HYDROGEN REFUELING STATIONS: SAFE FILLING PROCEDURES

Faudou, J-Y.[1], Lehman, J-Y.[2] and Pregassame, S.[3]
[1] AIR LIQUIDE, DICI, 33 Boulevard Valin, Paris, 75015, France
[2] AIR LIQUIDE, Engineering Dpt., 57 avenue Carnot, BP. 313, Champigny-sur-Marne, 94503, France
[3] AIR LIQUIDE, CRCD, 1 chemin de la Porte des Loges, B.P. 126, Jouy-en-Josas, 78354, France

ABSTRACT

Safety is a high priority for a hydrogen refueling station. Here we propose a method to safely refuel a vehicle at optimised speed of filling with minimum information about it. Actually, we identify two major risks during a vehicle refuelling: over-filling and over-heating. These two risks depend on the temperature increase in the tank during refuelling. But the inside temperature is a difficult information to get from the station point of view. It assumes a temperature sensor in a representative place of the tank and an additional connection between the vehicle and the station for data exchange. The refuelling control may not depend on this parameter only. Therefore, our objective was to effectively control the filling, particularly to avoid the two identified risks independently of optional and safety redundant information from the vehicle. For that purpose, we defined a maximum filling pressure which corresponds to the most severe following conditions: if the maximum temperature is reached in the tank or if the maximum capacity is reached in the tank. This maximum pressure depends on a few filling parameters which are easily available. The method and its practical applications are depicted.

1.0 INTRODUCTION

To introduce hydrogen in transport applications, safe refueling of the vehicles should be guaranteed. This operation is not easy to manage because of the high pressures (350bar or even 700bar) and the short refuelling time requested. The heat produced by the quasi adiabatic compression of the gas in these conditions may cause weak points and damages to the vessel which can lead to its rupture. Because of that, the step of vehicle refuelling is highly critical from safety point of view.

Pressure and temperature conditions into a pressure vessel define different domains that are presented in fig. 1 for a typical 350bar vessel. For transport applications, type III (metallic liner + composite) or type IV (polymeric liner + composite) vessels are usually used. These kind of vessels are certified for a given temperature window (usually -40 / +85°C).

This graph presents the operating window of the 350bar pressure vessel and four other domains that present a risk for the vessel:

- Low temperature domain (below -40°C)
- Over pressure domain (above 438bar)
- Over heating domain (above 85°C)
- Over filling domain (above 350bar at 15°C)

Over heating is a known risk which occurs especially when the remaining pressure in the vessel is low and when ambient temperature is high. The low temperature risk may occur only in cold filling cases. The over filling risk can occur in cold countries when the ambient temperature is low. In normal filling conditions, over pressure as compared to the service pressure is usually used to compensate the heat of compression. In low ambient temperature case, the filling can be stopped at high pressures but the temperature of the gas at the end of the filling could be not so high. When the pressure vessel is exposed to high temperature during the day, the pressure may then reach unexpected values.

