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Preliminary analysis of refilling cold-adsorbed hydrogen tanks

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Preliminary analysis of refilling cold-adsorbed hydrogen tanks

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Abstract. The effective storage of hydrogen is a critical challenge that needs to be overcome for it to become a widely used and clean energy source. Various methods exist for storing hydrogen, including compression at high pressures, liquefaction through extreme cooling (i.e. -253 °C), and storage with chemical compounds. Each method has its own advantages and disadvantages. MAST3RBoost (Maturing the Production Standards of Ultraporous Structures for High Density Hydrogen Storage Bank Operating on Swinging Temperatures and Low Compression) is a European funded Project aiming to establish a reliable benchmark for cold-adsorbed H2 storage (CAH2) at low compression levels (100 bar or below). This is achieved through the development of advanced ultraporous materials suitable for mobility applications, such as hydrogen-powered vehicles used in road, railway, air, and water transportation. The MAST3RBoost Project utilizes cutting-edge materials, including Activated Carbons (ACs) and high-density MOFs (Metal-organic Frameworks), which are enhanced by Machine Learning techniques. By harnessing these materials, the project seeks to create a groundbreaking path towards meeting industry goals. The project aims to develop the world's first adsorption-based demonstrator at a significant kg-scale. To support the design of the storage tank, the project employs Computational Fluid Dynamics (CFD) software, which allows for numerical investigations. In this paper, a preliminary analysis of the tank refilling process is presented, with a focus on the impact of the effect of the tank and hydrogen temperatures on quantity of hydrogen adsorbed.

1. Introduction

The importance of using clean and renewable energy sources has grown significantly to decrease the emission of greenhouse gases. In this context, hydrogen is recognized as a highly promising energy source [1]. It has the potential to serve as a clean energy carrier for generating electricity and heat. Nevertheless, the lack of efficient and safe storage systems remains a major challenge impeding the widespread adoption of hydrogen [2], [3].

There exist various techniques for hydrogen storage, each presenting its own advantages and disadvantages. One approach involves compressing hydrogen at high pressures, typically ranging from 350 to 700 bar. While this method is relatively straightforward and cost-effective, the tanks and equipment required to accommodate high-pressure hydrogen can be bulky and heavy. Another storage method involves liquefying hydrogen by cooling it to a temperature as low as -253°C. Although this approach needs specific equipment and insulation, it enables hydrogen to be stored at higher density. A third storage method involves combining hydrogen with a chemical compound, such as metal hydrides or hydrocarbons. These compounds can store hydrogen in a solid state, but they may require special handling and might not be as efficient in terms of hydrogen storage as the other methods.

Under the EU-funded Project MAST3RBoost, the Department of Energy, Systems, Territory, and Construction at the University of Pisa, in collaboration with Spike Renewables Srl, is currently engaged in the investigation of cold-adsorbed hydrogen storage (CAH2) at low compression levels, specifically 100 bar or below. This technique shows great promise as it enables the storage of hydrogen at high density while reducing volume. The focus of this paper will be on the Computational Fluid Dynamic (CFD) analyses, examining the impact of temperature on hydrogen absorption. Additionally, the study will explore the effects of different types of adsorbents

2. Cold-Adsorbed H2 Storage

As mentioned before an approach of storing hydrogen is through the adsorption of hydrogen using nonporous materials: hydrogen molecules are physically adsorbed within the pores of substances that have substantial surface areas and extensive gas-solid interfaces, such as zeolites, activated carbons (AC), and metal-organic structures (MOFs). This technique enables hydrogen to be stored at lower pressures, typically around 100 bar, in comparison to compressed hydrogen gas storage. Furthermore, it allows for storage at higher temperatures, around 77^{o} K, as opposed to the temperatures required for liquid hydrogen storage. Compared to chemical hydrogen storage, this adsorption approach offers quicker absorption and requires lower temperatures.

At 77^{o} K, the amount of hydrogen adsorbed becomes more significant compared to the gaseous hydrogen present in the tank, particularly at low pressures. This phenomenon is closely linked to changes in pressure and temperature within the tank [4]. Figure 1 shows the increasing density as a function of storage pressure for different types of adsorbent materials, with this effect becoming more pronounced as the temperature decreases. Notably, the most substantial disparity between the sorbent materials and the cryo-compressed case occurs around 100 bar and 77 K. The stored density of MIL-101 and compacted MOF-5, for instance, is 50% higher than that of CcH2 (45 versus 30 kg/m3) [5].

