**Proceedings of the 17th International Symposium on the Packaging and Transportation of Radioactive Materials
PATRAM 2013
August 18-23, 2013, San Francisco, CA, USA**

EVALUATION OF NEUTRON SHIELDING MATERIALS, TN VYAL B™ AND KOBESH EPR™ RESIN FOR INTERIM STORAGE CASKS

Akito OISHI
Kobe Steel, Ltd.
2-3-1, Shinhama, Arai-cho,
Takasago, Hyogo, 676-8670
Japan

Jun SHIMOJO
Kobe Steel, Ltd.
2-3-1, Shinhama, Arai-cho,
Takasago, Hyogo, 676-8670
Japan

Hiroaki TANIUCHI
Transnuclear, Ltd.
1-18-16, Shinbashi,
Minato-ku, Tokyo, 105-0004
Japan

ABSTRACT

Neutron shielding materials which used for interim storage casks are required to have an excellent neutron shielding performance and long-term stability such as heat and radiation resistances. The evaluations of stabilities against these conditions are necessary in order to reflect these characteristics into the designs of interim storage casks. Therefore, a series of tests of neutron shielding materials, TN Vyal B™ and Kobesh EPR™ resins are performed. TN Vyal B™ is vinylester based resin developed by TN International, and Kobesh EPR™ is Ethylene-Propylene-Rubber (EPR) based developed by Kobe Steel, Ltd.

The long-term heating tests up to 10,000hours are performed to estimate weight losses of both TN Vyal B™ and Kobesh EPR™ after 60 years storage by using Larson-Miller Parameter and Arrhenius equation. The heating tests in sealed condition are performed to estimate pressures after 60 years storage in resin areas considering the case of safety valves which release gas pressure are not set. Gas analyses of emitted gas indicate that the main component is carbon dioxide. Ion chromatography of emitted gas also indicates that the amount of acids in emitted gases such as formic acid, acetic acid and sulphuric acid are negligible. It is also confirmed that gamma-irradiation have no or negligible influence on weight loss or appearance of heated resins. The figure of TG-DTA indicates that these resins are stable up to approximately 230°C in both TN Vyal B™ and Kobesh EPR™ in the short term.

From the results of these tests, it is proved that these neutron shielding materials, TN Vyal B™ and Kobesh EPR™ resins have excellent thermal and anti-gamma-irradiation properties. These data are also used for the design and safety analysis of our casks to confirm the safety during long-term storage and transport.

1. INTRODUCTION

Neutron shielding materials used in interim storage casks is one of the most important materials for radiation safety. Usually, some kind of resin is used for this purpose, and a series of tests is needed for installation to our cask design because they are used under severe thermal and gamma-irradiation conditions.

Long-term heating tests are necessary to evaluate weight loss of resins for long-term storage. Resins are usually set in the lids, bottom and inside of outer shell of the cask and safety valves are usually set in these resin areas to release gas pressures. In case of safety valves are not set, heating tests in a sealed vessel are necessary to estimate gas pressures in resin areas. Gas analysis is performed to make sure that the gas emitted by resin is not containing corrosive components such as acids. Heating tests with or without gamma-irradiation are performed in order to confirm the influence of gamma-irradiation on weight loss of these resins.
For our cask design, TN Vyal B™ (here after called ''Vyal B'') and Kobesh EPR™ (here after called ''EPR'') are planned to use.
Vyal B resin developed by TN International, is composed of vinylester resin in a solution of stylene, aluminum hydroxide and zinc borate. EPR resin developed by Kobe Steel, Ltd. is Ethylene-Propylene-Rubber (EPR) based resin.
To examine the performance of neutron shielding materials Vyal B and EPR, a series of tests mentioned above are performed.

3. LONG-TERM HEATING TEST

To examine the weight loss of Vyal B and EPR, long-term heating tests are performed at three different temperatures.

