SolarPACES 2022, 28th International Conference on Concentrating Solar Power and Chemical Energy Systems
Receivers and Heat Transfer Media and Transport: Linear Systems
https://doi.org/10.52825/solarpaces.v1i.661

Published: 15 Dec. 2023

Determination of Hydrogen Content in Getter Material from Parabolic Trough Receivers

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Abstract. In this study, a procedure for analyzing the hydrogen content of used getter material is described based on mass spectrometry coupled to thermal gravimetry. It is shown that hydrogen masses per getter mass in the range of 2 – 15 mg/g can be quantified. At least three differently strong hydrogen binding situations are found with the thermal desorption program applied so far. Up to 450 °C only traces of hydrogen can be desorbed from the getter material with the applied method and up to 99% is released on heating up to 800 °C.

Keywords: Parabolic Trough, Vacuum Insulation, Getter Material, Hydrogen, Absorption

1. Introduction

Heat collecting elements (HCEs) for parabolic trough collector plants are equipped with vacuum insulations to minimize heat losses. Typical design pressures are below 0.001 mbar. [1] For maintaining the low pressure throughout the lifetime of a CSP plant the vacuum insulations are equipped with so-called getter materials. These absorb any gas permeating into the evacuated annular gap except for noble gases. Most relevant is hydrogen which is slowly formed in the organic heat transfer fluid at high operating temperatures. The gas permeates through the steel pipe of the HCE and hence, would accumulate in the evacuated annular gap if no getter material was present.

Non-evaporable getter (NEG) material is used which binds hydrogen reversibly. [2] At equilibrium conditions hydrogen pressure and hydrogen content of the getter material depend on the getter temperature. At a characteristic hydrogen content of the getter material the pressure in the annular gap of the HCE will increase beyond the designed vacuum pressure and heat losses will rise due to the excellent thermal conductivity of hydrogen.

Pumping speed and gas binding capacities of NEG materials are studied according to standard procedures. [3] The aim of this study is to provide a technique for determining the hydrogen content of used getter material collected from HCEs to learn about the condition of solar fields before any enhanced heat losses are caused by hydrogen. [1]

2. Approach

In general, non-evaporable getter materials absorb hydrogen reversibly. [2] Accordingly, the amount of collected hydrogen can be determined by baking out the material under controlled conditions. In this study this is done with a thermal gravimetric analyzer (TGA) unit (Netzsch STA 449 F5 Jupiter) which is coupled to a mass spectrometer (MS, Hiden HPR-20 EGA). NEG material was collected from unused and used solar receiver samples. Samples of the getter material are heated up in the TGA in a stream of highly purified argon (>99.9999%) and hydrogen desorbing from the getter material is detected in the exhaust of the TGA with the MS. The integral of the MS signal correlates with the amount of hydrogen when reproducible experimental conditions are applied. As no other gas than hydrogen was found to evolve from the NEG upon heating, the mass loss measured with the micro balance of the TGA can be correlated with the MS signal (s. Fig. 1). At low hydrogen masses (~below 2 mg) the uncertainty of the mass loss measurement increases. Between 2 and 15 mg, determination of hydrogen amount with MS and TGA unit differs less than 5%.

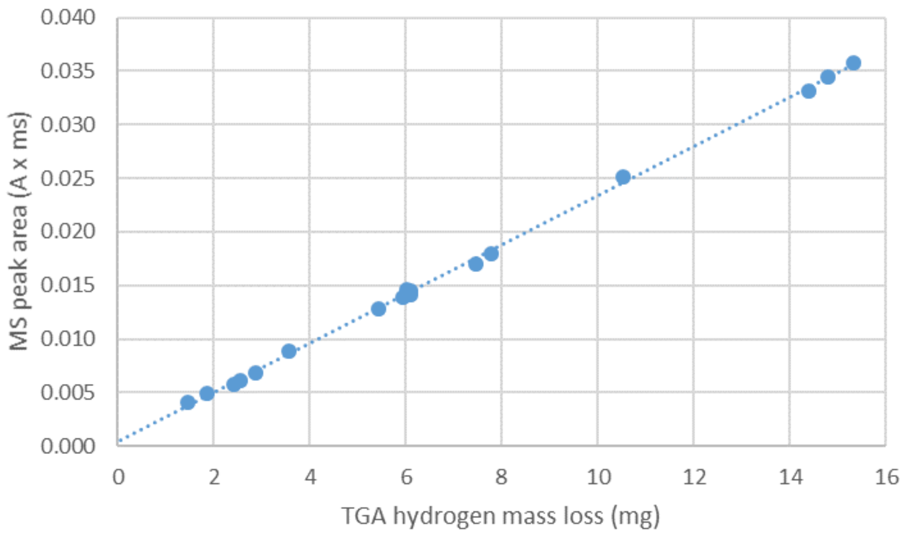

Figure 1. Correlation of the measured MS signal area with the TGA mass loss.

