THE APPLICABILITY OF LIQUID NEUTRON SHIELD TO A SPENT FUEL TRANSPORTABLE STORAGE CASK

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INTRODUCTION

It is advantageous to use liquid neutron shield for a spent fuel transportable storage cask, because of heat removal performance and manufacturing cost performance. In Japan, ethyleneglycol-water solution is used for HZ-75T and NH-25 transport casks which have been in operation for over 20 years. In the United States, there are many transport casks that use a water solution neutron shield. Also, a storage cask using an ethyleneglycol-water solution neutron shield with boron had been put to test use in the United States. Though the glycol-water solution as the neutron shield is satisfactorily practical as mentioned above, there are few reports concerning the change of its nature and the effect on the corrosion of cask materials under long time use.

The transportable storage cask developed by OCL and NFT uses propyleneglycol-water solution that is comparable to ethyleneglycol-water solution in shielding ability and antifreezing performance. The propyleneglycol-water solution has been introduced because propyleneglycol is accepted as a food additive and consequently there is no environmental problem even if the solution leaks out under hypothetical accidents.

In this study, the following items have been studied for the purpose of evaluating the change of the characteristics of propyleneglycol-water solution and its effect on the corrosion of cask materials under long time use for 40 to 60 years.

- Heat Acid Degradation of Propyleneglycol-water Solution
- Radiolysis of Propyleneglycol-water Solution
- Effect on the Corrosion of Cask Composition by Degradation Products

CONDITION FOR THE USE OF LIQUID NEUTRON SHIELD

The typical specifications of the NEO-type transportable storage cask developed by OCL and NFT, and thermal and radiation conditions for the use of liquid neutron shield of the cask are shown in Table 1. A temperature of 140°C was the basis used for the evaluation of heat acid degradation of propyleneglycol-water solution. The absorbed dose in the propyleneglycol-water solution is mostly caused by neutron exposure. The quantity of the absorbed dose is calculated by using Kerma factor and energywise neutron flux in the neutron shield. Though the neutron source strength becomes less as time goes on, the initial neutron flux was used to calculate the accumulated absorbed dose for 60 years conservatively. The calculated absorbed dose for the water and propyleneglycol without boron is about 500Gy/60years, and the dose is caused by proton exposure caused by elastic scattering between neutron and hydrogen nuclei. In the case of typical NEO-type cask design, 3000ppm of boron as a form of boric acid is added to the propyleneglycol-water solution to reduce the generation of secondary gamma ray. Therefore, about 1500Gy/60years of absorbed dose by exposure of alpha ray produced by $^{10}\mathrm{B}(n,\alpha)\,^{7}\mathrm{Li}$ reaction, is added to 500Gy/60years.

On the other hand, the absorbed dose by gamma exposure can be assumed to be almost equal to effective dose. Therefore, total absorbed dose of propyleneglycol-water solution for 60years is less than 3KGy, even if it is conservatively evaluated by neglecting the reduction of source intensity and using radiation flux at the maximum point in the neutron shield. An absorbed dose of about 6KGy was the basis used for the evaluation of radiolysis of propyleneglycol-water solution in this study, with consideration of a higher safety margin.

Table-1 Specifications of NEO-2521 Cask and Thermal and Radiation Conditions for Neutron Shield.

Loading	Capacity		21 PWR Fuel Assemblies		
	Burnup		cask average: 50,000 MWd/mtU		
			max.. fuel :55,000 MWd/mtU		
	Cooling Time		10 years		
	Heat Capacity		20kW/cask		
Temperature (℃)			Neutron Shield		
			Adjacent Part to Main Body	Center of Neutron Shield	Adjacent Part to Outer Shell of Cask
			136	132	—
Effective Dose (μSv/h)	Neutron		1.69×10^{4}	6.88×10^{2}	4.87×10^{1}
	Gamma Ray		1.65×10^{3}	1.12×10^{3}	6.32×10^{2}
	Total		1.86×10^{4}	1.81×10^{3}	6.81×10^{2}
Absorbed Dose (Gy/60years)	Neutron	PG	499	14.4	1.49
		3000ppmB	1480	349	8.88
	Gamma Ray		868	589	332
	Total		2847	952	342

