Optimization of a cold-adsorbed hydrogen tank during refilling using a Computational Fluid Dynamic (CFD) code.

Daniele Melideo
Dipartimento di Ingegneria dell'Energia, dei Sistemi, del Territorio e delle Costruzioni (DESTEC), Università di Pisa, Italy
e–mail: daniele.melideo@unipi.it

Lorenzo Ferrari
Dipartimento di Ingegneria dell'Energia, dei Sistemi, del Territorio e delle Costruzioni (DESTEC), Università di Pisa, Italy
e–mail: Lorenzo.ferrari@unipi.it

Paolo Taddei Pardelli
Spike Renewables Srl, Viale Manfredo Fanti, 217, 50137, Firenze, Italy
e–mail: paolo.taddei@spikerenewables.com

ABSTRACT

Hydrogen harbours the promise of serving as a significant clean energy resource; however, unlocking its full potential necessitates overcoming the crucial challenge of establishing efficient and economical hydrogen storage methods. To enable widespread adoption of hydrogen as an energy source, it is imperative to explore various storage approaches, including compression at elevated pressures, liquefaction through cooling to -253°C, and storage alongside chemical compounds, each presenting unique advantages and drawbacks.
The MAST3RBoost initiative (Maturing the Production Standards of Ultra-porous Structures for High-Density Hydrogen Storage Bank Operating on Swinging Temperatures and Low Compression) represents a European project with the primary objective of establishing a robust benchmark for cold-adsorbed H2 storage (CAH2) at low compression levels (100 bar or below). Activated Carbons (ACs) and high-density Metal-organic Frameworks (MOFs), the MAST3RBoost project aims to pave the way for a transformative approach. Its core mission involves the maturation of these materials to develop a ground-breaking adsorption-based demonstrator at the kilogram scale, thereby aligning with industry goals and fostering advancements in hydrogen storage technology. The design of the tank is supported by numerical investigation by mean of the use of Computational Fluid Dynamic (CFD) commercial code.
In this paper a study related to the optimization of the thermal and hydrogen flow distribution during the filling process is presented. The model has been previously validated against experiment using an axial symmetrical simplification of the geometry; a more detailed 3D model is now used to better reproduce the real case and understand the flow behaviour inside the tank.

KEYWORDS

Please supply six to eight keywords, which apply to your paper, after the abstract. This will assist in the preparation of an index for the Proceedings.

INTRODUCTION

The use of clean and renewable energy sources has become increasingly imperative in mitigating greenhouse gas emissions. Hydrogen emerges as a leading contender in this quest [1], heralded for its potential to serve as a clean energy carrier for both electricity and heat

production. However, the pervasive challenge hindering widespread hydrogen adoption remains the scarcity of efficient and safe storage solutions [2], [3].

Various methodologies for storing hydrogen exist, each presenting distinct advantages and drawbacks. One approach entails compressing hydrogen at high pressures, typically within the range of 350 to 700 bar. While relatively straightforward and cost-effective, this method necessitates heavy and bulky tanks and equipment. Another strategy involves liquefying hydrogen through extreme cooling to temperatures as low as -253°C, necessitating specialized equipment and insulation. Nonetheless, this technique enables higher-density hydrogen storage. Alternatively, hydrogen can be combined with chemical compounds like metal hydrides or hydrocarbons to store it in a solid state, albeit requiring specialized handling and potentially sacrificing efficiency compared to other methods.

In the framework of 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 investigating cold-adsorbed hydrogen storage at low compression levels, specifically targeting 100 bar or below. This approach shows promise by enabling high-density hydrogen storage with reduced volume. This paper will focus on Computational Fluid Dynamic (CFD) analyses, examining the influence of temperature and pressure on hydrogen absorption, while also exploring the impacts of various adsorbent types.

COLD-ADSORBED H2 STORAGE

An alternative method for hydrogen storage involves the adsorption of hydrogen using nonporous materials. In this process, hydrogen molecules are physically adsorbed within the pores of substances with extensive gas-solid interfaces, such as zeolites, activated carbons, and metal-organic structures (MOFs). This approach enables hydrogen storage at lower pressures, typically around 100 bar, in contrast to compressed hydrogen storage, and at higher temperatures, typically around 77º K, compared to liquid hydrogen storage. Furthermore, compared to chemical hydrogen storage, adsorption offers quicker absorption kinetics and requires lower temperatures.

At 77º K, the amount of hydrogen adsorbed predominates over the gaseous hydrogen inside the tank, particularly at low pressures. This phenomenon is closely linked to variations in pressure and temperature within the tank [4]. Figure 1 illustrates the density as a function of storage pressure for various types of adsorbent materials, showing that this effect becomes more pronounced at lower temperatures. The most significant disparity between sorbent materials and the cryo-compressed case is observed at approximately 100 bar and 77 K, where the stored density of MIL-101 and compacted MOF-5 is 50% higher than that of CcH2 (45 versus 30 kg/m3) [5].

