

Treatment of Hydrogen Fluoride Generated from the F-gases Decomposition Processes

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ABSTRACT

The objective of this study is to obtain the optimal conditions to remove hydrogen fluoride (HF) generated from a variety of F-gas treatment processes. First, we selected $\text{Ca}(\text{OH})_2$ and CaCO_3 as a reactant among the various alkali salts which have a high removal efficiency and a competitive price by forming a calcium fluoride precipitate. Additionally, various factors were investigated to improve the removal efficiency of HF. The conditions such as the settling time, agitating time and intensity, reaction temperature, and pH were considered as main factors. As a result, in the treatment process to remove HF through Ca-based alkali salts, the optimal conditions were a 120 min settling time, 30 min of agitation at 100 rpm, a pH of 4-8, and a reaction temperature of 40°C.

Key words: Hydrogen fluoride, Fluoride removal, Calcium hydroxide, Calcium precipitation, Alkali salts

1. INTRODUCTION

Fluorinated gases (F-gases), which were designated as greenhouse gases in the Kyoto protocol, contribute to the global greenhouse effect. F-gases consist of SF_6 (Sulfur hexafluoride), HFCs (Hydro fluorocarbons), PFCs (Perfluoro compounds), and NF_3 (Nitrogen trifluoride). They can commonly be present for a long time in the atmosphere because they have strong stability in the air. In addition, the amount of F-gases emitted is lower than other greenhouse gases, but their GWP (Global Warming Potential) is significantly higher.

In order to control F-gases, various technologies such as the pyrolysis process, catalyst process, and combus-

tion method have been developed. However, with the above-mentioned technologies, there are many problems such as a low decomposition efficiency, high operating cost, and the formation of by-products: NO_x , SO_x , HF, CO_2 , etc (Mi *et al.*, 2015; Park *et al.*, 2013; Wang *et al.*, 2004; Bonarowska *et al.*, 2001; Wang *et al.*, 1998). Afterward, the plasma process and electron-beam system have been exploited for improving previous technologies (Son *et al.*, 2016; Ryu *et al.*, 2012; Watanabe *et al.*, 2008; Kossyi *et al.*, 2001; Glocker *et al.*, 2000; Murphy *et al.*, 1998). Meanwhile, Park *et al.* (2013) reported that the plasma process obtained a high decomposition efficiency of PFCs when using hydrogen gas as an additive. Kim *et al.* (2013) and Ryu *et al.* (2015) also reported that the decomposition process of SF_6 by an electron-beam increased the removal efficiency when using hydrogen gas as a background gas. They commonly used hydrogen gas because it has an advantage in improving the decomposition efficiency. However, these processes form by-products such as HF, F_2 , etc. These by-products are generally removed by a wet scrubber using water. Accordingly, the dissolved by-products such as HF and F_2 with a high concentration are necessarily formed in these processes.

As a Korea standard, the emission allowance of fluoride, which is an acute and chronic toxic, is regulated as less than 3 mg/L discharged into rivers and 15 mg/L into the sea (Ministry of environment, 2007). Therefore, researches such as the sedimentation method, rare earth adsorption process, coagulation method using alum, ion-exchange process and electrophoresis to treat the fluoride in a solution have been continuously conducted (Kim *et al.*, 2011; Fang *et al.*, 2003; Lee, 2002; Povorov *et al.*, 2002; Na *et al.*, 1999; Haron *et al.*, 1995; Rao *et al.*, 1988).

Most of the processes to remove fluoride have been carried out for the treatment of drinking water with a low concentration range (20-200 mg/L). Therefore, these processes are unsuitable for application of wastewater with a high concentration of fluoride, directly.

Meanwhile, the sedimentation method has been used in the wastewater treatment process for a long time. Fluoride is removed by converting ionic materials to the insoluble precipitate in the wastewater. Precipitation has been widely used in the wastewater treatment process which is quickly able to reduce the concentration of the target substance and is economically feasible in spite of forming the sludge (Kang *et al.*, 2013; Kim *et al.*, 2007a, b; Kim, 2003; Raichur *et al.*, 2001).