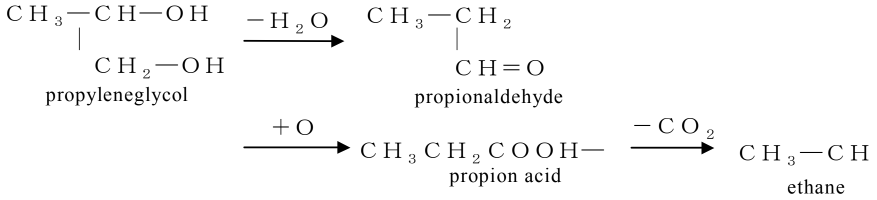
HEAT ACID DEGRADATION OF PROPYLENE-GLYCOL-WATER-SOLUTION

About 130cc propyleneglycol-water solution had been kept in a small stainless steel bottle with a constant temperature for a constant term. The bottle has a capacity of about 190cm^{3}. Two varieties of propyleneglycol-water solutions were used in the experiments. One was pure propyleneglycol-water solution produced by mixing 45% water with 55% propyleneglycol (PG). The other was water solution with 3000ppm of boron as a form of boric acid added to the pure propyleneglycol-water solution (PG (B)). The cavity of the bottle was filled with air. Though the (Type-A) bottle with elastomer gasket was initially used in the experiments, the (Type-B) bottle with metallic valve was used in some experiments, because Type-A bottle had slight leakage.

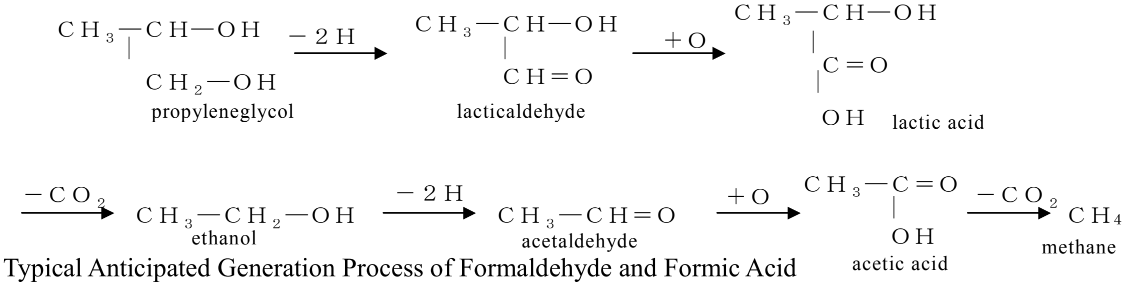
The products in the gas phase and liquid phase in the bottle were analyzed after heating for a certain period of time. The major products in the gas phase were hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), propene ($CH_3CH_2CH_3$), acetone (CH_3COCH_3) etc., in addition to nitrogen (N_2) and oxygen (O_2) which were compositions of enclosed air. Measured yields of major products in the gas phase are shown in Figure 1. It is considered that the analysis results for gases of Type-A bottle are very scattered compared with those of Type-B bottle, because of a small leakage of Type-A bottle during an experimental time. And also, there is the possibility of getting mixed with a little quantity of air at the time of sampling gas in the bottle. However, the quantity of carbon monoxide (CO) and carbon dioxide (CO_2) roughly shows time dependence as the same tendency as data of Type-B, although there is less reliability of quantitative value for analysis data using Type-A bottle.

