THE STUDY ON THE INTERNAL TEMPERATURE CHANGE OF TYPE 3 AND TYPE 4 COMPOSITE CYLINDER DURING FILLING

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ABSTRACT

The number of eco friendly vehicle, which is using green energy such as natural gas(NG) and hydrogen(H₂), is rapidly increasing in the world. Almost all of the car manufacturers are adopting the pressurizing fuel method to storage gas. The fuel storage system which can pressurize the fuel as high as possible is necessary to maximize the mileage of the vehicle. In Korea, the most important issue is that makes sure of safety of the fuel storage system, and several tests are performed to verify safety of the composite cylinder especially for Type 3 and Type 4. In this research, an empirical study on the internal temperature change of Type 3 and Type 4 composite cylinder during filling is performed by gas cycling test equipment. In order to measure the temperature, totally twelve sensors(every four sensors on the top, middle and bottom) are installed in each cylinder. As a consequence, large amount of compression heat is generated during rapid filling, and the result, temperature change in Type 4 is greater than Type 3, is confirmed depending on property of the liner material such as thermal conduction and thickness of carbon composite.

1. INTRODUCTION

The world's interest in replacement energy is increasing due to the depletion of natural resources, global warming, and environmental pollution. Amongst the replacement energies, hydrogen is the most likely eco-friendly energy to replace the fossil fuel [1]. Nations (mostly USA, Europe, and Japan) have researched on the safety regulations and codes for hydrogen since 2003 [2]. In order to apply hydrogen into vehicles, there were efforts being made to construct an infrastructure of economy for hydrogen which includes storage facilities and hydrogen products, and South Korea has been researching aggressively on hydrogen energy since 2005. Gas is compressed under high-pressure in order for natural gas and hydrogen to be used as fuels, and therefore, there is a need for inventing a fuel storage system which can store the fuel with highest possible pressure for longer travel distances. A composite cylinder which is safer and lighter is appropriate for high-pressure hydrogen gas. Especially, Type 3 and Type 4 composite cylinders are viewed as the safest amongst other composite cylinders because both of them are light. Type 3 is free from hydrogen embrittlement and Type 4 has superior endurance performance. This study measured and compared the changes in internal temperature of Type 3 and Type 4 composite cylinders which occurs when filling high-pressure gas in order to investigate how the composite cylinders being installed in vehicles which use high-pressure gas as fuels react to heat.

2. EVALUATION STANDARDS AND REGULATIONS OF COMPOSITE CYLINDERS

The international regulations for verifying the safety of composite cylinders for high-pressure hydrogen gas are all established or in effect in many countries such as the members of EU. The first hydrogen cylinder's safety standards were established in Europe as the UN EC No.406. Also, the U.S. is testing the cylinders with pressure outlined in North American CNG industrial standard of

ANSI/NGV2 2007, came up with their own modified standard, Modified ANSI/NGV2 2007(HGV), and testing the cylinders by installing them in hydrogen-fueled cars.

2.1 Test Items for Composite Cylinders

Composite cylinders are categorized into 4 types internationally and each type has different test items for testing safety. Composite cylinders for natural gas have to pass 13 safety test items, but for composite cylinders storing hydrogen, they have to pass 15 test items. Table 1 below lists the test items for composite cylinders. ANSI NGV 2(2007) is a safety evaluation standard for composite cylinders storing compressed natural gas which are installed in vehicles [3] and UN EC No.406(2010) is a safety evaluation standard for composite cylinders storing hydrogen gas for vehicles [4].

