§22. Chlorofluorocarbon Treatment Process by Micro Wave Pyrolysis and its Fixation Utilizing Concrete Waste

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Fluorinated hydrocarbons (Freon) have been used as refrigerants for air-conditioning systems for many years. Appropriate recovery and decomposition of Freon is now obligated based on the Montreal Protocol. Various treatment methods for Freon have been developed. However, these methods require high temperature to decompose Freon, and generate toxic gases such as hydrogen fluoride (HF) or hydrogen chloride (HCl). Alkali solutions, such as calcium hydroxide ($Ca(OH)_2$) solution are usually used to treat these decomposed gases. However, by using alkali solutions, secondary treatment of neutralized solution and salt sludge is required. Thus, development of more simple and effective treatment method is needed. Recently a new method which utilizes alkali metal oxide such as calcium or magnesium oxide (CaO or MgO) solid has been intensively investigated. In the study, we focused on concrete waste as an alkali metal source for fixation media of Freon decomposition gases. Waste concrete contains alkali calcium compounds, such as calcium hydroxide ($Ca(OH)_2$) and calcium silicate hydrate (e.g. $3CaO{\cdot}2SiO_2{\cdot}4H_2O$). These compounds can act as fixation media for fluorine. Furthermore, we tried to use micro wave heating method instead of conventional heating for Freon decomposition.

i) Materials

Waste concrete sample used in the study was obtained from Santoras Corp. The sample was grain with diameter of less than 5 mm. The calcium content ratio in the sample was measured to be about 11.3 wt%. The obtained sample was classified into three groups with sieving. HFC-134a, representative Freon, was used in the study.

ii) Methods

ii)-1 HFC-134a decomposition with conventional heating

Fig. 1 illustrates the experimental apparatus for thermal decomposition experiments of HFC-134a. A reaction tube (SUS316, =10.2 mm) passes through an electric furnace and was kept at reaction temperature. Waste concrete sample was packed in the center part of the tube. Gaseous nitrogen and HFC-134a were supplied to the reaction tube from each cylinder with mass flow controller. The flow rates were set at 80 mL/min and 20 mL/min, respectively. HFC-134a is thermally decomposed in the reaction tube and generates decomposition gas which contains hydrogen fluoride (HF). The decomposition gas is simultaneously fixed with waste concrete, or captured by sodium hydroxide (NaOH) solution. After 10 min, exhaust gas was collected into a sampling bag, and concentration of HFC-134a was analyzed with GC-TCD. Reaction temperature was varied 200~900°C. The amount of fluoride ion captured in NaOH solution was measured by ion electrode method.

ii)-2 HFC-134a decomposition with micro wave heating

For the experiment an electric furnace shown in Fig.1 was replaced by a micro wave heating system. Measurement of absorbed energy by reaction tube, generated HF amount, and qualitative analysis of exhaust gas were conducted. Surface temperature of waste concrete sample was measured with an IR thermometer. The waste concrete sample (0.6-1.2 mm, 1.242 g) mixed with activated charcoal (1.2-1.4 mm, 0.124 g) was placed in the reaction tub, and heated by micro wave.

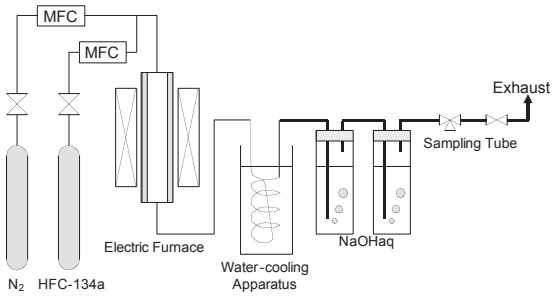

Fig. 1. Experimental apparatus for thermal decomposition experiments of HFC-134a

iii Results and discussion

iii)-1 HFC-134a decomposition with conventional heating

HFC-134a decomposition occurred at above 500°C, and decomposed gas was fixed in waste concrete. HFC-134a decomposition rate increased with an increase of HFC-134a concentration in supplied gas and reaction temperature. Particle size of waste concrete did not affect HFC-134a decomposition rate. Calcium reaction rate in waste concrete sample reached 40~50wt% after 10 min reaction. Under the condition of integral reactor (HFC-134a concentration: 19.82 mol%, space velocity: 601 h^{-1}, reaction temperature: 600°C), over 99.9% of HFC-134a decomposition rate was achieved over 20 min.

iii)-2 HFC-134a decomposition with micro wave heating

Fig. 2 shows the comparison of calcium reaction ratios with conventional heating and micro wave heating. As shown in the graph, almost same calcium reaction rate (=decomposed HF fixation rate) was observed.

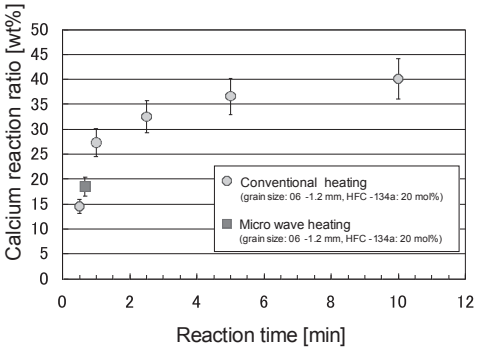

Fig. 2. Comparison of calcium reaction ratios with conventional heating and micro wave heating.

iv) Conclusion

Waste concrete can be utilized as a fixation media for fluorine. About 40-50wt% of calcium in waste concrete