op,t,max}$ is the number of hours per year at full operation temperature of the plant in hours/year, which is dependent on the weather data input, $V_{HTF,total}$ is the HTF volume during operation and $V_{HTF,hot}$ is the fraction of the HTF volume at maximum operation temperature. For the described case, 1000h of lab ageing would correspond to approximately 1 year of plant operation.

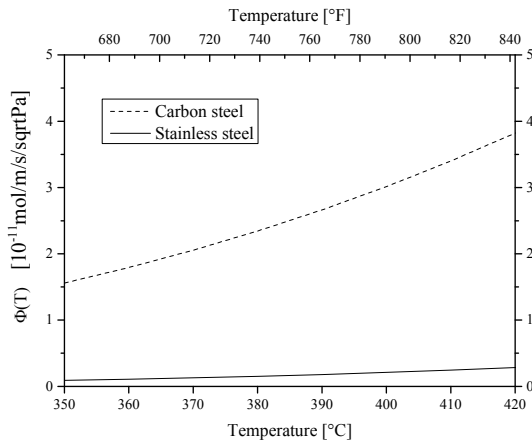


FIGURE 4. Hydrogen permeability used for absorber and for header/ joint piping material

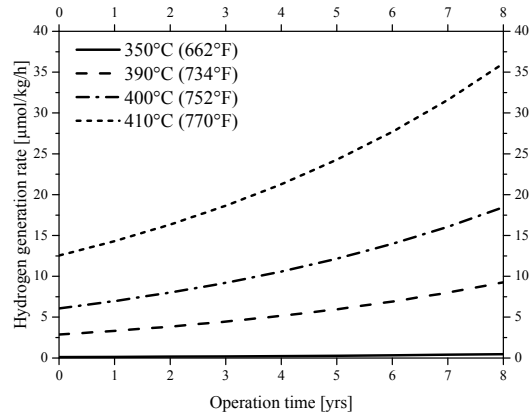


FIGURE 5. Hydrogen generation rate for fresh and pre-aged HTF for different temperature levels

The partial pressure p_2 for the permeation to ambient is set to $5 \cdot 10^{-2}$ Pa. The permeation properties of the stainless steel and carbon steel (header/joints) have been taken from literature [7], [8] and are shown in FIGURE 4. The solar field parameters have been chosen according to available data from literature, matching to a capacity of 75 MW without storage. Operation parameters have been calculated by using the weather data of Daggett, California. The amount of HTF in each module is calculated according to the operation temperature and the density of the HTF. At operation temperature approximately 30% of the HTF volume is pumped into the expansion vessel. 30% is in the hot header and 40% is in the cold header and in the loop (FIGURE 6).

TABLE 2. Parameter definition of solar field configuration for simulation model

Solar field		
Nbr. of Loops:	100	
Loop length:	800	m
Cold header length	~4000	m
Hot header length	~4000	m
Expansion tank volume	30-500	m ³
Solar-field inlet temperature:	300 (572)	°C (°F)
Solar-field outlet temperature:	380 – 410 (716 - 770)	°C (°F)
Power Block		
Turbine capacity (gross):	75,0	MW
Cooling method:	Wet cooling	

SIMULATION RESULTS

The aging effect of the HTF has been calculated for each module and time step. The resulting ageing time of the complete HTF has been calculated by summarizing the weighted contributions of each module.

The effective hydrogen partial pressure in the system is showing a significant seasonal variation with higher values in the summer and lower values in the winter (FIGURE 7). Without additional flushing in the expansion tank, the threshold value of 30 Pa is already surpassed in the first year of operation for operation temperatures of 390°C or higher.

