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Reduction of Fluorine-containing Industrial Waste Using Aluminum-solubility Method

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Abstract

About 30% of industrial waste from semiconductor plants is fluorine-containing waste. To decrease this we examined a new waste treatment method. This paper describes the theory, features and performance of this method.

In this method, fluorine contained in waste is fixated to AlF_3 using an aluminum treatment agent, which reduces fluorine in waste to a low concentration. Then AlF_3 is dissolved, and at the same time, a calcium treatment agent is added to substitute AlF_3 with CaF_2. By this method, the fluorine treatment performance was improved, decreasing fluorine-containing waste 75% or more than the conventional calcium precipitation method. Most of the aluminum treatment agent used for this new method can be reused, therefore the energy saving and cost reduction effect is high.

1. Introduction

Recently environmental protection is being given a great deal of attention, and standards to control the concentration of substances discharged from factories is becoming more strict every year.

The concentration of fluorine in waste water, for example, is defined as 15mg/l or less by the Water Pollution Control Law. This value is even 8mg/l or less depending on the local self governing body. Each factory performs the treatment of waste water and exhaust gas by various methods to meet these control values. These treatments generate an enormous amount of sludge, which are reclaimed as industrial waste. But the capacity of reclamation plants is already saturated, and decreasing industrial waste is an urgent problem.

Semiconductor plants are no exception, where large amounts of waste sludge is discharged. About 30% of waste sludge is generated when treating fluorine-containing waste water. To decrease the generation of this waste, various treatments have been examined. In newly established waste water treatment plants, a new system which uses calcium carbonate, is having good results.

We examined the treatment method using an aluminum-solubility method to decrease the fluorine-containing waste water treatment sludge generated from semiconductor plants. This paper first describes the current situation of fluorine-containing waste water treatment, then the principles, experimental methods and performance of treatment methods using an aluminum-solubility method are described.

2. Current situation of fluorine-containing waste water treatment

2.1 Coagulating sedimentation method using calcium hydroxide (conventional method)

The primary fluorine-containing waste water treatment method conventionally used was the coagulating sediment method*1 which uses calcium hydroxide $\{Ca(OH)_2\}$ as the treatment agent. Figure 1 shows the treatment flow.

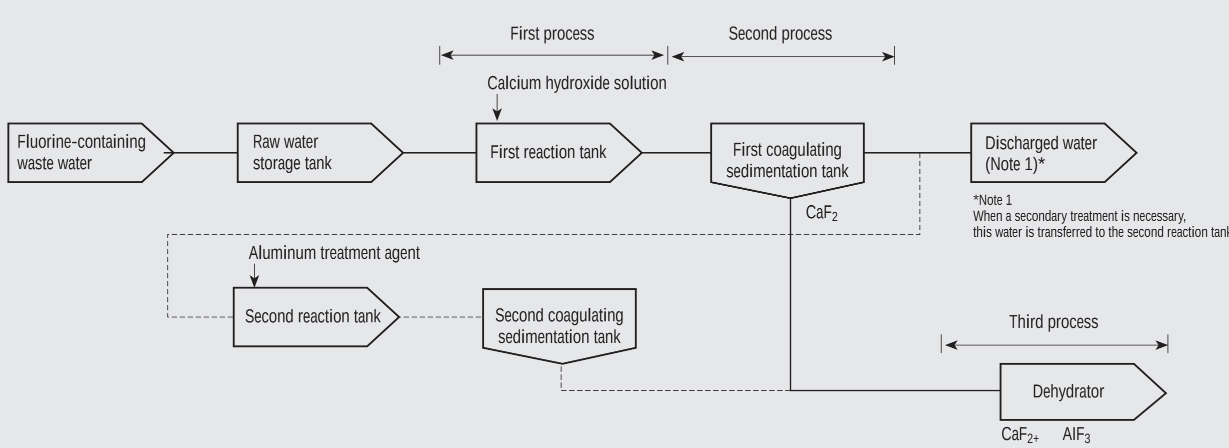

Figure 1: Treatment flow of fluorine-containing waste water (conventional method)

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*1 Coagulating sedimentation method is a method to sedimentate solid matter in the solution utilizing specific gravity differences.

