# PAC를 이용한 불소폐수 제거 효과

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# Removal Effects of Fluorine Wastewater using PAC

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## ABSTRACT

This paper describes the pH and PAC effect on the reduction of fluorine contained in industrial wastewater. We tried to find out the actual pH value and PAC which can make the best treatment efficiency. The main chemistry of this process is precipitation-coagulation. In this experiment, we used a small amount of $Ca(OH)_2$ for generating $CaF_2$ and two types of PAC for making $Al(OH)_3$ flock to adsorb fluorine and an aluminate ion. The best removal efficiency was obtained at pH 10, and PAC 2 (12% of $AlO_3$) can produce good treating condition than PAC 1 (17% of $AlO_3$) for low concentration and high concentration fluorine wastewater, respectively. We expect this method will make a significant contribution to treat the fluorine contained industrial waste water with short reaction time and easy handling.

**Keywords :** Poly aluminum chloride(PAC), Wastewater treatment, Fluorine, pH, Removal efficiency

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## 1. Introduction

Fluoride is often present in a variety of untreated industrial effluents, including those from chemical plants manufacturing organic fluorine compounds, aluminum smelters, phosphate fertilizers, semiconductor manufactu ring, glass and brick making industries, and coal power plants[3),13),15)]. The concentrations of fluoride in untreated industrial waste waters vary widely, and concentrations as high as 500 to 2,000 mg/L have been reported in effluents from semiconductor industry operations[5),6)]. Various treatment technologies based on precipitation[10)], ion exchange[9)], adsorption[17),18)], membrane process such as reverse osmosis[2)], nanofiltration[7)], electrodialysis[1),14)], and electro-chemical technology, including electro-coagul ation, electro-flotation and electro-chemical oxidation8), have been proposed for removal of fluoride from wastewater.

The industrial working process, which requires extremely high precision, generates both environmental and hazardous wastes.[16)] Some of previous studies prove that fluorine in water and wastewater can be treated to a desirable limit by adsorption or precipitation[4)]. Calcium salt and aluminum salt or lime precipitation of fluoride can reduce the residual fluoride concentration to 10-15 mg/L or lower[11),12)].

The most cost effective and common treatment method to remove fluorine is calcium salt precipitation. This method has also operational convenience and short reaction time. The salt is implemented by adding fixed amount of calcium salt which facts with fluoric ions in the wastewater.

$$Ca^{2+} + 2F \rightarrow CaF_2$$

It is two steps treatment process i.e. $CaF_2$ formation and fluorine adsorption by $Al(OH)_3$. First produces $CaF_2$ sludge and secondly generates a large a mount of fluorine containing $Al(OH)_3$ sludge.

Removing fluorine from wastewater : Generally fluorine contained wastewater treatment system is described into five processes. Each process is described as follows.

1) With pH control, the wastewater containing fluorine produces a calcium fluoride($CaF_2$) by adding calcium salt and in this process a small amount of sludge is produced also.

2) Sludge is separated from first treated water by solid-liquid separation.

3) Again, with pH control, the first effluent generates aluminum fluoride or makes $Al(OH)_3$ flock by adding aluminum compounds. The theoretical quantity of adding calcium is ; Calcium : fluorine = 1 : 2

4) The waste sludge is separated by solid-liquid separation.

5) Finally, the waste sludge is gone into the dehydrator.

Our current research also involves these

concepts. The objective of this study is to evaluate the pH and PAC effects on the reduction of fluorine concentration from the industrial wastewater.

## 2. Materials and Method

### 2.1. Experimental

Fluorine wastewater of low concentration (142 mg/L) and high concentration (1520 mg/L) was collected from Yeosu Industrial Complex area, South Korea. Initial pH was 3.7 and 3.01, respectively. This experiment was done two times for confirm in g the actual treating condition. Experiment was carried o ut using lab scale Jar reactor with controlling mixing speed(200 rpm) at farm power lab in Sunchon National University, South Korea. We tried to find out the pH(7, 8, 9, and 10) effects for the low concentration waste water and the PAC effects for high concentration fluorine waste water at the pH 7. Both experiments were done with same procedure. In the first step, $CaF_2$ (sludge 1) is generated, and fluorine adsorbing $Al(OH)_3$ (sludge 2) is generated in the second step. The quantity of sludge 2 is much larger than that of sludge 1. Therefore, the main part of total sludge generated is the $Al(OH)_3$ sludge produced in the second step.

### 2.2. Materials

The fluorine wastewater was used as a feed after diluting a concentrated calcium hydroxide for increasing pH. After 1st effluent, we used aluminum salt such as PAC in the second treatment. This experiment was done by using lab scale jar reactor.

### 2.3. Analytical

After settling the $Al(OH)_3$ flock at the bottom of reactor, we took the samples from the supernatant for measuring the fluorine

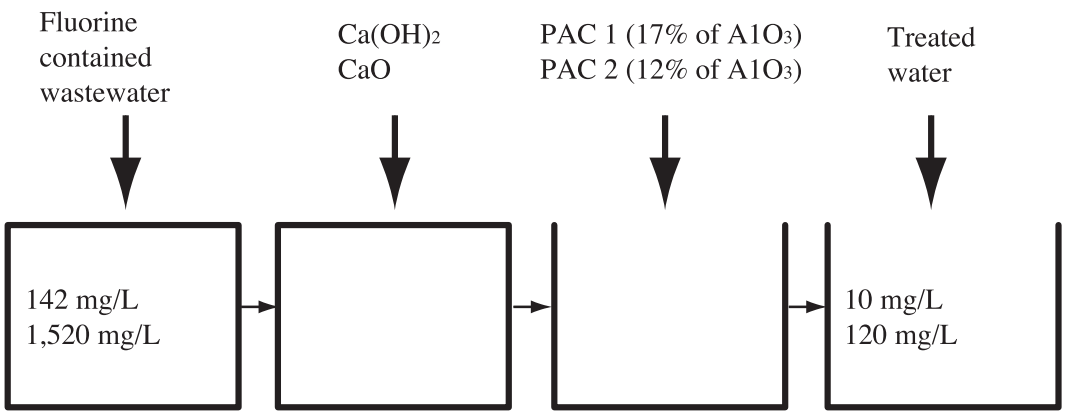


Fig. 1. Process flow diagram.

concentration. It was measured according to standard methods published by the American Public Health Association(APHA, 1998), using a DR/2800 spectrophotometer (Hatch, 1993).