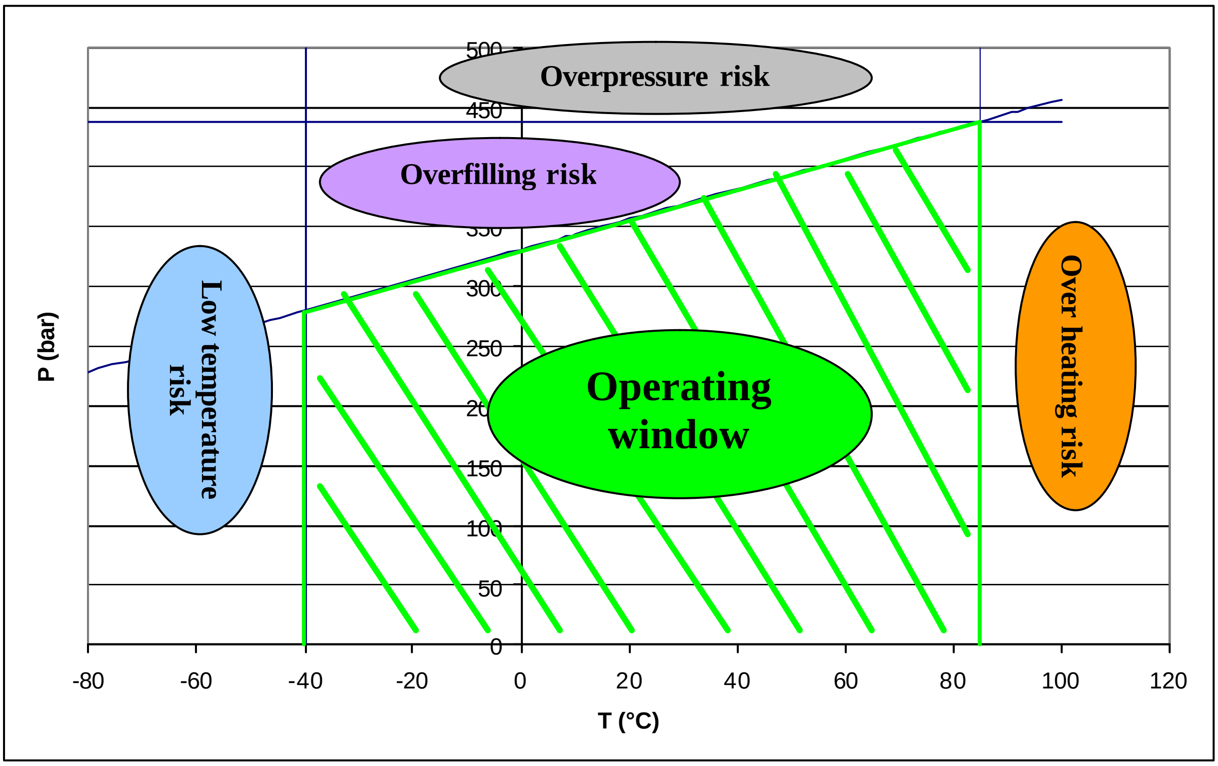

Figure 1: Operating and risk domain for a 350bar typical pressure vessel

The over pressure domain is quite easy to manage as the pressure measured in the filling hose during refueling is the same than the pressure in the vessel. This parameter is therefore easy to control.

The over heating, over filling and low temperature risks depend on the gas temperature evolution inside the vessel during the filling. This information is not easy to get for different reasons:

- To introduce a temperature sensor in the vessel may cause problems of gas tightness which are not easy to manage
- A second connection line between the vehicle and the station should be installed for the data exchange
- The temperature of the gas could be not homogeneous during the refuelling step. Highest temperatures are usually measured at the end of the vessel [1-2-5]. Therefore we should find the most appropriated place(s) for the temperature sensor(s) which will give a value representative of the whole vessel.

Moreover, such equipment will be installed by the vessel manufacturer or by the car manufacturer but will be used by the station operator. The station operator should then control the filling with unknown equipment which is not a reliable situation.

The filling control is therefore crucial for station operators independently of filling station control system. They should be able to safely refuel vehicles which do not communicate data about their on-board storage and particularly the gas temperature inside the pressure vessel.

For that purpose we developed a filling control tool which is able to predict when the station operator has to stop the filling to remain in the operating window of the pressure vessel. The predictive tool does not need any information from the vehicle and is presented more in details in the following part.

A similar tool already exists [1-2]. This tool uses the measured transferred mass which is not a reliable enough parameter for the moment. Moreover, the transferred mass measured could be used as an other controlling mean in our case which should be safer. A last point is that our tool takes into account the cold filling case. For passenger car for example, requirements are particularly demanding : short refueling time and high storage pressure are needed. Such requirements will be hardly met with an ambient temperature filling. Cold filling will therefore be a way to solve the issue of overheating.

2.0 FILLING CONTROL PROCEDURES

Two different procedures were defined depending on the filling process used to refuel the vehicle:

- A “warm filling procedure” when the filling gas temperature is close to ambient temperature
- A “cold filling procedure” when the filling gas temperature is below ambient temperature.

In the warm filling case, two risks have to be avoided: over heating and over filling. In the cold filling case, the two main risks that have to be avoided are the low temperature risk and over filling risk.

2.1. Warm filling procedure

During a vehicle refuelling, four main parameters have an influence on the final temperature reached:

- The rest pressure or initial pressure in the vessel before the filling
- The exterior temperature (ambient temperature)
- The filling speed
- The final pressure.