The purpose of this study was to find the optimal reactants and conditions to improve the removal efficiency of high concentration HF in the wastewater generated by the F-gas treatment processes using a variety of alkali salts. At the same time, optimal reactants were selected by investigating the price of alkali salts.

To do this, various influential factors were investigated to improve the removal efficiency of HF. The settling time (10-1200 min), agitating time (10-120 min), agitating intensity (100-300 rpm), pH (2-10) and reaction temperature (5-60°C) were considered as the main factors.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Experimental Materials

In this study, an aqueous HF solution diluted to 1% (Hydrofluoric Acid 49.0-50.0%, DUKSAN, Korea) was made to check the removal possibility of HF generated from various F-gases treatment processes. At this time, an aqueous HF solution is a corrosive and strong acid (pH: 1.16).

In order to investigate the removal efficiency of HF, we used a variety of alkali salts such as CaO, CaCl₂, CaCO₃ (DUKSAN, Korea), Ca(OH)₂, KOH (SAMCHUN, Korea), NaOH (DAEJUNG, Korea), and Na₂CO₃ (Junsei chemical Co., Ltd, Japan). Every alkali salt was used at a ratio of 0.1, 0.5, 1, 2, and 4% to find out the influence of the alkali salt concentration. The total reaction volume was 20 mL (HF: 10 mL, reactant: 10

mL). The settling time was 24 h to give sufficient time to make the precipitate.

2.2 Experimental Methods

To obtain the optimal conditions to remove HF, diverse influence factors such as the reaction time (min), agitating time (min), agitating intensity (rpm), pH, and reaction temperature (°C) were investigated in this study. Table 1 shows the detailed experimental conditions.

2.3 Analysis

All of the samples were analyzed after precipitation for 120 min, which were filtered by a 0.45 mm membrane filter (Acrodisc syringe filter, Pall Corporation, UK). To measure the removal efficiency of HF, the F⁻ concentration was analyzed using an ion chromatograph (Dionex ICS-900, Thermo Scientific, USA). The injected samples were diluted down 20-fold to adjust within the limit of the device. The calibration of the device was conducted using a standard solution (Dionex fluoride standard, 1000 mg/L, 99.9%, Thermo Scientific, USA) before analyzing the samples containing fluoride. The value of r² was 0.991 in the calibration of fluoride. Additionally, the detailed conditions are represented in Table 2.

A magnetic stirrer (DAIHAN scientific CO., Ltd, Korea) was used to investigate the effect of the agitating time (min) and intensity (rpm).

Control of the pH of the samples was conducted using 1 N and 5 N NaOH and H₂SO₄ solutions. The calibration of the pH meter (Orion star series, Thermo

Table 1. The experimental conditions of HF treatment.

Factors	Experimental condition
Settling time (min)	10, 20, 30, 60, 120, 240, 600, 1200
Agitating time (min)	10, 30, 60, 90, 120
Agitating intensity (rpm)	100, 150, 200, 250, 300
pH	2, 4, 6, 8, 10
Reaction temperature (°C)	5, 20, 40, 60

Table 2. Analysis conditions of ion chromatograph.

Factor	Analysis condition
Column	IonPac AS9-HC Analytical Column (4 × 250 mm) IonPac AG9-HC Guard Column (4 × 50 mm)
Suppressor	ASRS 300 (4 mm) Anion Self-Regeneration Suppressor
Eluent	9 mM Na ₂ CO ₃ (1.0 mL/min)
Injection volume	1 mL (manually controlled syringe system)
Detector	Digital conductivity detector
Pressure limit	0-3500 psi
Run time	5.5 min

Fisher SCIENTIFIC, USA) was performed before every experiment.

The magnetic stirrer with a heater (C-MAG HS 40, IKA, China) was used to raise the temperature to 40 and 60°C, and an incubated shaker (IS-971R, JEIO TECH Co., Ltd, Korea) was used to decrease and maintain the temperature at 5°C. The temperatures of all the samples were maintained for 1 hr.