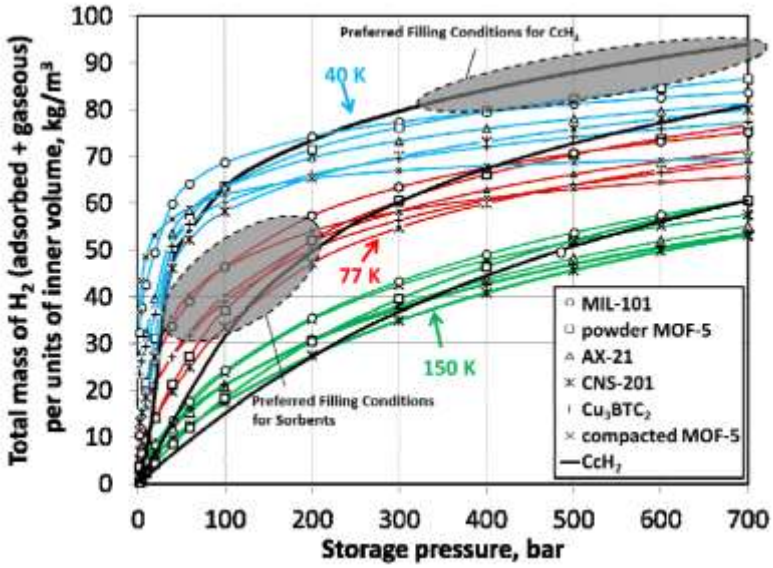

Figure 1. Total H2 density (including both adsorbed and gaseous phase) for different type of cryo-adsorbents

COMPUTATIONAL FLUID DYNAMIC (CFD) MODEL VALIDATION

The Computational Fluid Dynamics (CFD) model utilized in this study was crafted using COMSOL Multiphysics 6.1 software. Its accuracy was validated against both Test n. 20's experimental data [6], [7], and numerical findings from the filling procedure of a 2.5 L activated carbon tank [8]. To streamline computation and reduce processing time, an axially symmetrical mesh was employed, with temperature assessments concentrated at specific points.

The hydrogen storage tank, constructed of stainless steel and packed with adsorbents, is encased within a Dewar flask containing either room temperature water or liquid nitrogen coolant. Material characteristics for both the hydrogen tank and activated carbon are referenced from [8]. The adsorption isotherm for MOF-5 and activated carbon (AC) is described using a modified Dubinine-Astakhov (MDA) model [9].

Initially, the tank's pressure and temperature are set at 0.03208 MPa and 302º K, respectively. Cooling is facilitated using water at 302.5º K, with a heat transfer coefficient of 36 W/(m2 K) between the steel wall and room temperature water. Hydrogen influx into the tank occurs at a rate of 2.048e-05 kg/s, with the filling process lasting 953 seconds.

Simulation results depict pressure profiles within the tank aligning closely with experimental data, with a maximum pressure of 9 MPa reached by the end of the filling process. Figure *2* illustrates temperature profiles at some locations, demonstrating agreement between CFD results and experimental observations. CFD results are consistent with experimental findings, except for point Cw towards the end of filling, likely attributable to an inaccurate heat transfer coefficient between the steel wall and room temperature water. An in-depth model validation is reported in [10].