The first two parameters are imposed by the filling conditions. The last parameters are operating parameters and can be chosen by the station operators.

The safe filling procedure defined consists in determining a maximum on-board storage pressure before starting to fill as a function of the filling speed and of the imposed parameters so as to avoid the two identified risks:

- Over heating
- Over filling.

This maximum on-board storage pressure is a minimum of two independent functions:

- A first function which defines the final pressure for a 100% filling whatever the final temperature may be
- An other function which defines the final pressure corresponding to the maximum gas temperature (85°C for example) whatever the final H_2 mass stored may be

This procedure is summarized in fig. 2 which gives the final pressure as a function of the filling speed for a given rest pressure and a given ambient temperature.

As the maximum on-board storage pressure is the minimum of the two functions defined, if the final pressure of the filling is kept below this maximum pressure, we are sure that the gas temperature is below 85°C **and** that the mass is equal to or below a 100% filling.

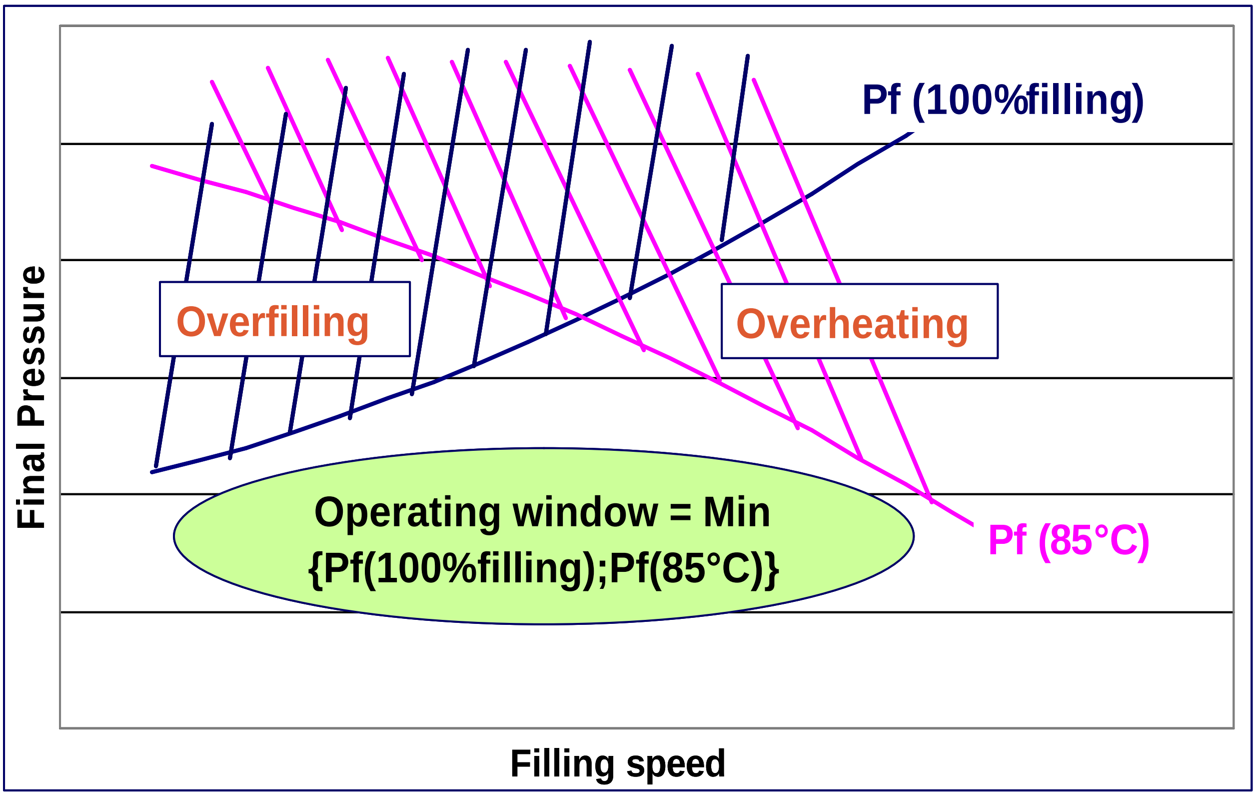

Figure 2: Maximum on-board pressure for a given rest pressure and a given ambient temperature

2.2. Cold filling procedure

Cold filling is used to compensate the heat of compression during the fast filling and thus to reach a 100% filling even if the rest pressure is low and/or the exterior temperature is high. Therefore the interest of the cold filling is to reach the 100% filling.