3. RESULTS AND DISCUSSION

3.1 Selection of Optimal Reactants

Generally, it has been reported that the removal efficiency of HF by a sedimentation method is affected by the concentration of the Ca-based reactants (Kim *et al.*, 2011; An *et al.*, 2009). Fig. 1 shows a variation of the removal efficiency by the initial concentration of Ca-based and KOH reactants (0, 0.1, 0.5, 1, 2, 4%). It was shown that Ca-based reactants have a high efficiency to remove HF. Although there are some differences in the removal efficiency in a low concentration range of the reactant, all Ca-based alkali salts with a concentration of 4% showed a level of more than 95%, commonly. However, CaO was exceptionally lower than the others. In the case of Ca-based alkali salts, insoluble calcium fluoride (CaF₂) was formed, and the fluoride was removed as a solid precipitate.

On the other hand, we were unable to find any changes in the F⁻ concentration when using the KOH as a reactant. We also obtained the same results when using Na-based alkali salts, although this is not represented in the figure. In addition, the precipitates of fluoride such as KF and NaF were not observed. Generally, the alkali salts except for Ca-based species are used to neutralize the wastewater containing HF, but fluoride was not able to be removed as a precipitate. It is only possible to modify the acidity to the neutrality of wastewater, which means that F⁻ ions exist in the solution (Kang *et al.*, 1999; Kust *et al.*, 1995). This result suggests that Ca-based alkali salts are appropriate to remove HF, easily and quickly, when using a sedimentation method. We could confirm that the KF and NaF

formed are excluded in this process because they are classed as toxic materials (CTEF, 2007).

3.2 Optimal Settling Time

The chemical reaction and price of all alkali salts used in this experiment are represented in Table 3. To

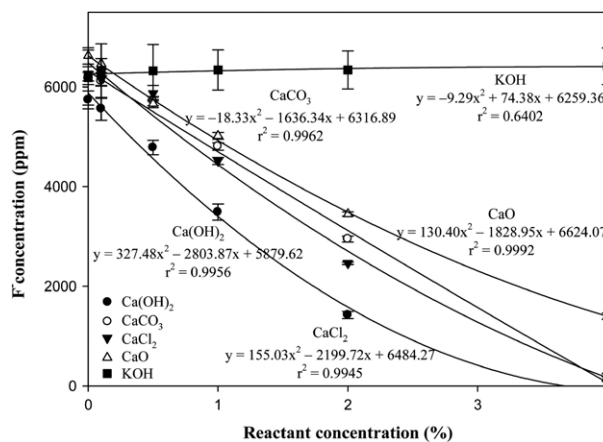


Fig. 1. Variation of F⁻ concentration by reactant type and concentration (settling time: 24 hr).

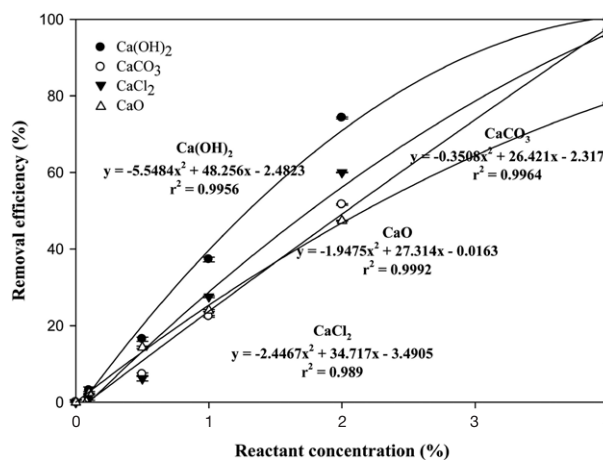


Fig. 2. Removal efficiency of HF by Ca-based alkali salts (settling time: 24 hr).

Table 3. Chemical reaction and price of alkali salts.