3. Results

Used getter material was heated up to 450 °C and after one hour, temperature was increased to 800 °C. Constant heating ramps of 20 K/min were applied. After five hours the samples were cooled down to ambient. Thermal lag of the sample was not specifically calibrated for the geometry of the sample and accordingly, “true” sample temperature is uncertain in this test. Up to three distinct peaks of hydrogen release have been found so far (Fig. 2). Most hydrogen is released during after heating up to 800 °C.

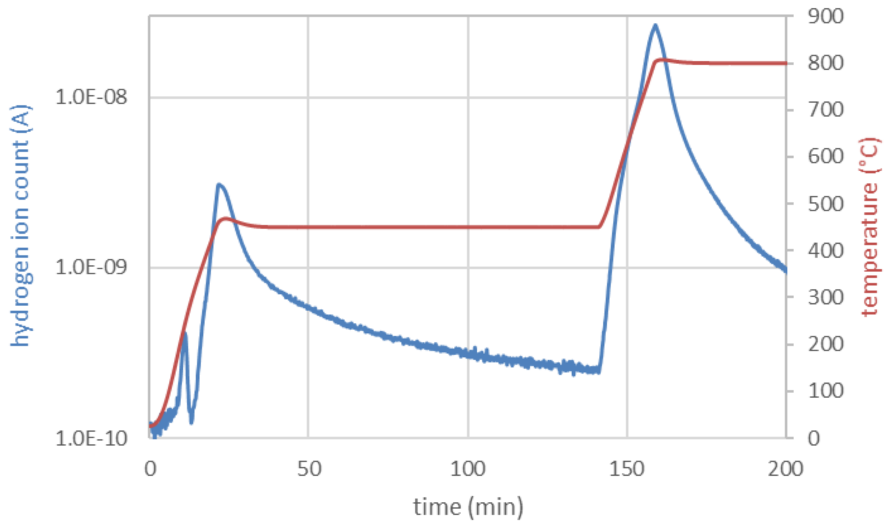

Figure 2. Hydrogen release during thermal desorption in the TGA unit.

According to the three hydrogen peaks at different temperatures, used getter material can contain hydrogen at least in three differently strong binding situations. Further studies are required to identify these binding sites and binding energies.

Most absorbed hydrogen is released during heating up to 800 °C. When specific amount of hydrogen per getter mass is about 3 mg/g or higher 99% of the hydrogen desorbs during heating up to 800 °C (Fig. 3). Accordingly, during heating up to 450 °C only 1% desorbs in most samples.

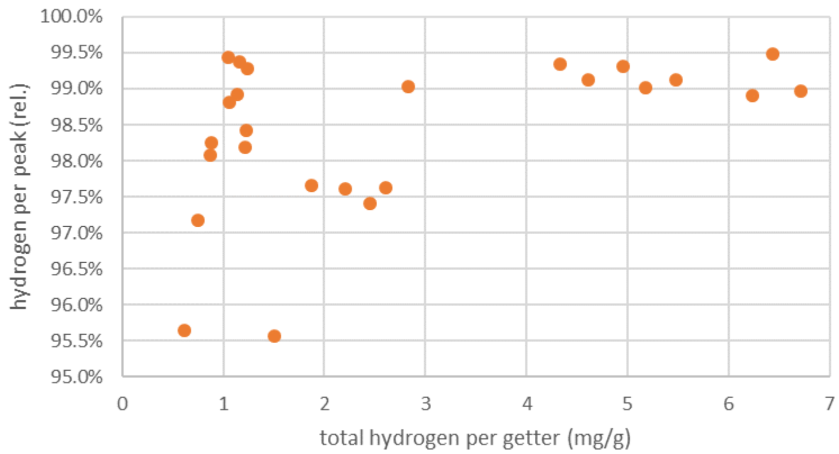

Figure 3. Relative amount of hydrogen desorbed during heating to 800 °C in relation to total desorbed hydrogen per getter mass.

Peak 1 and peak 2 do not occur separately in all samples. When total amount of hydrogen per getter is large, these peaks appear as one with the two-step thermal desorption program used in this study (Fig. 4). At very high hydrogen loads prolonged heating at 450 °C is even required to separate peak group 1 and 2 from peak 3.