3.1 Test conditions

Figure 1 shows test specimens of Vyal B and EPR. The diameter is 20mm and length is 70mm.
Specimens of Vyal B are heated at three different temperatures: 140, 160 and 170°C. On the other hand, specimens of EPR are heated at 140, 160 and 180°C. Heat duration is 10,000h for each temperature. These test conditions are introduced to estimate weight loss of these resins after 60 years by means of Larson-Miller Parameter (here after called ''LMP'') and Arrhenius equation.
Test specimens of Vyal B are heated without cover. On the other hand, test specimens of EPR are heated in a glass tube in accordance with the test condition of JIS K6257 (Accelerated aging test methods for vulcanized rubber). Figure 2 shows the test apparatus for EPR. Even though EPR is settled in the glass tube, air could go in and out from two tubes freely.

Vyal B

EPR

Figure 1. Test specimens for long-term heating test

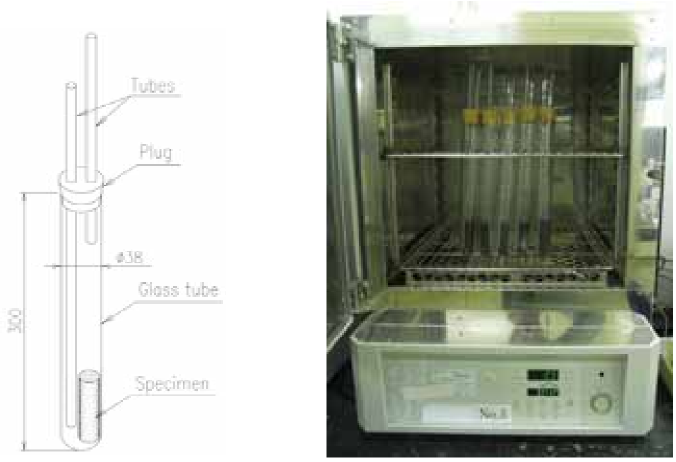
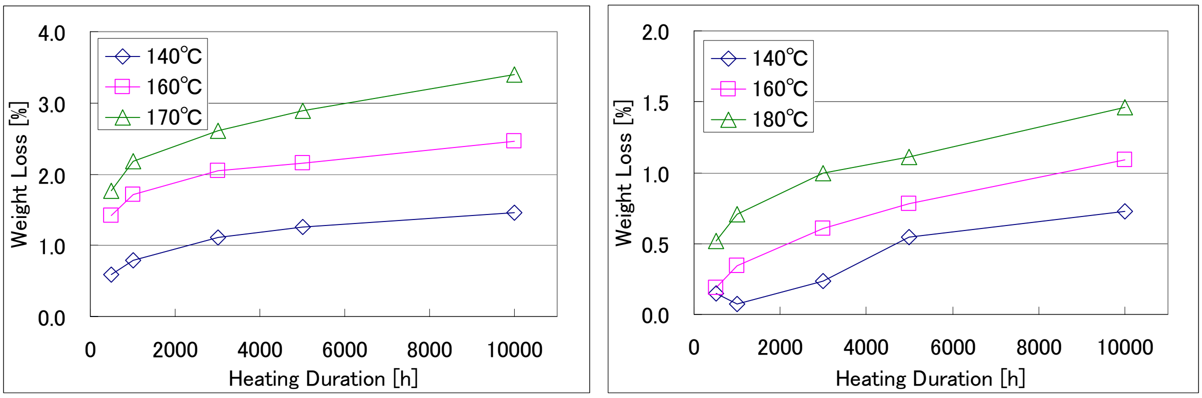


Figure 2. Heating apparatus for EPR

3.2 Weight loss of long-term heating test

Figure 3 shows the weight loss of the resins during long-term heating. The amount of weight loss increases in accordance with the increase of the heating temperature. The weight loss of EPR is less than Vyal B. This difference would come from the difference of testing conditions, opened and closed.



Vyal B EPR

Figure 3. Weight loss of resins during long-term heating

3.3 Evaluation of weight loss by LMP and Arrhenius equation

It is known that weight loss of resins can be evaluated by LMP and Arrhenius equation which include heating temperature and duration as parameters [1]. By using these evaluation methods, weight loss after long-term storage, such as 60 years, can be estimated.