ANSI NGV 2	(2007)			UN EC No.406(2010)							
Trad Pat	Ty	pe of	cylin	der	Track Park	Type of cylinder						
Test list	1	2	3	4	Test list	1	2	3	4			
Ambient Cycling Test	0	0	0	0	Ambient Temperature Pressure Cycle Test	0	0	0	0			
Environmental Test		\odot	0	\odot	Chemical Exposure Test		0	\bigcirc	\bigcirc			
Extreme Temperature Cycling	0	0	0	0	Extreme Temperature Pressure Cycle Test		0	0	0			
Hydrostatic Burst Test	\bigcirc	\odot	0	O	Burst Test	\bigcirc	0	\bigcirc	\odot			
Composite Flaw Tolerance Test		0	O	0	Composite Flaw Tolerance Test		O	O	O			
Drop Test		0	\odot	O	Impact Damage Test			O	O			
Accelerated Stress Rupture Test		0	O	0	Accelerated Stress Rupture Test		0	\bigcirc	O			
Bonfire Test	\odot	0	\odot	O	Bonfire Test	\bigcirc	\odot	\bigcirc	O			
Penetration Test	\odot	0	\odot	O	Penetration Test	\bigcirc	\odot	0	O			
Permeation Test				\odot	Permeation Test				\bigcirc			
Natural Gas Cycling Test				Ø	Hydrogen Gas Cycling Test			O	O			
Leak Before Break Test	\bigcirc	0			LBB Performance Test	\bigcirc	\odot	0	O			
Non-Destructive Examination (NDE) Defect Size Determination	O	O	O		Leak Test			O	O			
					Boss Torque Test				O			
					Hydraulic Test	\bigcirc	0	O	O			

Table 1. Design Qualification Tests for Composite Cylinders

○ : with welded metal liners

2.2 Gas Cycling Test

Only the samples that have passed the hydraulic pressure test, ambient hydraulic cycling test, and permeation test are allowed for gas cycling test due to safety concerns. The sample cylinder will contain the actual gas with 1.0 times more pressure than the nominal working pressure and held under 2 MPa for 1,000 times with repetitive pressurization and decompression. The filling time must be under 5 minutes during the test. During the test, a thermocouple should be placed at both metallic end bosses to measure temperature. If there is only one end boss, then a temperature sensor should be inserted on its opposite side to measure the temperature. A cylinder that was pressurized for 1,000 times should be tested for leakage after the cycling test and it also needs to be checked for any cracks between the plastic liner and another liner or between a plastic liner and an end boss, and for electrostatic leakage and such. The gas cycling test of composite cylinders for compressed natural gas and hydrogen is summarized in Table 2 below.

ANSI NGV 2(2007)	UN EC No.406(2010)
Test : Natural Gas Cycling Test	Test : Hydrogen Gas Cycling Test
Sampling : 1	Sampling : 1
Procedure : [Test Gas] Natural gas [Test Pressure] 10 percent of service pressure to service pressure [Test Cycles] 1,000 cycles The end boss at the valve end (the end where the fill/discharge occurs) may be grounded. Each cycle, consisting of the filling and venting of the cylinder, shall not exceed 1 hour.	Procedure : [Test Gas] Hydrogen gas [Test Pressure] ≤ 2,0 MPa and ≥ nominal working pressure [Test Cycles] 1,000 cyclesThe filling time shall not exceed 5 minutes. Temperatures during venting shall not exceed between -40 °C ~ +85 °C. The cylinder shall be thoroughly dried and pressurized for at least 3 minutes to nominal working pressure with leak test gas.Section the cylinder and inspect the liner and liner/end boss interface for evidence of any deterioration, such as fatigue cracking or electrostatic discharge.
 Requirement: a. Cylinders shall be thoroughly dried and pressurized to service pressure with a detectable gas or gas mixture. b. Cylinders shall be placed in an enclosure to permit detection of any leaks. c. Weld seams or spun enclosures in exposed metal parts be tested using liquid immersion or a leak detection solution compatible with the materials with which it comes into contact. Any leakage detected shall be cause for rejection 	Requirement : The cylinder shall be thoroughly dried and pressurized for at least 3 minutes to nominal working pressure with leak test gas. The liner and liner/end boss interface shall be free of any deterioration, such as fatigue cracking or electrostatic discharge.

