

LA-UR- 95-2464

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**Title:**

HYDROGEN VEHICLE FUELING STATION

**Author(s):**D. E. Daney, F. J. Edeskuty, M. A. Daugherty, F. C. Prenger,  
and D. D. Hill**Submitted to:**1995 Cryogenic Engineering Conference  
July 17-21, 1995  
Columbus, HO

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## HYDROGEN VEHICLE FUELING STATION

D. E. Daney, F. J. Edeskuty, M. A. Daugherty, F.C. Prenger, and D. D. Hill

Los Alamos National Laboratory  
Los Alamos, New Mexico, 87545, USA

### ABSTRACT

We describe a hydrogen vehicle fueling station that receives and stores hydrogen in liquid form and dispenses it either as a liquid or compressed gas. The economics that accrue from the favorable weight and volume advantages of liquid hydrogen support this concept both now and probably for some time to come. Our model for liquid transfer to a 120 L vehicle tank shows that transfer times under five minutes are feasible with pump-assisted transfer, or for pressure transfer with subcooling greater than 1 K. Our model for compressed gas transfer shows that underfilling of nearly 30 percent can occur during rapid filling. Cooling the fill gas to 214 K completely eliminates underfilling.

### INTRODUCTION

Because of the need to improve urban air quality, hydrogen-fueled vehicles have become a subject of increasing interest in recent years; in fact, a number of demonstration projects are planned or in progress around the world. Hydrogen fueling stations are essential to a practical demonstration of these vehicles. Furthermore, only a practical demonstration can accurately and convincingly address a number of issues such as safety, efficiency, design, and operating procedures. Of particular importance is safety which encompasses both technical risk and public perception of that risk. Regardless of whether the vehicle is powered by an internal combustion engine or fuel cell, or how hydrogen is stored on-board, the fueling station is the critical technology that links the local hydrogen storage facility and the vehicle.

A fundamental assumption guiding the Los Alamos National Laboratory (LANL) program is that the station should receive hydrogen in liquid form because of near term economics, which result from the favorable weight and volume advantages that accrue from shipping liquid rather than gas. This view is confirmed by our conversations with US industry (which delivered 92 percent of non-pipeline merchant hydrogen as liquid in 1993 <sup>1</sup>) and by systems studies (which favor LH<sub>2</sub> supplied fueling stations for capacities up to about 300 vehicles/day <sup>2</sup>). At least three methods of onboard fuel storage (liquid, compressed gas and metal hydride) are under consideration. Because it is unclear what the preferred method will be, or if there will be only one method, we are designing our fueling station to deliver hydrogen as either a liquid, high pressure gas, or low pressure gas so that it can accommodate vehicles with any type of fuel tank. Figure 1. illustrates the LANL fueling station concept.

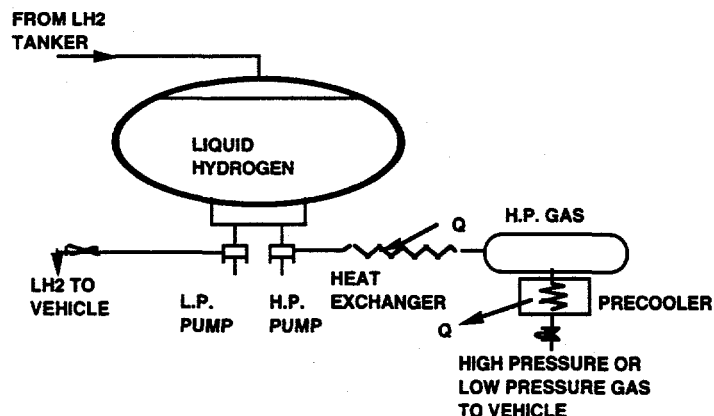


Figure 1. Los Alamos hydrogen fueling station concept.

Vehicle tank fill rates are an important consideration since refueling times must be short (less than five minutes) if the motoring public is to accept hydrogen as a fuel. In the case of liquid vehicle tanks, properly selected transfer and vent line sizes will give the required fill rates if venting is allowed. Because venting wastes hydrogen and is a minor safety hazard, no-vent filling is preferred. With no-vent filling, however, both the thermodynamic state (degree of subcooling) of the liquid in the supply tank and the amount of assist from a transfer pump strongly influence the fill rate. In the case of compressed gas vehicle tanks, fast filling causes significant heating in the tank which results in an underfilling. With compressed natural gas tanks, underfilling by as much as 20 percent is possible.<sup>3</sup> With hydrogen, because of its higher ratio of specific heats, underfilling up to 30 percent can be expected. We have developed models of both the liquid and gas fill processes to study fill rates and the tank heating phenomenon.

