Recovery of fluoride as perovskite-like minerals from industrial wastewater

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ABSTRACT

This study investigated the recovery of fluoride (626.5 mg/L) from an industrial wastewater as perovskite-like minerals. Effects of equilibrium pH (pH_{eq}), molar ratio of Na to F (Na/F), and types of pH reagents were examined. Fluoride was recovered and confirmed by XRD as elpasolite (K_2NaAlF_6) when pH reagent was KOH. High fluoride removal efficiency (>94.7%) was found at Na/F of 3/6, Al/F of 1/6, room temperature, and pH_{eq} range of 4.2–5.7. Satisfactory K_2NaAlF_6 recovery and fluoride removal were found as Na/F reduced to 1/6. Fluoride was recovered as cryolite (Na_3AlF_6) when NaOH was the pH reagent at Na/F of 12/6, Al/F of 1/6 and pH_{eq} range of 5.5–7.2, and good fluoride removal efficiency (>94.5%) was found. Size analysis and sedimentation test showed that both K_2NaAlF_6 and Na_3AlF_6 could be easily separated from water. The current study demonstrated simple and energy-efficient alternatives for fluoride recovery as potentially reusable minerals from wastewater.

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1. Introduction

Fluorine occurs generally in reduced form (fluoride, F^-) in combination with other minerals [1]. Most common fluoride-bearing minerals in the earth's crust include fluorite (CaF_2), fluorapatite ($Ca_5(PO_4)_3F$), cryolite (Na_3AlF_6) and villiaumite (NaF) [2]. Fluoride concentration in natural waters depends on various factors, such as temperature, pH, solubility of fluorine-bearing minerals, anion exchange capacity of aquifer materials, the nature of geological formations drained by water, and contact time of water with a particular formation [3].

Fluoride pollution has attracted worldwide concern over decades. Many industries generate significant amount of fluoride-containing wastewater, such as manufacturing of iron and steel, non-ferrous metal, chemical fertilizers, organic fluorine chemical products, and semiconductors [4]. Fluoride could be effectively removed by waste mud [5]. A basic aluminum carbonate nanosphere removes fluoride via the ion exchange between carbonate groups and fluoride [6]. Fluoride can also be effectively removed by Al-based coagulation and adsorption [7]. However, adsorption may not be suitable for concentrated fluoride-containing wastewater. Among all treatment technologies, chemical precipitation is the most economical and reliable way to remove high concentra-

tion of fluoride [8,9]. It is noted that sludge produced in wastewater treatment needs further treatment and disposal. Therefore, sludge minimization or utilization of sludge as valuable minerals has long been an important research topic [10–12].

Calcium fluoride (CaF_2) recovery in a fluidized bed reactor was reported by Aldaco et al. [13,14]. To ensure fluoride removal efficiency, it is very important to control the supersaturation degree in the crystallization reactor [13]. The synthesized CaF_2 from the reactor can be recycled and reused in the manufacturing of hydrofluoric acid. The fluoride recovery efficiencies in the reactor ranged from 70% to 80% [14].

On the other hand, some researchers have studied the recovery of fluoride as cryolite (Na_3AlF_6) and sodium silicofluoride (Na_2SiF_6) by simple precipitation [10–12,15]. The recovery rate of cryolite was about 75% under an influent fluoride concentration of 3500 mg/L at 50 °C [6]. Good control of pH and molar ratio of Al to F (Al/F) is the key [11,15]. Cryolite can be used as a fluxing agent for electrolytic aluminium production [16]. The chemical is also used as a protective and refining salt in the melting of light metals, for fireworks in pyrotechnics, and as a layer or host materials for optical applications [17].

Cryolite has a double perovskite structure. All of the Al^{3+} and one third of the Na^+ cations are sixfold coordinated (Na^{VI}) in the center of alternating $[AlF_6]$ and $[NaF_6]$ octahedra, whereas the remaining Na^+ ions are eightfold coordinated (Na^{VIII}) [16,18]. Materials with a perovskite-type structure (ABX_3) are of great interest in

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many fields of science and technology [16,19]. Their applications range from the use as catalysts, sensors, superconductors, or ferroelectric materials. Despite the structural similarities, the specific behavior of different perovskites varies substantially [16]. There is a large family of $A_2^I B^I M^{III} F_6$ compounds (A^I, B^I: monovalent cations; M^{III}: trivalent cation) with an elpasolite (K_2NaAlF_6) or cryolite ($NaNa_2AlF_6$, when A = B) structure derived from a perovskite superstructure with double cell edges [20].

The present study aimed to investigate recovery of fluoride as perovskite-like minerals from fluoride-containing industrial wastewater. The effects of equilibrium pH (pH_{eq}), molar ratio of Na to F (Na/F), molar ratio of Al to F (Al/F), and types of pH adjustment reagents were studied. Meanwhile, PHREEQC simulation was conducted to predict precipitation and speciation in the systems and results were compared with the experimental ones. Solubility products of solid phases included in simulation are listed in Table 1.

2. Materials and methods

The fluoride-containing wastewater was obtained from one of representative semiconductor manufacturers in Hsinchu Science Park, Taiwan. Sample was taken from equalization tank. The characteristics of industrial wastewater were analyzed using ion chromatography (IC, Dionex-100), inductively couple plasma-atomic emission spectrometry (ICP-AES: JY2000), pH meter, turbidity meter (Orbeco-Hellige 956-10). The fluoride concentration of wastewater was 626.5 ± 29.7 mg/L. The elements, such as Na, Al, Mg, K and Ca were lower than 1 mg/L or undetectable in the raw wastewater. The characteristics of the industrial wastewater are shown in Table 2.

