Thermal Behavior of Neutron Shielding Material, NS-4-FR, under Long Term Storage Conditions

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1. Introduction

NS-4-FR, Epoxy-Resin, has been widely used as a neutron shielding material for casks. It is recognized that the resin will degrade during storage and loose weight under high temperature conditions. Most of the examinations for the resin degrading behavior were conducted with rather small bare resin specimens. However, the actual quantity of neutron shielding is quite large and is covered by the cask body. To confirm the degrading behavior of the resin under the long-term storage conditions, we performed the test on the specimen with the same cross-section as the actual design, Hitz B69. The resin test vessels were made out of stainless steel and equipped with flange.

As the maximum allowable temperature of NS-4-FR is specified 150 °C in the supplier's catalogue, the tests were carried out at temperatures of 150 °C and 170 °C, the latter was selected to accelerate the degradation.
In addition, a test with temperature gradient between the both sides of specimen 130-150 °C was carried out to simulate temperature gradient in the actual cask.

2. Test Arrangement

Fig. 1 shows the test vessels. Two kinds of test vessels were prepared for the tests. One had a resin cross-section of 170mm×150mm and its height was 200mm. The other had the same cross section but its height was 400mm. The resin net weights were about 8.2kg and 16kg respectively.
The longer, 400mm-height, specimen was used for the test with temperature gradient in resin, on one side of which the panel heater was attached to give temperature gradient.
Fig.2 shows the Illustrations of the resin heating test arrangements. The resin vessels were heated in the electric furnaces.

3. Test Results

(1) Test 1 : 170°C Test

Fig. 3 shows the history of inner pressure of the resin vessel and resin temperature of 170°C test.
The resin temperature was increased stepwise, i.e. 90°C, 110°C, 130°C, 150°C, to 170°C, and kept at 170°C for 500 hrs, and then, decreased stepwise, i.e. 150°C, 130°C, to the room temperature.
The pressure rose to 0.97MPa(abs) at about 130hrs, and then gradually decreased to 0.93MPa at 500hrs. The specimen was cooled down to 150°C and kept for 48hrs. The pressure was 0.63MPa constant. The specimen was further cooled down to 130°C, and the pressure was 0.43MPa. The specimen was cooled down to the room temperature and the resin vessel pressure went back to almost atmospheric pressure. When opening the vessel, water drops were observed on the resin and flange surface. Captured water was totally 11.2 cm^3, and weight loss of the resin was 20g, or 0.24% of initial resin weight of 8245g.

(2) Test 2 : 150°C Test

Fig. 4 shows the pressure and temperature history of specimen for 150°C test.

The pressure rose to about 0.37MPa at 200hrs and seemed to saturate there, however, it began to rise from 1000 hrs and almost saturated at 1600hrs at about 0.6 MPa.

The specimen was cooled down to the room temperature after 2400hrs heating. The resin vessel pressure went back to almost atmospheric pressure.

A few water drops were observed on the resin and flange surface. The total amount was estimated less than 1 cm^3. The resin weight loss was 23g, or 0.28% of initial resin weight of 8202g.

(3) Test 3 : 130°C-150°C Temperature Gradient Test

Fig. 5-a shows the pressure and temperature history of the specimen for 130°C-150°C gradient test for 500hrs. The resin vessel pressure rose to about 0.25MPa at 500hrs, but was not saturated. The specimen was cooled down to the room temperature and the pressure went back to almost atmospheric pressure. No weight loss and no water drops were observed.

After two months interval, the same specimen was heated again to the same temperature. (Fig. 5-b)

The pressure was 0.37MPa at accumulated heating period of 4500hrs, and was still rising.

4. Discussion

(1) Resin weight loss

Table 1 shows the resin weight loss of each test. The weight loss was observed in Test 1 and Test 2, i.e., 0.24% at 170°C×500hr test and 0.28% at 150°C×2400hr test respectively. There was no weight loss at Test-3a, i.e. 150°C-130°C×500hr test.

Nuclear Power Engineering Corporation (NUPEC) measured weight loss with small specimens of NS-4-FR in both open and enclosed environments. Where in open environment test, the bare specimens were heated in an electric furnace and in enclosed environment test, the resin specimens put in small vessels were heated in an electric furnace. The vessels were kept atmospheric pressure in the enclosed environment test.

