Experimental Studies on Long-term Thermal Degradation of Enclosed Neutron Shielding Resin

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INTRODUCTION

Resins which have high Hydrogen atom content are effective for Neutron shielding and are recently used for neutron shielding material of spent fuel shipping casks. As the resins themselves are easily burned at relatively low temperature, which could be the problem during the fire test condition, mixture of resin and fire retardant which main component is a hydroxide compound is usually used as shielding material. The fire retardant prevents resin from burning by decomposing of the hydroxide compound under fire test condition.

When these resins are used for neutron shielding material of cask, their temperature rises during the transportation by decay heat of spent fuel. Therefore, thermal degradation of resin (hereafter called as "heat weight loss") at the operating temperature should be paid attention.

Furthermore, when the resin is used for neutron shielding material, there are two cases. One is to put it on the outside surface of the cask and the other is to enclose it between two layers. In former case, the heat weight loss occurs in air of which study report can be obtained. On the other hand, the latter is the reaction in the enclosed environment which study report can be seldom obtained. Therefore, the study of the heat weight loss in the enclosed environment was carried out for long term period assuming the operating time of the real cask .

TEST MATERIAL

Test material is NS-4-FR supplied by BISCO CO. LTD, U.S.A. Raw materials are epoxi resin, hardener and fire retardant. They are mixed together and hardened according to the manu-

facturing manual supplied by BISCO. NS-4-FR is the neutron shielding material which contains about 60% of aluminium hydroxide as fire retardant.

TEST

Tests were carried out in order of basic material test, open test, enclosed test and long term cyclic test which simulates the operation term of cask. The test results are explained as follows.

Basic material test

TG tests which can be performed comparatively easily were carried out in order to study basic thermal characteristics of the test material. The test conditions are as follows.

Condition	Case 1	Case 2
Atmospheric gas	Air&N_2	Air&N_2
Gas Flow Rate(cc/min)	150	200
Temp. Rising Rate(°C/min)	3	10
Max.Temperature(°C)	220	530

Heat weight loss could not be detected in the Case 1. The results of Case 2 are as follows.

(1) The weight loss of the test specimen in nitrogen gas was much smaller than that in air between 300°C and 380°C which were shown in Fig 1. It indicates that the test materials are decomposed and loose its weight by oxygen in air and by heat within the temperature range.

(2) Comparing the results between test material and NS-4- FR without fire retardant, the weight loss of latter is less than that of former until 360°C as shown in Fig. 2. It indicates that the weight loss of former is mainly due to the decomposition of aluminium hydroxide as fire retardant. This result means that the decomposition of aluminium hydroxide is important for the weight loss during low temperature. And it is necessary to select a suitable grade of aluminium hydroxide, as the decomposition temperature depends on the purity and grain size of aluminium hydroxide.

TG test results can not be used directly for long term degradation data because the test specimen was pulverized to very small size, and reaction and diffusion is very rapid, but they can be good reference information.

Open test

Open tests were performed varying the shape of test specimen and temperature to study heat weight loss in air. The results are as follows.

(1) Effect of shape of test specimen
To study the effect of the shape, cubic and cylindrical test specimens with nearly equal weight were tested. It was observed that the heat weight loss of latter which had larger surface area was always larger than that of the former. It indicates that effects of surface oxidation and surface diffusion are important factors for the heat weight loss.

(2) Effect of temperature
The heat weight loss at 125°C, 150°C, 175°C and 200°C are shown in Fig.3 as a function of time. The increase of the heat weight loss is observed in 200°C test after 1000 hr. It is supposed that generation of continues crack inside of the test specimen makes it easy to diffuse the decomposed resin component and water.

Enclosed test

Supposing that the neutron shielding material is filled in the enclosures tests were conducted to study the effects of enclosed condition to the heat weight loss. The tests were performed on test specimen in the sealed stainless steel container with Ar atmosphere.

(1) Sealed stainless steel container
Seal container is shown in Fig. 4, of which lid is welded to seal the cavity of the container perfectly. Enough height of container cavity is provided to avoid the effect of welding heat to the test specimen. Ar gas seal hole is seal-welded and cooled immediately by water after replacing air with Ar gas.