Attempts were made to evaluate what the filling gas temperature could be to reach a 100% filling [3]. Actually, during a vehicle refuelling, five main parameters have an influence on the final temperature reached:

- The rest pressure or initial pressure in the vessel before the filling
- The exterior temperature
- The filling speed
- The filling gas temperature
- The final pressure.

The first two parameters are imposed by the filling conditions. The last parameters are operating parameters. Either the final pressure or the filling gas temperature can be imposed by the process. For example, if the filling process uses high pressure buffers where H_2 is stored at 400bar to fill a 350bar on-board storage, the final pressure is less than 400bar. If the station is equipped with an ethylene glycol cooling machine, the minimum filling temperature is -20°C.

The safe filling procedure defined consists in setting either the final pressure or the filling gas temperature (for example considering the filling process used), and determining the other parameter as a function of the first parameter, the filling speed and the imposed parameters in order to reach a 100% filling.

Of course the final pressure should be less than the maximum pressure (438bar for example) so as to avoid over heating and should be more than 280bar to avoid the low temperature risk.

Fig. 3 summarizes this procedure giving the final pressure for a given filling speed and a given filling gas temperature.

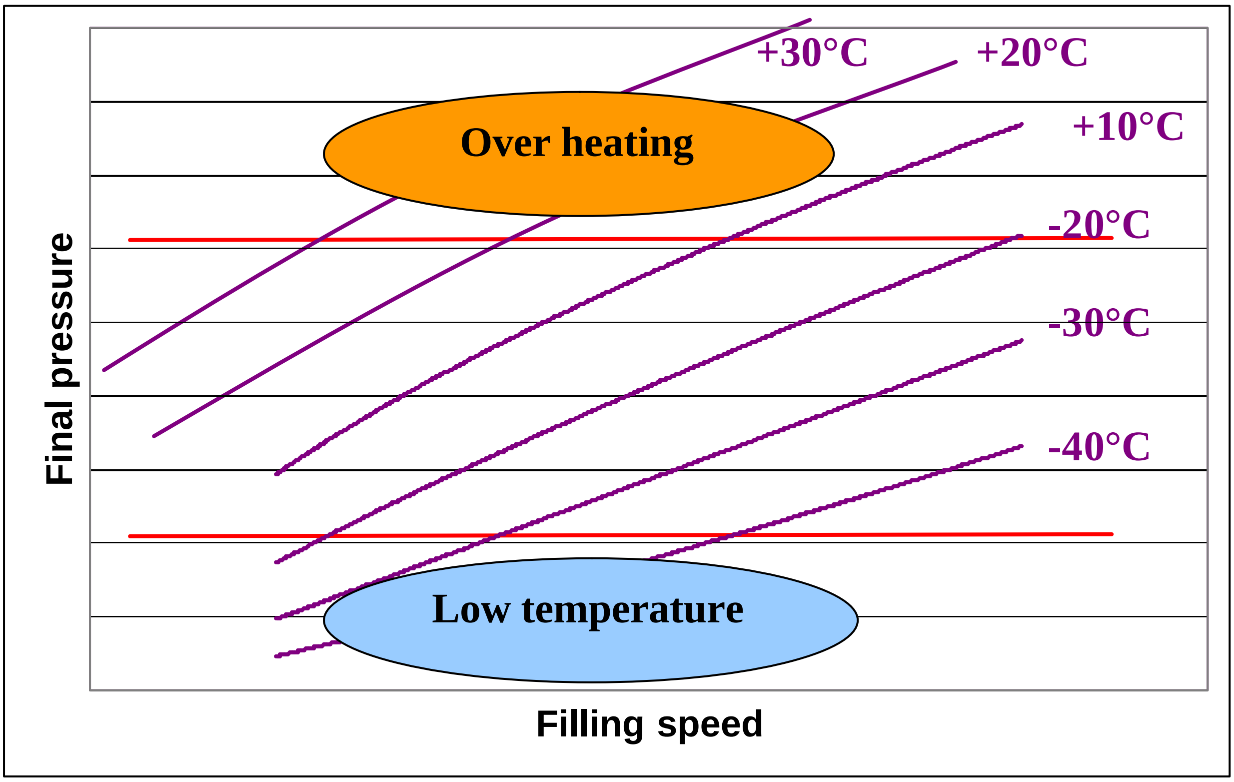

Figure 3: Final pressure for a given rest pressure and a given ambient temperature

If the filling is stopped at the final pressure calculated and if the filling temperature is kept at the set value (or the contrary), we are sure to reach a 100% filling staying in the operating window of the vessel.

