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EXECUTIVE SUMMARY OF THE THESIS

Pipe-in-pipe solutions for hydrogen transport employing fibre-reinforced polymers: material assessment and application evaluation

TESI MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY – INGEGNERIA DEI MATERIALI E DELLE NANOTECNOLOGIE

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1 Introduction

Within the energy transition towards decarbonisation, hydrogen is expected to play a key role to enable sector integration and reduce emissions in hard-to-abate sectors. However, the development of a hydrogen infrastructure is essential to kick-start a true H_2 economy.

For the transport of large quantities over long distances, pipelines are the most efficient, economical and environmentally safe option. Within this context, the pipe-in-pipe system appears as an attractive solution, because it allows pure hydrogen to be transported in a pipe inserted inside an existing gas network pipeline, while continuing to supply natural gas in the annular section. However, research is required to study the implications and consequences of this innovative solution, both in terms of fluid dynamics and material suitability.

2 State of the art

This chapter summarises the state of the art of hydrogen transport via pipeline, as well as the challenges and possible solutions for the materials used.

2.1 Material suitability

Exposure to hydrogen under pressure in metallic pipes generates adverse effects on mechanical and fracture properties, which can be summarised by the term hydrogen embrittlement (HE). The main effects are a reduction of ductility by 20-50%, fracture toughness and an increase of one to two orders of magnitude in fatigue crack growth rate compared to exposure to air [1]. The susceptibility of steel can be estimated based on chemical composition, a first representative index of which is the carbon equivalent (CE), and, for gas pipes, the transmission network is at greater risk than the distribution network due to the higher pressures and strengths of the materials typically used.

The use of polymeric materials is currently limited to the distribution grid. The results of tests carried out on polyethylene (PE), widely used, showed no deleterious effect on mechanical properties and microstructure after exposure to this gas for years. Fibre-reinforced polymers are promising materials for pipes working with hydrogen at high pressures and are obtained from the dispersion of fibres in a polymer matrix, whose synergetic operation allows for superior mechanical properties and anisotropic behaviour. Different combinations are possible, using thermoplastic or thermosetting matrices and choosing between different fibre types. The most common are glass, aramid and carbon fibre, of which the last is the one with better mechanical properties but also higher cost, while glass fibre results in better barrier properties according to literature.

2.2 Hydrogen-natural gas blending

One possibility that is increasingly being considered is to transport hydrogen as a blend with natural gas, retrofitting the existing gas network to reduce CAPEX and start laying the foundations for sustained hydrogen use. There are several maximum H_2 concentrations in natural gas in different countries, such as 2% in Italy and 10% in Germany, which aim to be increased following several completed and ongoing projects focusing on the applicability of this solution to the current infrastructure and required adaptations. Indeed, the injection of H_2 into the gas leads to substantial changes in both the physical and combustion properties of the gas. Blending, however, does not in principle exclude the possibility of consuming pure hydrogen, as specific membranes can be used to separate it from NG, though increasing the complexity of the system.

2.3 Hydrogen pipelines

Today, there are more than 4500 km of pipelines around the world, mainly made of carbon steel, typically to connect production sites with chemical industries and refineries [2]. The European Industrial Gases Association (EIGA) guidelines specify design criteria for the steels used in such pipelines, which must have hardness of less than 22 HRC, including welds, with possible pre- or post-welding heat treatment [3].
FRP pipes are promising for hydrogen service, performing well at high pressures, where plain polymers fail, and bringing improvements in weight, handling, welding and joining. They are interesting for the inner pipe in the pipe-in-pipe system.
The simplest FRP pipe concept consists of using a single material and can be produced via multi-filament winding (MFW), an innovative technique allowing 48 tows, typically pre-impregnated with resin (towpregs), to be wound around a mandrel that moves horizontally and rotates around its axis. Eventually, non-crimped structures are obtained, arranging unidirectional layers on top of each other and each with a specific orientation.

