Decomposition Degree of Chlorofluorocarbon and Hydrochlorofluorocarbon

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Hydrochlorofluorocarbons (HCFCs), which have a smaller ozone depleting propensity than the chlorofluorocarbons (CFCs) replacements, have been developed and produced. However, HCFCs decompose more readily than CFCs. Studying their decomposition degree is useful for increasing their recovery efficiency and minimizing their environmental impact. It is concluded that the amount of produced heavy metal ions was caused by a variation in the pH due to the HF and HCl, and the recovery of HCFC141b is more difficult than CFC113 or HCFC123.

Chlorofluorocarbons (CFCs) affect the depletion of the ozone layer[1] and have a greenhouse effect.[2] Therefore, the hydrochlorofluorocarbons (HCFCs), which have a smaller effect on ozone depletion and global warming, have been developed and produced. The HCFCs contain a hydrogen atom and therefore decompose more readily than CFC. There is an urgent need for the recovery of the replacement compounds with energy-savings. The principle gaseous phase, atmospheric degradation products of HCFC141b and HCFC123 are $CFCl_2CHO$, $C(O)FCl$, CO, and CO_2 and $CF_3C(O)Cl$, CF_3OH, $C(O)F_2$, and CO, respectively.[3] While in the liquid phase, HF and HCl are also produced. We have reported the recovery efficiency of HCFCs using surface modified activated carbons.[4] The study of the CFC decomposition has been reported by many investigators.[5,6] However, little work on the study of HCFC decomposition during their recovery using activated carbon has been done so far.

The solvents used were 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113), 1,1-dichloro-1-fluoroethane (HCFC141b), (Central Glass Co., Ltd., Tokyo, Japan) and 1,1-dichloro-2,2,2-trifluoroethane (CFC123) (Central Glass Co., Ltd., Tokyo, Japan). Activated carbon was commercially obtained from JXN 4x6 (Japan Carbon Co., Ltd., Tokyo, Japan). The activated carbon used for the recovery of CFCs and HCFCs was added during the decomposition. The decomposition degree of the CFCs and HCFCs were measured as follows: activated carbon (approximately 2 g), distilled water (25 g), and the CFCs or HCFCs (20 g) were put in an autoclave and incubated at 120 ℃. The mixture was allowed to cool to 25 ℃ before being filtered through a funnel covered with filter paper (Toyo, No. 2) The chloride ion, pH, and the heavy metals in the distilled water after decomposition were measured to elucidate the decomposition degree of the CFCs and HCFCs. The chloride ion was measured using the Japanese Industrial Standard method.[7] The content of heavy metals was measured based on atomic absorption spectrometry, respectively. The C-F bond stabilizes the CFC and CFC replacement molecules. It is consider that HF is the principal factor of the corrosion materials. Therefore, the amount of produced heavy metals was analyzed, because the corrosion materials other than HF might be produced. HCFC141b was used for evaluating the effect of temperature on the decomposition. The decomposition of HCFC141b occurred at temperatures of 80, 100, and 120 ℃. There are some HCFCs adsorbed onto the activated carbon after desorption by water vapors. These HCFCs might be decomposed by many recyclings of the activated carbon. The decomposition degree increased with increasing temperature (Table 1) and the amount of distilled water (Table 2). In the case of adding twice the water, the amount of produced chloride ion and heavy metals increased. These results indicated that the decomposition of HCFCs was accelerated by hydrophilic solvents (water) or the rise of internal pressure of the autoclave.

Table 1. Effect of Temperature on Decomposition Degree

Temperature	Amount Produced / mg			pH
	Cl	Fe	Ni	
80	2.5	0.7	0.1	2.8
100	30.0	1.8	0.4	1.8
120	310.0	130.0	23.0	1.1

Table 2. Effect of Water Quantity on Decomposition Degree

Water Quantity / g	Amount Produced / mg			pH
	Cl	Fe	Ni	
25	310.0	130.0	23.0	1.1
50	400.0	140.0	34.0	1.1