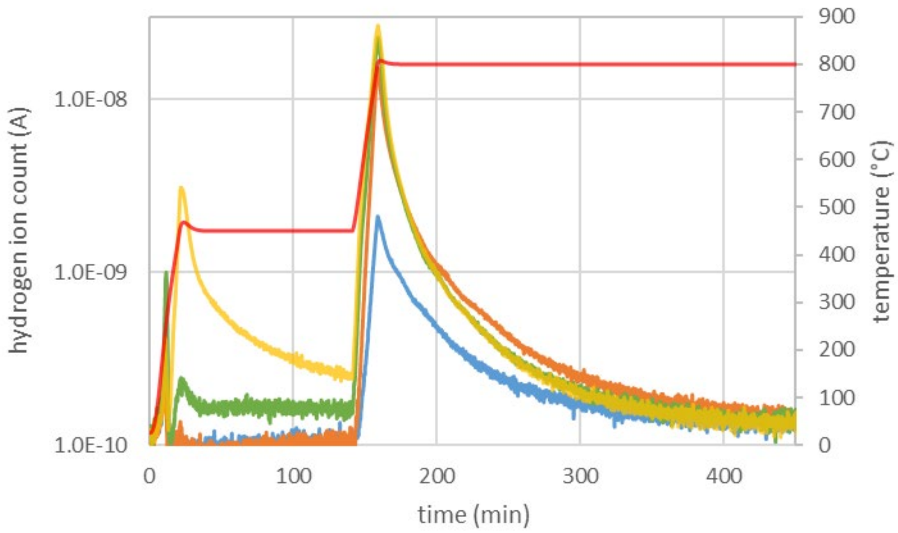

Figure 4. Desorption of hydrogen from used getter material with 1 mg/g (blue), 4 mg/g (orange), 7 mg/g (green) and 9 mg/g (yellow) specific hydrogen on heating up to 450 °C and 800 °C (temperature in red).

4. Discussion

NEG reported to be used for solar thermal receiver applications are based on zirconium alloys with vanadium, iron, yttrium and other metals like St2002, St 787 or St777. [4] While the absorption characteristics of these materials are not reported in scientific literature the St707 getter material has been studied by several authors. [5-7] According to *Benvenuti*, hydrogen pressure (p) of St707 depends on the amount of absorbed gas (q) and the getter temperature (1) with p in mbar, q in mbar * l / g and T in Kelvin. (q can be transformed into mass of hydrogen per mass of getter material with the ideal gas law using 23 °C as defined in [3].)

$$\log(p) = 5.14 + 2\log(q) - 6250/T \quad (1)$$

According to Burkholder's studies on heat losses of a solar receiver at 350 °C, significantly rising losses will start when pure hydrogen with pressures of 1 Pa (0.01 mbar) or higher is present in the annular insulating gap. [8] Considering St707 such pressure can be reached below 10 mg/g hydrogen per getter material when getter temperatures close to 300 °C are reached at operating conditions of a receiver (Fig. 5).

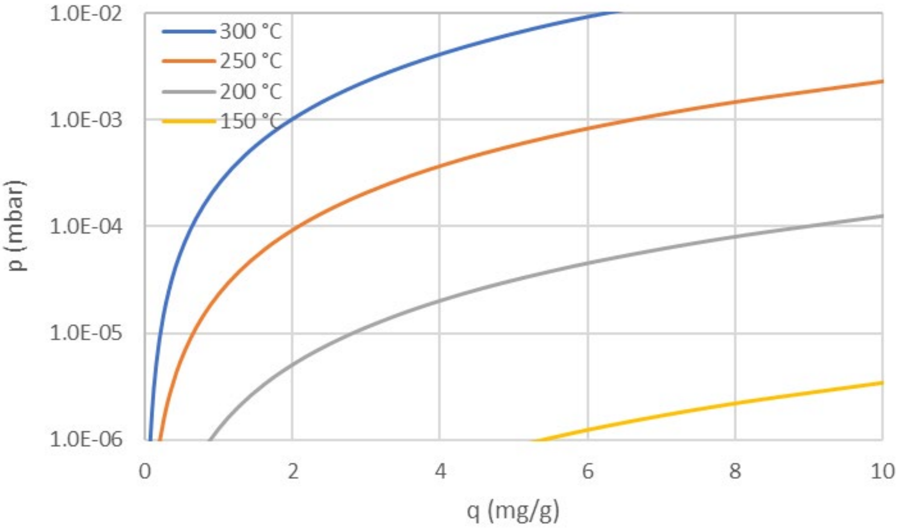

Figure 5. Hydrogen absorption isotherms of St707 calculated with equation (1).

Accordingly, the getter material and its specific hydrogen absorption characteristics as well as getter operating temperature in a specific receiver have to be defined to allow evaluation of the results of hydrogen analysis presented in this study. Moreover, it has to be confirmed whether the characteristics of unused getter remain stable after years of thermal stress as to be expected in solar receiver operation.

From the analytical results obtained so far, it is expected that specific hydrogen absorptions in the range of 10 - 15 mg/g will cause significant accumulation of molecular hydrogen in the annular gap of solar receivers.

The technique described in this study allows to analyse the hydrogen content already accumulated in a solar field. For evaluating the degree of saturation follow-up studies are in progress with typical unused getter material qualities for use in solar receivers.

Data availability statement

No additional data are available to this publication.

Underlying and related material

No additional material is available to this publication.

Author contributions

The author has developed the measurement procedure, performed and evaluated the measurements on his own.

Competing interests

The author declares no competing interests.

Funding

The author would like to express his gratitude for the public funds that were granted for the research project “Active Hydrogen Control in Solar Thermal Parabolic Trough Plants” (Hyrec³) by the Federal Ministry for Economic Affairs and Climate Action (BMWK) of Germany.

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