Alkali salts	Chemical reaction	Price (\$/Ton)	Ref.
CaCO ₃	HF + CaCO ₃ → 2CO ₂ + CaF ₂ + H ₂ O	75-95	Yasui <i>et al.</i> (2012)
Ca(OH) ₂	2HF + Ca(OH) ₂ → CaF ₂ + 2H ₂ O	110-160	Kowalski <i>et al.</i> (1999)
CaCl ₂	HF + CaCl ₂ → CaF ₂ + HCl	240-260	James <i>et al.</i> (2000)
CaO	HF + CaO → CaF ₂ + H ₂ O	140-160	Wang <i>et al.</i> (2013)
KOH	HF + KOH → KF + H ₂ O	400-500	Cook <i>et al.</i> (2003)
NaOH	HF + NaOH → NaF + H ₂ O	900-1200	Cook <i>et al.</i> (2003)
Na ₂ CO ₃	2HF + Na ₂ CO ₃ → 2NaF + CO ₂ + H ₂ O	280-350	Quicker <i>et al.</i> (2015)

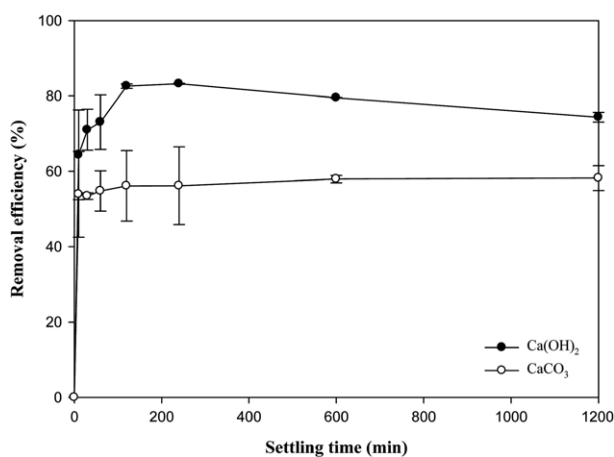


Fig. 3. Removal efficiency of HF with respect to settling time.

obtain the optimum condition to remove HF, Ca(OH)_2 and CaCO_3 were selected among the all alkali salts because both reactants have a high removal efficiency of HF and a competitive price (Ca(OH)_2 : \$110-160/ton, CaCO_3 : \$75-95/ton). To investigate the influence of each parameter, the concentration of both reactants was fixed at 2%.

Fig. 3 shows the concentration of F^- by the settling time. The removal efficiency was gradually increased to 88% as the time passed to 240 min when using Ca(OH)_2 . After that, the removal efficiency was slightly reduced. In the case of using CaCO_3 , the removal efficiency was increased to 58% based on the elapsed time until 1200 min. This means that the removal efficiency of Ca(OH)_2 is better than CaCO_3 as a reactant, but the stability of the precipitate with the time of CaCO_3 is more than Ca(OH)_2 . However, in case of the the CaCO_3 , it can be a waste of time and money when operating after 120 min because the variation of removal efficiency is minimal. Therefore, we confirmed that the optimal settling time of both reactants is fixed at 120 min because the removal efficiency of the two materials with time was stable after 120 min.

3.3 Optimal Agitating Conditions

In order to examine the influence of the agitating conditions, we conducted an experiment in the agitating time and intensity. Fig. 4 shows that the F^- concentration was commonly decreased according to the agitating time when using Ca(OH)_2 and CaCO_3 as the reactant. F^- concentration of Ca(OH)_2 and CaCO_3 were respectively reduced from 999.70 and 2790.31 ppm to 668.06 and 2275.95 ppm after a 10 min reaction, respectively. It seems that agitation contributed to a mixing of both fluoride ions and Ca ions in the solution.

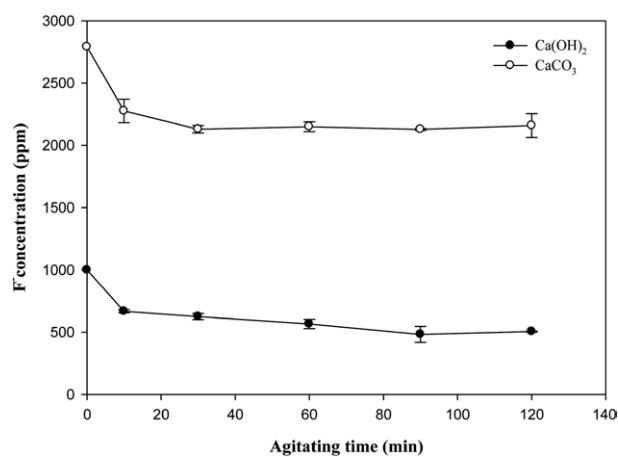


Fig. 4. Variation of F^- concentration with regard to agitating time.

