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Measurement of the Radiolysis Gases Generated in the Waste Forms by External Irradiation

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1. Introduction

All radioactive waste drums, if they disposed in a permanent disposal site, could be exposed ~ 10^{+8} rads from the incorporated radionuclides during the 300 years' surveillance period. As a result of that exposure, the structural stability of the waste forms can be deteriorated owing to the swelling, the generation of the radiolysis gases and the volatile materials. And furthermore the waste forms can be caused the safety of the disposal site not to keep. So to prevent from deteriorating the waste forms, we must evaluate or test the waste form against the external irradiation, but there is no any kind of standard test methods for the irradiation except recommendations in several countries. NRC/BTP of USA recommends to carry out the irradiation test for the waste forms that incorporated the organic materials or ion-exchange resins and that is over 10^{+9} rads of the cumulative expected exposure dose rate, and insists to decide the effects (specimen size, irradiation temperature and dose rate) to calculate a G-value. France recommends to irradiate to the 10^{+7} rads with a dose rate = 2 x 10^{+4} rads/hr and to calculate. In Korea, there are no any recommendations for the irradiation test but MOST Notification No. 2005-18 describes that the waste forms must have a sufficient strength to keep their structural integrity under the expected situations in handling stage and the expected pressure and temperature in a disposal step.

In this study, we choose the wastes generated in a large and their solidification matrix used in popular, and put their small amount to the vial by using a high vacuum pump, and irradiated to the 10^{+8} rads in a 5.43 x 10^{+6} rads/hr. Finally we analyzed the type and amount of the generated radiolysis gases.

2. Methods and Results

2.1 Preparation of Waste and Waste Form

In consideration of the generation amount and the solidification matrix used in popular, the cemented and paraffin waste forms incorporated the borate wastes, the cemented waste form incorporated the ion-exchange resins, and miscellaneous waste(decontamination paper) were chosen. The 1.1 g per several wastes were put into the pyrex tube and evacuated air by using the rotary vacuum pump below 0.1 torr. Under the pressure of 0.1 torr , the pyres rubes were sealed.

Figure 1. Specimens for Irradation

2.2 Irradiation Test

For the irradiation of specimens from the external radiation source, the pyrex tubes contained the specimens were installed in a small turn-table in a round type. And the 72,023.9 Ci of Co-60 source irradiated the pyrex tube until 10^{+8} rads with a constant dose rate, 5.43 x 10^{+5} rads/hr.

And after the irradiation, the pyrex tube was put into the vacuum chamber known the volume, and then was broken under vacuum. At this time the pressure change was measured by the baratron, and the partial pressure of individual gases measured with the precision gas mass analyzer(Finnigan MAT 271) to analyze the individual gaseous species. – 60 °C cryogenic trap was used for the remove of moisture.

Fig. 2 is the pretreatment apparatus to measure the individual gas amount.

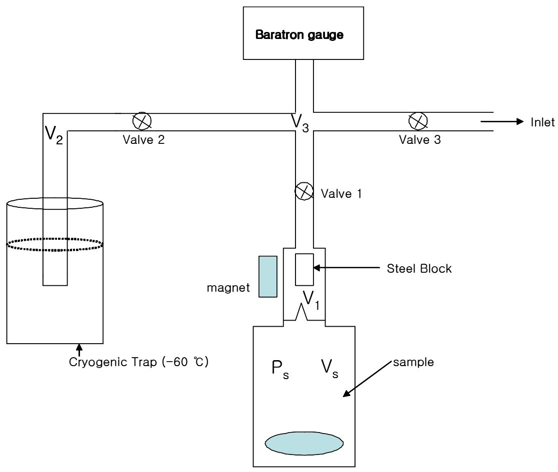

Figure 2. Apparatus to measure the gas amount

After the above apparatus was under vacuum, the nitrogen gas of 5 cm^3 · atm was inserted to the system($V_s + V_1 + V_2 + V_3$) and then measured the system volume through the measurement P_{N2}.