LMP

$$\Delta w = a \cdot T \cdot (C + \ln(t)) + b$$

Δw : Weight loss [%]
T : Temperature [K]
t : Time [h]
a , b , C : Constant [-]

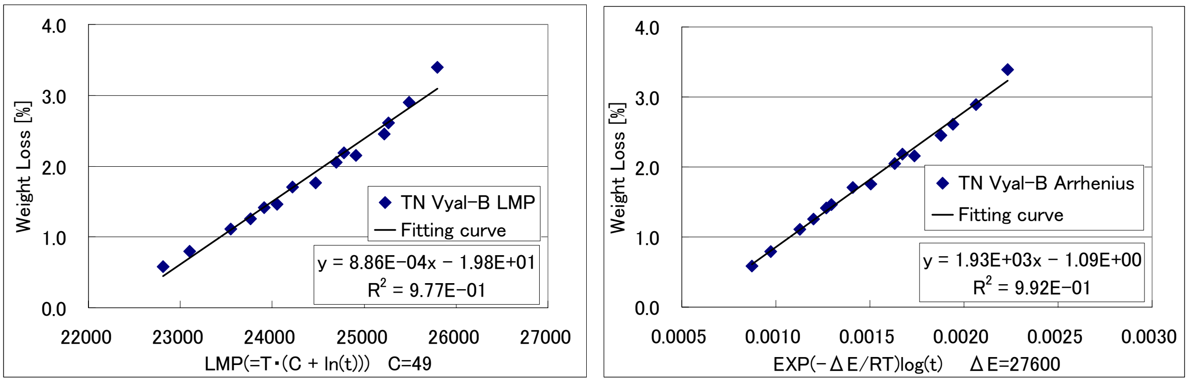
Arrhenius equation

$$\Delta w = C1 \cdot \exp(-\Delta E / RT) \cdot \log(t) + C2$$

Δw : Weight loss [%]
T : Temperature [K]
t : Time [h]
ΔE : Activation energy [J / mol]
R : Gas constant [J / (mol $\cdot$ K)]
$C1$, $C2$: Constant [-]

3.4 Evaluation of weight loss of Vyal B

Figure 4 shows the example of evaluations of weight loss of Vyal B by LMP and Arrhenius equation. In these evaluations, constant ''C'' in LMP and Activation energy '' ΔE'' in Arrhenius equation are not specified. In these examples, these two parameters are decided by least-square method. Constant ''C'' is 49 and activation energy '' ΔE'' is 27600 in this example.



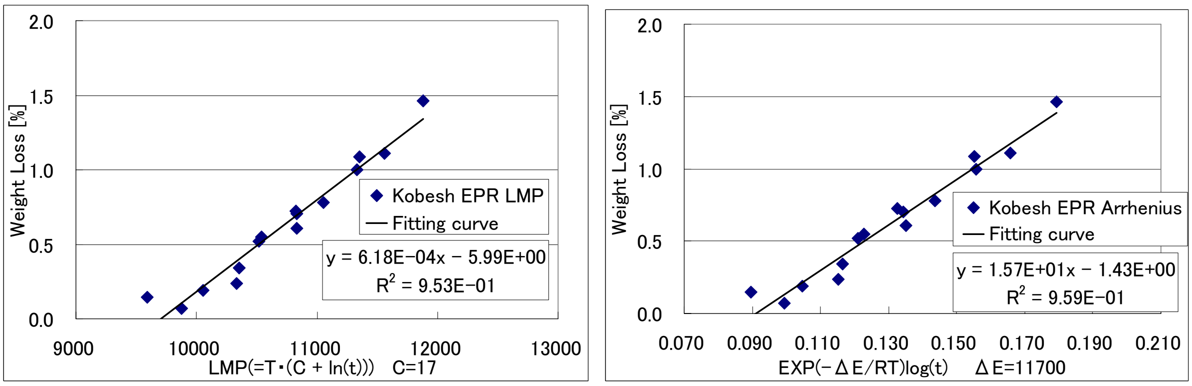
LMP Arrhenius equation

Figure 4. Evaluations of weight loss of Vyal B by LMP and Arrhenius equation

By using these figures, weight loss after 60 years storage at continuous 160 °C is 4.2% by LMP and 4.1% by Arrhenius equation. In the long-term storage condition of casks, actual temperature of resin is gradually decreased. Taking into consideration of decreasing of resin temperature, weight loss after 60 years storage at 160 °C (initial temperature) is 3.4% by LMP and 2.8% by Arrhenius equation. These evaluations are examples at one temperature. Weight loss is possible to be evaluated at any temperature.