(2) Test Condition
Continuous test and cyclic test of 110 hr heating and 58 hr cooling which simulated the actual operating condition of cask were performed at 125°C, 150°C and 175°C. The test duration was from 8 to 16 weeks.

(3) Test Results
Test results are shown also in Fig.3. Main results are as follows.

(a) Test Results at 125°C
The heat weight loss at 1512 hr continuous test and that at 1760 hr cyclic test were negligible. The heat weight loss at this temperature is regarded as insignificant.

(b) Test Results at 150°C
The heat weight losses at both 1224 hr continuous tests, 990 hr cyclic test and 1760 hr cyclic test were almost 1/3 of that of open test.

(c) Test Results at 175°C
The heat weight losses at both 1600 hr continues test, 1210 hr cyclic test and 1760 hr cyclic test were almost half of that of open test.

(d) Due to the few test specimens and short test period, data scattering was observed in the test results . However, heat weight loss of enclosed test is clearly less than that of open test except those at 125°C when no heat weight loss was observed.

Long term cyclic test at 150°C
In order to avoid scatter in test results and to estimate heat weight loss during long term use of cask, long term cyclic tests at 150°C were conducted, where temperature supposed was the maximum working temperature of neutron shielding material during transportation. The results are shown in Fig. 5. Total test specimens were 18 and maximum test period was 56 weeks. One cycle is composed of 110 hr heating and 58 hr cooling which is same as the enclosed test above. The heat weight loss for 56 weeks was about 1.1%.

DISCUSSION

The relation between heat weight loss W(%) and test period D(day) is given from Fig. 5, as follow.

$$W=100.63-0.218\times\log D$$

Using this equation the heat weight loss for 20 years W_{20}(%) can be estimated as follow.

$$W_{20}=100.63-0.218\times\log(20\times365)$$
$$=1.87(\%)$$

From the calculation above it is enough to have the cask design margins of 2.0% heat weight loss even if the scattering in the test results are taken into account.

Water drops were observed on inside surface of sealed container when the lid was cut off to open and to take out the test specimen from the container after test. It is considered that these drops prevented the temperature rise of test specimen by evaporating during the test and reduced the heat weight loss of the specimen.

From the results, it is concluded that NS-4-FR is effective as neutron shielding material of cask, especially when it is used in enclosed condition.