Table 2. Comparison of Gas Cycling Test Standards for Composite Cylinders

3. EXPERIMENT

3.1 Outline of the Experiment

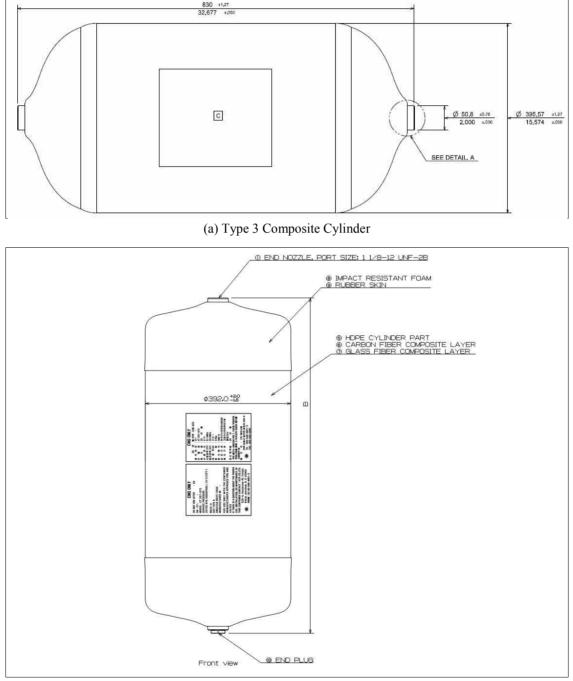
The outline of the experiment is as follows.

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Test Item : Natural Gas Cycling Test
Purpose : Comparison of internal temperature change within Type 3 and Type 4 composite cylinders when filling high-pressure gas
Test Subject : Type 3 70 liters CNG cylinder 1ea, Type 4 71 liters CNG cylinder 1ea
Testing Period : 2013. 3. 7 ~ 3. 9
Testing Pressure : less than 2 MPa ~ 20.7 MPa, 22 MPa (holding for 60secs at peak)
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3.2 Composite Cylinders Subject to the Test

This study used Type 3 and Type 4 composite cylinders for which can store up to 70 and 71 liters of natural gas with 20.7 MPa pressure for the experiment. As you can see from Table 3 below, Type 3 composite cylinder is made of Al6061-T6 material along with seamless aluminium liner and fully wrapped in T700 carbon fiber/epoxy in helical and hoop winding. Fig. 1(a) is showing the measurements of Type 3 cylinder such as the liner thickness around the cylinder 4.3 mm, thickness of composite layer 8.3 mm, and the external diameter of the cylinder 395 mm. Fig. 1(b) is showing the

measurements of Type 4 composite cylinder such as the liner thickness around the cylinder 7.5 mm, thickness of composite layer 11 mm, and the external diameter of the cylinder 396 mm. Type 4 cylinder storing up to 71 liters of natural gas is made of HDPE(high density polyethylene), and liner is fully wrapped with carbon fiber/epoxy material.



(b) Type 4 Composite Cylinder

Figure 1. Blueprint of Composite Cylinders for Testing

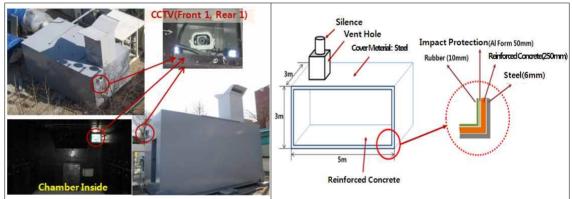
Table 3 below shows the specifications of the testing cylinders.

Cylinder Type	Type 3	Type 4
Liner Material	AL6061-T6	HDPE
Approved Gas	CNG	CNG
Water Capacity (L)	70	71
Weight (kg)	28	28
Diameter (mm)	395.57	392
Length (mm)	830	900
Service Pressure (MPa)	20.7	20.7

Table 3. Specification of Cylinder

3.3 Experiment Method

Both Type 3 and Type 4 composite cylinders took in compressed natural gas with 20.7 MPa twice and 22 MPa once with a natural gas cycling test equipment which can pressurize up to 38 MPa. Each cylinder was maintained for 60 seconds at the target pressure, and then gas started to release. With the pressure data, which was from the closest pressure sensor to test cylinders, the pressurization and withdrawal were controlled. Fig. 2 explains the equipment used in the experiment such as test chamber, compressing equipment, recovery equipment, etc. Also, Fig. 3 shows the set up of the composite cylinders. Fig. 3 explains composite cylinders set up.