1. First process (first reaction tank)
   Calcium hydroxide is added to fluorine-containing waste water, and the pH is controlled. Fluorine ions that dissolve in the waste water combine with calcium ions and is deposited as calcium fluoride.

   $$2\,HF + Ca(OH)_2 \rightarrow CaF_2\downarrow + 2\,H_2O$$

2. Second process (first coagulating sedimentation tank)
   Since calcium fluoride is alkaline and exhibits low solubility, solid and liquid can be easily separated by using the coagulating sedimentation method. The separation speed can be accelerated by adding macromolecular flocculant. Supernatant liquid after solid-liquid separation is discharged as treated water and the sedimentated portion is recovered as sludge.
3. Third process (dehydrator)
   Recovered sludge is decreased in volume by a dehydrator and is disposed of as industrial waste.

2.2 Problems of conventional methods

Calcium hydroxide, which is frequently sold as slaked lime, is generally inexpensive. But the solubility of calcium hydroxide is low, so the quantity of calcium hydroxide that dissolves in water as calcium ions is very little. Therefore, a large amount of the treatment agent must be added to treat the concentration of the treatment target fluorine. Excess calcium hydroxide added in the waste water is recovered with calcium fluoride as waste sludge, which is a cause to increase waste sludge more than necessary. Also because of low solubility, calcium hydroxide can decrease the concentration of fluorine in treated water only to 15mg/l. To further decrease this concentration to 8mg/l or less, a secondary treatment (second reaction tank - second coagulating sedimentation tank) using an aluminum treatment agent is required.

3. Reduction of fluorine-containing waste sludge

3.1 Concept

Under certain conditions, aluminum exhibits a higher bonding strength with fluorine compared with calcium. Aluminum can therefore remove fluorine in waste water down to a lower concentration. The problems of aluminum are that aluminum is much more expensive than the calcium treatment agent, and sludge generated after treatment has a poor dehydrating capability. For these reasons, aluminum is inappropriate for high concentration fluorine treatment, and therefore is mainly used for low concentration fluorine waste water.

Focusing on the high fluorine removal capability of aluminum, and the good dehydrating capability and low cost of calcium, we examined a treatment method that decreases waste sludge.

3.2 Waste water treatment using aluminum-solubility method

We experimented with a waste water treatment based on an aluminum-solubility method, and checked the effect. With this method, a calcium treatment agent is added to the sludge generated after treating fluorine-containing waste water with an aluminum treatment agent, and the aluminum of aluminum fluoride is substituted with calcium. Aluminum in sludge dissolves, and is recovered and reused as an aluminum treatment agent. Figure 2 shows the waste water treatment flow of this aluminum-solubility method. This waste water treatment system is separated into five processes. Each process is described below.

1. First process
   The recycled aluminum treatment agent, recovered in the fourth process, is added to the fluorine-containing waste