According to the NUPEC's examinations, the weight loss (ΔW) can be estimated by following equations [1];

Open Environment : $\Delta W(\%)=1.39\times10^{-3}\cdot (T+273.15)(38.2+\ln t)-24.5$ (a)

Enclosed Environment: $\Delta W(\%)=5.69\times10^{-4}\cdot (T+273.15)(77.6+\ln t)-19.2$ (b)

Where; T: Resin Temperature (°C)

t: Heating Period (hr)

Using above equations (a) and (b), the resin weight loss of Test 1 and Test 2 can be calculated as follows;

170°C×500hr : (a) 2.86%, (b) 1.93%

150°C×2400hr : (a) 2.55%, (b) 1.36%

From similar experiments, the weight loss of NS-4-FR at 150°C×2400hr in the enclosed environment can be estimated to be about 0.7% [2], and 1.3%[3]. It was also reported that the weight loss in enclosed system was almost 1/3 of one in open environment test [2].

Comparing to these results, the weight loss of large amount of resin in the containment vessel as measured in Test 1 and Test 2 were considerably small.

(2) Effect of high temperature

Fig. 5-c is the figure combined of Fig.5-a and Fig. 5-b, to coincide with the cool down start time of Fig. 5-a and the steady state attained time of Fig. 5-b. The pressure history seems continuous as if there was no effect by two months interval. Accordingly, it is considered that the pressure rise and resin degradation are governed by only high temperature circumstance.

(3) Pressure at high temperature

The pressure came back to almost atmospheric pressure after cool down in every test. From the results, it can be indicated the pressure will be estimated as the sum of steam pressure and partial air pressure in the void.
Table 2 shows the partial air pressure calculated from the measured initial resin weight, resin volume, vessel void and calculated resin expansion. Fig.6 shows the relationship between (measured vessel saturation pressure) vs. (steam saturation pressure + air pressure in the vessel void) in Table 2, which shows good correlation.

(4) Behavior of resin at high temperature

Fig. 7 shows the pressure history of each test where time axis is log scale. From these data, it can be considered that the pressure rise takes place at three stages as illustrated in Fig. 8.

Stage 1. Pressure rises immediately to 0.2-0.23MPa(abs) from atmospheric pressure, where expansion of resin seems to govern the pressure.

Stage 2. After slight decrease of the pressure in the latter half of stage 1, the pressure increased gradually to the certain saturation pressure. At this stage, small amount of water may be contributed to the pressure in addition to the air expansion.

Stage 3. After keeping the pressure constant for a while, it begins to rise again and come close to the saturation pressure discussed in (3) above.

The saturation time at 170°C was about 130hrs and that of 150°C was 1600hrs. The saturation time depend keenly on the resin temperature.
Based on the assumption that the relation between the pressure saturation time ts (hrs) and the resin temperature Ts(°C) can be described by the degradation parameter (Ts+273.15)･ (log ts +C), as shown (1) above, the saturation time ts (hrs) and turning point time tp (hrs) at any temperature are calculated by the equation below. The calculations were shown in Table 3, which explains the reason why the pressure has not saturated in Fig5-b.,

$$\log (ts) = 10221/(Ts+273.15)-20.95$$

$$\log (tp) = 10782/(Ts+273.15)-22.48$$

6. Conclusion

(1) Resin (NS-4-FR) weight reduction at 150°C×2400hr was less than 0.3%, which is considerably smaller than the one estimated by the existing correlations. The resin weight loss would be practically negligible for actual casks, provided the resin temperature is maintained below 150 °C.

(2) The maximum pressure of the neutron shielding space of actual casks filled with resin can be estimated as the sum of the steam saturation pressure and air pressure.

(3) The final saturation time keenly depends on the resin temperature.

As resin design temperature will be usually rather lower than the allowable limit, and in the meantime, the resin temperature will decrease further during storage, neither the pressure saturation nor water condensation seems to occur during their design storage period.

References :

[1] Nuclear Power Engineering Corporation, "The Demonstration Examination for Metal Cask Storage Technology Establishment." 2003 Edition (Japanese).

[2] Ryoji ASANO, Nagao NIOMURA, "Experimental Studies on Long-term Thermal Degradation of Enclosed Neutron Shielding Resin", PATRAM 1992.

[3] T. Shirai, et-al, "Evaluation Test on the Thermal Stability of Resin as Neutron Shielding Material for Spent Fuel Transport Cask", PATRAM 1998.

