Radiation Decomposition of Trichlorofluoromethane in Flow System under ^{60}Co γ -Ray Irradiation

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Irradiation experiments of CCl_3F were carried out with ^{60}Co γ -rays using the irradiation facility of the flow system. In the system, CCl_3F was irradiated at 5.7 kGy/h ($5.7 \times 10^5 \text{ rad/h}$) and -30°C . The decomposition behavior of CCl_3F and the influence of impurities in the circulating gas on the decomposition were examined. The result was compared with that of ampoule scale.

The decomposition yield of CCl_3F and the yields of radiolytic products (fluorocarbons) increased in proportion to the absorbed dose. The decomposition yield per Mrad of CCl_3F was $0.0246 \text{ mol\%/Mrad}$ ($G=2.9$). This value was equal to 1.8 times that of the ampoule scale. The marked influence of impurities (air, CH_4 , I_2) was recognized for the yields of halogen ions.

Key Words: radiation decomposition, trichlorofluoromethane, cobalt-60, degradation products, flow system

1. Introduction

The removal of ^{85}Kr by the solvent absorption process has been undertaken in the flow system equipped with an absorber column and a stripper column at the ^{85}Kr recovery plant¹⁾. In the process, the solvent has been subject to radiation damage by ^{85}Kr β -rays. In our previous papers^{2)~4)}, the radiolysis of 4 fluorocarbons (CCl_3F , CCl_2F_2 , $\text{C}_2\text{Cl}_4\text{F}_2$ and $\text{C}_2\text{Cl}_3\text{F}_3$) by ^{60}Co γ -rays was examined under various conditions in the batch system (ampoule scale). Several other studies^{5)~9)} on the radiolysis of fluorocarbons have been also conducted in the ampoule scale. The G-values for the decomposition of fluorocarbon and the formation of the degradation products were obtained, and the decomposition behavior of fluorocarbon in the

ampoule scale was elucidated by these studies. Present study deals with the decomposition behavior of CCl_3F by ^{60}Co γ -rays in a flow system which simulates the ^{85}Kr recovery plant.

The radiation damage of fluorocarbon in the flow system must be different from the case of the ampoule scale, because the decomposition may be affected by the continuous removal of the degradation products generated, and in addition, by the impurities in the off-gas at the fuel reprocessing. Accordingly, it is difficult to predict the decomposition behavior of fluorocarbons in the flow system from the results of the ampoule scale.

In the present study, the irradiation experiments were carried out with ^{60}Co γ -rays using the irradiation facility of the flow system, in which ^{60}Co source of 2.442 PBq (66 kCi) was installed instead of ^{85}Kr . Nitrogen gas was used in the place of the off-gas as circulating gas and CCl_3F was used as fluorocarbon. The decomposition behavior of CCl_3F and the influence of impurities on the decomposition were examined under the above conditions and the results obtained were compared with those of

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Fig. 1 Flow sheet of fluorocarbon and circulating gas during irradiation.

the ampoule scale presented in the previous paper²⁾.

2. Experimental

2.1 Fluorocarbon irradiation facility

This irradiation facility consists of reaction vessel, gas circulation apparatus, stripper column, fluorocarbon circulation apparatus, and vacuum exhaust apparatus. The whole facility is made of stainless steel and forms an airtight system. The reaction vessel alone is installed in ^{60}Co irradiation cell. The fluorocarbon in the reaction vessel is irradiated with ^{60}Co γ -rays. Cooling jackets are attached to main parts except the reaction vessel. The fluorocarbon is controlled at constant temperature by a coolant passing through these jackets. Figure 1 shows the course of the fluorocarbon and the circulating gas during the irradiation.

(1) Reaction vessel: This part consists of a single reaction vessel. It is the part that the fluorocarbon poured from the absorber column (inlet) is irradiated and sent to the stripper column (outlet). The capacity of the reaction vessel is 1.9 l (400×206×31 mm). It is immersed in a thermostat shown in Fig. 2. The aqueous calcium chloride (30%) is used as the coolants, and cooled by refrigerator during the irradiation.