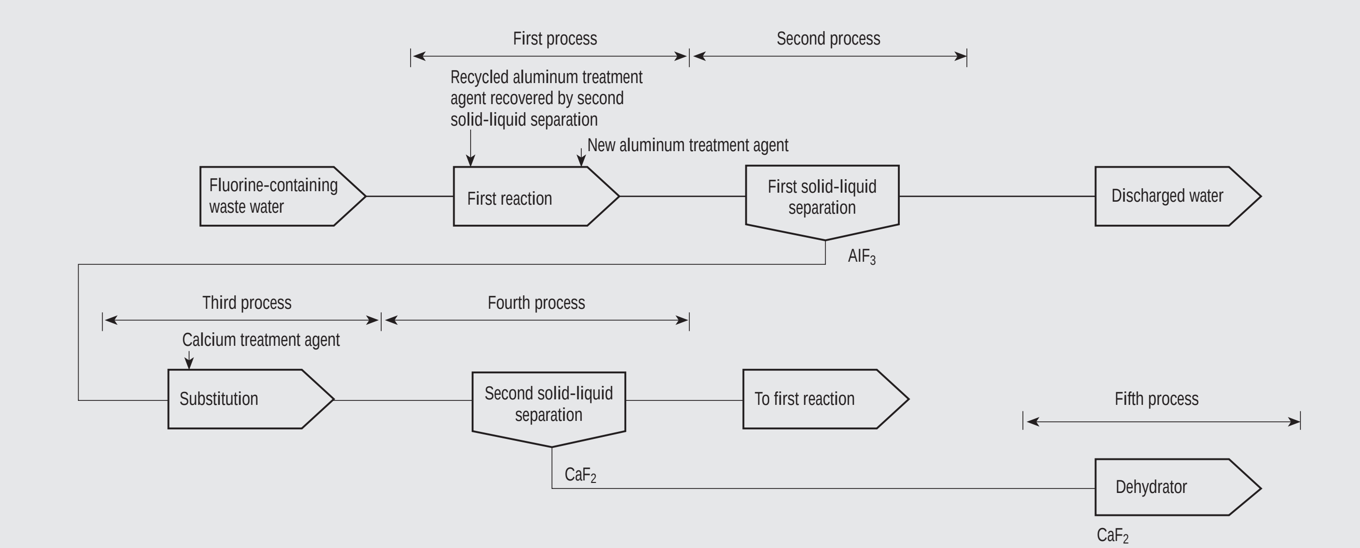

Figure 2: Treatment flow of waste water using aluminum-solubility method

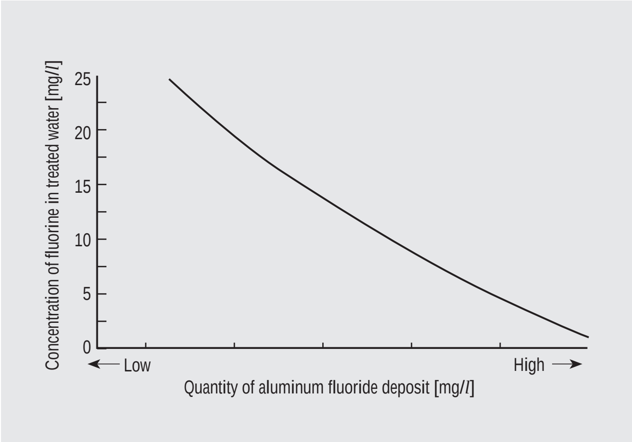

Figure 3: Quantity of aluminum fluoride deposit vs. concentration of fluorine in treated water

water. When this is insufficient for the fluorine treatment, a new aluminum treatment agent is added. By pH control, fluorine contained in waste water is deposited as aluminum fluoride, then fluorine in waste water is removed by removing aluminum fluoride. The following chemical formula shows the reaction of hydrofluoric acid and ammonium fluoride with the aluminum treatment agent.

$$3\,HF + AlO_2 \xrightarrow{-NaOH} AlF_3\downarrow + H_2O + OH^-$$

$$3\,NH_4F + AlO_2 \xrightarrow{-NaOH} AlF_3\downarrow + 3NH_4^+ + O_2$$

$$6\,NH_4HF_2 + 4\,AlO_2^- \xrightarrow{-NaOH} 4\,AlF_3\downarrow + 6\,NH_4^+ + 2\,O_2 + 2\,H_2O + 2\,OH^-$$

Figure 3 shows the relationship between the volume of deposit of aluminum fluoride*2 and the concentration of fluorine in treated water*3 obtained from our experiment. From Figure 3 we determined the quantity of aluminum required to add for fluorine treatment.

2. Second treatment

Recovered sludge is separated from treated water by solid-liquid separation. We measured the concentration of aluminum in recovered sludge, and confirmed that 85% of aluminum can be recovered.