Table 1 Resin Weight Loss

Test No.	Test Condition (Max. Pressure)	Initial Resin Weight	Resin Weight Loss		Remarks
1	170°C×500hr (0.972MPa)	8245g	20 g	0.24%	Slight Water Drops are observed on resin and flange surface. Water captured: 11.2 cm3.
2	150°C×2400hr (0.598MPa)	8202g	23g	0.28%	Slight Water Drops are observed on resin and flange surface. Less than 1 cm3.
3-a	150/130°C×500hr (0.250MPa)	16033g	0g	0.0%	No weight loss and water observed.
Pre. Test	150°C×500hr (0.375MPa)	8192g	0g	0.0%	No weight loss and water observed.

Table 2 Resin Vessel Saturation Pressure

Test No.	Initial State			Press. History Fig.	Steady (Saturated) State						
	Resin Weight (g)	Resin Volume (cm^3)	Void Space (cm^3)		Temp. (°C)	Resin Expansion (cm^3)	Void Space (cm^3)	Steam Saturation Pressure (MPa)	Air Pressure (MPa)	Total Calculated Pressure (MPa)	Measured Pressure (MPa)
1	8245	4673	927	Fig.3	170	221	706	0.792	0.195	0.987	0.972
					150	191	736	0.476	0.178	0.654	0.632
					130	162	765	0.270	0.163	0.433	0.416
2	8202	4718	883	Fig.4	150	193	690	0.476	0.181	0.657	0.598
3	15955	9588	1112	Fig.5	150-130	321	791	0.361	0.194	0.555*	0.31*

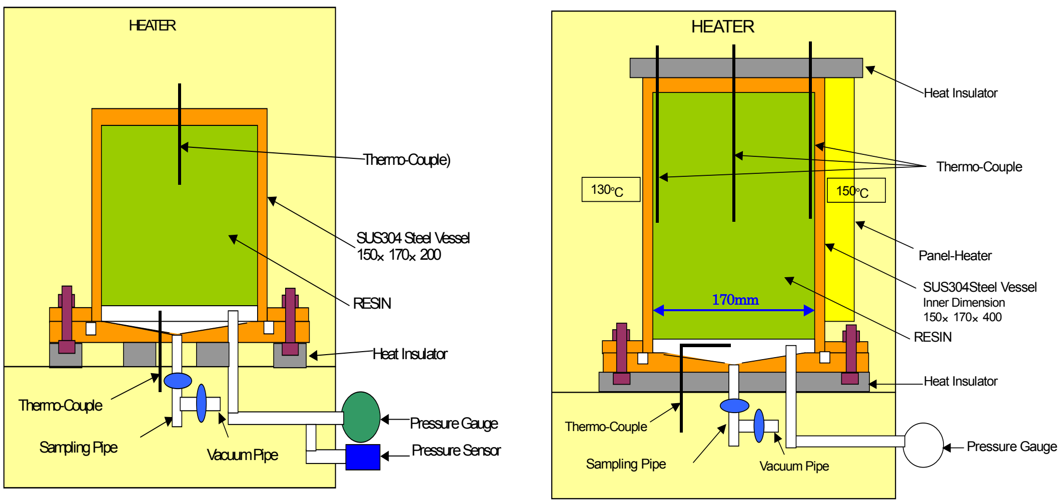
Resin Thermal Exp. Coeff.: 1.05×10^{-4}/°C、 SUS: 1.2×10^{-5}/°C

*) not saturated

Table 3 Estimated Saturation Time and Turning Point Time.

Resin Temp. °C	170°C	150°C	140°C	130°C	110°C
Saturation time ts	130hrs	1600hrs	6200hrs	25300hrs=1050days	532000hrs=60.8yrs
Turning Point time tp	71hrs	1000hrs	4140hrs	18400hrs=760days	456000hrs=52.2yrs

Fig.1　Test Vessels of Neutron Shielding Material (NS-4-FR)



Resin Uniform Temp.　　　　Resin Gradient Temp.