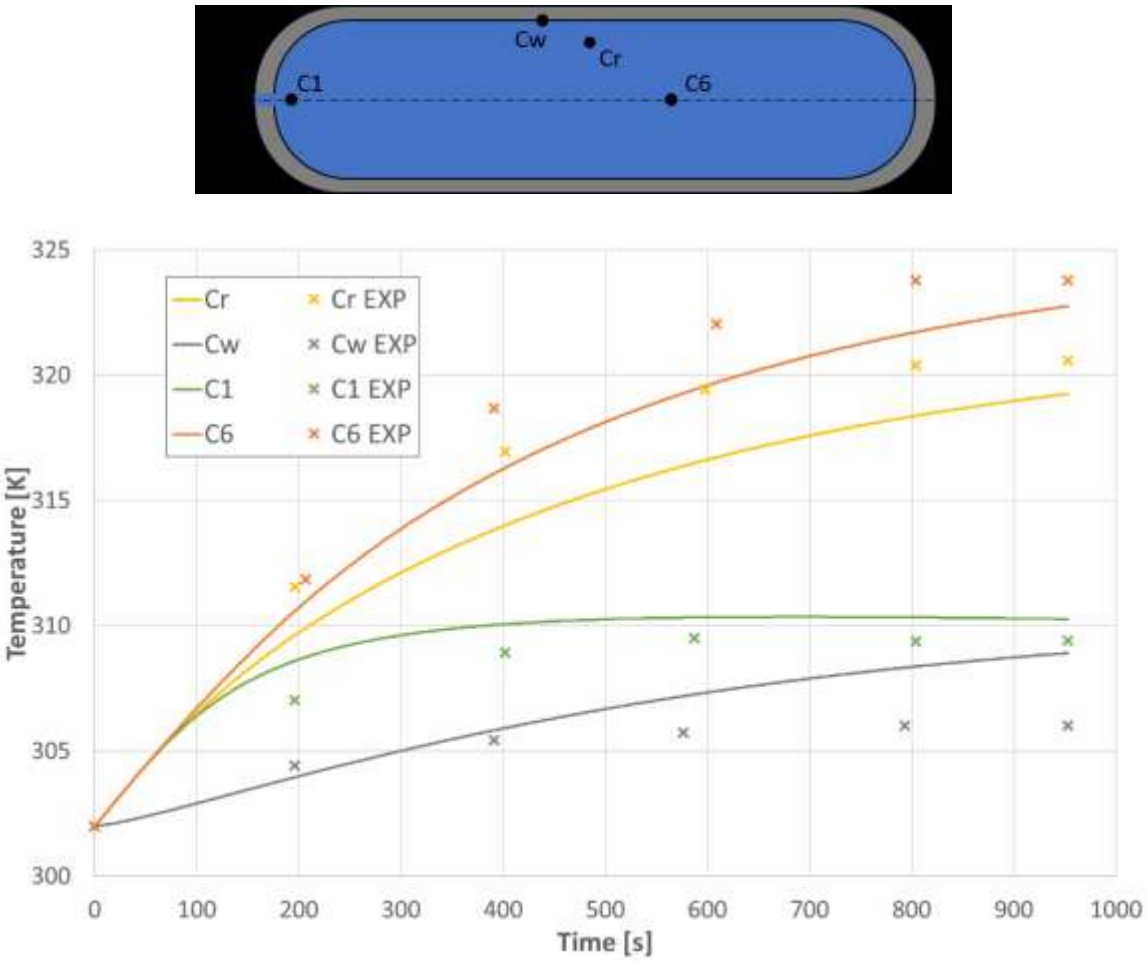

Figure 2. Temperature profile at selected locations during the filling compared with the experimental data

EFFECT OF INTERNAL COOLING SYSTEM (2D AXIAL-SYMMETRICAL SIMULATIONS)

In the previous simulations, an ideal constant temperature on the wall of the tank has been imposed in order to guarantee a constant low temperature at the tank boundaries during the filling; that situation is not feasible in the “real world”. A more realistic configuration has been analysed considering the presence of a cooling system inside the tank; the internal cooling system is composed of a spiral coil with nineteen turns, covering approximately the length of the tank itself (see Figure 3); nitrogen is circulated inside it, being a readily available fluid in the market, at a temperature of 77 K. In this study, a simple imposition of 77 K on the wall of the "spiral coil" throughout the filling time will be considered, which is a further simplifying assumption, not focusing on the cooling system, which may be subject to further study in the future developments of this project. The hydrogen enters the tank through an injector: it consists of eleven equally spaced levels, each equipped with four holes with a diameter of 5 mm; the lance is bottom-closed.

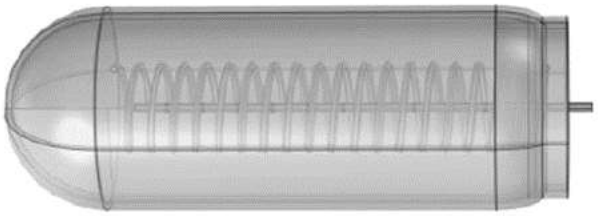

Figure 3. Tank geometry with the internal spiral coil and hydrogen injector

Firstly, 2D axial symmetrical simulations have been performed, to study the tank's response during the filling process and estimate the hydrogen mass stored in tank (i.e. adsorbed and gaseous), and the refrigeration effect in the system to counteract the heat generated by compression and that related to the adsorption phenomenon itself. Two configurations have been considered for the study, with and without the cooling system as reported in Figure 4.

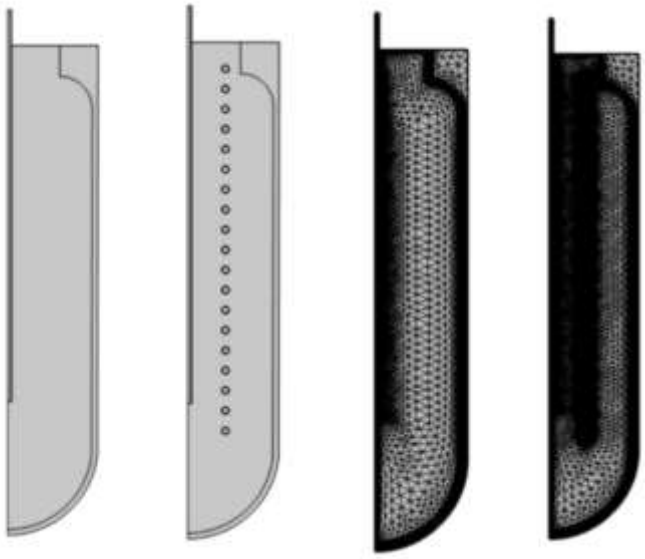

Figure 4. 2D axial symmetrical geometry and mesh with and without schematic cooling system

The contours of the temperature and absolute adsorption for the two configurations at the end of the filling (i.e. 500 s) are reported in Figure 5: it is possible to observe how the refrigeration system reduce the presence of "hot" zone, which benefits the adsorption phenomenon.