The experiment was conducted at room temperature in plastic beakers using a conventional jar test apparatus. The pH was adjusted to desired value by 5 M KOH (laboratory reagent grade, Fisher Scientific) or NaOH (pellets, laboratory reagent grade, Fisher Scientific), then the measured amount of NaCl (99.5%, Acros) and $AlCl_3 \cdot 6H_2O$ (99%, Acros) were added into 500 mL industrial wastewater to control Na/F and Al/F. In jar test, 3-min rapid mixing at 90 rpm was applied, followed by 20 min of slow stirring at 30 rpm. After settlement for 30 min the supernatants were sampled and filtered using a 13-mm syringe filter with a 0.45 μm PVDF membrane (Chrom Tech). The residual fluoride concentration of the supernatants was measured by IC (Dionex-100). The wet sample was filtered through a 0.22 μm mixed cellulose ester membrane (Advantec) and rinsed by 500 mL ultra-pure water until the conductivity was constant. The filtrated cake was dried at 110 °C for 3 h. Dry samples of precipitates were analyzed by X-ray diffraction (XRD) and field-emission scanning electron microscope (FESEM/EDS). The concentration of fluoride was examined by ion chromatography (ICS-1000, Dionex). A mixture of 3.5 mM of Na_2CO_3 (99.8%, Acros) and 1 mM of $NaHCO_3$ (99.5%, Acros) was prepared as IC eluent. Each sample was filtered by a 0.45 μm PVDF membrane and filled into 20-mL plastic bottle, which was

Table 1
Solubility products of solid phases used in thermodynamic modeling by PHREEQC at 25 °C.

Aluminum trifluoride, AlF_3	$AlF_3 \rightarrow Al^{3+} + 3F^-$	−2.96[a]
Aluminium hydroxide, $Al(OH)_3$	$Al(OH)_3 \rightarrow Al^{3+} + 3OH^-$	−31.50[a]
Cryolite, Na_3AlF_6	$Na_3AlF_6 \rightarrow 3Na^+ + Al^{3+} + 6F^-$	−33.84[a]
Gibbsite, $Al(OH)_3$	$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$	−22.80[a]
Aluminium hydroxyfluoride, $AlF_2(OH)$	$AlF_2(OH) \rightarrow AlF^{2+} + OH^-$	−15.70[b]

[a] PHREEQC database.
[b] Ref. [23].

Table 2
Characteristics of the fluoride-containing industrial wastewater.

Constituent	Value
pH	3.8 ± 0.1
Conductivity (μs/cm)	1.932 ± 2.7
Turbidity (NTU)	1.0 ± 0.2
Fluoride (mg/L)	626.5 ± 29.7
Nitrate (mg/L)	298.8 ± 53.7
Ammonia (mg/L)	217.1 ± 12.2
Silicon (mg/L)	1.5 ± 1.2

stored in refrigerator under 4 °C before analysis. The filtrate was diluted at a range from 10 to 100 times and the residual fluoride concentration was analyzed by IC. The ICP-AES was used to analyze the concentration of metal elements.

The crystalline structures of precipitates were examined by the X-ray diffraction (Bruker D2 PHASER). The Cu target was used to generate Cu Kα ray. The Cu Kα line at 1.5406 Å was used as the source of diffraction. The working voltage and current were fixed at 50 kV and 10 mA, respectively. Samples were analyzed at a range of 2θ from 10° to 70° with the interval of 0.02° and scan rate of 0.25°/min.

The morphology of the precipitate was examined by the field-emission scanning electron microscope (FESEM, JSM-6500F, JEOL). The samples were coated with gold for 100 s to enhance the conductivity. The acceleration voltage was set at 15 kV and the pressure in charmer was kept below 4.41×10^{-4} Pa. The particle size of precipitates was measured by a light scattering instrument (Mastersizer, Hydro-2000).

3. Results and discussion

3.1. KOH as pH reagent for elpasolite

According to previous studies [10–12], pH value is a significant parameter for producing Na_3AlF_6 during precipitation process. In order to investigate the effect of pH, the alkaline reagent was required to adjust the pH value of the fluoride-containing industrial wastewater. Moreover, since sodium ion (Na^+) of NaOH was a reactant in the process, pH of solution was thus adjusted by 5.0 M KOH. In this experiment, Na/F and Al/F were kept at 3/6 and 1/6, respectively. As shown in Table 3, fluoride concentration decreased from initial concentration of 626.5 mg/L to below 35 mg/L at pH_{eq} range from 3.31 to 5.67, and the removal of fluoride could reach >92% in the pH range, but decreased at pH > 7.15.

Fig. 1 shows the comparison of XRD patterns between precipitates recovered at various pH_{eq} from the wastewater and commercial cryolite (Na_3AlF_6), (97.4%, First Chemical). The crystal structure of precipitates was not in conformity with commercial Na_3AlF_6, but was identified as elpasolite (K_2NaAlF_6) from the Joint Committee on Powder Diffraction Standards (JCPDS) of 22-1235. Since the molar

Table 3
Effect of equilibrium pH (pH_{eq}) on fluoride removal using KOH as pH reagent (Na/F = 3/6, Al/F = 1/6).

pH_{in}[a]	pH_{eq}	KOH added (mL)	[K^+] (mol/L)	F removal (%)
4.57	3.31	1.80	0.0180	92.7
5.50	4.20	1.81	0.0181	96.2
6.87	5.11	1.87	0.0187	94.7
7.40	5.67	1.90	0.0190	95.5
7.55	7.15	2.00	0.0200	33.1
9.00	7.79	2.05	0.0205	18.6
9.60	8.15	2.98	0.0298	21.0
10.7	9.16	3.00	0.0300	16.4

[a] pH_{in}: initial pH.