3.0 FILLING CONTROL TOOL

3.1 Presentation of the tool

The maximum on-board storage pressure as defined in paragraph 2.1 and the filling gas temperature as defined in paragraph 2.2 were estimated thanks to a simulation tool developed by AIR LIQUIDE. This tool is able to predict the gas temperature evolution during fast filling process and was described in several papers [4-6]. This simulation tool was successfully validated with high pressure hydrogen in a full scale 350bar hydrogen pilot station located in Sassenage (FRANCE). Knowing the filling conditions (rest pressure, exterior temperature, filling speed, final pressure and filling gas temperature), the tool is able to accurately calculate the final gas temperature reached.

With this tool we were able to realize tables that directly give the maximum on-board storage pressure or the filling gas temperature. Table 1 is an example for warm filling and table 2 is an example for cold filling. The figures given in both tables depend of course of the vessel type and geometry.

Table 1. Example of on-board maximum pressure for a type 3, 350bar vessel (bar).

Filling speed = 1bar/s		Exterior temperature (°C)		
		0	20	40
Rest pressure (bar)	1	401	430	158
	100	383	413	401

In table 1, blue cases mean that the filling is limited by the mass (100% filling reached), orange cases mean the filling is limited by temperature (85°C reached).

Table 2. Example of filling gas temperature for a type 3, 350bar vessel (°C).

Filling speed = 1bar/s Final pressure = 400bar		Exterior temperature (°C)		
		0	20	40
Rest pressure (bar)	1	0	-20	-40
	100	32	0	-35

When exterior temperature is very low, cooling is not necessary (yellow cases). Ambient temperature is low enough when for example the rest pressure is 1barA and the exterior temperature is 0°C. When the rest pressure is 100bar and the exterior temperature is 0°C, we had to fill the vessel with hot gas to reach a 100% filling at 400bar. In that case of course, it makes no sense and we should stop the filling at a lower pressure than 400bar. For that purpose the first procedure can be used to calculate the final pressure needed in that case.

In order to easily use this kind of tool in a refueling station we found the following mathematical relations:

Pf (100% filling) = f(V, T0, P0) (1)

Pf (85°C) = f(V, T0, P0) (2)

Pmax = Min{Pf(100%filling), Pf(85°C)} (3)

Te = f(Pf, V, T0, P0) (4)

where

- for warm filling : Pf (100%filling) is the final pressure for a 100% filling (bar), Pf(85°C) is the final pressure corresponding to the maximum temperature (bar), Pmax is the maximum on-board pressure (bar)
- for cold filling : Te is the filling gas temperature (K), Pf is the final pressure (bar)
- V is the filling speed (bar/s), T0 is the exterior temperature (K) and P0 is the rest pressure (bar).

The relations (1) to (4) have a good accuracy (5%). For the moment they depend on the vessel type and geometry. We are currently working on a generalized tool.

With these relations, the predictive tool can be easily programmed in the control unit of any refuelling station.

3.2 Examples of the operation board

Fig. 4 shows two examples of operation boards for the warm filling procedure.

The interest of showing these operation boards is to illustrate what could be the limiting parameter is:

- mass, in the first example
- temperature, in the second example.

As can be seen, three parameters are necessary to calculate the maximum on-board pressure: the exterior temperature and the initial pressure which are imposed, and the filling speed which is the operator choice. The filling speed is equivalent to the refuelling time: any of these 2 parameters can be used to calculate the maximum on-board pressure.