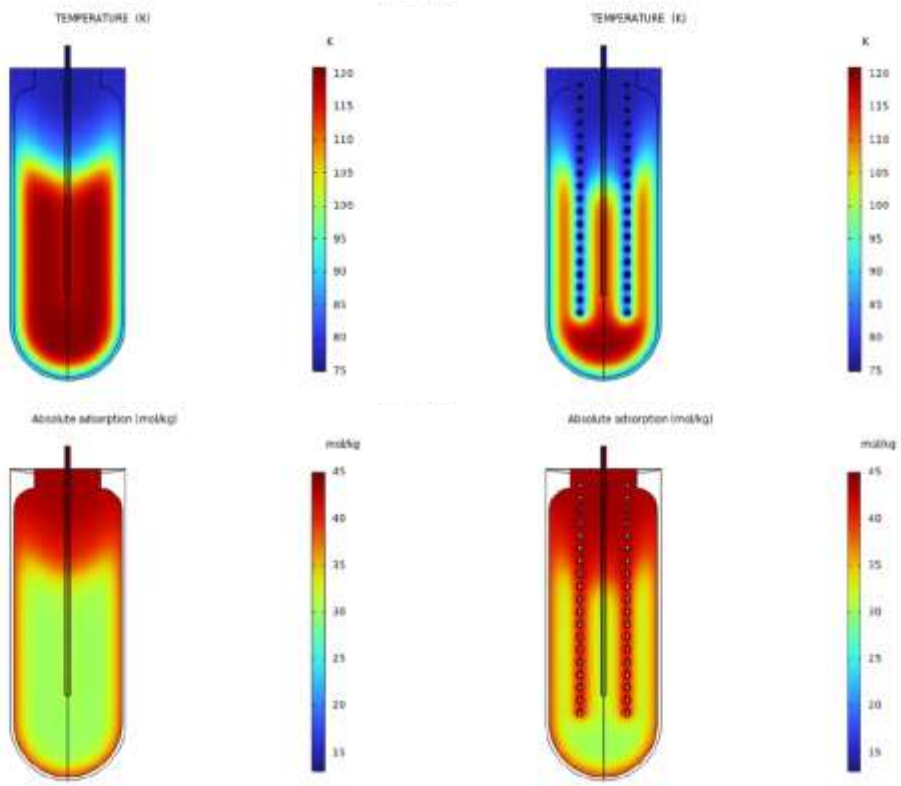

Figure 5. Temperature and absolute adsorption for the two configurations at the end of the filling (i.e. 500 s)

The mass of hydrogen stored (i.e. adsorbed hydrogen mass, gaseous mass, and total mass) during the filling for the two configurations are reported in Figure 6. The use of the cooling system has a positive effect on the stored mass in the system at the end of the process, with an increase of approximately 60 g in the total mass. This leads to the conclusion that the inclusion of the internal refrigeration system in the tank, despite resulting in a reduction of available space of about 0.5 litres out of the total tank capacity, benefits the process. The heat management issue can become much more significant when considering scenarios closer to reality, such as the non-adiabatic nature of the tank, or as we will see in the continuation of the study, the introduction of hydrogen at temperatures higher than 77 K.

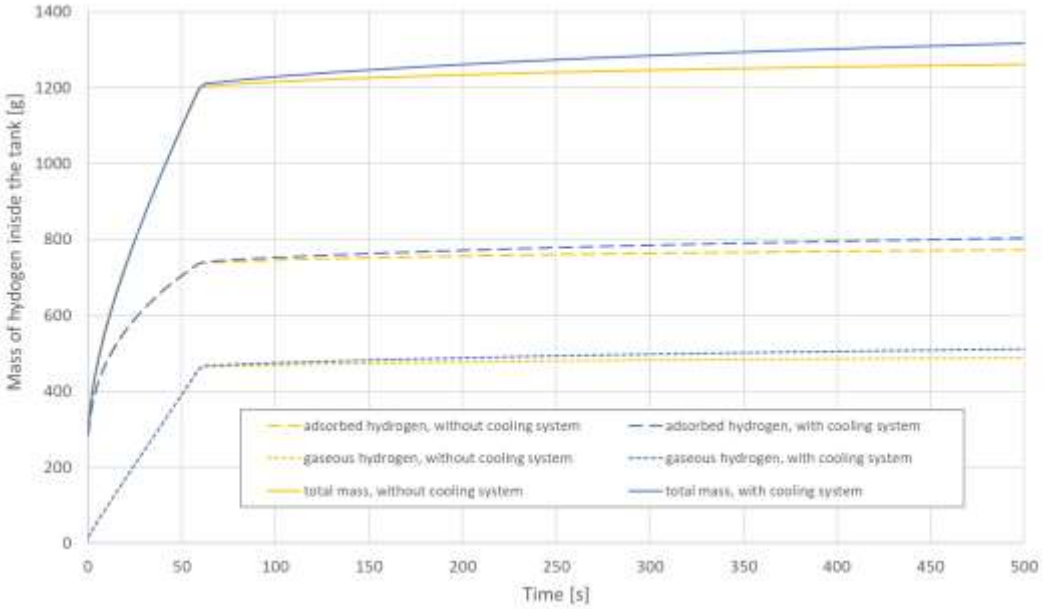

Figure 6. Mass of hydrogen stored during the filling for the two configurations

3D AXIAL-SYMMETRICAL SIMULATION WITH THE PRESENCE OF COOLING SYSTEM

The simulation of the whole tank with the presence of the cooling system has been performed in order to study the possible 3D effect on the temperature and absolute adsorption distribution inside the tank during the filling. It is possible to observe how a low temperature distribution is mainly located at the top of the tank (see Figure 7) especially at the beginning of the filling; the absolute adsorption distribution is affected by the temperature distribution.