The major products in the liquid phase were acetone (CH_3COCH_3), methanol (CH_3OH), ethanol (C_2H_5OH), dimethyldioxane isomer ($C_6H_{12}O_2$), hydroxypropanone ($HOCH_2COCH_3$), formaldehyde (HCHO), acetaldehyde (CH_3CHO), propionaldehyde (CH_3CH_2CHO), glycol acid ($HOCH_2COOH$), formic acid (HCOOH), acetic acid (CH_3COOH) etc., in addition to dipropyleneglycol ($(HOC_3H_6)_2O$) which was an composition of initial solution. Measured yields of major products in the liquid phase are shown in Figure 2. The measured hydrogen power (pH) value of (PG) shifted to about 4.0 to 4.5 from the initial value of about 7 during the heating term. On the other hand, the measured pH value of (PG (B)) was slightly reduced from the initial value of about 4 as time went on. Typical anticipated generating process of detected organic acid and aldehyde which is the precursor of acid, are shown as follows:

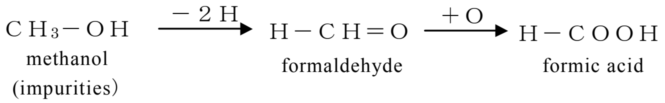
① Typical Anticipated Generation Process of Propionaldehyde and Propion Acid



② Typical Anticipated Generation Process of Acetaldehyde and Acetic Acid



③ Typical Anticipated Generation Process of Formaldehyde and Formic Acid



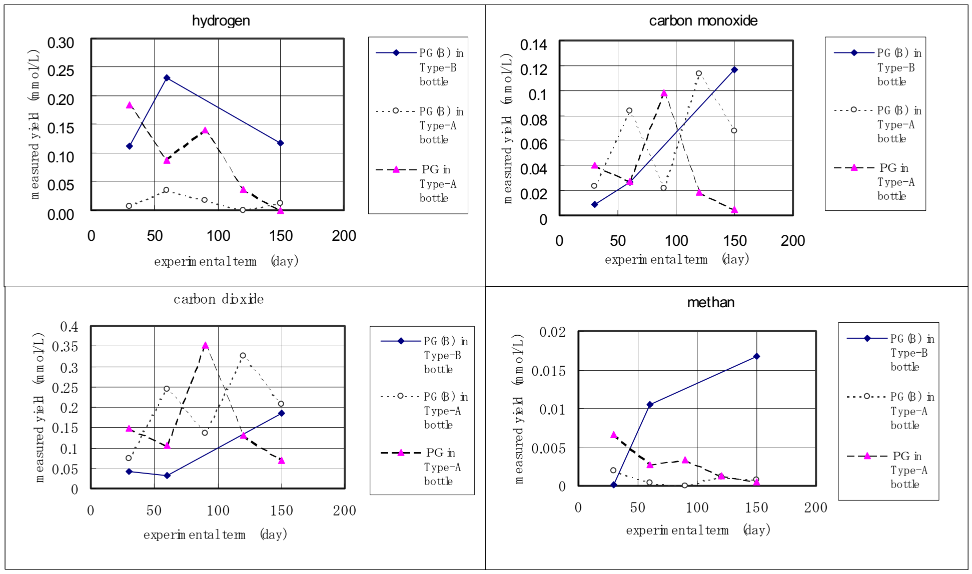


Figure1 Measured Yields of Products in Gas Phase for Heat Acid Degradation Experiment of Propylenglycol-water Solution at 140℃