Ambient temperature	20	°C	instantaneous measure
Initial pressure	100	bar	fixed measure
Filling speed	**1**	**bar/s**	operator choice
Maximum allowed pressure	**413**	**bar**	estimation
Fillling rate	100%		estimation
Final temperature	65	°C	estimation
Total filling time	5,2	min	estimation
Actual pressure in the filling hose		bar	instantaneous measure
Actual filling time		min	instantaneous measure
Actual pressure in the tank		*bar*	*optional*
Actual temperature in the tank		*°C*	*optional*

measure
operator choice
estimation
filling limiting parameter
optional information

Ambient temperature	40	°C	instantaneous measure
Initial pressure	100	bar	fixed measure
Filling speed	**1**	**bar/s**	operator choice
Maximum allowed pressure	**401**	**bar**	estimation
Fillling rate	92%		estimation
Final temperature	85	°C	estimation
Total filling time	5,0	min	estimation
Actual pressure in the filling hose		bar	instantaneous measure
Actual filling time		min	instantaneous measure
Actual pressure in the tank		*bar*	*in option*
Actual temperature in the tank		*°C*	*in option*

measure
operator choice
estimation
filling limiting parameter
optional information

Figure 4: Examples of the operation board

This filling speed (or the refuelling time) can be chosen manually (by the operator) or automatically (by the control unit of the station) depending on a compromise between the time and the filling rate constraints. For public use, an automatic control would be safer. The operator just has to connect the station to the vehicle and then the control unit can calculate the maximum on-board pressure (using optimisation algorithms) and starts the filling operation.

4.0 RISK EVALUATION DURING FAST FILLING

Table 3 and table 4 give an idea the final conditions (hydrogen mass stored or final gas temperature) if such a filling control is not used and if the final pressure of the filling is 438bar.

Table 3. Final temperature if final pressure is 438bar (°C).

Filling speed = 1bar/s		Exterior temperature (°C)
		40
Rest pressure (bar)	1	**100°C**
	100	87°C

In case of over heating risk (when the exterior temperature is high and/or when the rest pressure is low), the gas temperature can reach 100°C, or even more for higher exterior temperature.

Table 4. Final H2 mass stored if final pressure is 438bar (%).

Filling speed = 1bar/s		Exterior temperature (°C)	
		0	20
Rest pressure (bar)	1	107%	102%
	100	110%	105%

In case of over filling risk (when the exterior temperature is low and/or when the rest pressure is high), over filling can be as high as 110% if the gas temperature increases to 85°C and the pressure reaches 495bar. It will be even higher for lower temperature and higher rest pressure.

These results show that on one hand, such a predictive tool is necessary to avoid any dangerous situation as the one presented below. On the other hand, as the constraints in storage pressure and in refuelling time will go stronger and stronger, it might be worth to investigate new materials that stand higher temperatures.

5.0 CONCLUSIONS

Refueling step is highly critical from safety point of view. During this process, the vessel is subject to high temperature gradients and to high pressures (because of the over-pressure usually used to compensate the compression heat). This is why this operation has to be carefully managed despite the fact that the station operator has usually no information return from the vehicle.

In order to manage this situation, AIR LIQUIDE is developing all the necessary tools to safely handle with this operation. One of the first tools developed was a modeling tool which is able to predict the gas temperature evolution during filling process. This tool was validated with high pressure hydrogen for fast filling situation with a good accuracy. The complementary tool is a filling management tool which can be easily implemented in a refueling station. This tool is able to predict what the safest way to refuel a vehicle is and forms the subject of a patent pending. Two different tools are developed (for warm and cold filling) and of course these tools can be combined. The interest of such a predictive tool is that the filling is controlled with the pressure measured in the filling hose only (and eventually the filling gas temperature). The final conditions are then calculated prior to any filling operation and no additional data is needed from the vehicle during the filling process. As the maximum on-board storage pressure can be calculated automatically by the station control unit, the filling process can be fully automatic and therefore safer.

This tool was first developed for a safety interest but can also be used to optimize the filling. Actually fast filling has two antagonistic constraints: the refueling time and the refueling rate. Such a predictive tool can also help to choose the best way to refuel the vehicle finding a compromise between both refueling time and refueling rate and always keeping in mind the safety priority.

At the current step of the study the tool depends on the vessel type and geometry. In the hypothesis of a spread use of hydrogen vehicles and that different vehicles can be refueled in the same station, this is not sufficient. For that purpose we are currently working on a generalized tool.

6.0 DISCLAIMER

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