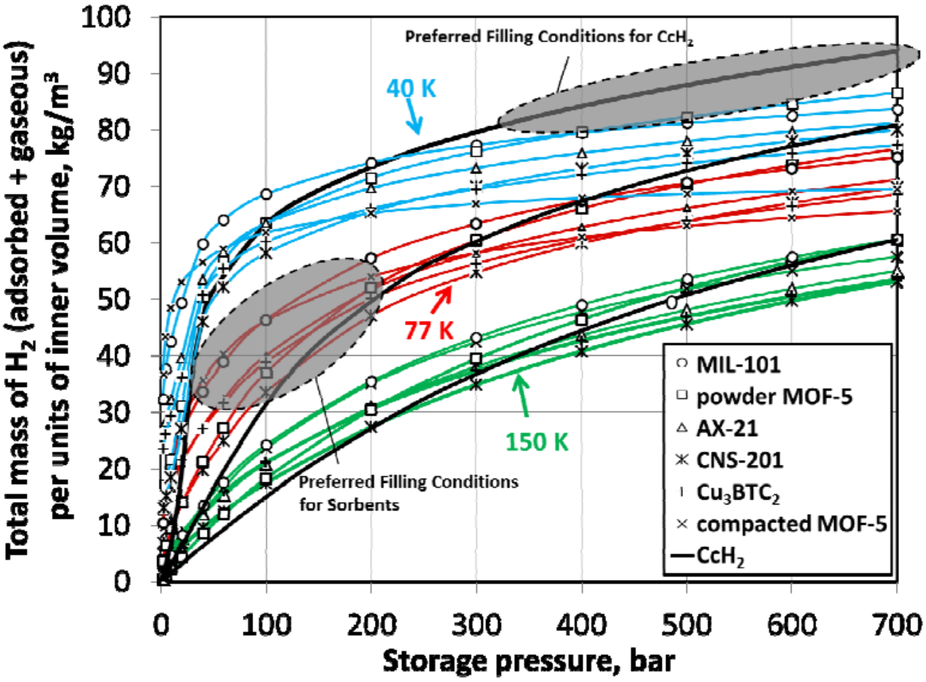

Figure 1. Total H2 density (including both adsorbed and gaseous phase) for different type of cryo-adsorbents

3. Computational Fluid Dynamic (CFD) model validation

The Computational Fluid Dynamics (CFD) model used in this work was developed using the commercial software COMSOL Multiphysics 6.1. The model was validated by comparing it against experimental data from Test n. 20 [6], [7], as well as numerical results obtained from the filling process of a 2.5 L tank with activated carbon [8]. To reduce the number of nodes and, as a consequence, the computational time, an axially symmetrical mesh was generated, and the temperatures calculated during the filling process were compared at specific locations, as indicated in Figure 2.

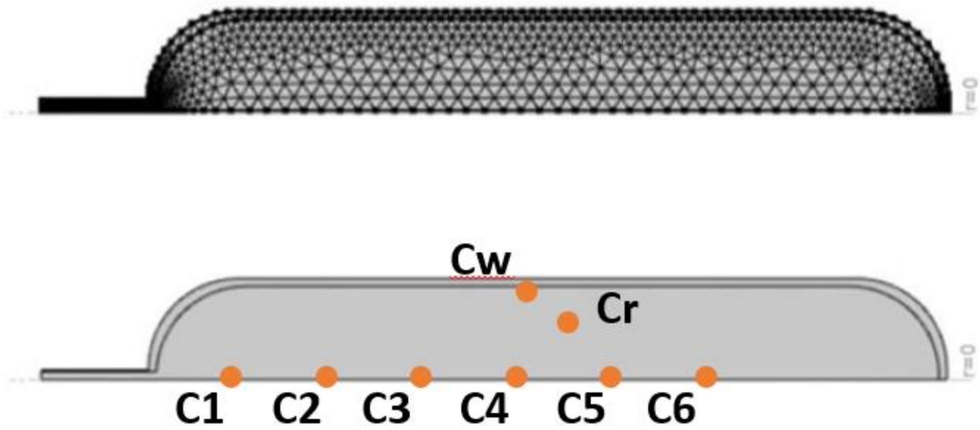

Figure 2. Computational grid and monitor point locations

The hydrogen storage tank is a stainless-steel container packed with adsorbents and is put into a Dewar flask filled with coolant (room temperature water or liquid nitrogen). Material properties of hydrogen tank and activated carbon properties are taken from [8]. A modified Dubinine-Astakhov (MDA) adsorption model [9] is used to describe the adsorption isotherm for MOF-5 and activated carbon (AC).