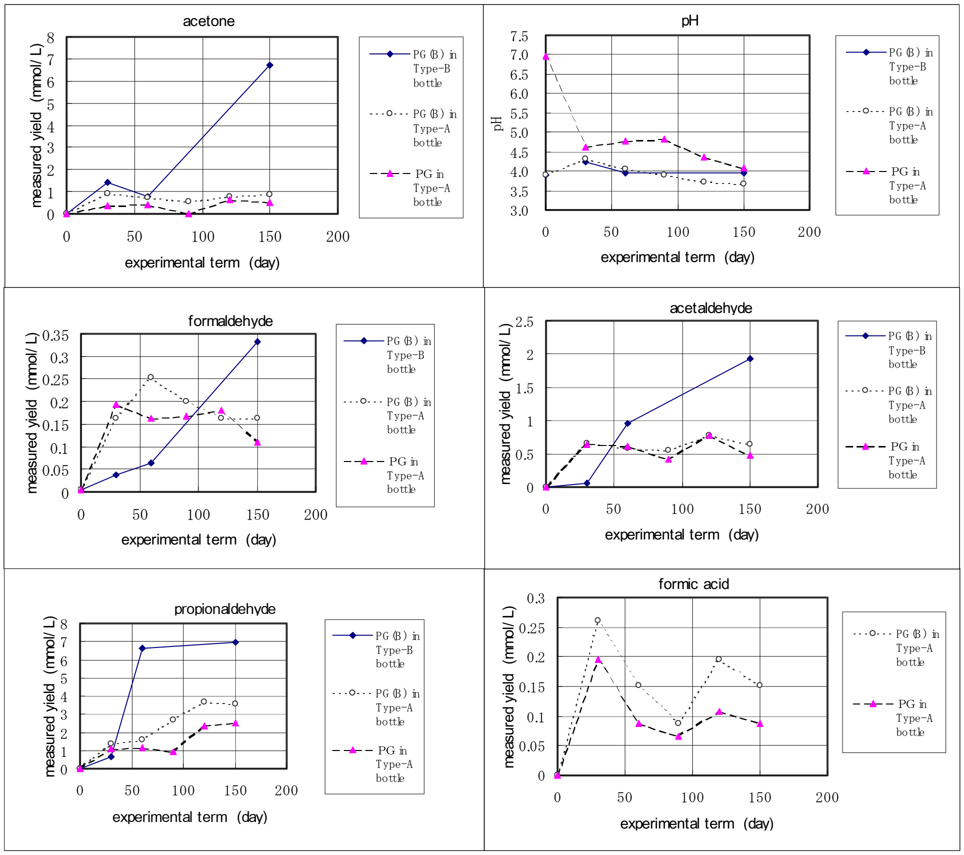


Figure2 Measured Yields of Products in Liquid Phase for Heat Acid Degradation Experiment of Propyleneglycol-water Solution at 140℃

RADIOLYSIS OF PROPYLENE GLYCOL WATER-SOLUTION

About 73cc propyleneglycol-water solution had been exposed by ^{60}Co gamma ray in a small Pyrex ampule. The ampule has a capacity of about 108cm^3. Four varieties of ampules with propyleneglycol-water solution were used in the experiments. Two types of ampules contain (PG) or (PG (B)) as the same solution used in the heating experiments with air in the cavity. Third one contains propyleneglycol-water solution purged with nitrogen, and its cavity is filled with nitrogen gas (PG (N_2)). Fourth one contains propyleneglycol-water solution heated with a constant temperature of 140°C for three months beforehand (PG (3M)). The cavity of this ampule is filled with air. Gamma irradiation was also carried out with simultaneous heating, too. In this experiment, ampules were soaked in silicone oil kept at a constant temperature during irradiation.

The products in the gas and liquid phase in the ampule were analyzed after irradiation for a certain period of time. The major products in the gas phase were hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), acetone (CH_3COCH_3), dimethyldioxane isomer ($C_6H_{12}O_2$), etc., in addition to nitrogen (N_2) and oxygen (O_2) those were compositions of enclosed air. The relation between the quantity of major products in the gas phase and exposure is shown in Figure 3. The yields of hydrogen (H_2), carbon monoxide (CO), methane (CH_4), and acetone (CH_3COCH_3) in the gas phase increase along exposure, and show irradiation temperature dependence except for hydrogen (H_2).