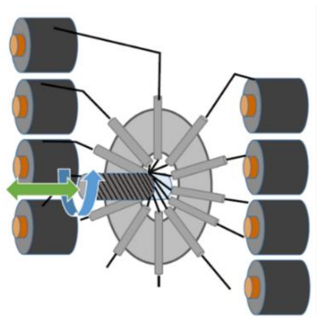

Figure 2.1 - MFW working principle [4]

This concept can be developed and involve several layers, each with its own task [5]. Starting from the inside, one has a liner in contact with hydrogen, with good barrier properties and even made from polymers such as HDPE, the FRP core which must withstand mechanical stresses, and an outer protective layer, depending on the working environment. Sandwiched between these are other minor interface and barrier layers to ensure better performance.

3 Roughness tests on FRP

The roughness of a pipe wall is crucial in determining the pressure losses during fluid transport. Measurements are made on specimens of carbon fibre- and glass fibre-reinforced epoxy resin (CFRE and GFRE, respectively) and glass fibre-reinforced polypropylene (GFRPP) using a digital microscope. Using the depth-from-focus (DFF) method, it generates a 3D image of the surface to be analysed by superimposing images at different focal planes and allows line measurements of surface roughness to be carried out. The arithmetic mean roughness is used later in this work for the pipe-in-pipe model and both the inner and outer surfaces of the test specimens are considered, as both are in contact with the gas. In the following calculations, the average of R_a in circumferential and longitudinal direction are used as surface roughness and their values are shown in Table 3.1.

Table 3.1 - FRP roughness values

	Internal surface	External surface
ε_{CFRE} [μm]	0.359	0.447
ε_{GFRE} [μm]	0.638	1.757
ε_{GFRPP} [μm]	0.606	0.628

It is worth noting that these values are two orders of magnitude lower than those typical of commercial steel, in the order of 50 μm.

4 Permeation test

Gas permeation involves the transmission of a gas through a material and comprises several fundamental steps, including adsorption, absorption, diffusion, and desorption. Diffusion is the time-determining step and is driven by the flow of matter aiming to equalize a concentration difference. Permeability is defined as the product of the diffusion coefficient D and the solubility coefficient S that relates the concentration and pressure of a gas at the barrier's surface.

$$P = D\,S$$

The equipment used for the tests consists of the Automated Measurement and Control Box (AMB) from the company iChemAnalytics GmbH and the ElyFlow test cell from Gaskatel. The tests are conducted by adapting the electrochemical method in patent [6], originally developed for metallic materials as a simplification of the ISO 17081 standard procedure, to non-conductive FRPs, being less expensive and safer in its application than the manometric method in ISO 15105 standard.
The fundamental principle involves measuring the current generated by the oxidation of hydrogen atoms, which are electrolytically produced in a loading cell. These atoms adsorb and diffuse through the sample to the so-called oxidation cell. Since the samples made of FRP need to be electrically conductive, one of the production steps involves depositing a palladium coating using sputtering, which also acts as a catalyst for the hydrogen oxidation reaction (HOR), ensuring that diffusion is transport limited. However, further investigations need to be carried out regarding the influence of this coating on the reliability of the results since permeation can only occur in atomic form in metals, unlike polymers.
For each hydrogen atom that diffuses, an electron is emitted due to the HOR, and therefore, it's possible to correlate the hydrogen flow with the permeation current (see equation (4.1)). This is achieved by subtracting the passivation current, which is caused by the exposure of the metallic coating to the electrolyte in the oxidation cell, from the total measured current.

$$J_H = \frac{I_{perm}/A}{F} \tag{4.1}$$

To determine the diffusion coefficient, there are three possible methods that refer to the transient regime of diffusion. Two of these methods correlate the sample thickness with the time required to reach a permeation current equal to a certain fraction of the steady-state current (lag time and breakthrough methods), while the last one involves fitting the experimental data with Fick's second law (see Figure 4.1).

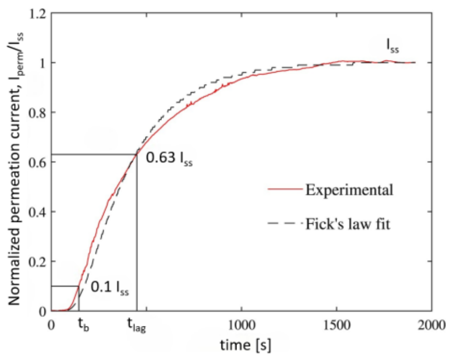

Figure 4.1 - Visual representation of thresholds for different D calculation methods

However, the results obtained from experimental tests are not satisfactory and appear to be incorrect, since the trend of the current over time is anomalous. Improvements to experimental devices are suggested and, for subsequent calculations, values obtained by literature models will be used, as detailed in the thesis.