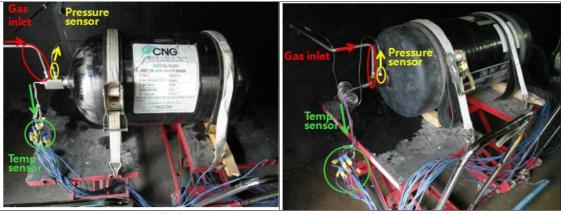


(a) Structure of Safety Chamber for Gas Cycling Test



(b) Compressing and Recovery Equipment for Natural Gas(Max pressure: 38 MPa)

Figure 2. Gas Cycling Test Equipment

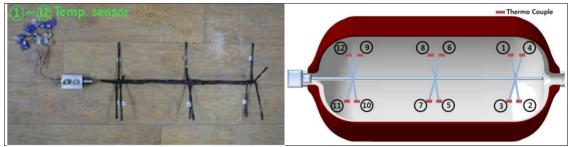


(a) Type 3 Cylinder

(b) Type 4 Cylinder

Figure 3. Set Up of Composite Cylinders

A sensor to check for temperature change within the cylinder was created as Fig. 4(a) shows below. 12 t-type thermocouple temperature sensors were equipped from the gas injection hole and the sensors were made with flexible plastic-like material to be able to be inserted through tiny holes of the cylinders [5]. Also, in order to handle the cylinder, specially threaded plug(1.124 12UNF) was used, and O-ring which made it possible for the cylinder to handle up to 35 MPa. In Fig. 4(b), 12 temperature sensors are able to sense heat from the gas injection hole and all possible angles inside the cylinder(above, below, left, right, up, down, middle, back).



(a) Actual Temperature Sensor

(b) Location of the Sensor Within the Cylinder



(C) Setting Up the Temperature Sensor

Figure 4. Structure and Set Up of the Temperature Sensor

A pressure sensor was set up on the front of the testing cylinder to check the testing pressure, and an exclusive computer program was used to control the gas cycling test. All data was set up to be collected once every second and all testing and monitoring scenes were generated and saved into video files to establish data.

4. TEST RESULTS AND DISCUSSION

4.1 Temperature Change

When testing the cylinder's integrity, pressure tests are mostly conducted with water, because of safety issues. However in this research, because of the actual use of the cylinder, internal temperature measurements from natural gas pressure were taken from full-wrapping Type 3, Type 4 cylinders which have low thermal conductivity. In this test, Type 3 and Type 4 cylinders were each tested under 20.7 MPa twice, and 22 MPa once with pressure and internal temperatures equal. The test compared the amount of time each cylinder was able to hold the target pressure. Fig. 5 shows the internal temperature changes after Type 3 Cylinder was pressurized to 20.7 MPa, and the average temperature at 20.7 MPa 1st and 2nd test was determined as $30.3 \,^{\circ}$ C and $29.7 \,^{\circ}$ C.

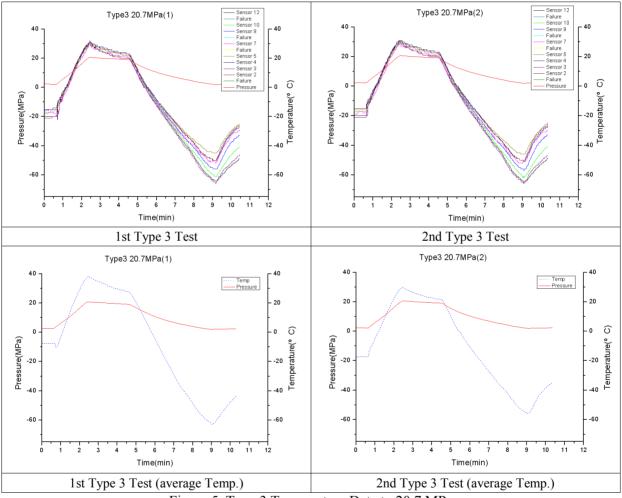


Figure 5. Type 3 Temperature Data to 20.7 MPa

Fig. 6 shows Type 4 cylinder's internal temperature changes after it was pressurized to 20.7 MPa, and the average temperature for tests 1 and 2 was determined to be 38 °C and 33.5 °C. The cylinders in this test were built to hold 20.7 MPa, but to observe the progress of internal temperature, the cylinders were put under 22 MPa pressure and the resulting internal temperatures were recorded. Fig. 7-8 shows Type 3 and 4 cylinders' internal temperature changes under 22 MPa pressure, and the average temperatures were 30.2 °C and 33.8 °C respectively.