The initial pressure and temperature of the tank are 0.03208 MPa and 302^{o} K, respectively. To cool the tank, water at 302.5^{o} K is used, and the heat transfer coefficient between the steel wall and the water at room temperature is 36 W/(m2 K). Hydrogen enters the tank at a rate of 2.048e-05 kg/s, and the filling process takes 953 seconds.

The pressure profile obtained from the simulation within the tank are in line with the experimental data. The maximum pressure attained inside the tank at the end of the filling process is 9 MPa.

Figure 3 shows a comparison of the temperature profiles at various locations along the axis of the tank during the filling process, in relation to the experimental data: the CFD results are in agreement with the experimental data. It should be noted that, overall, the CFD results tend to slightly underestimate the experimental data, except for the aforementioned point C1, which is situated near the tank inlet.

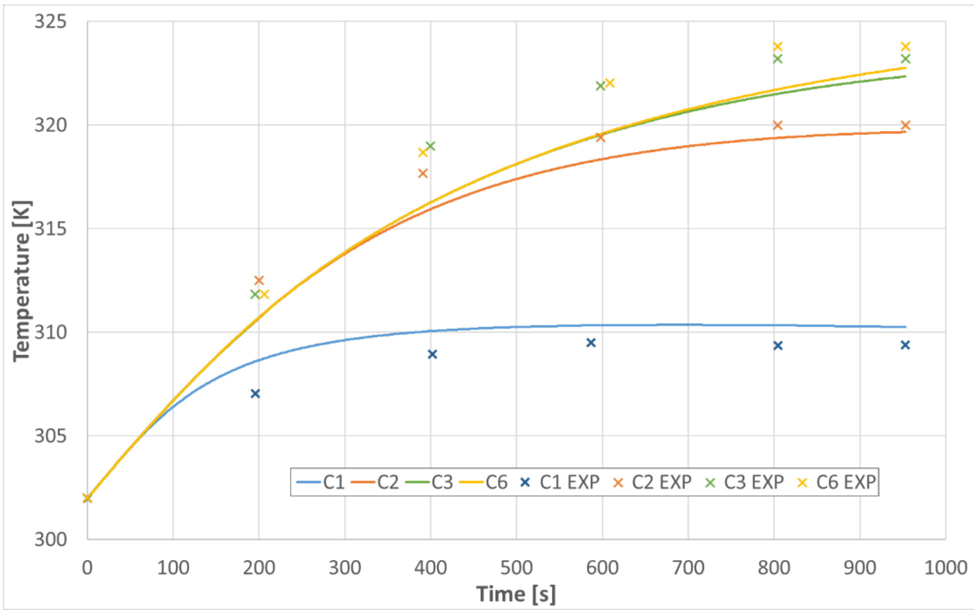

Figure 3. Temperature profile at selected locations during the filling compared with the experimental data

A comparison of the temperature profiles near the tank wall at different locations during the filling process, alongside the corresponding experimental data are represented in Figure 4. For this case as well, the CFD results are in line with the experimental data. However, it is worth noting that point Cw deviates from the expected trend of the experimental values towards the end of the filling process. This discrepancy is likely due to the utilization of a non-accurate heat transfer coefficient between the steel wall and the water at room temperature.

The gaseous hydrogen mass and the adsorbed hydrogen mass at the end of the filling are 8.7g and 11g respectively; those values are the same of the one calculated in [8].