## FUELING STATION DESIGN

Figure 2 shows a detailed schematic of the LANL fueling station that will receive hydrogen as a liquid and dispense it as either liquid, high pressure gas or low pressure gas. Near the center of the schematic is the liquid hydrogen (LH2) dewar which receives liquid from a commercial LH2 tanker truck. We anticipate that this dewar will be a leased Customer Service Station, as it is known in the trade.

For LH2 refueling, a centrifugal pump assists the transfer. From the pump the LH2 flows to the vacuum-insulated valve box where the flow is automatically regulated by sequencing solenoid valves with a microprocessor controller. Prior to the start of liquid transfer, the connecting lines are vacuum purged and checked for leaks by the pressure rise technique. The microprocessor, via a control line, sequences the vehicle tank valves and shuts off the vehicle ignition interlock. Under normal transfer conditions there will be no venting from the vehicle tank once the lines are cooled down. To prevent venting to the atmosphere of any gas generated in line cooldown, a gas holder, compressor, and gas storage cylinders are provided. This collected gas maintains the dewar pressure and supplies gaseous hydrogen for gaseous hydrogen (GH2) refueling.

For GH2 refueling, a pump-vaporizer unit ( a high pressure piston pump in combination with a heat exchanger ) generates high pressure hydrogen gas. To reduce the size of the pump-vaporizer required, high pressure gas storage cylinders are provided. These are interconnected for cascade-type discharge, which maximizes their effective storage capacity. As with liquid discharge, valve sequencing is automatic; and a vehicle ignition interlock prevents the vehicle from starting during refueling. A chiller, located between the GH2 storage tanks and vehicle coupling, reduces vehicle tank heating during fast filling.

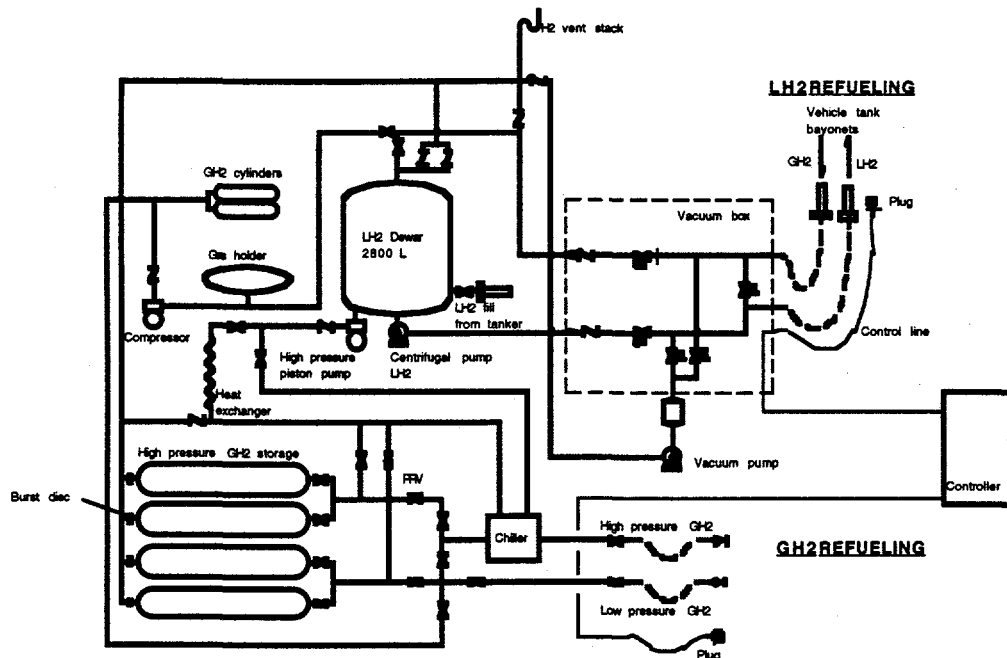


Figure 2. Detailed Schematic of Los Alamos hydrogen fueling station.