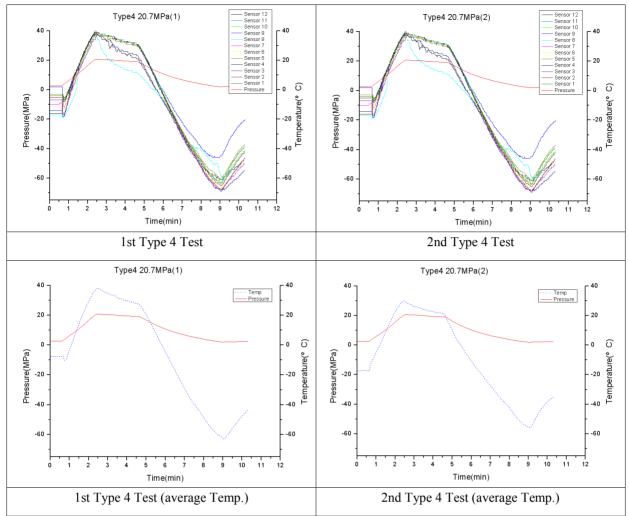


Figure 6. Type 4 Temperature Data to 20.7 MPa

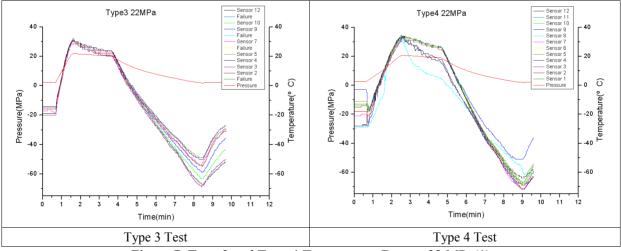


Figure 7. Type 3 and Type 4 Temperature Data to 22 MPa(1)

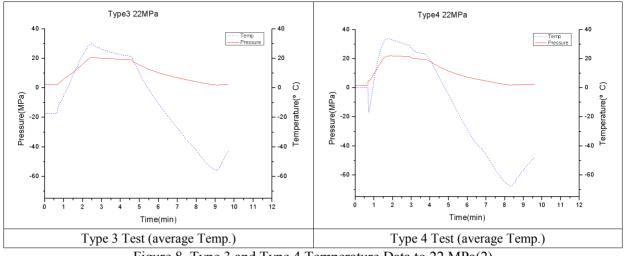


Figure 8. Type 3 and Type 4 Temperature Data to 22 MPa(2)

After comparatively analyzing Fig. 5-7, Type 4 cylinder has average temperatures 3~7 °C higher than Type 3 cylinder in all areas at 20.7 MPa, and about 3 °C higher at 22 MPa. Also Hydrogen gas regulation UN EC No.406(2010) states that the gas should not be below -40 °C when releasing, but in this test all types of cylinders were pressurized with gas below -40 °C. Fig. 9 shows how long each cylinder can maintain pressure after reaching the target pressure, and its average temperature. Type 4 cylinder can hold 20.7 MPa for 8 seconds on average, and Type 3 cylinder holds for 4 seconds on average. Under 22 MPa, Type 4 cylinder holds for 7 seconds while Type 3 holds for 3 seconds on average.

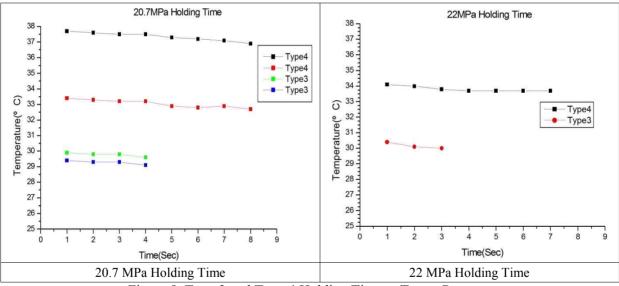


Figure 9. Type 3 and Type 4 Holding Time at Target Pressure

4.2 Temperature Data for Holding

Table 4 through 10 shows the minor temperature changes during the target pressure duration, and shows the amount of time maintained, and average temperature. Through the tables, Type 4 average temperature was higher than Type 3, and in case of time maintaining maximum pressure, Type 4 was longer than Type 3. In view of the results, it can be seen that Type 3's heat transference is higher than Type 4's, enabling it to quickly disperse its internal temperature. It was verified that there is a bigger internal temperature change in Type 4 cylinder.