3.5 Evaluation of weight loss of EPR

Figure 5 shows the example of evaluations of weight loss of EPR by LMP and Arrhenius equation. Constant ''C'' is 17 and activation energy '' ΔE'' is 11700 in this example.



LMP Arrhenius equation

Figure 5. Evaluations of weight loss of EPR by LMP and Arrhenius equation

Weight loss after 60 years storage at continuous 140 °C is 1.7% by LMP and 1.6% by Arrhenius equation. Taking into consideration of decreasing of resin temperature, weight loss after 60 years storage at 140 °C (initial temperature) is 1.5% by LMP and 1.0% by Arrhenius equation. These evaluations are examples at one temperature. Weight loss is possible to be evaluated at any temperature.

4. HEATING TEST IN SEALED CONDITION

To examine the increase of gas pressure in resin installed areas for long-term storage, heating tests in sealed condition are performed. In this test, resins are heated within a sealed vessel (carbon steel). Volume ratio of resin and air is similar to actual cask designs.

4.1 Test conditions

Table 1 shows the test condition of heating test in sealed vessel. Volume ratio of resin is approximately 90% in the vessel. Figure 6 shows the apparatus of this test.

Table 1. Test condition of heating test in a sealed vessel

Resin	Heating temperature [°C]	Specimen size [mm]	Measured specimen volume [cm^3]	Measured sealed vessel volume [cm^3]	Volume ratio of resin and air [%(resin : air)]
Vyal B	120	ϕ 51×95	193.3	222.7	87:13
	150	ϕ 50×95	200.0	220.6	91:9
EPR	140	ϕ 50×90	190.0	220.6	86:14

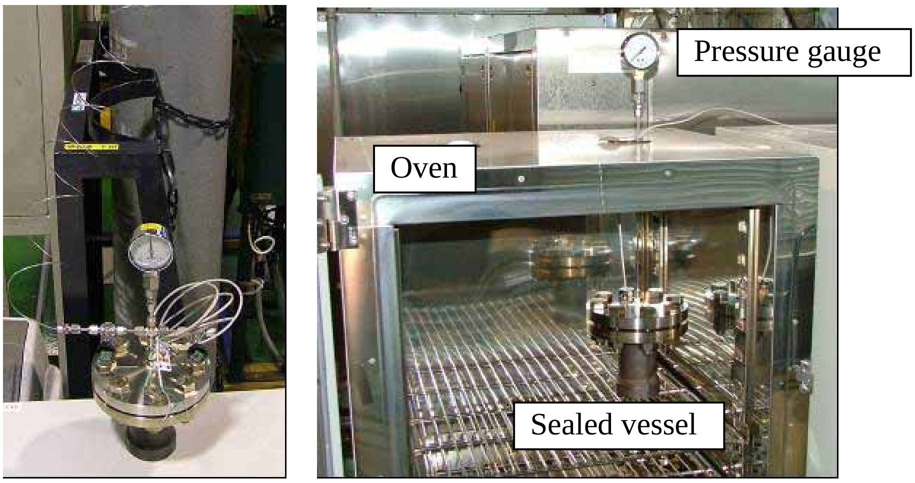


Figure 6. Apparatus for heating test in sealed condition

4.2 Pressure in sealed vessel of Vyal B

Heating tests in sealed condition of Vyal B are performed at two different temperatures, 120 and 150°C.

Figure 7 shows the pressure in sealed vessel and fitting equations of Vyal B. Fitting equations are derived after 1,000 hours at 120°C and 2,600 hours at 150°C. From these fitting equations, estimated pressure at 120°C after 60 years storage is approximately 0.75 MPa(abs). 0.6 MPa(abs) is due to the emitted gas generated by long-term heating and another 0.15 MPa(abs) is due to the air expansion initially existed in the vessel. Estimated pressure at 150°C after 60 years storage is approximately 1.1 MPa(abs). 0.9 MPa(abs) is due to the emitted gas and another 0.2 MPa(abs) is due to the air expansion. The major component of emitted gas is carbon dioxide.