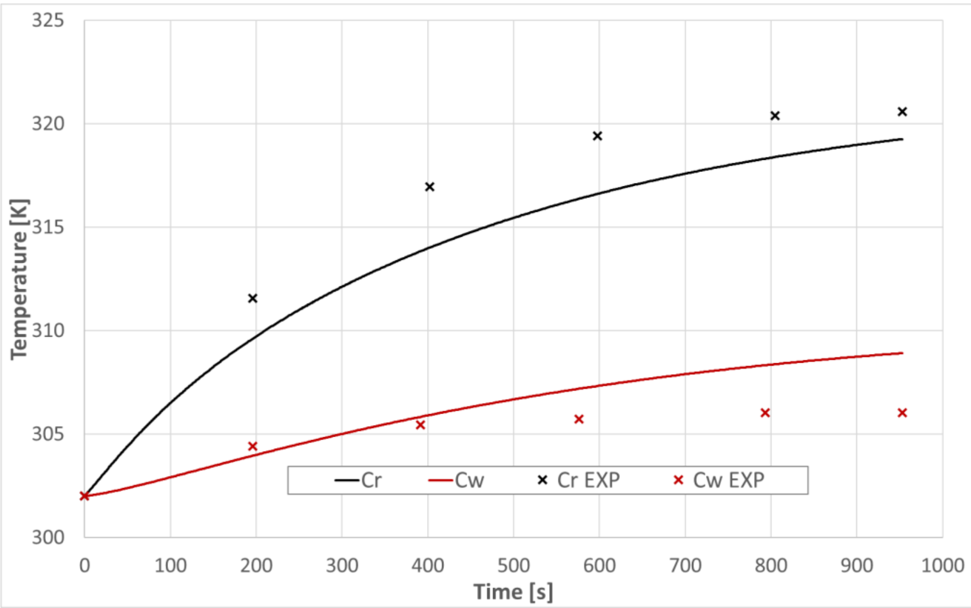

Figure 4. Temperature profile at selected locations close to the tank wall during the filling compared with the experimental data

Figure 5 shows the temperature contours (on the left-hand side) and the absolute absorption (on the right-hand side) at the end of the filling process (i.e. 953 s). Notably, it is evident that as the temperature decreases, the absorption of hydrogen increases.

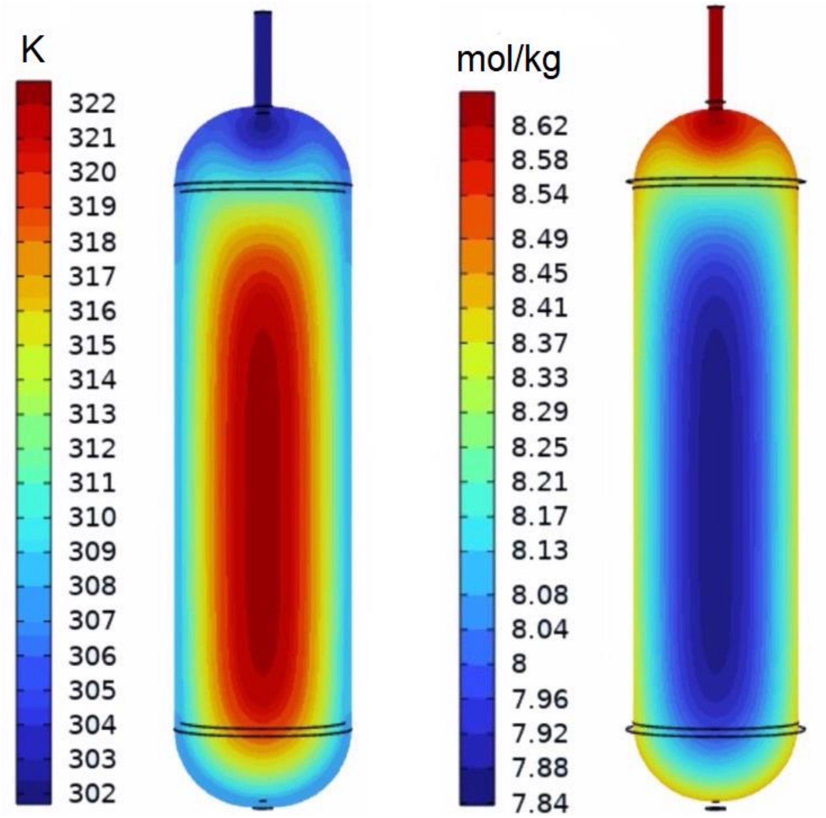

Figure 5. Temperature contours (a) and absolute adsorption (b) at the end of the filling

4. Simulation results

In a previous study [10], the same CFD model was further used to simulate the tank filling process with the presence of activated carbon (AC) under different conditions; simulations were conducted with varying inlet hydrogen temperatures (77º K, 150º K, and 233º K) and different initial tank temperatures (233º K, 150º K, and 77º K); as result, lower temperatures, whether it is the initial or the inlet temperature, result in a higher quantity of hydrogen being stored; in addition, for all the scenarios, more than half of the total hydrogen stored in the tank is adsorbed by the activated carbon.