Fig.2　Resin Heat Degradation Test Equipment

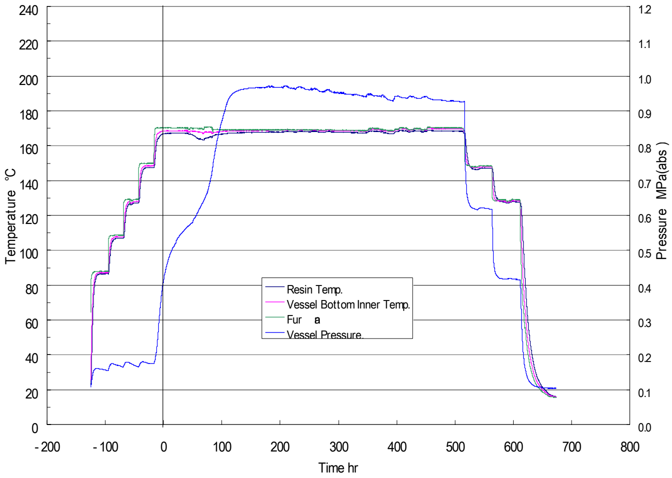


Fig.3 170°C×500hrs Test

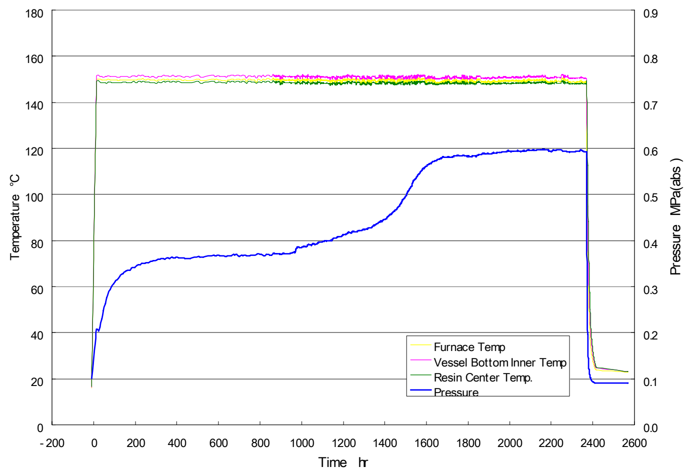
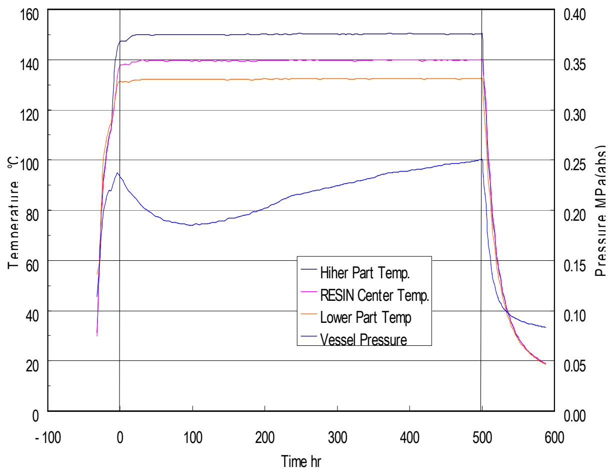
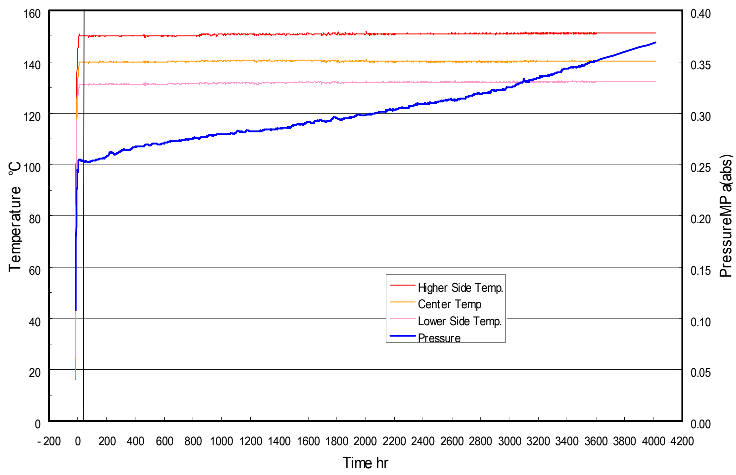