Estimated pressure evaluated by this test is conservative because temperature of this test is continuous condition. In actual storage condition of interim casks, resin temperature will gradually decrease.

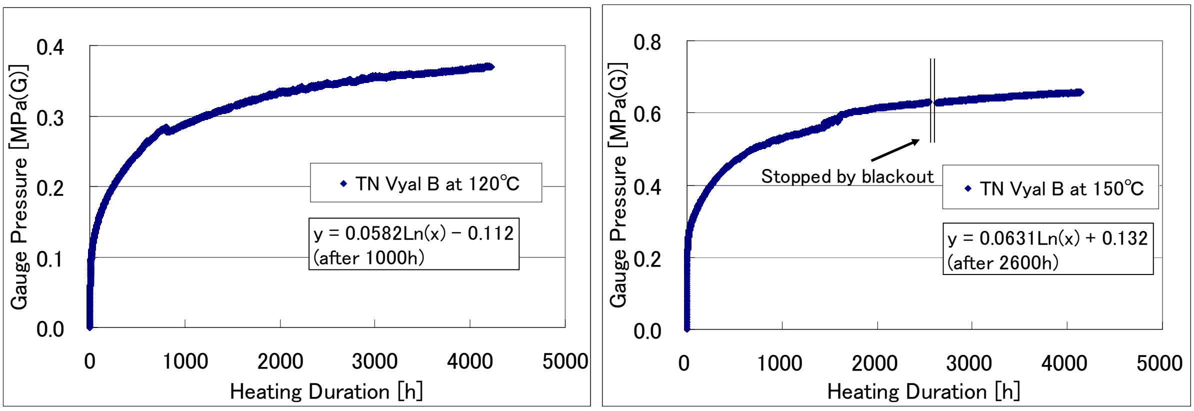


Figure 7. Pressures in sealed vessels and fitting equations of heating tests of Vyal B

<u>4.3 Pressure in sealed vessel of EPR</u>

Heating test in sealed condition of EPR is performed at 140°C. Figure 8 shows the pressure in sealed vessel of EPR. In this test, gauge pressure is saturated at approximately 0.32 MPa(abs) (0.22 MPa(G)). 0.07 MPa(abs) is due to the emitted gas and another 0.25MPa(abs) is due to the air expansion. The major components of emitted gas are carbon dioxide and carbon hydride.
Estimated pressure evaluated by this test is conservative because temperature of this test is continuous condition. In actual storage condition of interim casks, resin temperature will gradually decrease.

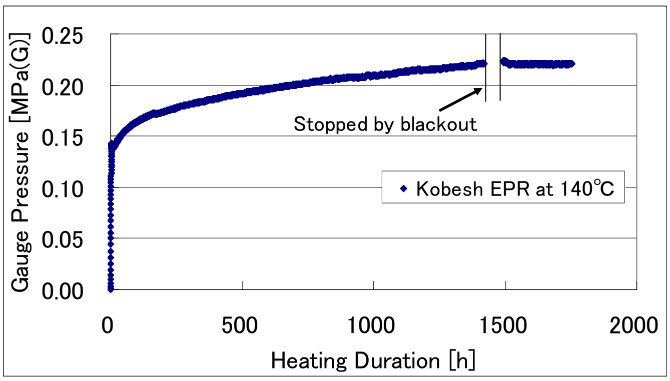


Figure 8. Result of heating test of EPR

5. ANALYSIS OF EMITTED GAS BY ION CHROMATOGRAPHY

To confirm the amount of corrosive gases, such as acids, in emitted gas, gas analysis tests by ion chromatography are performed.

5.1 Test conditions

Resins are heated at 150°C for 30 days in a sealed vessel. Specimen size is ϕ 20mm and 70mm long. Emitted gas is absorbed in 0.2% of hydrogen peroxide solution (H_2O_2). Components of emitted gas in this solution are evaluated by ion chromatography analysis.