$$5\ cm^3 \cdot atm = P_{N2} \cdot (V_s + V_1 + V_2 + V_3) \ \ (at\ 22\ ℃)$$
$$(V_s + V_1 + V_2 + V_3) = 5\ cm^3 \cdot atm / P_{N2}$$

And then $V_s \cdot P_s$ could be calculated through Psys(equilibrium pressure between the system and the pyrex tube).

$$V_s \cdot P_s = P_{sys} \cdot (V_s + V_1 + V_2 + V_3)$$

So total pressure(Ps) is the summation of the individual gases' pressure.

$$P_s = P_1 + P_2 + P_3 + P_4$$

2.3 Gas Amount Generated from the wastes

As a result of the analysis, the generated gases were H_2, CH_4, amines, N_2, CO, Ethane, O_2, and CO_2.

Table 1 shows the partial pressure(%mole/mole) of the main gases of the above-analyzed gases, and the volume(cm^3) of pyrex tube contained the wastes. Table 2 shows the amount(cm^3.atm) of the main gases of the above-analyzed gases.

The amount gas volume was larger in paper wastes than other wastes. The main gas in the generated radiolysis gases was hydrogen gas. Hydrogen in the borate-cement waste form would be generated in the crystal water but would be generated in hydrocarbon of organic materials in other waste forms and wastes.

In general the cemented waste form was known well as the stable form but the reason that the generation of gas in the cemented waste form incorporated ion-exchange resins was larger, was due to the degradation of the functional groups(specially, amine group) of ion-exchange resins.

Of the organic material, total gas amount, H_2, and CH_4 were generated much more in paper wastes than other wastes.

Table 1. Individual Partial Pressure(%mole/mole) in Generated Gases and the Volume of Pyrex Tubes

Waste Type	No	H_2	CH_4	Amines	Total (cm^3.atm)	Pyrex Volume
Cement-Borate	1	97.79	0.17	0.00	0.03	11.36
	2	93.90	0.32	0.00	0.03	11.46
	3	91.62	0.83	0.00	0.03	11.32
Paraffin-Borate	1	87.39	0.39	0.00	0.18	10.78
	2	90.90	0.34	0.00	0.20	11.56
	3	78.17	0.32	0.00	0.12	11.24
Cement-Resins	1	55.56	1.09	39.00	0.11	11.50
	2	12.81	0.05	0.57	0.79	11.99
Papers	1	57.94	0.15	0.00	0.52	11.50
	2	72.53	0.15	0.00	0.45	11.46
	3	66.20	0.31	0.00	0.42	11.50

Table 2. The Volume(cm^3.atm) of the Radiolysis Gases Generated in the waste type

Waste Type	No	H_2	CH_4	Amines	Total (cm^3.atm)
Cement-Borate	1	0.029	5.00E-05	0	0.029
	2	0.027	9.30E-05	0	0.029
	3	0.031	0.00028	0	0.034
Paraffin-Borate	1	0.155	0.00069	0	0.178
	2	0.177	0.00067	0	0.195
	3	0.096	0.00039	0	0.123
Cement-Resins	1	0.062	0.00122	0.044	0.112
	2	0.101	0.00042	0.004	0.788
Papers	1	0.298	0.00077	0	0.515
	2	0.324	0.00067	0	0.447
	3	0.279	0.00132	0	0.422

3. Conclusion

The results of the irradiation to the waste and waste forms with 10^{+8} rads as follows;

- The type and the generation amount of the radiolysis gases were different to the waste type. The generation amount was larger in the organic wastes and in the waste forms incorporated the organic wastes.
- The most of the generated radiolysis gases was hydrogen and the order of the generation in other gases was CO_2 > CO > methane > ethane.
- The cemented waste forms were known as the very stable forms against to the radiation, but unexpectedly the waste forms incorporated ion-exchange resins generated the radiolysis gases much more. The reason was expected due to the anionic resins(amine functional group).