3. Third process

A calcium treatment agent is added to the recovered sludge. By pH control, aluminum of aluminum fluoride is substituted with calcium and is deposited as calcium fluoride. Figure 4[1] shows the relationship between the logarithmic solubility of metal ions and pH. From Figure 4, we assumed that the aluminum and calcium status changes due to the pH value change, and determined an optimum pH value after experiment. The following formula shows the reaction between aluminum fluoride sludge and the calcium treatment agent.

$$2\,AlF_3\downarrow + 3Ca^{2+} \xrightarrow{-NaOH} 3CaF_4\downarrow + 2\,AlO_2^- + 4H^+ + 2Na^+$$

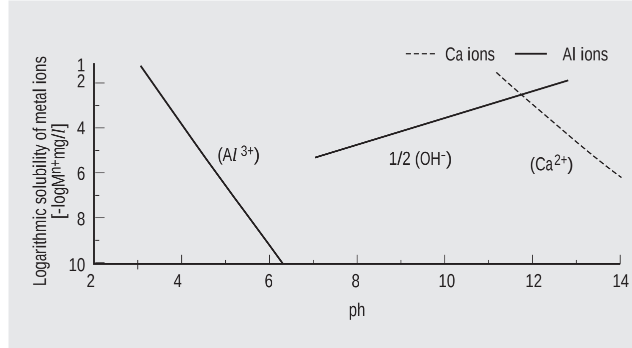

Figure 4: Relationship between solubility of metal ions and pH

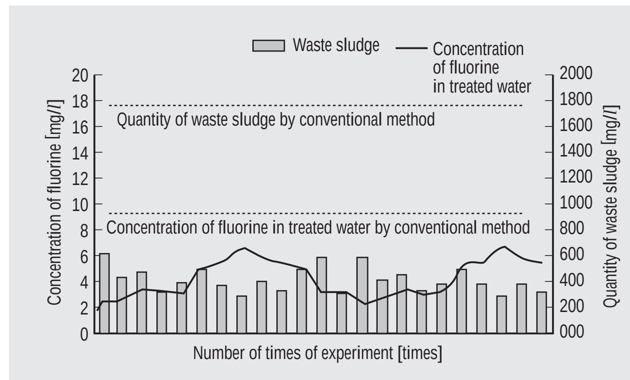

Figure 5: Quantity of waste sludge and concentration of fluorine in treated water

When aluminum fluoride dissolves and fluorine becomes unstable, aluminum of aluminum fluoride is substituted with calcium and is deposited as calcium fluoride. The theoretical quantity of adding calcium is calcium : fluorine = 1:2.

Based on the above result, we determined the quantity of the aluminum treatment agent and the calcium treatment agent to add that is required for the removal of fluoride and for substitution.

4. Fourth process

Waste sludge and the recycled treatment agent (dissolved aluminum) are separated by solid-liquid separation.

5. Fifth process

The volume of waste sludge is decreased by the dehydrator.

3.3 Result of experiment using aluminum-solubility method

Figure 5 shows the relationship between the quantity of waste sludge and the concentration of fluorine in treated water. As this figure shows, fluorine in waste water was removed down to a low concentration. Compared with conventional treatment methods, the concentration of fluorine in treated water was lowered, and waste sludge was decreased 75%.

*2 Quantity of aluminum fluoride deposit was measured as mass of suspended matter based on measurement JIS K0102-14.2 analysis method.

*3 Concentration of fluorine in treated water was measured based on fluorine concentration measurement JIS K0102-34.1 analysis method.

For the experiment, we used actual waste water from a semiconductor factory. The concentration of fluorine in this waste water was 120mg/l.

4. Conclsion

Aiming at decreasing the quantity of fluorine-containing waste sludge, we confirmed the effect of a waste water treatment method using an aluminum-solubility method.

We continued experiments nearly 60 times and treatment was stable throughout these experiments, with no drop in treatment capability. Compared with conventional methods, the aluminum-solubility method can decrease waste sludge 75% as dry weight, and 88% if an ordinary dehydrator is used. The fluorine removal ratio can also be improved. This waste water treatment method, based on an aluminum-solubility method, has high potential to be installed in already established waste water treatment plants after small scale modifications.

We are planning to examine the aluminum treatment agent recovery method and a stable supply method aiming at implementing a system that can be installed in already established waste water treatment plants.

With the 21st century close at hand, environmental problems are becoming more serious. We will make efforts in environmental protection from various aspects so that the natural environment and factories can coexist.

5. Reference

1. Industrial Water and Waste Water Guide, 2nd Edition, Industrial Water and Waste Water Guide Editorial Committee, (1973): 407.