Time (sec)	Sensor 1	Sensor 2	Sensor 3	Sensor 4	Sensor 5	Sensor 6	Sensor 7	Sensor 8	Sensor 9	Sensor 10	Sensor 11	Sensor 12	Average	Pressure (MPa)
1	\setminus /	31	29	31	29	\backslash	28	\setminus /	30	30	\backslash /	31	29.9	20.7
2	$ \rangle /$	31	29	31	29		28		30	30		30	29.8	20.7
3	X	31	29	31	29	X	28	X	30	30	X	30	29.8	20.7
4		31	29	31	28		28		30	30		30	29.6	20.7
Average	$/ \land$	31.0	29.0	31.0	28.8	$/ \land$	28.0	$/ \land$	30.0	30.0	$/ \land$	30.3	29.8	

Table 4. Temperature Data of Type 3 for Holding at 20.7 MPa(1st)

Table 5. Temperature Data of Type 3 for Holding at 20.7 MPa(2nd)

Time (sec)	Sensor 1	Sensor 2	Sensor 3	Sensor 4	Sensor 5	Sensor 6	Sensor 7	Sensor 8	Sensor 9	Sensor 10	Sensor 11	Sensor 12	Average	Pressure (MPa)
1		30	28	31	29	/	27	/	30	30		30	29.4	20.7
2	$ \rangle /$	30	28	31	29		27		30	29	\setminus	30	29.3	20.7
3	ΙΧ	30	28	31	29	X	27	X	30	29	Χ	30	29.3	20.7
4	$]/ \setminus$	30	28	31	29		27		30	29		29	29.1	20.7
Average	$/ \land$	30.0	28.0	31.0	29.0	$/ \land$	27.0	$/ \land$	30.0	29.3	$/ \setminus$	29.8	29.3	

Table 6. Temperature Data of Type 4 for Holding at 20.7 MPa(1st)

Time (sec)	Sensor 1	Sensor 2	Sensor 3	Sensor 4	Sensor 5	Sensor 6	Sensor 7	Sensor 8	Sensor 9	Sensor 10	Sensor 11	Sensor 12	Average	Pressure (MPa)
1	38	39	39	38	38	37	37	34	38	38	39	37	37.7	20.7
2	38	39	39	37	38	37	37	34	38	38	39	37	37.6	20.7
3	38	39	39	37	37	37	37	34	38	38	39	37	37.5	20.7
4	38	39	39	37	37	37	37	34	38	38	39	37	37.5	20.7
5	38	38	38	37	37	37	37	34	38	38	39	37	37.3	20.7
6	38	38	38	37	37	37	37	33	38	38	39	36	37.2	20.7
7	38	38	38	37	37	37	37	33	38	38	38	36	37.1	20.7
8	38	38	38	37	37	37	37	31	38	38	38	36	36.9	20.7
Average	38.0	38.5	38.5	37.1	37.3	37.0	37.0	33.4	38.0	38.0	38.8	36.6	37.3	

Table 7. Temperature data of Type 4 for holding at 20.7 MPa(2nd)

Time	Sensor	Average	Pressure											
(sec)	1	2	3	4	5	6	7	8	9	10	11	12		(MPa)
1	34	34	34	33	33	33	33	32	33	34	34	34	33.4	20.7
2	34	34	34	33	33	33	33	31	33	33	34	34	33.3	20.7
3	34	34	34	34	33	33	33	30	33	33	34	33	33.2	20.7
4	34	34	34	34	33	33	33	30	33	33	34	33	33.2	20.7
5	33	34	34	34	33	33	33	29	33	33	34	32	32.9	20.7
6	33	34	34	34	32	33	33	29	33	33	33	32	32.8	20.7
7	33	34	34	34	32	33	33	31	34	33	33	31	32.9	20.7
8	33	34	34	32	32	32	33	31	34	33	33	31	32.7	20.7
Average	33.5	34.0	34.0	33.5	32.6	32.9	33.0	30.4	33.3	33.1	33.6	32.5	33.0	