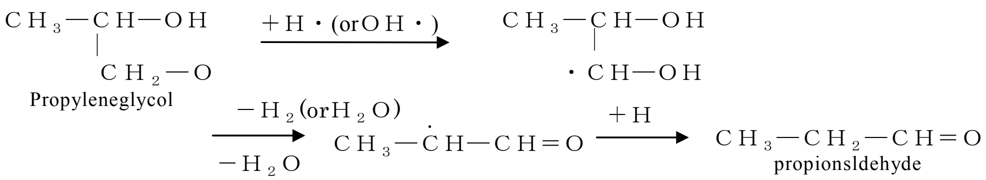
The major products in the liquid phase were acetone (CH_3COCH_3), methanol (CH_3OH), ethanol (C_2H_5OH), dimethyldioxane isomer ($C_6H_{12}O_2$), hydroxypropanone ($HOCH_2COCH_3$), formaldehyde (HCHO), acetaldehyde (CH_3CHO), propionaldehyde (CH_3CH_2CHO), oxalic acid ($H_2C_2O_4$), formic acid (HCOOH) etc., in addition to dipropylene glycol ($(HOC_3H_6)_2O$), which was an composition of initial solution. The relation between the quantity of major products in the liquid and exposure is shown in Figure 4. The yield of every aldehyde, which is precursor of acid, increases along exposure. There is no significant change of measured pH value. The yields of acetone, acetaldehyde, and propionaldehyde show irradiation temperature dependence. From the facts described above, it is concluded that there is not such a significant chain reaction on radiolysis of propyleneglycol-water solution at a high temperature of 140°C, though it is recognized that the yield of acetone at 140°C is about six times as much as the yield of at room temperature. By comparing (PG (3M)) with (PG) on pH and the yield of formic acid in Figure 4, it can be seen that the yield of acid is dominated by previous heating. It is also considered that the yield of every aldehyde is less affected by dissolved oxygen, whereas the yield of hydrogen and acetone in (PG (N_2)) become about 20% and 40% less respectively by eliminating air. It is known that the yields of radiolysis products conversely increase in proportion as the dose rate decreases, if the accumulated absorbed dose is the same. In fact, in this study, it was recognized that the radiolysis yield of acetone under one-fourth the basic dose rate increased 1.6 times as much as one under a basic dose rate. 1.8mmol/liter propyleneglycol would be analyzed for 6kGy dose if G-value of propyleneglycol would be considered to be about 3. Although this radiolysis quantity is not so much, the effect of dose rate above mentioned must be considered as future problem.

Typical anticipated generation process of detected organic acid and aldehyde which is the precursor of acid, are shown as follows:

① Radiolysis of Water

$H_2O \longrightarrow \cdot H + \cdot OH^- + e^-aq$

② Typical Anticipated Generation of Propionaldehyde



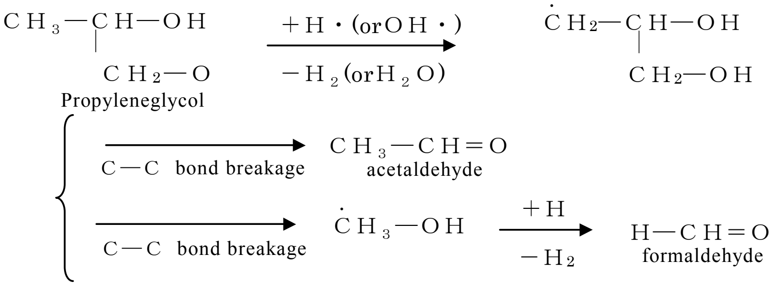
$$CH_3-\underset{\displaystyle CH_2-O}{\underset{|}{C}}H-OH \xrightarrow{+H\cdot\ (or\ OH\cdot)} CH_3-\underset{\displaystyle \cdot CH-OH}{\underset{|}{C}}H-OH$$

$$\xrightarrow[-H_2O]{-H_2(or\ H_2O)} CH_3-\dot{C}H-CH=O \xrightarrow{+H} CH_3-CH_2-CH=O$$

Propyleneglycol

propionsldehyde

③ Typical Anticipated Generation Process of Acetaldehyde and Formaldehyde



$$CH_3-\underset{\displaystyle CH_2-O}{\underset{|}{C}}H-OH \xrightarrow[-H_2(or\ H_2O)]{+H\cdot\ (or\ OH\cdot)} \dot{C}H_2-\underset{\displaystyle CH_2-OH}{\underset{|}{C}}H-OH$$