5 Fluid dynamic model

A fluid dynamic model was developed to assess the competitiveness of the pipe-in-pipe concept compared to alternatives, considering the influence of above discussed roughness and H_2 permeation. To describe the gas flow, a 1D steady-state finite volume model was used, discretizing the pipe into small volumes characterized by constant gas properties. The assumptions are: (i) constant pipe section; (ii) 1D flow; (iii) compressible fluid; (iv) newtonian fluid; (v) isothermal flow.

The compressibility factor *Z* is one of the factors that most influences the behaviour of the transported gas, and it is an indicator of the deviation from ideal behaviour. Since the study conducted in this thesis focuses on a single pipe with a limited number of sections, it is possible to use the complete formulation. It is decided to estimate it, as well as other thermophysical properties, by using the library REFPROP, which relies on experimental data and continuously updated and validated mathematical models.

There are also various correlations for the friction factor depending on the flow conditions. When in the turbulent regime, the implicit Colebrook-White equation provides the most accurate results. However, explicit equations like the Hofer formula are often preferred for their simplicity while still maintaining accuracy.

6 Fluid dynamic assessment: blend transport

A fluid dynamics analysis of the transport of an H_2-NG blend is performed as a reference, as this is currently the most investigated option.

The composition of natural gas considers an Algerian gas (89.9% CH_4, 8.4% C_2H_6, 1.2% C_3H_8, 0.5% N_2) and analysed percentages of hydrogen in the blend are 0%, 2% (limit in Italy), 5% (maximum in Spain), 10% (in Germany), 20% (frequently used in blending projects), 50%, 80%, 90% and 100%, to consider also substantial concentrations.

The analysis focuses on the transmission network, and parameter values will be typical of the first species of pipeline, according to the classification in Italy. We consider metallic pipes with a diameter of 0.7 m and roughness of 46 μm operating in two distinct scenarios, which differ in initial and final pressures (at the compressor station), p_{in} and p_{fin} respectively. Scenario A represents the national network, with p_{in} = 70 bar and p_{fin} = 50 bar, while Scenario B represents the regional network, with p_{in} = 50 bar and p_{fin} = 30 bar. Two different cases are studied and are presented below: "Constant energy" and "Retrofit".

6.1 Constant energy

The energy flow rate $\dot{E}$ of blends is imposed equal to that of pure NG (2207 MW), to simulate a null variation in the amount of energy received by final users. Being the higher heating value (HHV) of H_2 (12.09 MJ/Sm³) lower than that of NG (39.73 MJ/Sm³), a larger volume flow rate *F* is required for blends. Also pressure losses increase for the blend and reach a maximum for an H_2 fraction close to 80%, corresponding to a minimum of the distance at which the compressor station is located, i.e. L_{fin} (see Table 6.1). This behaviour beyond a certain H_2 fraction is due to the larger contribution to pressure losses of the velocity increase, compared to the decrease in density. In general, velocities for the 100% H_2 are more than three times those of NG.

Table 6.1 - Volume flow rate and compressor station distance (Constant energy)

	% H_2	**0%**	**20%**	**80%**	**100%**
	F [kSm³/h]	200.0	232.3	451.0	657.2
A	**L_{fin} [km]**	1060	880	600	720
B	**L_{fin} [km]**	680	580	400	480

Comparing the two scenarios, the average pressure drop per km of the national grid is around 1.5 times that of the regional grid, while velocities are higher in the latter, due to lower pressures for the same volume flow.

6.2 Retrofit

This analysis aims at simulating the retrofit of the existing infrastructure, imposing the distance L_{fin} of compressor stations equal to natural gas, 1060 km for scenario A and 680 km for B.

Figure 6.1 shows the development of volume and energy flow rate as the hydrogen percentage increases, respectively. F increases monotonically, E reaches a minimum for percentages close to 80%, beyond that there is a more abrupt increase in F than a decrease in HHV.