## HYDROGEN TRANSFER MODELS

### Liquid Transfer

Our liquid hydrogen transfer model is based on a computer code developed by Daney and co-workers at NIST<sup>4</sup> which simulates both vented and non-vented transfer between the fueling station tank and the vehicle tank. It is a thermodynamic model developed from the differential mass and energy balances applied to both the fueling station tank and vehicle tank, and it uses actual hydrogen properties. We consider both single-phase conditions (that occur during the initial cooldown of an empty tank) and two-phase conditions (that occur after liquid begins to collect in the tank). Either pump-assisted or pressure induced H<sub>2</sub> transfer can be analyzed. The program accepts a wide range of input variables, including heat leaks, tank temperatures, and piping and equipment specifications.

The model begins with the first law of thermodynamics for an open system

$$dU = dQ + h_1 dm_1 + h_2 dm_2 \quad (1)$$

which for single-phase conditions in the vehicle tank gives

$$dT = \frac{\phi T dm + \frac{(h_1 - h)}{C_v} dm_1 + \frac{dQ}{C_v}}{\rho V + \frac{m_w C_w}{C_v}} \quad (2)$$

as the differential temperature equation and

$$dp = \frac{\phi [\theta dm + (h_1 - h) dm + dQ - m_w C_w dt]}{V} \quad (3)$$

as the differential pressure equation prior to venting.

For two-phase conditions in the vehicle tank the change in mass of the liquid phase is given by

$$dm_\lambda = \frac{-\frac{\rho_\lambda}{\rho_v}(dm_1 - dm_2) - \rho_\lambda \left[ m_\lambda \left( \frac{\partial v}{\partial p} \right)_\lambda + m_v \left( \frac{\partial v}{\partial p} \right)_v \right] dp}{1 - \frac{\rho_\lambda}{\rho_v}} \quad (4)$$

and the differential pressure equation prior to venting is

$$dp = \frac{\left[ h_1 - u_v + \frac{\rho_\lambda}{\rho_v}(u_\lambda - h_1) \right] dm_1 + dQ \left( 1 - \frac{\rho_\lambda}{\rho_v} \right)}{F(p)} \quad (5)$$

where

$$F(p) = m_\lambda \left[ \left( \frac{\partial u}{\partial p} \right)_\lambda \left( 1 - \frac{\rho_\lambda}{\rho_v} \right) + \rho_\lambda \left( \frac{\partial v}{\partial p} \right)_\lambda (u_v - u_\lambda) \right] + m_v \left[ \left( \frac{\partial u}{\partial p} \right)_v \left( 1 - \frac{\rho_\lambda}{\rho_v} \right) + \rho_v \left( \frac{\partial v}{\partial p} \right)_v (u_v - u_\lambda) \right] - m_w C_w \left( \frac{\partial T}{\partial p} \right)_{\text{sat}} \left( 1 - \frac{\rho_\lambda}{\rho_v} \right) \quad (6)$$

### Gas Transfer

Our analysis of the temperature rise that occurs during the filling of compressed gas vehicle tanks assumes perfect mixing in the vehicle tank and no heat transfer with the tank wall. For the adiabatic case, combining equations (2) and (3) to eliminate  $m$  gives

$$dT = \left\{ \frac{v \left[ \phi T + \frac{(h_i - h)}{C_v} \right]}{\phi [\theta + (h_i - h)]} \right\} dp \quad (7)$$

as the differential temperature equation for the tank. If we assume an ideal gas equation of state, then integration of equation (7) gives

$$T_2 = T_1 \left\{ \frac{\left( \frac{p_2}{p_1} \right)}{1 + \left( \frac{p_2}{p_1} - 1 \right) \left( \frac{T_1}{\gamma T_1} \right)} \right\} \quad (8)$$

Equation (8) has the interesting property that as the pressure ratio,  $p_2/p_1$  increases without limit

$$\frac{T_2}{T_1} \rightarrow \gamma \quad (9)$$

for the case of an ambient gas supply temperature ( $T_i = T_1$ ). This approach to a fixed temperature ratio, in contrast to an increase with out limit for a closed, adiabatic system, results from the cooling effect of the incoming gas.