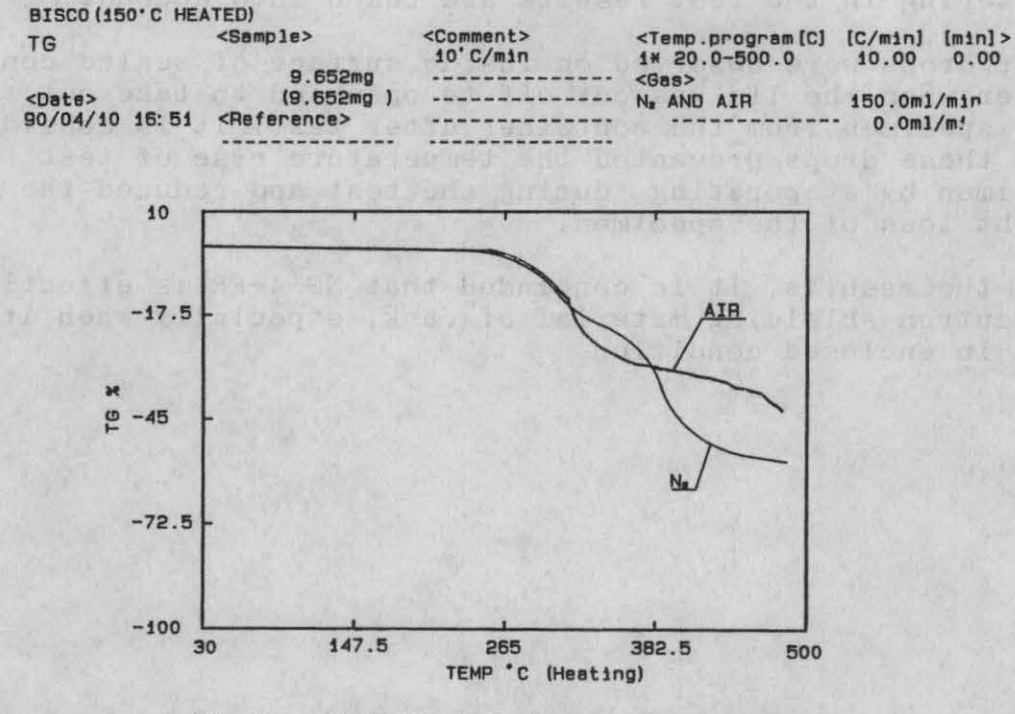

Fig 1 TG OF NS-4-FR IN AIR AND NITROGEN

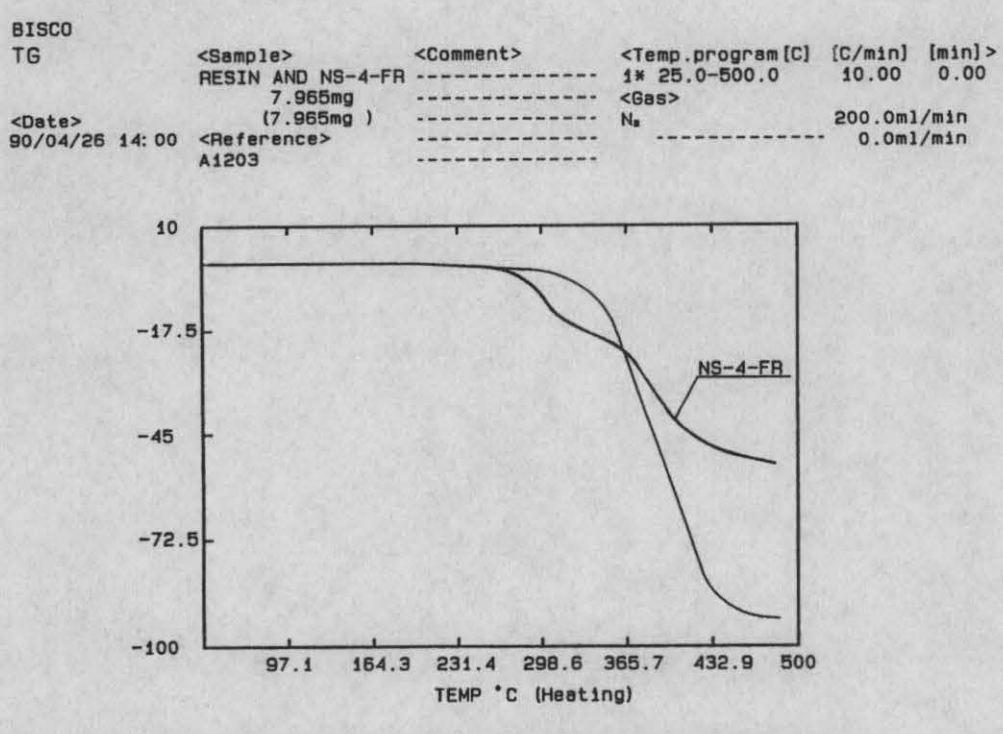

Fig 2 TG OF NS-4-FR W/O FIRE RETARDANT

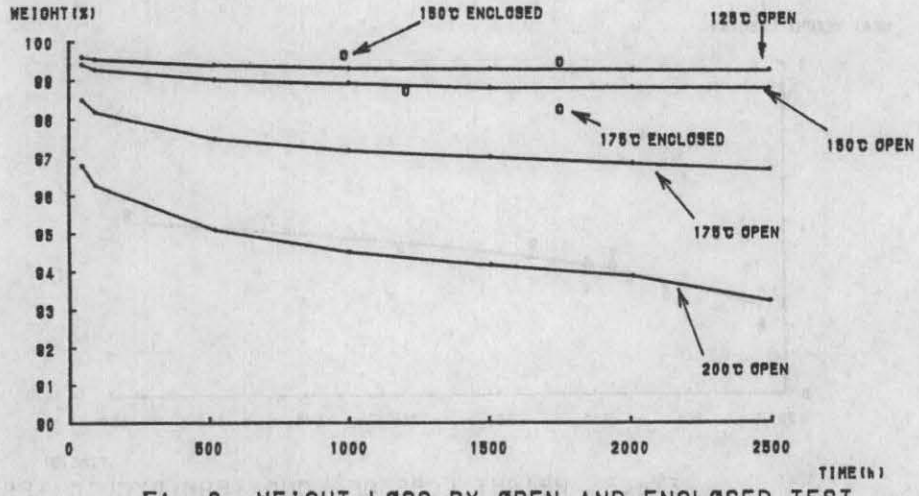