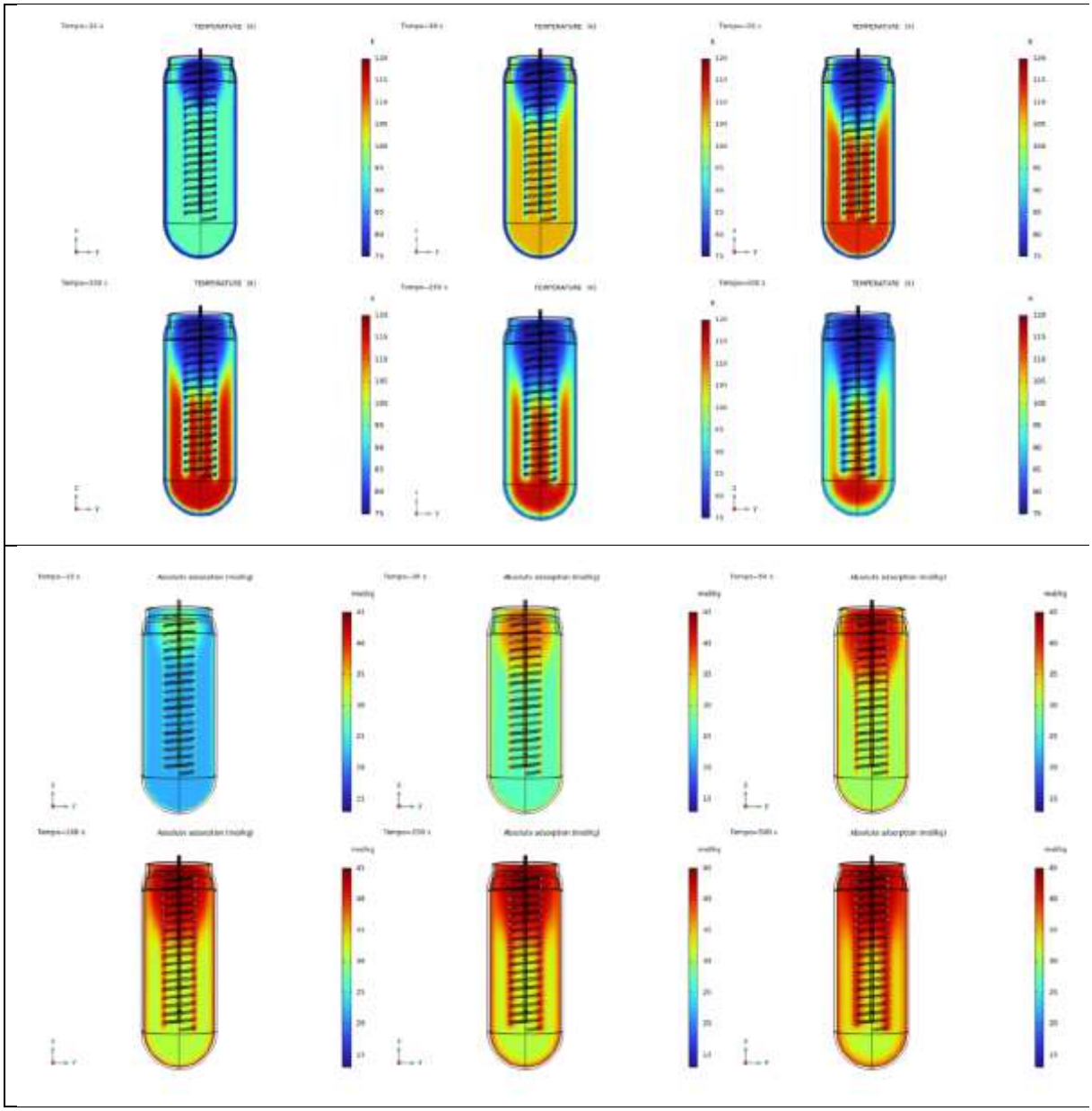

Figure 7. Temperature and Absolute adsorption distribution at different times during the filling (10 s, 30 s, 50 s, 100 s, 250 s and 500 s)

At the end of the filling the adsorbed hydrogen mass, the gaseous mass, and the total mass are 852 g, 542g and 1394 respectively.

The effect of different adsorbent material

The distinction between utilizing MOF5 (Metal-Organic Framework 5) and activated carbon in hydrogen adsorption tanks lies in their structural and adsorption characteristics. MOF5 comprises a crystalline framework of metal ions interconnected by organic ligands, forming a porous structure with defined channels and a large surface area. In contrast, activated carbon consists of amorphous carbon structures with irregular pores and a highly porous network. Regarding adsorption capacity, MOF5 generally demonstrates high adsorption capabilities due to its structured pores, enabling efficient hydrogen uptake. On the other hand, activated carbon, while also possessing good adsorption properties, typically exhibits lower capacities than

MOF5 due to its larger, less defined pore structure. In terms of selectivity, MOF5 may offer preferential adsorption of hydrogen over other gases, depending on its chemical composition and pore size distribution. Activated carbon, relying primarily on physical adsorption, may display less selectivity compared to MOF5. Regarding stability, MOF5's stability can vary depending on its composition, with some materials prone to degradation under certain conditions. In contrast, activated carbon tends to be more stable and less susceptible to degradation, making it suitable for long-term use in hydrogen adsorption applications.