The inlet gas temperature,  $T_i$ , required to give a final temperature,  $T_2$ , equal to the initial gas temperature,  $T_1$ , is found from equation (8) to be simply

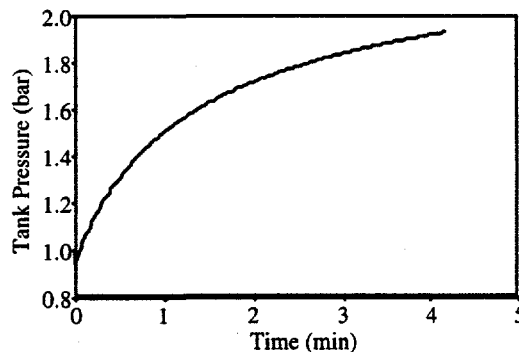
$$T_i = \frac{T_1}{\gamma} \quad (10)$$

Thus, there is a single inlet temperature -- 214 K for hydrogen initially at 300 K -- that will maintain a constant tank gas temperature for all pressure ratios.

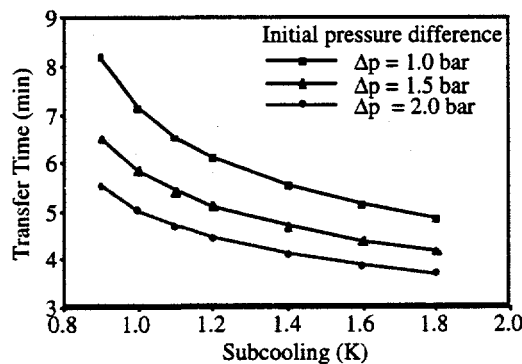
## MODELING RESULTS

### Liquid Transfer

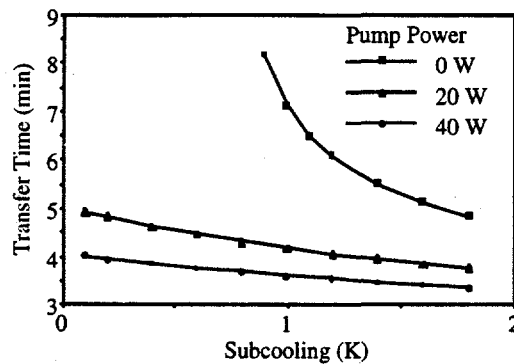
We are using our liquid transfer model to investigate the effects on transfer time of the initial conditions in the vehicle tank, the pressure and degree of subcooling in the supply tank, transfer-pipe size and configuration, and transfer-pump power. Figure 3, which shows the rise in vehicle tank pressure during a pump assisted, no-vent transfer, illustrates the detail inherent in the model. Figure 4, which gives the transfer time as a function of supply tank subcooling and initial pressure difference, illustrates the importance of subcooling. Close to 0.9 K of subcooling is required, and more is desirable if there is no pump to assist the transfer. For the 1/2-inch line in these simulations, rapid (below 5 minutes) transfer is feasible with good subcooling. Figure 5 shows that use of a centrifugal transfer pump can further reduce the transfer time as well as extend the supply tank operating range. For vented transfer, of course, no subcooling is required in the supply tank. Figure 6, which gives transfer time as a function of transfer pipe size, illustrates how the model aids in the design of individual components. A 16 mm ( 5/8-inch ) diameter transfer line size appears to be a good compromise between fast transfer times and easily handled flexible lines with low thermal mass.



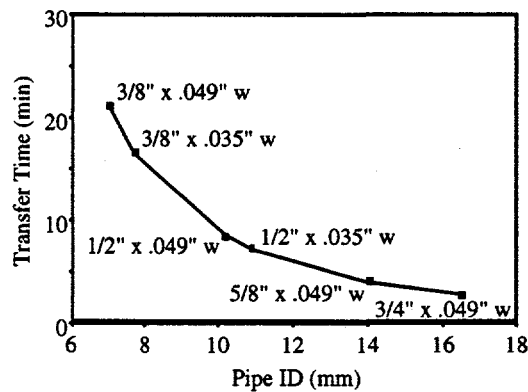
**Figure 3.** Typical vehicle tank calculated pressure history during pump-assisted, no-vent LH2 transfer with 1.0 K of subcooling. Initial vehicle tank pressure is 1.0 bar. Initial pressure difference is 1.0 bar. Pump power is 20 W.



**Figure 4.** Effect of supply tank subcooling on calculated LH2 transfer time for no-vent pressure transfer. Initial vehicle tank pressure is 1.0 bar.



**Figure 5.** Effect of transfer-pump power on calculated LH2 transfer time for no-vent transfer. Initial pressure difference is 1.0 bar. Initial vehicle tank pressure is 1.0 bar.