5.2 Gas component analysis by ion chromatography

Table 2 shows the gas components. It is confirmed that the amount of acids in emitted gases which cause corrosion of metal is negligible.

Table 2. The quantitative value of each ion of 0.2% of H_2O_2

Resin	Quantitative value in 0.2% of H_2O_2 solution			Units
	Formic acid $HCOO^-$	Acetic acid CH_3COO^-	Sulfuric acid SO_4^{2-}	
Vyal B	0.01	0.03	<0.005	[mg / 50ml]
EPR	<0.003	0.080	<0.03	[mg / 20ml]

6. HEATING TEST WITH GAMMA-IRRADIATION

To evaluate the influence of gamma-irradiation on these resins for long-term storage condition, heating tests with or without gamma-irradiation are performed, and the difference of weight loss and appearance is investigated.

6.1 Test conditions

Specimens are set in the stainless cases without sealing which simulate resin environment in casks and heated with or without gamma-irradiation. Total dose is set taking 60 years storage condition into consideration.

Figure 9. Appearance of test cases

Table 3. Test condition of heating test with or without gamma-irradiation

Gamma-rays condition	Specimen size [mm]	Heating temperature [°C]	Dose rate [kGy/h]	Heating duration [h]	Total dose [kGy]
Non-irradiation	ϕ 20×70	140	0	50	0
Irradiation			1.8		90

6.2 Influence of gamma-irradiation on weight loss and appearance

Weight losses are shown in Table 4. There are no remarkable differences in these two conditions. In appearance, there are also no differences in both resins.

Table 4. Weight-loss of Vyal B and EPR

Resin	Weight-loss [%]	
	Non-irradiation	Irradiation
Vyal B	-0.294	-0.289
EPR	-0.043	-0.046

7. THERMOGRAVIMETRIC-DIFFERENTIAL THERMAL ANALYSIS (TG-DTA)

Thermogravimetric-differential thermal analyses are performed to investigate thermal resistances of these resins.

7.1 Test conditions

These tests are performed under air atmosphere. Increasing rate of temperature is 10°C /min. Temperature is increased from room temperature up to 1000°C.

7.2 Thermal resistance of these resins

Specific changes in TG-DTA start to appear at approximately 230°C in both Vyal B and EPR. These results indicate that these resins are stable under these temperatures in the short term.

SUMMARY OF EVALUATION

From the long-term heating tests, by using LMP and Arrhenius equation, weight losses of both Vyal B and EPR after 60 years storage are estimated. Weight loss of Vyal B at continuous 160°C is approximately 4% in both evaluations and EPR at continuous 140°C is approximately 2%. Taking into consideration of decreasing of resin temperature, weight loss of Vyal B is approximately 3% and EPR is approximately 1%. Compared with LMP and Arrhenius equation, estimated weight loss by LMP is higher than that of Arrhenius equation.

From the heating test in sealed condition, pressures in resin areas after 60 years storage are estimated. Estimated pressures in sealed vessels of Vyal B after 60 years storage are 0.75 MPa(abs) at 120°C and 1.1 MPa(abs) at 150°C. Pressure in sealed vessel of EPR is saturated at 0.32MPa(abs) at 140°C. Main component of gas emitted by resins is carbon dioxide.

The gas analysis by ion chromatography makes it clear that the amount of acids in emitted gases such as formic acid, acetic acid and sulphuric acid is negligible.

It is confirmed that gamma-irradiation have no or negligible influence on weight loss and appearance of heated resins.

The figure of TG-DTA indicates that these resins are stable up to approximately 230°C in both Vyal B and EPR in the short term.

CONCLUSIONS

From the results of these tests, it is proved that these neutron shielding materials, Vyal B and EPR resins have excellent thermal and anti-gamma-irradiation properties. These data are also used for the design and safety analysis of our casks to confirm the safety during long-term storage and transport.

REFERENCES

[1] Japan Nuclear Energy Safety Organization, “Heisei 15, Corroborating Tests Report for Metal Cask Storage Technology”, (2004). (in Japanese)