In order to reproduce a filling similar to the one used in the hydrogen refueling station, a simulation imposing a pressure at the inlet of the tank has been done: as indicated in Figure 6, the pressure rises from 1 bar to 100 bar in 60 seconds and then the pressure in maintained constant for the whole simulation. The material properties of the tank are the described in session 3 and the adsorbent material in a MOF-5 [11]; the initial tank temperature is 77º K and the hydrogen enter the tank at 233º K. The total simulation time is 2500 seconds.

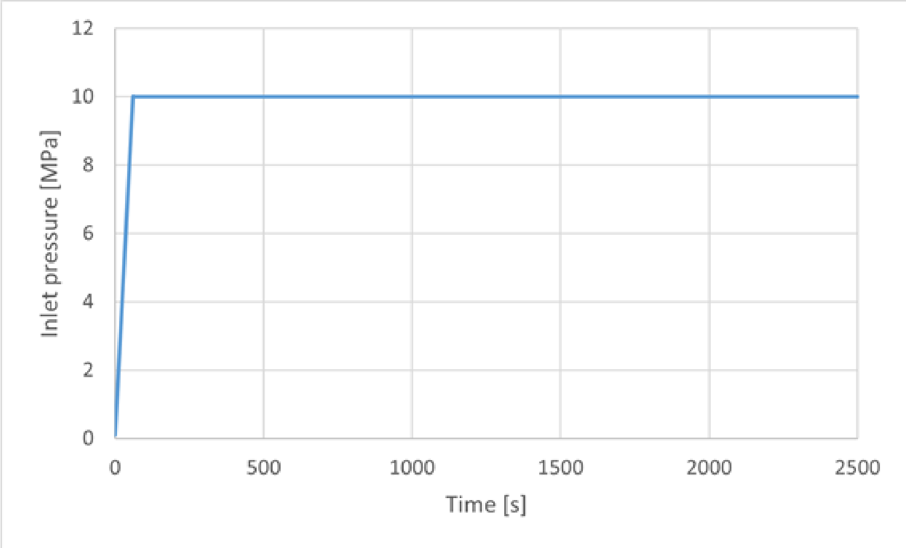

Figure 6. Inlet pressure profile

The hydrogen mass flow rate entering the tank reaches the maximum value (i.e. 0.9 g/s) at the end of the pressure ramp (i.e. 60 s); after the pick the mass flow rate decreases as shown in Figure 7.