Two different type of adsorption material have been used in the simulation and compared to evaluate the effect on the hydrogen mass stored in the tank during the filling: Activated Carbon (AC) and compacted MOF-5; their material properties are reported in Table 1.

Table 1. Activated carbon and compacted MOF-5 material properties

Properties	Activated carbon (AC) [8]	Compacted MOF-5 [11]
Bulk density ρb[Kg/$m3$]	269.00	269.00
Specific heat Cp [J/Kg K]	825	742.5
Conductivity k [W/m K]	0.76	0.30
Bed porosity ϵ	0.49	0.13
Particle diameter dp [mm]	2.00	0.04
Permeability [m^2]	1.7e-08	2.0e-13

A comparison between AC and MOF-5 in terms of adsorbed hydrogen mass, gaseous mass, and total mass during the filling is reported in Figure 8. The analysis of stored mass evolution shows two different trends for the different materials: MOF-5 has a steeper curve toward the end of the filling compared to the AC. Additionally, regarding the distribution of adsorbed and gaseous hydrogen, in the case of M.O.F-5, approximately 92% of the total stored mass comprises adsorbed mass on the porous material, whereas with AC, the adsorbed mass constitutes 61% of the total mass.

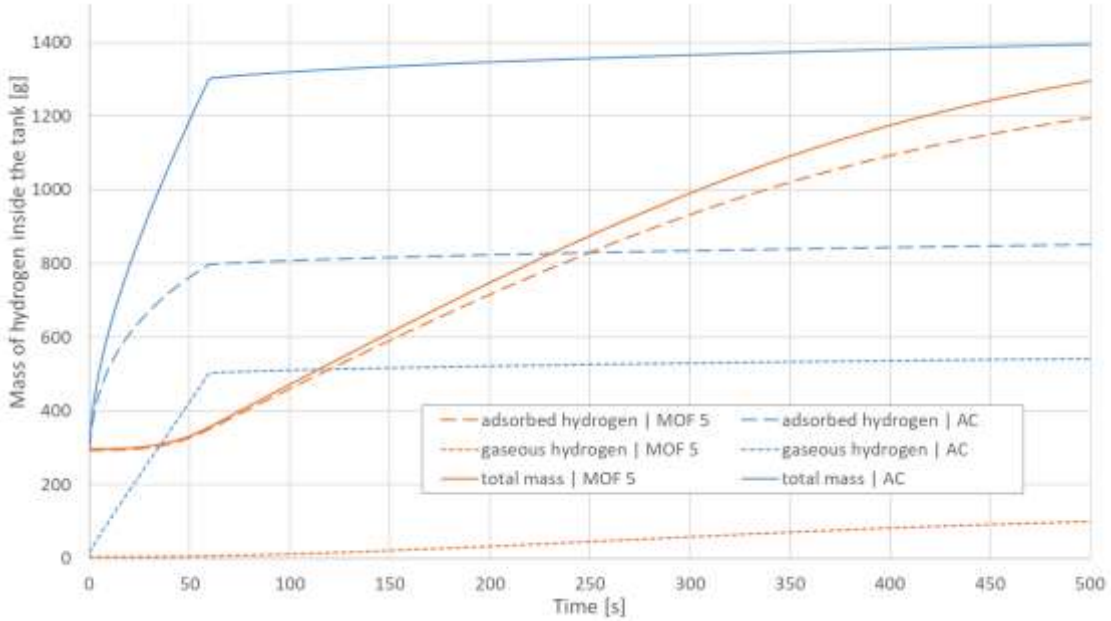

Figure 8. Adsorbed hydrogen mass, gaseous mass, and total mass during the filling

It is also observed that in the case of filling with MOF-5, the value of potential maximum saturation of the porous bed at the end of filling is significantly lower compared to the case with AC (see Figure 9).

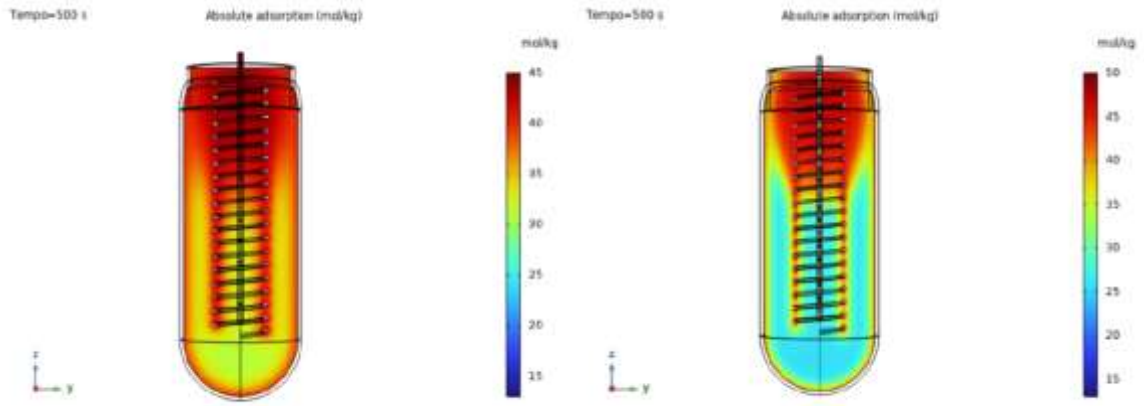

Figure 9. Absolute adsorption at the end of the filling for the two materials (AC on the left and MOF-5 on the right)

Analysing the pressure evolution inside the tank for the two materials (see Figure 10), it is possible to observe AC case has a different behaviour compare to MOF-5 case: the latter consistently remains above the curve representing the imposed inlet pressure of the tank, probably due to the greater hindrance offered by the denser adsorbent material to the passage of the hydrogen flow. Furthermore, it is observed that in the case of MOF-5, the target pressure of 100 bar imposed by the boundary conditions is not reached, unlike the case with A.C.