Table 6. Temperature Data of Type 5 for Holding at 22 With														
Time	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Average	Pressure
(sec)	1	2	3	4	5	6	7	8	9	10	11	12	j	(MPa)
1	\setminus /	31	31	32	29	\setminus /	28	\setminus /	30	31	\setminus /	31	30.4	22
2	\bigvee	31	31	31	29		29		30	30		30	30.1	22
3	\wedge	31	30	31	29		29		30	30		30	30.0	22
Average	$/ \setminus$	31.0	30.7	31.3	29.0	/	28.7	$/ \setminus$	30.0	30.3	\vee	30.3	30.2	

Table 8. Temperature Data of Type 3 for Holding at 22 MPa

	Tuble 7. Temperune Dun of Type Flor Holding in 22 Mili													
Time	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Sensor	Average	Pressure
(sec)	1	2	3	4	5	6	7	8	9	10	11	12	j	(MPa)
1	33	35	34	34	34	33	34	33	35	35	35	34	34.1	22
2	33	35	34	34	34	33	34	32	35	35	35	34	34.0	22
3	33	35	34	33	34	33	34	32	35	35	35	33	33.8	22
4	33	34	34	32	34	33	34	31	35	35	35	34	33.7	22
5	32	35	34	32	34	33	34	31	35	35	35	34	33.7	22
6	32	35	34	32	34	33	34	31	35	35	35	34	33.7	22
7	32	35	34	32	34	33	34	31	35	35	35	34	33.7	22
Average	32.6	34.9	34.0	32.7	34.0	33.0	34.0	31.6	35.0	35.0	35.0	33.9	33.8	

Table 9. Temperature Data of Type 4 for Holding at 22 MPa

Table 10. Results of Filling Test

Turne	20.7 MPa	Temp. (°C)	22 MPa T	emp. (°C)	Holding time (sec)			
Туре	Max	Min	Max	Min	20.7 MPa	22 MPa		
Type3 (A)	30.3	-56.1	30.2	-58.1	4	3		
Type4 (B)	38.0	-66.6	33.8	-67.9	8	7		
B - A	+7.7	-10.5	+3.6	-9.8	+4	+4		

5. CONCLUSION

In this study, gas cycling test was performed in order to figure out the relationship between the internal temperature and composite material-made Type 3 and Type 4 cylinders. The temperature change and the time of holding pressure, when natural gas was pressurized to 20.7 and 22 MPa, were analyzed with 12 thermal sensors inserted into two composite cylinders. The following conclusion was reached.

1) Change of internal temperature : It was observed that Type 4 cylinder maintained higher internal temperature compared to Type 3 cylinder by $3\sim7$ °C on average under 20.7 MPa and by 3 °C under 22 MPa.

2) Maintainability of target pressure : Both of Type 4 cylinders were able to maintain 20.7 MPa for 8 seconds, but both of Type 3 cylinders were only able to maintain the same pressure for only 4 seconds. At 22 MPa, Type 4 maintained for 7 seconds, but Type 3 maintained for 3 seconds.

3) Temperature change during gas discharge : All cylinders fell below -40 °C during the experiment

As a result of this research, there is a bigger internal temperature change in Type 4 cylinder and a longer heat exchange time. Through this, it is verified that the internal aluminum liner of Type 3 cylinder distributes internal heat faster than the internal HDPE liner of Type 4 cylinder. In addition to,

UN EC No.406(2010) does not allow temperature below -40 °C during gas discharge, but all cylinders fell below -40 °C during the experiment. These results verify the need for controlling the gas leak speed in experiments following the regulations. The advanced study on the internal temperature change when using hydrogen gas based on this result will be performed. We hope that this study helped readers to understand the internal temperature change within fully wrapped composite cylinders Type 3 and Type 4.

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