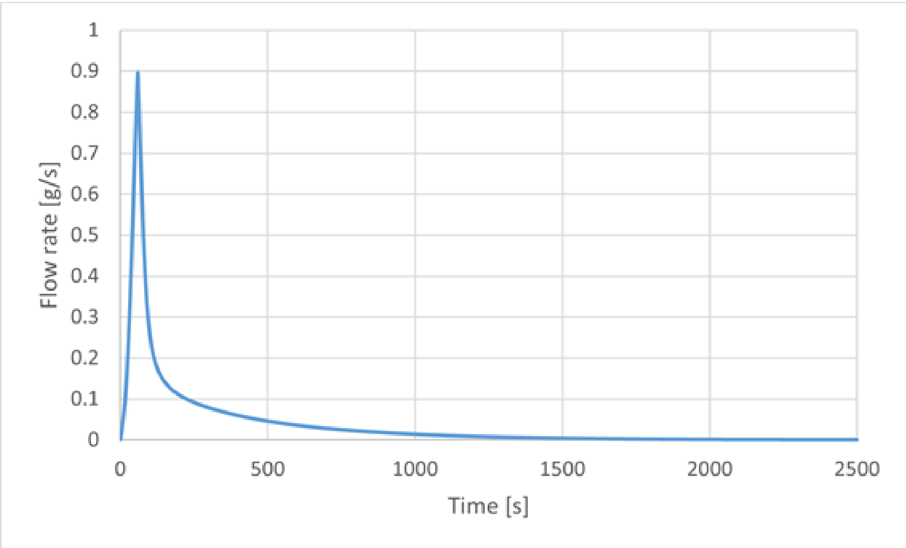

Figure 7. Hydrogen mass flow rate

The temperature profile at selected locations during the filling are reported in Figure 8: in all probes, except for Cw (i.e. the one close to the tank wall), the temperature rises rapidly due to the entry hydrogen at higher temperature, the compression work, and the heat released during adsorption; the Cw probe is affected by the nitrogen cooling system at 77 K, considering the steel tank wall has good thermal conductivity and a small thickness. Almost half of the tank is the zone more effected by the hydrogen inlet temperature: the probes close to the tank inlet, namely C1, C2, C3 and C4 are the ones with higher temperatures compared to the other probes.

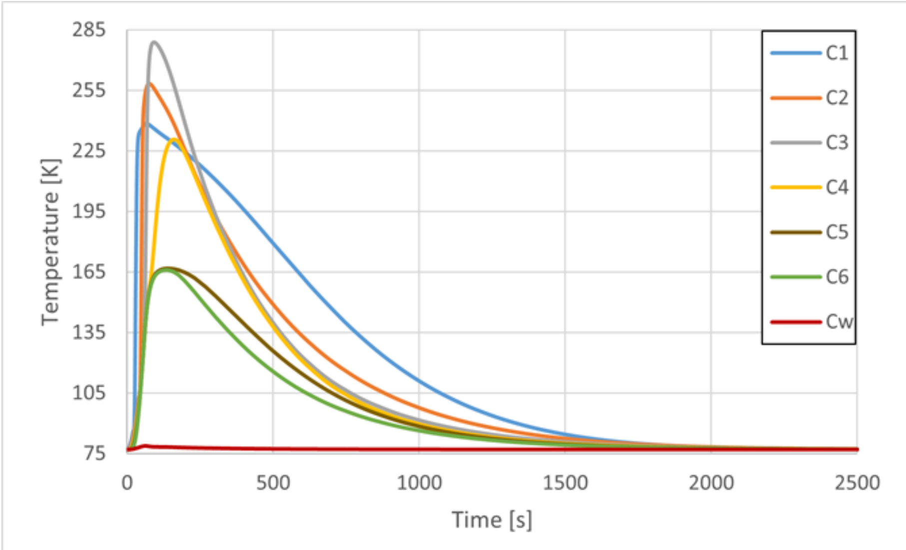

Figure 8. Temperature profile at selected locations during the filling

That phenomenon is also confirmed by plotting the temperature contours at different simulation times (see Figure 9): at 91 second the maximum temperature inside the tank is reached, with the presence of a hot spot close to the tank inlet, while the zone close to the wall is the effect by the cooling system where the temperature is the lowest; continuing with the filling process, the temperature of the tank decreases and it becomes uniform towards the end of the simulation. Figure 10 confirms the strong relation between the temperature and the absolute adsorption: as the temperature decreases, the absorption of hydrogen increases.