The gas velocity follows the same trend as F, increasing for larger fractions of H_2, and from scenario A to B.

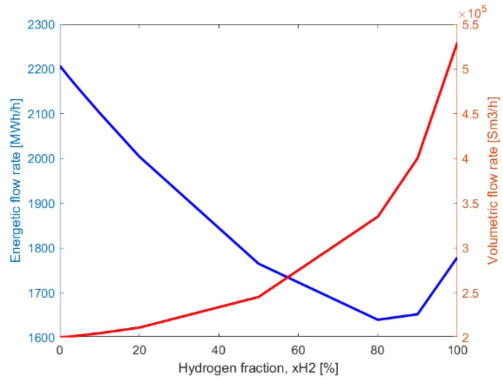

Figure 6.1 - Volume and energy flow rate

7 Fluid dynamic assessment: pipe-in-pipe system

The pipe-in-pipe system consists of the insertion of a smaller diameter pipe inside a larger pipe, allowing the transport of hydrogen inside the former and natural gas in the annular section. This also follows the future consumption projected in the net zero emission scenario, with continued use of natural gas and increasing use of hydrogen, and a possible future stop of natural gas flow, with the use of annulus as a safety cushion gas layer.
The fluid-dynamic model used is the 1D model presented in Section 5. Accordingly, the analysis holds for both concentric and eccentric systems, since resulting turbulence is not accounted for.

7.1 Model details

The inner pipe, with a diameter of Di, is made of GFRE, CFRE or GFRPP, and its respective roughness analysed in Section 3, the outer pipe is a metal pipe of the first species of the existing NG network, with a roughness of 46 μm and diameter Do. The annulus is modelled as an equivalent pipe with a diameter equal to the hydraulic diameter, i.e., $D_o - D_i$, and for the calculation of the friction factor of the natural gas flow, a roughness equal to the weighted average over the fluid-wetted areas of the FRP and steel roughness was considered.
The flow rates of the "Retrofit" case seen in Section 6.2 are used to make an analogy and are divided between H_2 and NG. The various pipe-in-pipe cases are still referred to in terms of the H_2 fraction in the overall transported gas, as with the blend. Only the 50% and 80% H_2 cases are investigated, as they justify the development of a pipe-in-pipe system (nor too low, neither pure hydrogen).
Again, scenarios A and B described in Section 6 are considered.

7.2 Influence of diameter ratio

The results are limited to GFRE since it has been confirmed that the different roughness of the three FRP materials has negligible effects on fluid dynamics and GFRE will be considered in a following analysis on permeation.
Increasing Di/Do ratio, keeping the value of Do fixed, for the same fraction of hydrogen, the pressure drop of H_2 decreases and that of NG decreases. They are also greater when considering the boundary conditions imposed for the regional network. The "optimum" diameter ratio was considered to be that at which the pressures of the two gases on the two sides of the FRP pipe are equal, allowing H_2 and NG to be compressed at the same compressor station at an acceptable distance and to focus on hydrogen permeation. For the inner tube, the mechanical requirements are neglected as it is subjected to zero pressure difference and pressure fluctuations are not considered in this preliminary work, while the outer tube is already designed for such conditions. This optimum value is obtained by minimising the root mean square error (RMSE) of the pressure difference between H_2 and NG evaluated in n sections and taking zero as the target value:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(p_{H2,i} - p_{NG,i})^2}{n}} \tag{7.1}$$

The optimum diameter ratio results equal to 0.40 for 50% H_2 and 0.53 for 80% H_2 in both scenarios, thus not depending on pressure. This value is the one used in the subsequent analysis.
In Table 7.1 the distance of the compression stations obtained in the optimum condition is compared with those required in the "Retrofit" case for the blend seen in Section 6.2. As the table shows, the distance between compression stations is significantly lower than in the blend configuration. Accordingly, the CAPEX required for the pipe-in-pipe system are higher since it is required a frequency of compressor stations that is five times that for the blend. The compression power of the blend is lower than that of the pipe-in-pipe, but OPEX are not that influenced being both values about 0.015-0-035% of the transported energy.