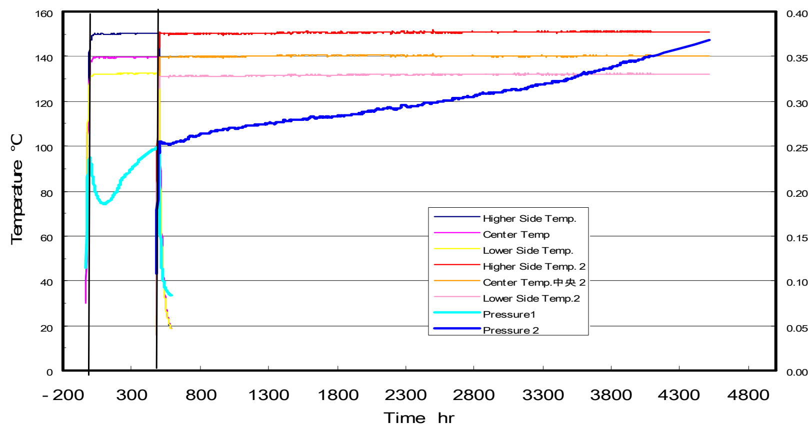
Fig.4 150°C×2400hrs Test



a. 0-500hr



b. 500hr-



C. a+b

Fig.5 130°C-150°C Test

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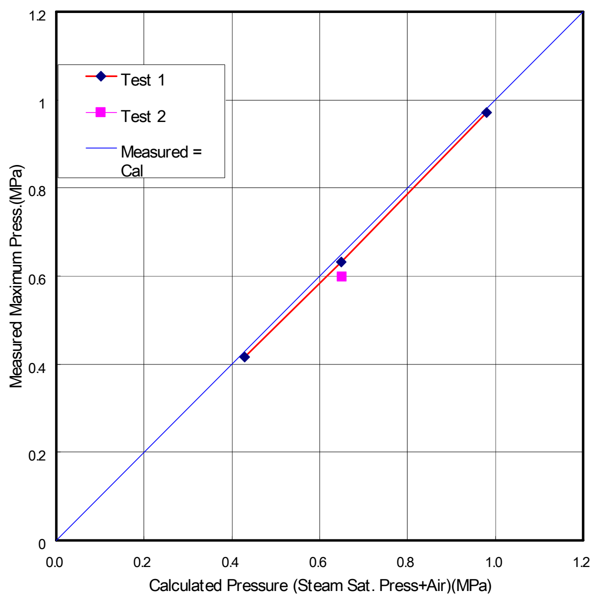

Fig.6 Measured and Calculated Saturation Pressure

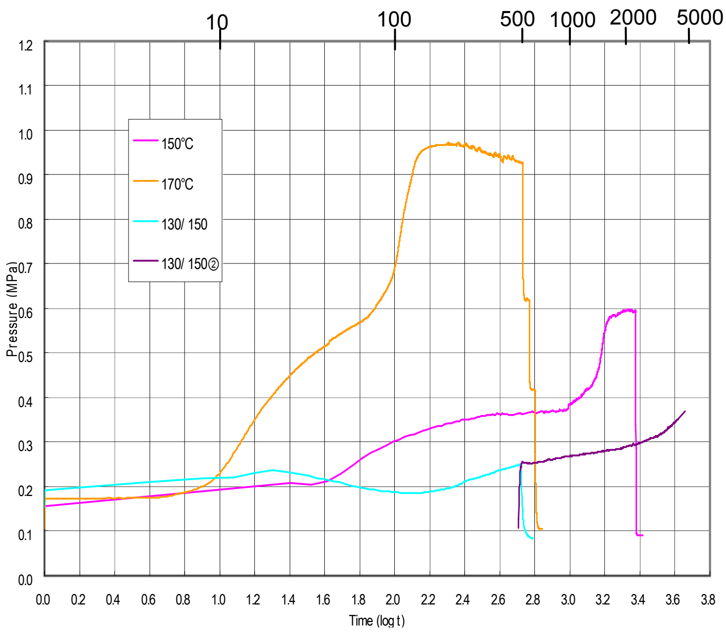

Fig. 7 Pressure Histories (Time log scale)

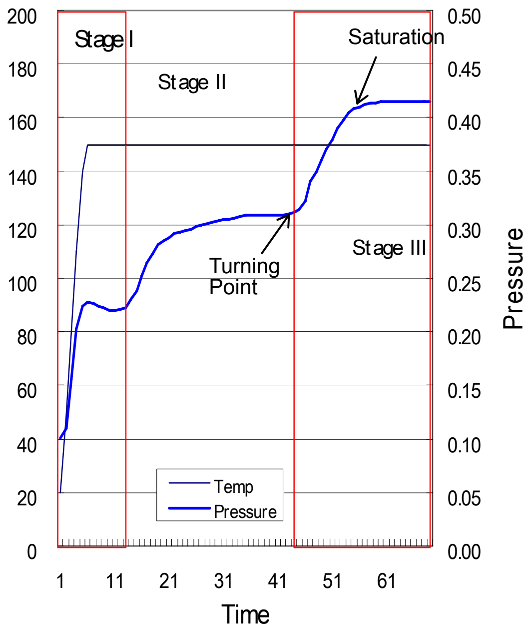

Fig . 8 Typical Pressure History