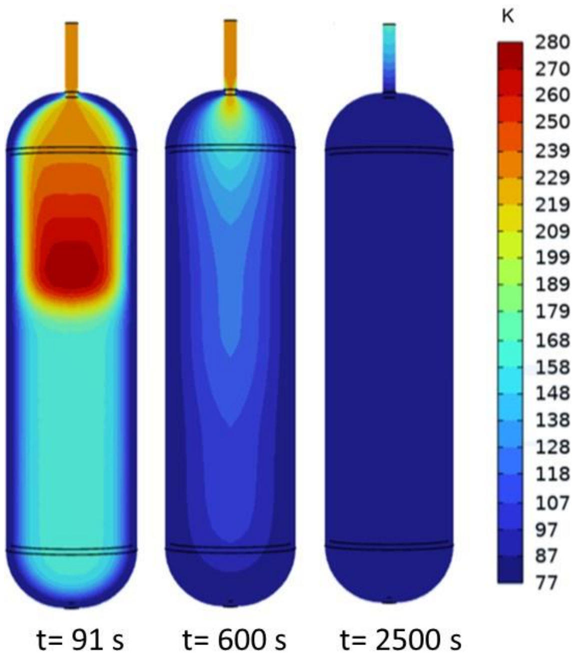

Figure 9. Temperature contours at 91, 600 and 2500 seconds

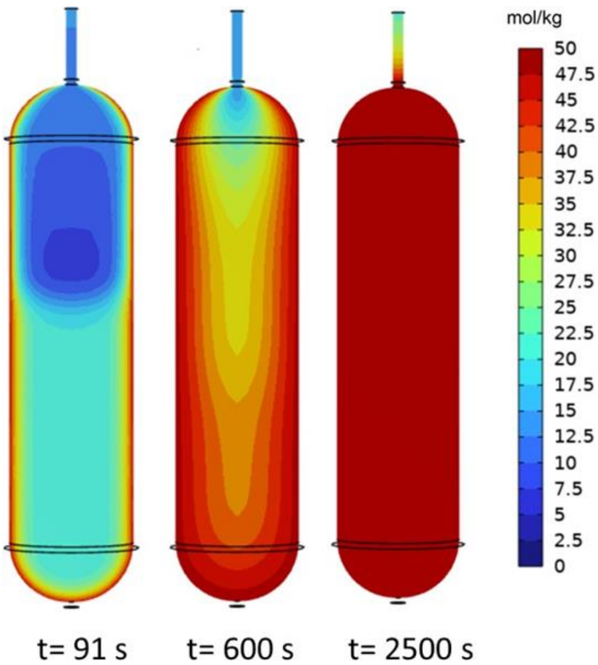

Figure 10. Absolute adsorption at 91, 600 and 2500 seconds

The adsorbed, gaseous, and total hydrogen masses stored inside the tank during the filling are reported in Figure 11. The adsorbed mass at the end of the filling process is 100 g, while the mass of gaseous hydrogen accumulated in the empty portions of the material is only 10 g due to the density of MOF-5 (up to 400 kg/m3); therefore, the total quantity of hydrogen stored in the 2.5 L tank for a filling time of 2500 s is 110 g.

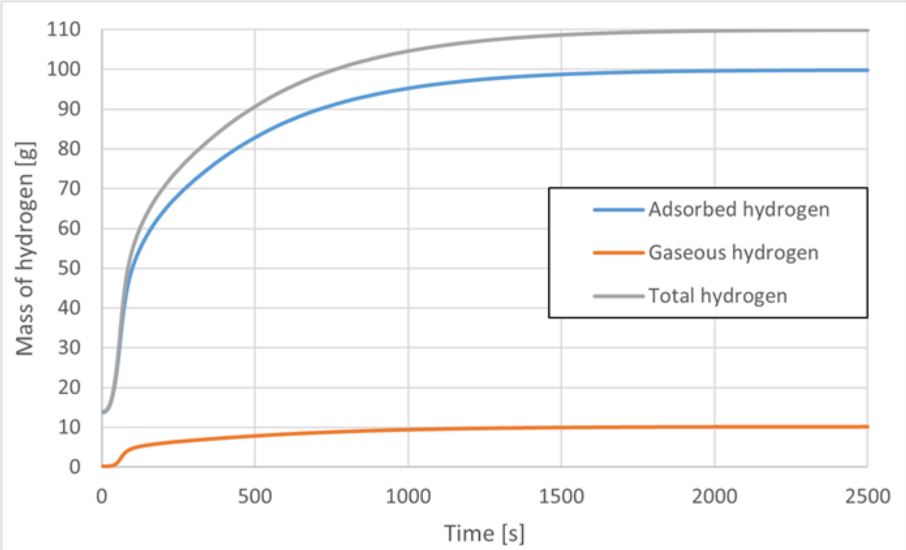

Figure 11. Adsorbed, gaseous, and total masses stored inside the tank during the filling

5. Conclusions

A validated CFD model has been used to simulate the hydrogen tank filling process in the presence of adsorbent materials. In a previous study, the same model has been utilized to investigate the impact of various factors, including inlet temperature, inlet pressure ramp rate, and initial tank temperature, on the quantity of hydrogen stored at the end of the filling process. In this study a filling of a 2.5-liter hydrogen tank with MOF-5 adsorbent material has been simulated imposing a pressure profile at the inlet. The hydrogen temperature inside the tank and the absolute adsorption has been analyzed: it has been observed that lower temperatures led to higher absolute absorption of hydrogen. the total quantity of hydrogen stored in tank for a filling time of 2500 s is 110 g, with the adsorbed mass 10 times bigger than the hydrogen accumulated in the empty portions of the material.

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