**Figure 6.** Calculated dependence of LH2 transfer time on pipe diameter for no-vent pressure transfer. The degree of subcooling is 1.0 K. The geometry is: 9.2 m of straight pipe, 2.6 m of flexible pipe, eight elbows and five globe valves.

## Gas Transfer

The warming that occurs in a compressed gas hydrogen vehicle tank during a fast fill with ambient temperature (300 K) gas is illustrated in Figure 7. The curve, generated from equation (8), represents the limiting case of negligible heat transfer from the gas to the tank wall, such as would occur during rapid filling. The associated underfilling of the tank is illustrated in the Figure 8. Because the weight and volume penalties associated with compressed gas vehicle tanks seriously degrade vehicle performance<sup>5</sup>, reducing the loss of capacity due to fast filling becomes particularly important. As discussed above, precooling the fill gas to 214 K holds the tank gas at ambient temperature thus eliminating the problem of underfilling.



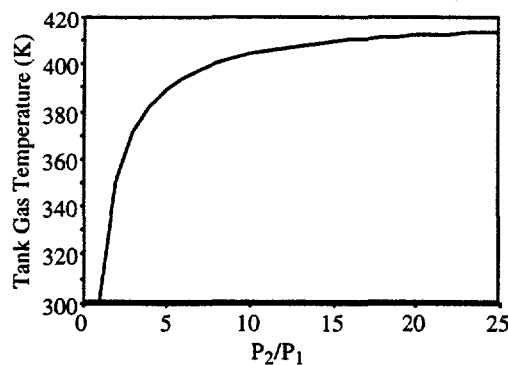


Figure 7. Warming in a GH2 fuel tank during fast fill. These calculations are for the limiting adiabatic case.

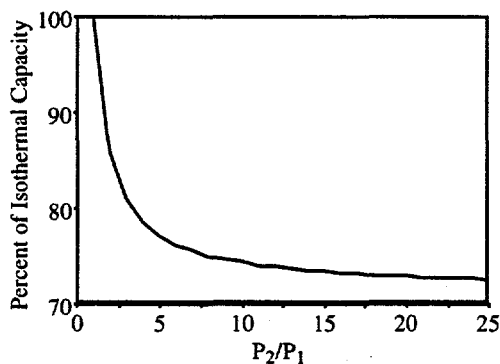


Figure 8. Calculated percent of isothermal GH2 tank capacity that results from an adiabatic fill. The asymptote at high pressure ratios is 71.4 percent full.

## CONCLUSIONS

Refueling hydrogen powered vehicles in less than five minutes and without venting is feasible with a properly designed fueling station. In the case of LH2 refueling, this goal requires either pump-assisted transfer or pressure transfer with subcooling greater than 1 K. In the case of compressed gas refueling, the fill gas should be precooled to reduce or eliminate fuel tank underfilling that results from compression warming due to rapid fill. Precooling the fill gas to 214 K should completely eliminate the problem for hydrogen.

## NOMENCLATURE

$C_p$	specific heat capacity at constant pressure
$C_v$	specific heat capacity at constant volume
$C_w$	specific heat capacity of tank wall
$h$	specific enthalpy; unsubscripted, it refers to single-phase fluid in tank.
$m$	mass; unsubscripted, it refers to single-phase fluid in tank.
$p$	tank pressure
$Q$	heat transferred to tank fluid
$s$	specific entropy
$t$	time
$T$	temperature
$u$	specific internal energy

U	total internal energy of fluid within tank
v	specific volume of fluid within tank; unsubscripted, it refers to single-phase fluid.
V	tank volume

#### Greek symbols

$\gamma$	specific heat ratio, $C_p/C_v$
$\theta$	heat of expulsion, $-\rho \left( \frac{\partial h}{\partial p} \right)_p$
$\phi$	Grüneisen parameter $\phi$ , $\frac{1}{\rho} \left( \frac{\partial p}{\partial u} \right)_p = \frac{\rho}{T} \left( \frac{\partial T}{\partial p} \right)_s$
$\rho$	density

#### Subscripts

i	inlet gas
v	vapor phase
$\lambda$	liquid phase
1	fill stream in liquid fill model; initial gas temperature in gas fill model
2	vent stream in liquid fill model; final gas temperature in gas fill model

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