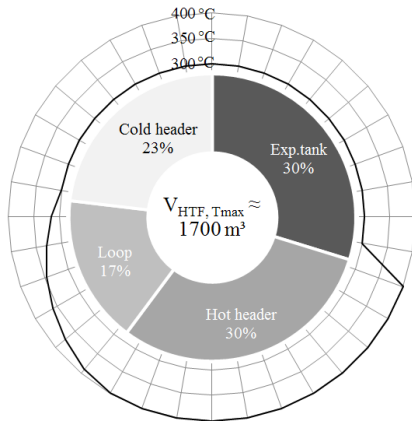


FIGURE 6. Distribution of HTF volume and appendant temperature levels at operation temperature of 400°C (752°F) within the solar field components

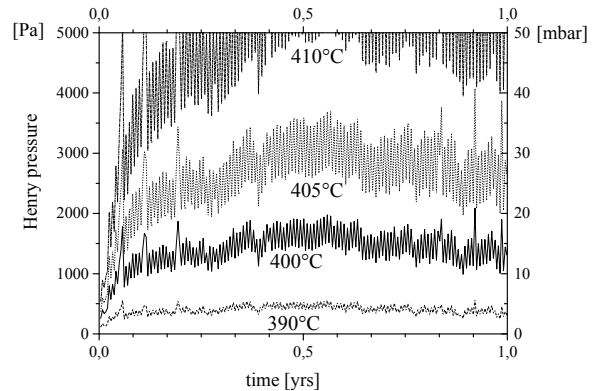


FIGURE 7. Hydrogen partial pressure in the expansion tank for different operation temperatures over one year after start of operation without HTF treatment (fresh HTF)

The hydrogen pressure level is continuously increasing with time due to the ageing effect of the HTF, roughly doubling in the period of 8 years. By adding the venting option to the model, the hydrogen partial pressure in the expansion tank is limited to the threshold value of 30 Pa. Due to the different generation and loss rates of each module, the pressure is not constant over the whole system. The highest hydrogen pressure is reached at the end of the hot header pipe and at the hot end of the loop. At 390°C maximum operation temperature the calculated hydrogen venting rate is in the range of 1 mol/h.

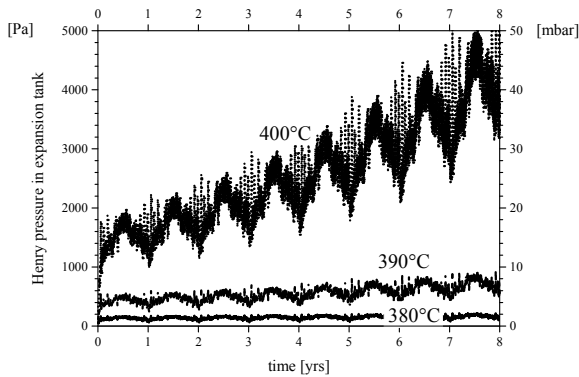


FIGURE 8. Hydrogen pressure in the expansion tank for different operation temperatures over a time period of 8 years without HTF treatment

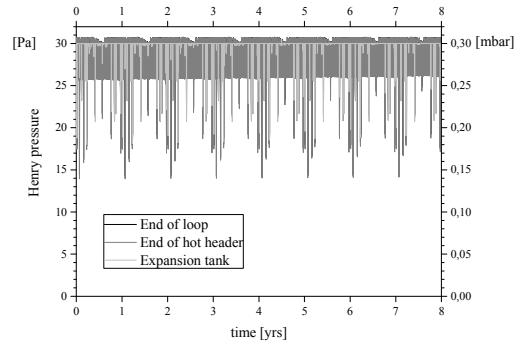


FIGURE 9. Hydrogen pressure at the hot end of the loop, in the hot header and in the expansion tank at 400°C with venting