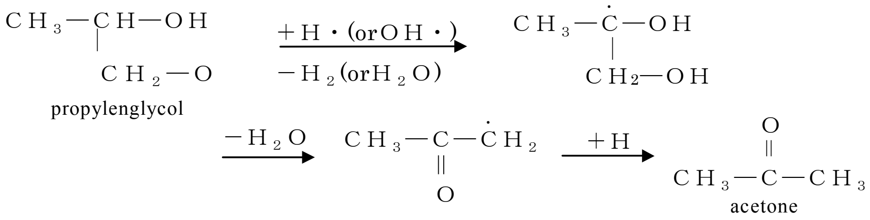
$$\left\{\begin{array}{l} \xrightarrow[\text{C—C bond breakage}]{} CH_3-CH=O \\ \xrightarrow[\text{C—C bond breakage}]{} \dot{C}H_3-OH \xrightarrow[-H_2]{+H} H-CH=O \end{array}\right.$$

Propyleneglycol

acetaldehyde

formaldehyde

④ Typical Anticipated Generation Process of Acetone



$$CH_3-\underset{\displaystyle CH_2-O}{\underset{|}{C}}H-OH \xrightarrow[-H_2(or\ H_2O)]{+H\cdot\ (or\ OH\cdot)} CH_3-\underset{\displaystyle CH_2-OH}{\underset{|}{\dot{C}}}-OH$$

$$\xrightarrow{-H_2O} CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-\dot{C}H_2 \xrightarrow{+H} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

propylenglycol

acetone

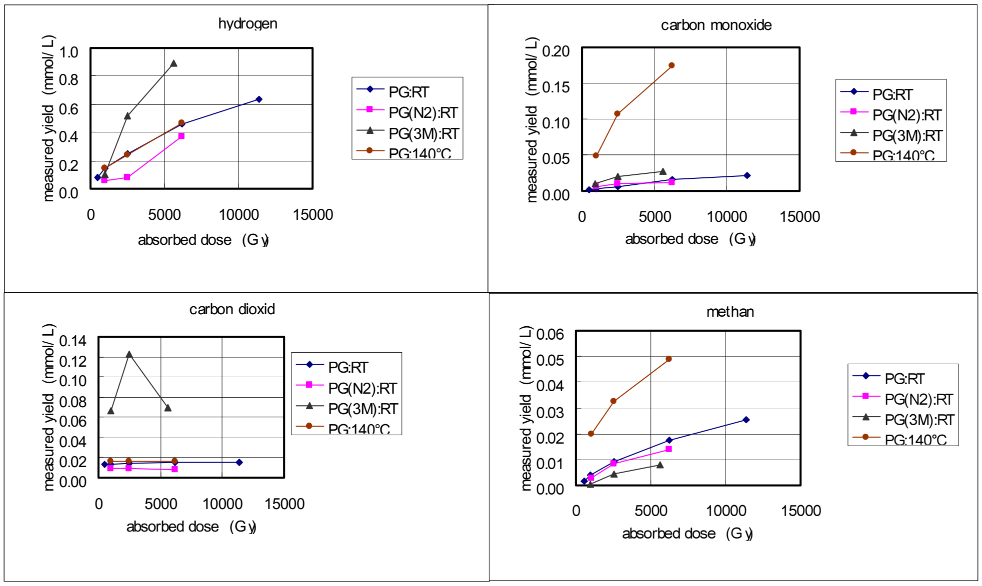


Figure3 Measured Yields of Products in Gas Phase for Radiolysis of Propyleneglycol-water Solution