The amount of Cl ion and heavy metals produced by the decomposition of HCFC141b is shown in Figure 1. The amount of produced chloride, iron, chromium, and nickel ions increased with increasing decomposition time. The impurities of CFC113

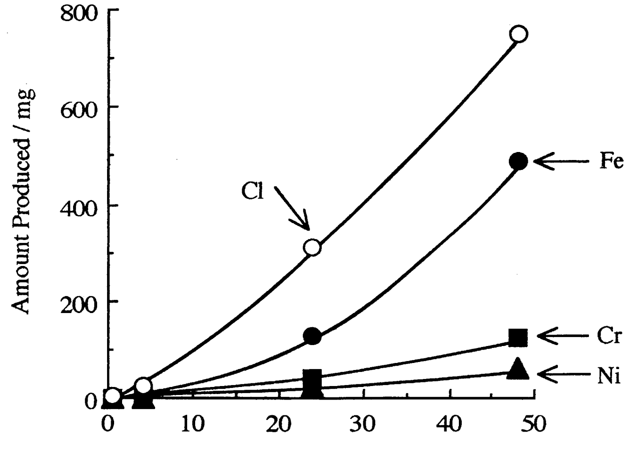

Figure 1. Elution Degree of Chloride and heavy metal ions with Elapsed time

and HCFC123 were much less than those of HCFC141b. CFCs are extremely stable compounds, while HCFCs are more unstable than CFCs because of the hydrogen atoms in these molecules. The molecules of CFC113 and HCFC123 are stabilized by some C-F bonds. The internal pressure of the autoclave during HCFC141b, HCFC123, and CFC113 decomposition was about 8, 10, and 5 kg/cm^2, respectively. It is considered that some elution of the chloride, iron, chromium, and nickel ions are from the internal walls of the autoclave due to reaction with hydrogen chloride and hydrogen fluoride produced by the decomposition of HCFC141b. Hence, the water phase was colorless after a 30 minutes HCFC141b decomposition. The color became darker when the decomposition time was increased. The color of the water phase during the decomposition of HCFC123 and CFC113 scarcely changed. It is considered that the changing color of the water phase was caused by the nickel ion.

Recently, a hydrochlorofluorocarbon (HCFCs) mixture, which has a lower decomposition, was developed and produced. We evaluated the decomposition of a mixture of the CFC or HCFCs. The mixed solvents used were S1; CFC113 : HCFC123 (1:1), S2; CFC113 : HCFC141b (1:1), and S3, HCFC123 : HCFC141b (1:1). The results of the CFC113, HCFC123, and HCFC141b decompositions are shown in Table 3. The decomposition time of CFC113 and HCFC123 or HCFC141b is 66 and 24 h, respectively. It is assumed that the molecular stability decreased in the order of CFC113, HCFC123, and HCFC141b. The results of the S1, S2, and S3 decompositions are shown in Table 4. The decomposition time of S1 and S2 or S3 is 66 and 24 h, respectively. S2 and S3 are easier to decompose than S1 which does not contain HCFC141b. The amount of chloride ion produced is large in the order of S1, S3, and S2. The amount of heavy metals increased in the order of S1, S2, and S3. The following conclusions were developed. (1) HCFCs decompose more readily than CFCs, (2) HF and HCl were produced due to the HCFCs decomposition products corroding the stainless steel, and (3) The amount of produced heavy metal ions was caused by the variation in pH due to HF and HCl.

Table 3. Decomposition of CFC and CFC Replacements

Sample	Amount Produced / mg			pH
	Cl	Fe	Ni	
CFC113[a]	3.5	0.5	0.2	2.8
HCFC123[b]	0.8	0.2	0.2	3.7
HCFC141b[b]	310.0	130.0	23.0	1.1

[a]Decomposition time of 66 h. [b]Decomposition time of 24 h.

Table 4. Decomposition of Mixture Solvents

Sample	Amount Produced / mg			pH
	Cl	Fe	Ni	
S1[a]	6.0	0.9	0.5	6.4
S2[b]	150.0	54.5	9.8	2.7
S3[b]	100.0	67.0	12.0	2.9

[a]Decomposition time of 66 h. [b]Decomposition time of 24 h.

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