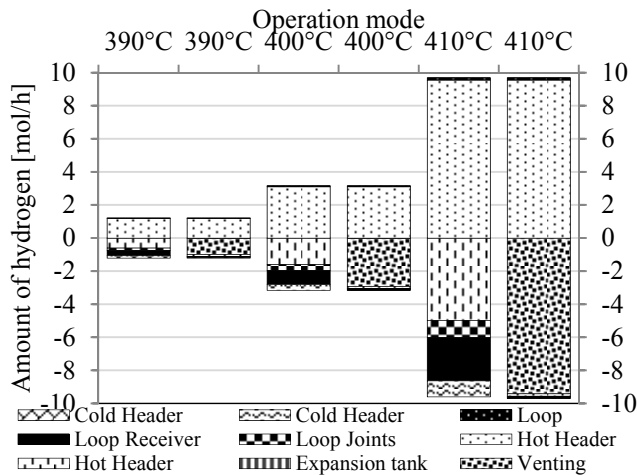


FIGURE 10. Hydrogen generation and hydrogen loss rates in each module for operation temperature 390°C – 410°C, 1,3,5: no venting, 2,4,6: with venting

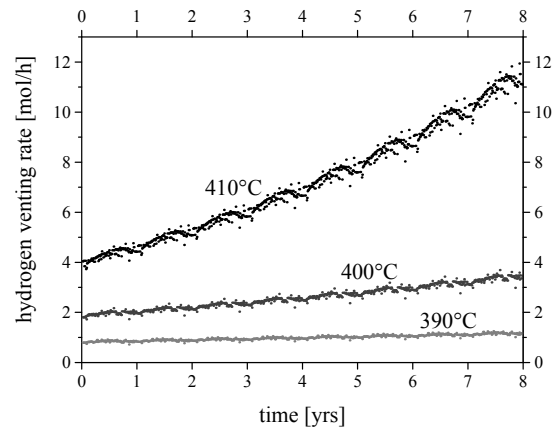


FIGURE 11. Increase of hydrogen venting rate over time for operation temperature of 390°C, 400°C and 410°C

CONCLUSION

Hydrogen generation and hydrogen balance have been simulated for the HTF system of a parabolic trough plant. Similar hydrogen generation rates have been derived from different test methods, from direct hydrogen measurement during aging and from analysis of the degradation products. Nevertheless, due to the high uncertainty caused by extrapolation of the experimental data in time and temperature, and the application of a relatively simple plant model, results should be construed more in a qualitative than in a quantitative way. Following the model output, nearly all hydrogen is generated in the hot part of the header pipe. For all considered cases it is mandatory to apply an effective hydrogen removal method in order to keep the threshold value of 30 Pa in the system. Overheating is significantly accelerating the HTF degradation process and can cause radical fast hydrogen pressure rise. In order to get more reliably quantitative values, a more detailed model has to be developed and real data of operation plants should be used to fit the model.

NOMENCLATURE

TABLE 3. List of constants and parameters

Parameter / constant	Value	Used in equation no.
$\dot{c}_{H_2,0}$	2,9 $\mu\text{mol/kg/h}$	(1)
τ	$4,3 \cdot 10^{-5}$ 1/h	(1)
H_a	278 kJ/mol	(1)
Φ_0 (HCE)	$8,53 \cdot 10^{-8}$ mol/m/s/ $\sqrt{\text{Pa}}$	(6)
H_0 (HCE)	59,4 kJ/mol	(6)
Φ_0 (header pipes)	$1,17 \cdot 10^{-7}$ mol/m/s/ $\sqrt{\text{Pa}}$	(6)
H_0 (header pipes)	46 kJ/mol	(6)

TABLE 4. List of abbreviations:

Parameter	Unit	Parameter definition
A	m^2	Surface through which permeation takes place
s	m	Wall thickness
p	Pa	Pressure
Φ	mol/m/s/ $\sqrt{\text{Pa}}$	Permeability
n	mol	Amount of substance
c	mol/kg	Concentration
T_0	K	Reference temperature of the power plant, e.g. 663K=390°C=734°F
T_i	K	Temperature of the i^{th} power plant module (see Figure 3)
H	-	Henry-coefficient, temperature dependent
H_0, H_a	kJ/mol	Activation energies
t, dt	h	Time, time step

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