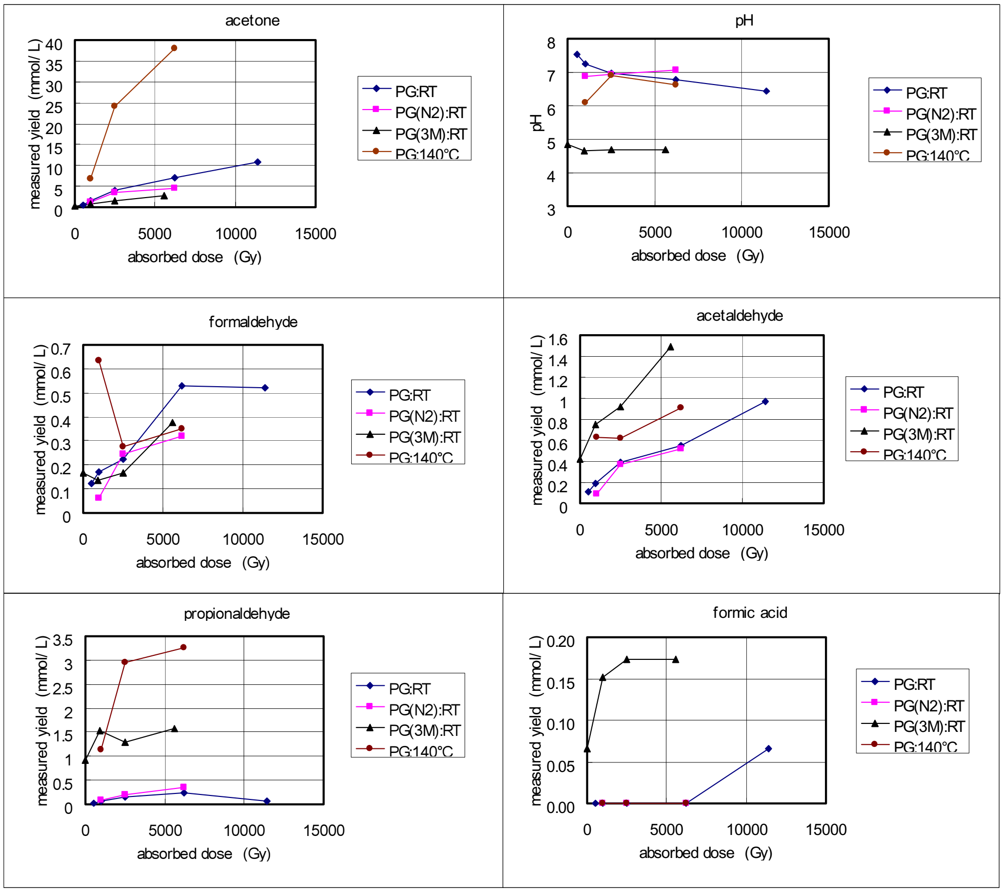


Figure4 Measured Yields of Products and pH in Liquid Phase for Radiolysis of Propyleneglycol-water Solution

EFFECT ON THE CORROSION OF CASK COMPOSITION BY DEGRADATION PRODUCTS

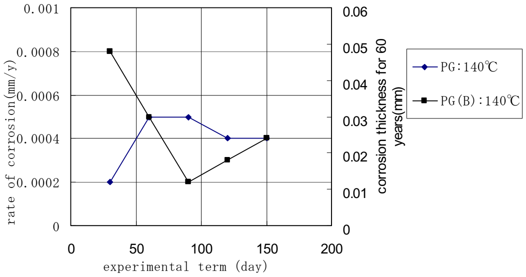


Figure5 Experimental Results of Stainless Steel Corrosion in PG and PG(B) at 140°C

It is necessary to provide stainless steel as the structural material surrounding propylenglycol-water solution neutron shield because of acid corrosion proofing. To evaluate the rate of corrosion for stainless steel, some small specimens (35mm long, 10mm wide, 3mm thick) were soaked in the (Type-A) bottle during the above mentioned heating experiments. The rates of corrosion for stainless steel in (PG) and (PG (B)) at a temperature of 140°C are shown in Figure 5. From this experimental result, the corrosion of stainless steel is not substantial.