(2) Gas circulation apparatus: This part consists of the absorber column and a gas holder.

Fig. 2 Arrangement of reaction vessel in thermostat.

It is the part that a fraction of circulating gas is dissolved in the fluorocarbon in the absorber column by contacting the circulating gas with the fluorocarbon which flows in parallel. The capacity of the absorber column is 125 cc (43 mm ϕ ×500 mmh), and MacMahon's packings of 159 g are filled up in it. The gas holder is a vessel for the adjustment of pressure and its capacity is 1.6 l (114 mm ϕ ×160 mmh).

(3) Stripper column: This part consists of the stripper column, still, reflux condenser and cold trap. It is the part that the circulating gas dissolved in the fluorocarbon is released by contacting the fluorocarbon flowed from the reaction vessel with the vapor of fluorocarbon generated in the still. Most of the fluorocarbon vapor is condensed at the reflux condenser and returns to the stripper column, while the circulating gas returns to the gas holder through the

cold trap. By the removal of the degradation products (low boiling point) in the circulating gas and the fluorocarbon vapor at the cold trap, the circulating gas returning to the absorber column becomes dry state.

The capacity of the stripper column is 580 cc ($43\text{ mm}\phi \times 400\text{ mmh}$), and MacMahon's packings of 118 g are filled up in it. The capacity of the still is 1 l ($102\text{ mm}\phi \times 130\text{ mmh}$), and a mantle heater (500 W) is attached to the outside of it. Both the reflux condenser and the cold trap are the double cylindrical structure, and these sizes are $37\text{ mm}\phi \times 100\text{ mmh}$ and $43\text{ mm}\phi \times 200\text{ mmh}$, respectively.

(4) Fluorocarbon circulation apparatus: This part consists of the fluorocarbon cooler and circulating pump. It is the part that the fluorocarbon flowed through the still is cooled and sent to the absorber column again. The fluorocarbon cooler is a heat exchanger of hose line form. The size of the pipe is $10\text{ mm}\phi \times 300\text{ mmL}$ and the heat-transfer area is 100 cm^2 . The circulating pump is metallic diaphragm type.

(5) Vacuum exhaust apparatus: The part which consists of vacuum pumps and a cold trap controls the exhaust of the whole facility.

2.2 Irradiation experiment

The irradiation of fluorocarbon was carried out according to the following procedure. The facility was evacuated to 1×10^{-2} Torr by means of the vacuum pumps, and was filled with the deaerated fluorocarbon (CCl_3F) of 6.41 kg. Then, main parts were cooled at constant temperature, and the circulating gas of a fixed volume was charged into the facility. The circulating gas was dissolved in the fluorocarbon at the absorber column by the circulation of fluorocarbon with the circulating pump. The circulation amount of fluorocarbon was set at 2 l/h.

By heating the still at 25°C , the stripper column was led to the reflux state. After reaching the reflux state, the fluorocarbon in the reaction vessel shown in Fig. 2 was irradiated with ^{60}Co source of 2.442 PBq (66 kCi). The irradiation was carried out continuously for 50 h at 5.7 kGy/h ($5.7 \times 10^5\text{ rad/h}$) and -30°C .

The pressure was kept below 684 Torr during the irradiation.

Small fractions of the circulating fluorocarbon were collected from the valve SV_4 after 10, 22, 32, 42 and 50 h. The total liquid in the cold trap was also collected through the valve SV_3 after 25 and 50 h. These samples were analyzed by the same method in the previous paper⁴⁾. The fluorocarbon was finally taken out of the facility.