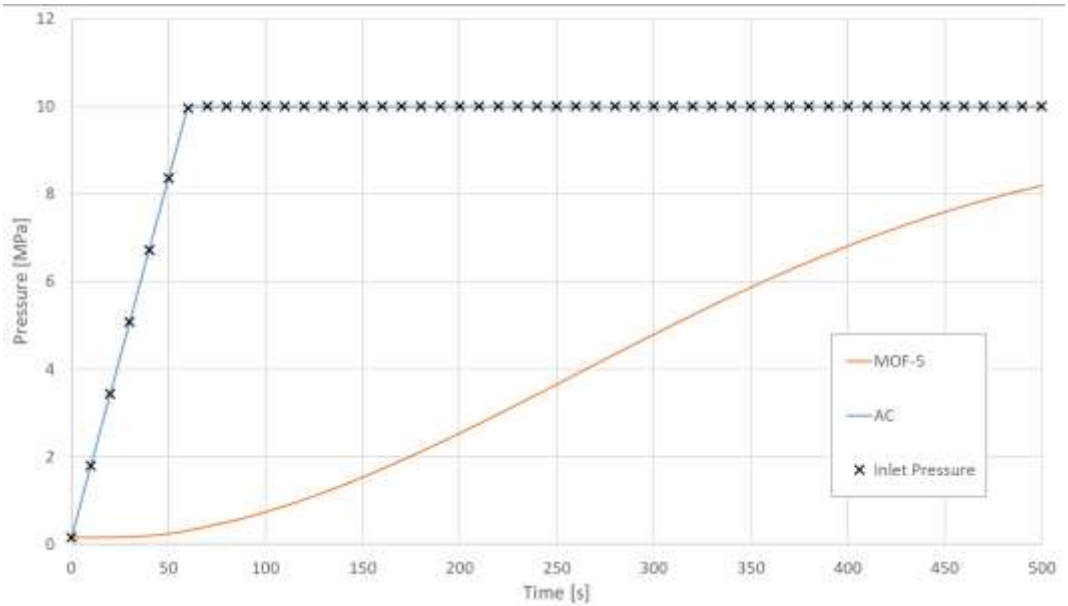

Figure 10. Tank pressure profiles inside the tank

The inlet mass flow rate for the two cases is reported in Figure 11; it is possible to observe that in the case of filling with MOF-5, there is a peak value around 3 g/s, significantly lower than the 60 g/s recorded in the case of AC. Furthermore, the peak in the two cases occurs at different times: while for activated carbon, it occurs practically at the beginning of the filling, in the case of MOF-5, it is reached after 60 seconds. This phenomenon confirms the slower dynamic in the

case of MOF-5, likely influenced by the denser nature of the material itself, which thus poses a greater obstacle to the passage of hydrogen flow in the tank.