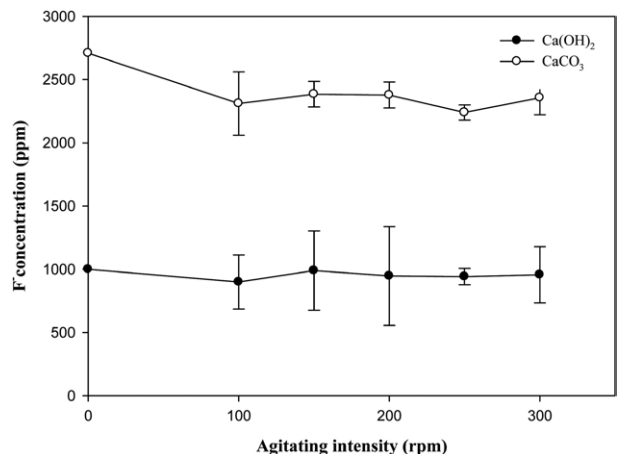


Fig. 5. Changes of F^- concentration by agitating intensity.

However, the variation of F^- concentration after 10 min was slight, although the F^- concentration was continuously decreased to 120 min. This result means that agitation has a limitation in continuously enhancing the removal efficiency. In addition, agitation for a long period of time is not effective. Some researchers acquired similar results. Kim *et al.* (2011) reported that the removal efficiency of HF by a sedimentation method using Ca(OH)_2 , CaCO_3 , and CaCl_2 was not visibly affected by the agitating time.

The influence of agitating intensity is represented in Fig. 5. It was found that the agitating time was fixed at 10 min with reference to a previous experiment. As a result, the F^- concentration of Ca(OH)_2 and CaCO_3 decreased from 999.70 and 2790.31 ppm to 899.43 and 2310.16 ppm at 100 rpm, respectively. Comparing the two reactants, while using Ca(OH)_2 was unaffected by

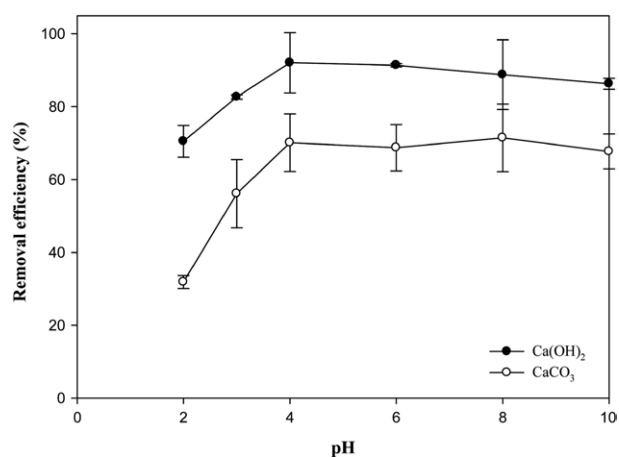


Fig. 6. Removal efficiency of HF with respect to pH.

the agitation intensity, CaCO_3 was influenced by it. However, the effect of the increasing agitation intensity by two reactants to remove HF was not mutually considerable. These results indicate that agitation has an advantage in improving the removal efficiency even though the impact according to a variation of the agitation time and intensity was not considerable. It was determined that agitation contributes to reducing the F^- concentration by mixing the solution, and interrupts the formation of the precipitate as CaF_2 , simultaneously. This is consistent with the results obtained by other researchers (Kang *et al.*, 2013; Kim *et al.*, 2011). They also studied the variation of agitation intensity to improve the removal efficiency of HF, but there was little effect on the F^- concentration. In addition, An *et al.* (2010) and Lee *et al.* (2002) reported that calcium fluoride was able to be separated in the mixing process caused by agitation, which interrupt the enhancement in the removal efficiency. Therefore, proper conditions to enhance the removal efficiency through agitation should be necessarily considered.

Conclusively, the optimal agitation conditions to enhance the removal efficiency are 10 min of time and 100 rpm of intensity considering the economy to operate the HF removal process in the field.