2.3 Dosimetry

The fluorocarbon in the reaction vessel which is installed in the ^{60}Co irradiation cell and immersed in the thermostat at -30°C , was irradiated with ^{60}Co γ -rays as shown in Fig. 2. Accordingly, it is impossible to measure directly the absorbed dose of the fluorocarbon by the ferrous sulfate dosimeter. The average dose D_T absorbed in the whole fluorocarbon (CCl_3F 6.41 kg) of the flow system was approximately calculated by making the following corrections for the dose rate I_d ($=6.6\text{ kGy/h}$ ($6.6 \times 10^5\text{ rad/h}$)) which was measured by the ferrous sulfate dosimeter under the coolant temperature of 20°C at the position of the reaction vessel in the thermostat.

$$D_T = I_d \cdot f_1 \cdot f_2 \cdot f_3 \cdot t \\ = I_d (e^{-\mu_1 x} / e^{-\mu_2 x}) (\mu_t / \mu_d) (W_1 / W_2) t \quad (1)$$

where f_1 is the correction for the absorption coefficient of γ -rays due to the difference in the coolant temperature of the thermostat, f_2 is the conversion factor for the absorbed dose from the dosimeter solution to the fluorocarbon, and f_3 is the correction for the dilution due to the non-irradiated fluorocarbon; μ_1 and μ_2 are the linear absorption coefficient of γ -rays in the coolant at 20 and -30°C , respectively ($\mu_1 = 0.0835$, $\mu_2 = 0.0850\text{ cm}^{-1}$)¹⁰⁾; x is the thickness of the coolant ($=5\text{ cm}$), and μ_d and μ_t are the mass absorption coefficient of γ -rays in dosimeter solution and fluorocarbon (CCl_3F), respectively ($\mu_d / \mu_t = 0.480/0.553$). W_1 ($=3.03\text{ kg}$) is the amounts of the fluorocarbon irradiated and W_2 ($=6.41\text{ kg}$) is the amounts of the fluorocarbon charged in this facility. Finally, t ($=50\text{ h}$) is the irradiation time. From these values, 3 corrections are

$$f_1=0.992, f_2=0.868, \text{ and } f_3=0.473. \quad (2)$$

After all, the average absorbed dose D_T was 134 kGy (1.34×10^7 rad) in the experiment of 50 h.

3. Experimental Results and Discussions

3.1 Decomposition test

The variations in the composition of the circulating fluorocarbon and the liquid from the cold trap were measured. The absence of CCl_2F_2 in the circulating fluorocarbon may be due to the stripping of the product from the stripper column. Compared with CCl_2F_2 , most of the components with higher boiling point were stored in the circulating fluorocarbon. Halogen components were fairly stripped from the stripper column; Cl^- remained more in the circulating fluorocarbon than F^- . Each of the stripped component was trapped in the cold trap.

The decomposition yield of CCl_3F and the yields of radiolytic products (fluorocarbons) were determined on the basis of the analytical values of the circulating fluorocarbon and the liquid from the cold trap. As shown in Fig. 3 and 4, the decomposition yield of CCl_3F and the yields of radiolytic products increased in proportion to the absorbed dose.

In Table 1 are given the amounts of the degradation products in the circulating fluoro-

Fig. 3 Variation in decomposition yield of CCl_3F with absorbed dose (Decomposition test). Dose rate: 5.7×10^5 rad/h, Temperature: -30°C , Circulating gas: N_2 . (1 Mrad = 10 kGy)

Fig. 4 Variation in yield of fluorocarbons with absorbed dose (Decomposition test). Dose rate: 5.7×10^5 rad/h, Temperature: -30°C , Circulating gas: N_2 . (1 Mrad = 10 kGy)

carbon and the liquid from the cold trap. The accurate measurement of the amounts of the fluorocarbon, the liquid and several components in both liquids is difficult, since the decrease of the amount of fluorocarbon at each sampling gives rise to the disagreement between the compositions of the circulating fluorocarbon and the sample collected for analysis. Thus, the amounts of the circulating fluorocarbon and the liquid from the cold trap at an end of irradiation were adopted as the amounts of both liquids, and the analytical values for the circulating fluorocarbon at the end of irradiation were taken as the average composition. As is evident from this table, Cl^- of 42% and F^- of 83% are stripped from the stripper column, respectively.