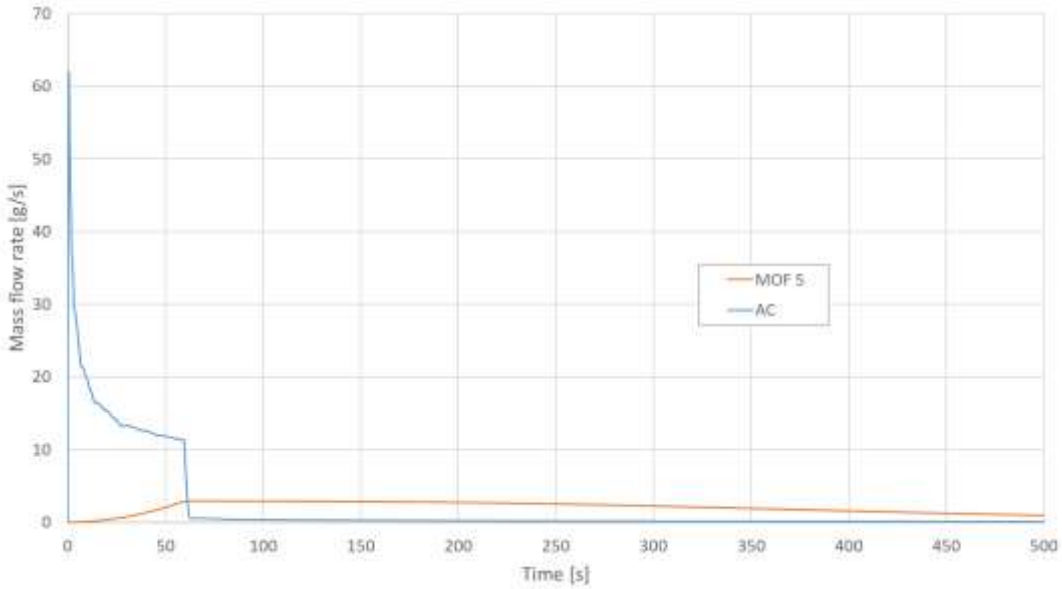

Figure 11. Mass flow rate during the filling for the two cases

CONCLUSION

Computational Fluid Dynamic (CFD) simulations have been performed in order to a cold-adsorbed hydrogen tank during the refilling process, based on a validated model. By investigating the influence of temperature, absolute adsorption, and the presence of an internal cooling system on hydrogen absorption and storage dynamics, insights were gained into enhancing the efficiency and effectiveness of hydrogen storage systems. The presented study firstly analysed the effect of the presence of a refrigeration system within the tank, which improved the stored mass despite a reduction in available space. This finding highlights the potential for leveraging advanced cooling mechanisms to enhance the performance of hydrogen storage systems, a critical aspect in advancing the adoption of hydrogen as a clean energy resource.

Moreover, the comparative analysis between different adsorbent materials, particularly Activated Carbon (AC) and compacted MOF-5, revealed nuanced trends in stored mass evolution and pressure behaviour during the filling process. MOF-5 exhibited a slower dynamic response and a lower potential maximum saturation compared to AC.

Furthermore, the observed discrepancies in pressure evolution inside the tank between the two materials (particularly the inability of MOF-5 to reach the target pressure of 100 bar imposed by boundary conditions) underscore the importance of material selection and system design in achieving desired operational outcomes. Additionally, the peak inlet mass flow rate in the case of MOF-5 was significantly lower than AC, indicating the influence of material properties on hydrogen flow dynamics within the tank. This highlights the need for a comprehensive understanding of material characteristics and their impact on system performance when designing hydrogen storage systems.

Overall, these findings emphasize the complexity of hydrogen storage dynamics and the importance of integrating advanced computational modelling techniques with experimental

validation to optimize system performance. Further research endeavours are warranted to explore alternative adsorbent materials, refine system designs, and address operational challenges to realize the full potential of hydrogen as a clean energy carrier.

ACKNOWLEDGMENT

MAST3RBoost is a funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European union or the European health and digital executive agency. neither the European union nor the granting authority can be held responsible for them.

Project funded under the National Recovery and Resilience Plan (NRRP), Mission 4 Component 2 Investment 1.3 - Call for tender No. 1561 of 11.10.2022 of Ministero dell'Università e della Ricerca (MUR); funded by the European Union – NextGenerationEU.

NOMENCLATURE

AC	Activated Carbons
CAH2	Cold-Adsorbed H2
CFD	Computational Fluid Dynamic
EU	European Union
MDA	Modified Dubinine-Astakhov
MOFs	Metal-organic Frameworks

REFERENCES

[1] IEA (International Energy Agency). The Future of Hydrogen. Rep Prep by IEA G20, Japan 2019. https://doi.org/10.1787/1e0514c4-en.

[2] Rivard E, Trudeau M, Zaghib K. Hydrogen storage for mobility: A review. Materials (Basel) 2019;12. https://doi.org/10.3390/ma12121973.

[3] Tzimas E, Filiou C, Peteves SD, Veyret J. Hydrogen Storage : State-of-the-Art and Future Perspective. 2003.

[4] Sdanghi G, Schaefer S, Maranzana G, Celzard A, Fierro V. Application of the modified Dubinin-Astakhov equation for a better understanding of high-pressure hydrogen adsorption on activated carbons. Int J Hydrogen Energy 2020;45:25912–26. https://doi.org/10.1016/j.ijhydene.2019.09.240.

[5] Petitpas G, Benard P, Klebanoff LE, Xiao J, Aceves M. A Comparative Analysis of the Cryo-compression and Cryo-adsorption Hydrogen Storage Methods 2014.

[6] Xiao J, Wang J, Cossement D, Bénard P, Chahine R. Finite element model for charge and discharge cycle of activated carbon hydrogen storage. Int J Hydrogen Energy 2012;37:802–10. https://doi.org/10.1016/j.ijhydene.2011.04.055.

[7] Xiao J, Peng R, Cossement D, Bénard P, Chahine R. CFD model for charge and discharge cycle of adsorptive hydrogen storage on activated carbon. Int J Hydrogen Energy 2013;38:1450–9. https://doi.org/10.1016/j.ijhydene.2012.10.119.

[8] Xiao J, Hu M, Bénard P, Chahine R. Simulation of hydrogen storage tank packed with metal-organic framework. Int J Hydrogen Energy 2013;38:13000–10. https://doi.org/10.1016/j.ijhydene.2013.03.140.

[9] Chahine MRPBR. Gas adsorption process in activated carbon over a wide temperature range above the critical point . Part 1 : modified Dubinin-Astakhov model 2009:43–51. https://doi.org/10.1007/s10450-009-9149-x.

[10] Melideo D, Ferrari L, Taddei Pardelli P. Preliminary analysis of refilling cold-adsorbed hydrogen tanks. J Phys Conf Ser 2023;2648:012042. https://doi.org/10.1088/1742-6596/2648/1/012042.

[11] David Tamburello, Hardy B, Sulic M, Kesterson M, Corgnale C, Anton D. Compact cryo-adsorbent hydrogen storage systems for fuel cell vehicles. ASME 2017 Fluids Eng Div Summer Meet 2018.