3.4 Optimal Reaction Temperature and pH

The variation of the removal efficiency was studied in a pH range of 2 to 10, as shown in Fig. 6. Additionally, the pH of both unadjusted samples is approximately 3. The results indicate that the removal efficiencies of Ca(OH)_2 and CaCO_3 at a pH of 4 were 92% and 70%, respectively. In a pH range of 4-8, the removal efficiency was commonly maximum. In addition, at a pH of 10, the removal efficiency slightly decreased. This result indicates that the removal efficiency of

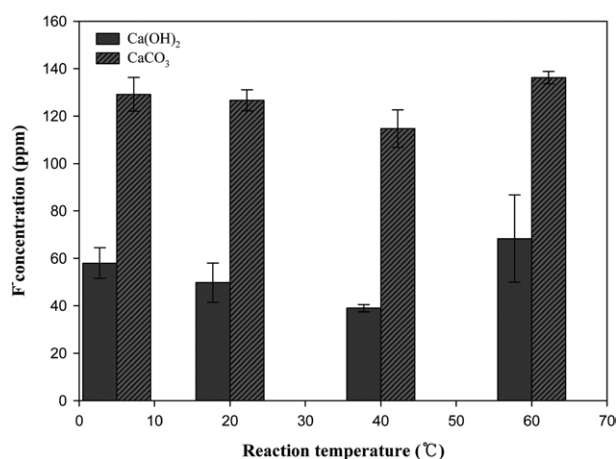


Fig. 7. F^- concentration by reaction temperature.

both reactants is affected by the pH of the solution and is highest in a neutral range. We found similar results in previous studies. Raichur *et al.* (2001) reported that the removal of HF in the waste water was closely associated with the pH. In addition, it was studied that, within the acidic pH range, the form of the fluoride is converted into HF and H_2F_2 , which interfere in the precipitation reaction of calcium. In the alkaline pH range, the removal efficiency was gradually declined, which is due to competition of the hydroxyl ions with the fluoride (Kim *et al.*, 2011; Kim *et al.*, 2007a; Lee *et al.*, 2006; Huang *et al.*, 1995; Wu *et al.*, 1995). Therefore, it is important that the pH be adjusted within a neutral range to obtain the maximum removal efficiency. Therefore, when using Ca(OH)_2 and CaCO_3 as a reactants, the optimal condition is commonly a pH of 4.

Fig. 7 shows the influence of temperature (5, 20, 40, 60°C) on the F^- concentration. This part was conducted to adjust only the temperature using an incubator and heater. We confirmed that the F^- concentrations of both Ca(OH)_2 and CaCO_3 were steadily decreased to 800.94 and 2294.32 ppm with the temperature until 40°C, respectively. However, at 60°C, it was rapidly increased. The Gibbs free energy of the precipitate equation for Ca(OH)_2 and CaCO_3 was -205.660 and -128.886 kJ at room temperature which was calculated by the HSC program (HSC chemistry, Outotec, Germany). It was also indicated that the precipitate reaction is spontaneous in all ranges of temperature, and its spontaneity is increased with a temperature increase. However, at a temperature of 60°C, it was considered that water evaporation was observed, which affected the reduction in the removal efficiency of HF.

Some researches obtained similar results. Kim *et al.* (2007b) reported that the precipitation reaction of fluorine was the endothermic reaction. In addition, they

considered that the precipitation reaction of fluorine has a spontaneous tendency, and the spontaneity is raised with an increase in the temperature until 55°C. In addition, in a previous study by Yang *et al.* (1999), the results demonstrated that while the difference between 25 and 16.5°C was not considerable, the F⁻ removal efficiency decreased rapidly when the temperature was decreased to 8.5°C.

4. CONCLUSION

In this study, a sedimentation method using Ca-based alkali salts was used to remove high concentration HF generated from the F-gas treatment process. As a result, the optimal conditions were a 120 min of settling time, 30 min of agitation at 100 rpm, pH of 4-8, and a reaction temperature of 40°C. These results are applicable to an industrial wastewater treatment process containing a high concentration of HF (such as F-gas treatment process, semiconductor wastewater treatment process). However, additional studies such as on the composition of by-products and their influence should be carried out to apply the technique in the actual field.

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