The decomposition yield per Mrad (energy decomposition) of CCl_3F , and the yields per Mrad (energy yields) of halogen ions and radiolytic products (fluorocarbons) are shown in Table 2, along with the experimental results²⁾ of ampoule scale performed under the same irradiation conditions. These yields were calculated from the amounts of products presented in Table 1 and the dose (134 kGy (1.34×10^7 rad)) absorbed in the CCl_3F . The energy decomposition of CCl_3F was 0.0246 mol%/Mrad. G-value (2.9) obtained from the experiment of flow system was equal to 1.8 times that of

Table 1 Amounts of degradation products in circulating fluorocarbon and liquid from cold trap. Dose rate: 5.7 kGy/h (5.7×10^5 rad/h), Temperature: -30°C , Irradiation time: 50 h, Circulating gas: N_2 , CCl_3F : 6.41 kg

	Decomposition test		Impurities test	
	Circulating fluorocarbon	Cold trap	Circulating fluorocarbon	Cold trap
Amount of halogen ion (g)				
F^-	0.010	0.0475	0.073	0.157
Cl^-	0.293	0.216	1.79	0.228
Amount of fluorocarbon (mol)				
U_1 (unknown)	0	0.00036	0	0.00087
CCl_2F_2	0	0.0125	0.0196	0.00679
U_2 (unknown)	0	0.00006	0	0.00035
CCl_4	0.0418	0.00008	0.0537	0.00002
$\text{C}_2\text{Cl}_4\text{F}_2$	0.0854	0.00003	0.0595	0.00001
$\text{C}_2\text{Cl}_5\text{F}$	0.0152	0.00002	0.0163	0

Table 2 Comparison of energy yields of flow system with those in ampoule scale (energy decomposition, G -value, energy yield). Dose rate: 5.7 kGy/h (5.7×10^5 rad/h), Temperature: -30°C (1 Mrad=10 kGy)

	Flow system		Ampoule scale
	Decomposition test	Impurities test	
Energy decomposition (mol%/Mrad)			
CCl_3F	0.0246 ($G=2.9$)	0.0248 ($G=2.6$)	0.0150 ($G=1.6$)
Energy yield ($\mu\text{g/g} \cdot \text{Mrad}$)			
F^-	0.66	2.7	2.8
Cl^-	5.8	23.2	27.5
Energy yield (mol%/Mrad)			
U_1	0.00006	0.00014	0
CCl_2F_2	0.00197	0.00419	0.00235
U_2	0.00001	0.00006	0.00010
CCl_4	0.00660	0.00847	0.00410
$\text{C}_2\text{Cl}_4\text{F}_2$	0.0135	0.00936	0.00705
$\text{C}_2\text{Cl}_5\text{F}$	0.00241	0.00256	0.00106
$\text{C}_3\text{Cl}_5\text{F}_3$	0	0	0.00011

ampoule scale. The formation ratios of radiolytic products obtained from this experiment is shown in Table 3 along with those obtained from ampoule scale. In the present experiment, $\text{C}_2\text{Cl}_4\text{F}_2$ increased and CCl_2F_2 decreased compared with the results of ampoule scale.

The explanation for the above differences may be ascribed to the removal of halogen

components from the circulating fluorocarbon by the stripping, and to the reaction of halogen components and constituent materials. Since the halogen components in the circulating fluorocarbon are continuously removed in this flow system, the reaction of the primary radical $\text{CCl}_2\text{F}^\cdot$ with halogen radical ($\text{Cl}^\cdot$, $\text{F}^\cdot$) decreases. Thus, the recombination of $\text{CCl}_2\text{F}^\cdot$ increases,

Table 3 Comparison of formation ratio of degradation products in flow system with those in ampoule scale

Degradation product	Formation ratio (%)	
	Flow system	Ampoule scale
CCl_2F_2	8	14
CCl_4	27	29
$\text{C}_2\text{Cl}_4\text{F}_2$	55	49
$\text{C}_2\text{Cl}_3\text{F}$	10	7
$\text{C}_3\text{Cl}_5\text{F}_3$	0	1

and the decomposition of CCl_3F is also promoted. Since metals are used as constituent materials of the irradiation facility, it is also presumed that the halogen radicals are disappeared by the contact with metal.