### 2.4. Principle of treatment process

The main chemistry of this process is the conventional precipitation. The ion

product ($Ca^{2+}$ and $F^{-}$) by applying calcium hydroxide is formed into $CaF_2$ in the homogeneous liquid phase according to the following reaction.

$$H^{+} + F^{-} \rightarrow HF$$
$$Ca^{2+} + 2OH^{-} \rightarrow Ca(OH)_2$$
$$2HF + Ca(OH)_2 \rightarrow CaF_2\downarrow + 2H_2O$$
$$Al^{3+} + 3OH^{-} \rightarrow Al(OH)_3$$

Finally, fluorine adsorbing $Al(OH)_3$ sludge is separated from the water and settles at the bottom of it.

## 3. Result and Discussion

### 3.1. Effect of pH

For this experiment we collected actual wastewater from Yeosu industrial complex area. For treating low concentration of fluorine wastewater, $Ca(OH)_2$ was used to form $CaF_2$, and PAC 2(12% of $AlO_3$) was added to make $Al(OH)_3$ flock with different pH(7, 8, 9 and 10).

Fig. 2 shows the relationship between the pH and the concentration of fluorine in treated water. As shown in the figure, fluorine in wastewater was removed down to a low concentration. Comparing among pH, we got the lower value of fluorine 10.2 mg/L with 92.81% fluorine removal efficiency at pH 10(Table 1).

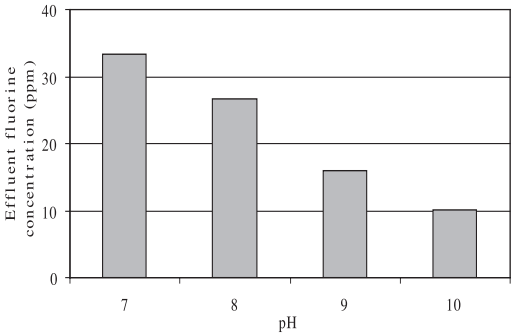


Fig. 2. Relationship between pH and fluorine concentration in effluent water.

### 3.2. Treatment performance of PAC

For high concentration fluorine wastewater(1520 mg/L), we used CaO for the first treatment and PAC 1(17% of $AlO_3$) and PAC 2(12% of $AlO_3$) for the second treatment with controlling pH 7. In the second treatment PAC 1 of 350 ppm has the same value of $AlO_3$ with PAC 2(12%) of 496 ppm. We found out the PAC effect to treat this wastewater. Table 2 shows that better effluent was obtained from the PAC 2 of 496 ppm than from the PAC 1 of 350 ppm. Using PAC 1, we got the final fluorine concentration 240 mg/L with 92.1% of removal efficiency and using PAC 2, we got 120 mg/L with 84.21% of removal efficiency

Table 1. Treatment procedure of low concentration fluorine wastewater

| No | 1st Treatment ; 25% $Ca(OH)_2$ 20 min reaction + 20 min settle | | | 2nd Treatment ; PAC 2(12% of $AlO_3$) 20 min reaction + 20 min settle | | | |
|---|---|---|---|---|---|---|---|
| | Quantity (Raw water) (ml) | pH | Input $Ca(OH)_2$ (ml) | 1st effluent (ml) | Input (PAC 2) (ppm) | Final Conc. (mg/L) | Removal efficiency (%) |
| 1 | 600 | 7 | 0.7 | 500 | 80 | 33.4 | 76.47 |
| 2 | 600 | 8 | 0.8 | 500 | 80 | 26.6 | 81.26 |
| 3 | 600 | 9 | 0.9 | 500 | 80 | 16.0 | 88.73 |
| 4 | 600 | 10 | 1.1 | 500 | 80 | 10.2 | 92.81 |
| Influent wastewater fluorine concentration=142 mg/L | | | | | | | |

Table 2. Treatment procedure of high concentration fluorine wastewater

| Reagent | Treatment | | | 2nd Treatment | | | Removal efficiency (%) |
|---|---|---|---|---|---|---|---|
| | Quantity (Raw water) (ml) | pH | Input CaO, (gm) | 1st effluent (ml) | Input PAC (ppm) | Final Conc. (mg/L) | |
| PAC 1 | 600 | 7 | 9.61 | 500 | 350 | 240 | 84.21 |
| PAC 2 | 600 | 7 | 9.61 | 500 | 496 | 120 | 92.10 |
| Influent wastewater fluorine concentration=1520 mg/L | | | | | | | |

## 4. Conclusion

This study demonstrates that industrial wastewater containing fluorine can be efficiently treated by precipitation method. The combined use of calcium salt and PAC can be a process to enhance the removal efficiency. Comparing PAC1 (17% of $AlO_3$) and PAC 2 (12% of $AlO_3$), we obtained the better efficiency from PAC2. It is very important to select the pH value and PAC which influence on the fluorine removal efficiency.

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