Fig.3 WEIGHT LOSS BY OPEN AND ENCLOSED TEST

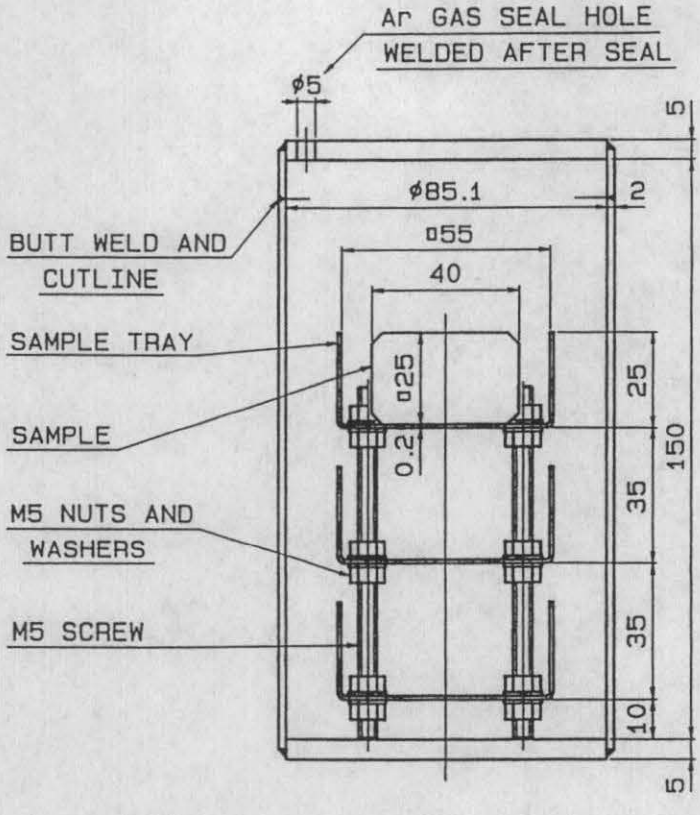

Fig 4 SEALED STAINLESS STEEL CONTAINER

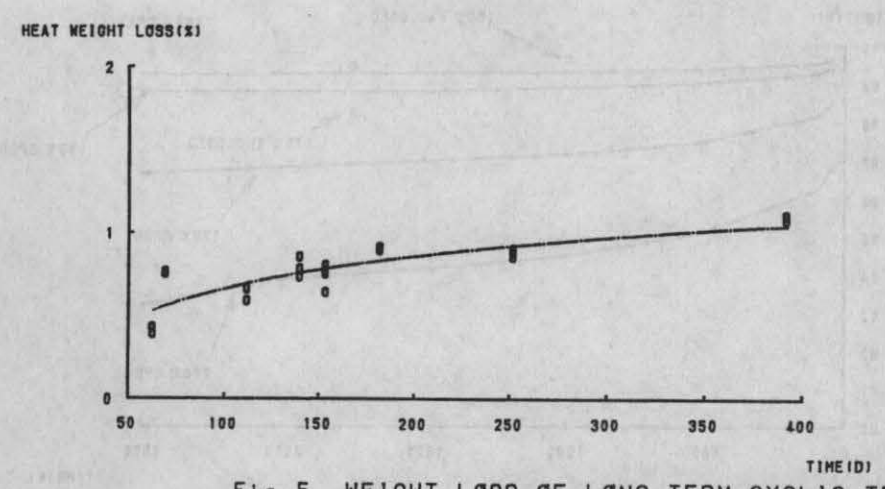

Fig.5 WEIGHT LOSS OF LONG TERM CYCLIC TEST