3.2 Impurities test

Influence of impurities on the decomposition of CCl_3F (6.41 kg) was examined by the addition of the impurities having the same composition as the off-gas at the fuel reprocessing. The mixed gas (4.1 l) of air (99.9%) and CH_4 (0.1 %) was used as circulating gas and I_2 (12 $\mu\text{g/g}$ CCl_3F) was added to CCl_3F in the reaction system. Irradiation was performed under the same condition as the decomposition test. Compositions of the circulating fluorocarbon and the liquid from the cold trap were determined and the result was compared with that of the decomposition test.

As indicated in Table 1, the amounts of halogen ions in the liquid from the cold trap did not vary much by the addition of the impurities, while those in the circulating fluorocarbon increased. The total amounts of halogen ions increased consequently. Above result is in agreement with the result in the irradiation experiments of ampoule scale²⁾. Moreover, small amount of CCl_2F_2 was detected in the circulating fluorocarbon, and the components with high boiling point in the liquid from the cold trap decreased. This cause seems to be due to the lack of the stripping effect by insufficient heating of the still rather than influence by the addition of the impurities.

In Table 2 are shown the comparison of the energy decomposition of CCl_3F and the energy

yields of degradation products in 3 experiments. The value (0.0248 mol%/Mrad) of the energy decomposition of CCl_3F in the impurities test is almost the same as that of the decomposition test.

4. Conclusion

The irradiation experiments of CCl_3F were carried out with ^{60}Co γ -rays using the irradiation facility of the flow system. The decomposition yield of CCl_3F and the yields of radiolytic products increased in proportion to the absorbed dose. The energy decomposition of CCl_3F was estimated as 0.0246 mol%/Mrad ($G=2.9$). This value was equal to 1.8 times that of the ampoule scale. It is considered that such difference in the experimental results of 2 systems is attributed to the promotion of the decomposition with the continuous removal of the degradation products. The formation of halogen ions was promoted by the addition of impurities (air, CH_4 , I_2). Further, irradiation experiments of CCl_3F are intended to be performed in both batch and flow system with ^{85}Kr β -rays, to investigate the relationship between decomposition yield and absorbed dose.

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References

- 1) J.R. Merriman, et al.: K-L-6201 (1972)
- 2) T. Yamamoto and N. Ootsuka: *J. Nucl. Sci. Technol.*, **17**, 913 (1980)
- 3) T. Yamamoto and N. Ootsuka: *ibid.*, **18**, 913 (1981)
- 4) T. Yamamoto and N. Ootsuka: *Radioisotopes*, **31**, 469 (1982)
- 5) J.R. Merriman and J.H. Pashley: K-1770 (1968)
- 6) T. Tominaga, et al.: *Chem. Lett.*, 871 (1972)

- 7) T. Tominaga, et al.: *Radiochem. Radioanal. Lett.*, **21**, 211 (1975)
- 8) Power Reactor and Nuclear Fuel Development Corporation: Studies on Radiolysis of Flon-112 (unpublished data) (1973)
- 9) A.R. Kazanjian and D.R. Horrell: *J. Phys. Chem.*, **75**, 2217 (1971)
- 10) K. Kimura: "Hoshasen Databook", (in Japanese), p. 158, Chijin Syokan, Tokyo (1961)

要 旨

^{60}Co γ 線照射下の流通系における トリクロロフルオロメタンの放射線分解

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流通式の照射装置を用いて, ^{60}Co γ 線による CCl_3F の照射実験を行った。照射は線量率が 5.7 kGy/h ($5.7 \times 10^5 \text{ rad/h}$), 温度が -30°C の下で行い, CCl_3F の分解挙動, および分解に及ぼす不純物の影響について調べた。さらに, 本試験結果とアンブル規模の試験結果との比較を行った。

CCl_3F の分解率とフロロカーボン系化合物の収率は, いずれも吸収線量に比例して増大した。 CCl_3F のエネルギー分解率は $0.0246 \text{ mol\%/Mrad}$ ($G=2.9$) であり, これはアンブル規模の試験結果に比べて 1.8 倍大きかった。不純物 (air, CH_4 , I_2) の影響は, ハロゲンイオンの収率に対してのみ, 著しく認められた。

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