Table 7.1 - Distance of compressor stations for the optimum pipe-in-pipe and blend

	% H_2	50%	80%
A	$L_{fin,PIP}$ [km]	211	200
	$L_{fin,BLEND}$ [km]	1060	
B	$L_{fin,PIP}$ [km]	128	121
	$L_{fin,BLEND}$ [km]	680	

7.3 Hydrogen permeation through the FRP inner pipe

In this section, an analysis of hydrogen permeation through the GFRE inner tube with fibre volume fraction of 60% is carried out, using a theoretical model and interpolating literature data, resulting in a permeability of $1.14 \cdot 10^{-10}$ mol/(m.s.MPa). For both scenarios and H_2 fractions, there is no relevant benefit in terms of permeation reduction beyond 10 mm in wall thickness (instead it might be required due to mechanical issues, not considered). The permeation flow as a function of wall thickness for the 50% H_2 case is shown in Figure 7.1.

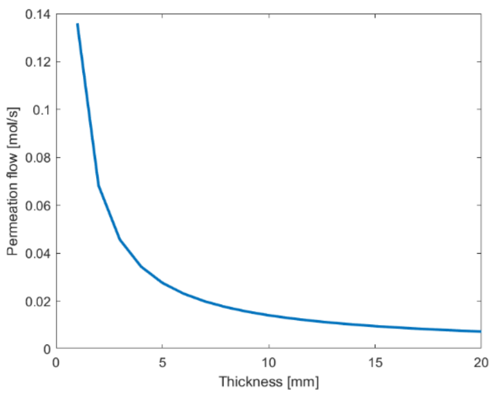

Figure 7.1 - H_2 permeation flow as a function of wall thickness for 50% H_2, scenario A

An assessment at the end of the pipe is then made of the contamination of the NG flowing through the annular section for a thickness of the GFRE pipe of 10 mm and the results are shown in Table 7.2.

Table 7.2 - NG contamination at pipe outlet by permeated hydrogen

	% H_2	$\dot{n}_{H2,perm}$ [mol/s]	$ppm_{H2,out}$
A	50%	0.0140	0.970
	80%	0.0169	2.142
B	50%	0.0061	0.413
	80%	0.0075	0.928

In all scenarios, the final concentration of hydrogen in natural gas is about 0.5-2 ppm and the effect of this injection is insignificant on NG quality.

8 Conclusions

This thesis is first aimed at the experimental characterisation of fibre-reinforced polymers (FRP) as promising materials for hydrogen transport in pipelines, and then to develop a numerical fluid dynamics analysis of the pipe-in-pipe system as an alternative to blend transport for retrofitting the existing natural gas network. Two scenarios representing the national and regional grids are distinguished.

FRPs show roughness that is two orders of magnitude lower than typical metal pipes (in the order of 0.5-1 μm and 50 μm respectively). The differences between the various analysed FRP materials (CFRE, GFRE, GFRPP) are not relevant for pressure drops in transmission pipes due to the large diameters. This is why GFRE was chosen for the inner pipe of the pipe-in-pipe system. Adopting a fluid dynamic model and performing a permeation analysis, an optimal diameter ratio of 0.40 or 0.53, depending on whether the hydrogen transported is 50% or 80% of the total gas, together with a wall thickness of 10 mm, has been identified. This guarantees virtually unchanged NG quality in the annulus without unnecessary increase in weight and cost, allowing mechanical stresses to be neglected and compressing the two gases at the same distance of more than 200 km for the national network and 120 km for the regional. Both values are far lower than in an equivalent case of blend transport, about one-fifth, and this significantly increases the infrastructure CAPEX. The compression power required for the pipe-in-pipe is 10-20% higher than that for the blend, but both values are in the order of 0.02-0.04% of the energy flow rate and their influence on OPEX is very limited.

Further research should focus on obtaining accurate permeation data for FRPs, either with the electrochemical method, also studying the influence of the Pd coating, or with an upgrade, e.g., using molecular H_2 gas directly. In addition, for more comprehensive results, the mechanical stresses associated with pressure fluctuations and, in a 2D model, the influence of the degree of eccentricity of the inner tube on the fluid dynamics must be considered.

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