ANTIFREEZING PERFORMANCE OF PROPYLENEGLYCOL-WATER SOLUTION

It was investigated whether the antifreezing performance of propylenglycol-water solution would change by heat acid degradation and radiolysis. Glass transition temperature, cold crystalization peak temperature, and melting peak temperature of the propyleneglycol-water solution that was heated for 5 months at 140°C and had irradiation of 6 kGy, were measured by using a Differential Scanning Calorimetry (DSC). In result, no particular change of the antifreezing performance of the propyleneglycol-water solution was recognized.

YIELD OF ACID

It is well known that casing organic matter produces aldehyde and acid by heat degradation and radiolysis. The acid causing corrosion is produced in the propyleneglycol-water solution by bonding with oxygen to aldehyde as mentioned above. It can be considered that the source of supplying oxygen is dissolved oxygen and hydrogen peroxide produced by radiolysis for water. It is conservatively estimated that the quantity of dissolved oxygen is about 60 mg/liter, assuming the quantity of dissolved oxygen for propyleneglycol-water solution is the same with the one for pure alcohol. On the other hand, 0.3mmol/liter oxygen (9.6mg/liter oxygen) would be produced for 6kGy dose, assuming G-value of hydrogen peroxide for propyleneglycol-water solution is about 1. Assuming all of 100mg/liter (6.2mmol/liter) oxygen including oxygen for hydrogen peroxide would be used for production of formic acid roughly, 6.2 mmol/liter (285 mg/liter) formic acid would be produced. Therefore, it is considered that it is satisfactorily conservative to use 1000mg/liter (1000ppm) formic acid solution for future study of corrosion.

SUMMARY

The summary is as follows:

- It can be seen from the results of experiments that the organic acid causing corrosion was not produced much, though various organic matters were produced by heat acid degradation and radiolysis.
- Though the heat acid degradation experiment carried out no more than 5 months in this study, it is considered that the production of organic acid would stop at a point of time when the resolved oxygen was completely spent. Therefore, it is considered that it is satisfactorily conservative to use 1000mg/liter (1000ppm) formic acid solution for future study of corrosion.
- No particular change of the antifreezing performance of the propyleneglycol-water solution by heat acid degradation and radiolysis was recognized.
- It can be seen from the results that the use of propyleneglycol-water solution as the neutron shield for a transportable storage cask, is applicable for long time use under the condition that stainless steel or the stainless overlay is used for the corrosion proofing against the water-solution.

ACKNOWLEDGEMENT

In this study, the radiolysis experiment was carried out in cooperation with Research Institue for Advanced Science and Technology of Osaka Prefecture University.

REFERENCES

[1] Walter J. Rossiter. Jr., Paul W. Brown and McClure Godette, “The determination of Acidic Degradation Products in Aqueous Ethylene Glycol and Propylene Glycol Solution Using Ion Chromatography”, Solar Energy Materials 9 (1983) 267-279

[2] ICRU REPORT, “Neutron Dosimetry for Biology Medicine”

[3] J. W. T. Spinks and R. J. Woods; An Introduction to Radiation Chemistry, Third Edition, John Wiley & Sons, Inc., 1990.

[4] S. Gordon, K. M. Schmidt and J. R. Honekamp; Radiat. Phys. Chem., 21, 247 (1983) "An Analysis of the Hydrogen Bubble concerns in the Three-Mile Island UNIT-2 Reactor Vessel"

[5] W. Burns and P. B. Moore; Radiat. Effects, 30, 233 (1976) "Water Radiolysis and Its Effect upon In-Reactor Zircaloy Corrosion"

[6] G. R. Sunaryo, Y. Katsumura, D. Hiroishi and K. Ishigure; Radit. Phys. Chem., 44, 273 (1994), "Radiolysis of Water at Elevated Temperatures I - Irradiation with g-rays and Fast Neutrons at Room Temperature"