A study on the low-temperature wet synthesis of hydrofluoric acid from synthetic calcium fluoride and waste sulfuric acid

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Abstract. An innovative method for utilizing synthetic calcium fluoride (CaF₂), recovered from fluoride-containing semiconductor wastewater, and waste sulfuric acid (H₂SO₄) to produce hydrofluoric acid (HF) was investigated. The research was set to study the low-temperature production of HF via the reaction of synthetic CaF₂ and waste H₂SO₄. The impact of H₂SO₄ concentration and total volume (H₂SO₄ + H₂O)/CaF₂ ratio, drying temperature of synthetic CaF₂ on HF productivity were investigated in this study. HF yield increased with increasing H₂SO₄ concentration and total volume/CaF₂ ratio under room temperature. In addition, the HF produced in the reactions involving the 105 °C-dried synthetic CaF₂ were higher than the 600 °C-dried synthetic CaF₂ ones. The study will not only find uses for this semiconductor wastes but also provide a greener alternative to the current commercial production of HF.

Keywords: HF productivity, Synthetic CaF₂, Waste sulfuric acid

1. Introduction
Fluoride, as hydrofluoric acid (HF) or ammonium bifluoride (NH₄-HF), and piranha solution (sulfuric acid, H₂SO₄ + hydrogen peroxide, H₂O₂), are extensively used in the semiconductor and nanotechnology industries as etchants. This leads to generation of waste that contains substantial amounts of these etchants. For example, it is reported that an 8-inch integrated circuit fabrication facility produces around 350 – 700 m³/d of fluoride-containing wastewater with a concentration around 500 – 2000 mg/L [1]. Huang and Liu [2] reported fluoride concentration in semiconductor wastewater could reach up to 3500 mg/l and account for 40 % of the hazardous waste from these industries.

Currently, the fluoride-containing wastewater is usually treated via coagulation using Ca(OH)₂ and/or CaCl₂ [3, 4]. The Ca²⁺ ions react with the F⁻ ions to form CaF₂ [5, 6]. The production rate of CaF₂ is estimated to be approximately 1.0 kg per ton of F⁻-containing wastewater [7].
used in different industrial sectors e.g. as flux in the manufacturing of glass ceramic or an additive in cement [8]. However, most of it end up in landfills [1]. Because of the low solubility of Calcium salts, the coagulation process does not remove all the fluoride in the wastewater, for e.g. when Ca(OH)$_2$ is used, the fluoride concentration left in the wastewater can be as high as 15 mg/l [2]. Therefore, because the slurry still contains free F$^{-1}$, it has limited usage for e.g. in Taiwan only 1 % wt. can be used in the cement and most of it is usually disposed of in landfills [9]. The waste H$_2$SO$_4$ solution from the semiconductor industry is usually neutralized and disposed, however, there has been some current effort of purifying and reusing as an etchant [10].

The use of synthetic CaF$_2$ and waste H$_2$SO$_4$ can be a green alternative in the production of HF. The synthetic CaF$_2$ formed through the reaction of fluoride-containing wastewater with CaCl$_2$ can be reacted by the waste sulfuric acid to yield HF as shown in equation (1). The synthetic CaF$_2$ which initially is in form of slurry is dried before the reaction.

$$\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HF} + \text{CaSO}_4$$ (1)

The objective of this research was to study the low-temperature formation of HF and the quantification of the absorbed-HF yield from the reaction of synthetic CaF$_2$ and waste H$_2$SO$_4$ received from a semiconductor industry. This waste to resource study will not only find uses for this semiconductor wastes but might provide a greener alternative to the current commercial production of HF.

2. Experimental

The experiments were carried out in two different reactors, a 250-mL Polyethylene (PE) reactor and a tailored stainless-steel reactor coated with Teflon. Behind the stainless-steel reactor, a condensing tube and three bottles with water used for absorbing hydrofluoric acid, were attached to the nozzle on the cover and were installed under considerable ice, at temperature of 4°C. The reactions conducted in the PE reactor were maintained at room temperature while in the stainless-steel reactor, a heater was incorporated to raise the temperature of the reactions. Reagent grade CaF$_2$ was used in this study to represent the commercial CaF$_2$ while synthetic CaF$_2$ and waste H$_2$SO$_4$ were obtained from one of the semiconductor manufacturing companies in Taiwan. Before the experiments, samples of the synthetic CaF$_2$ were preheated by drying to 105°C and 600°C. Various concentrations of H$_2$SO$_4$ solution, 40%, 50%, 60%, 70% and 80%, were prepared using 98% H$_2$SO$_4$ and distilled water.

During the reaction in the stainless-steel reactor, the hydrofluoric acid would gradually generate in the reactor and partly vaporized into the gas phase and was collected by the condensing tube and three absorbing bottles.

2.1 Synthetic CaF$_2$ and Waste H$_2$SO$_4$ Analysis

The chemical analysis of the synthetic CaF$_2$ and Waste H$_2$SO$_4$ was carried out by Sociétée Générale de Surveillance (SGS) company. The determination of the weight percentage of CaF$_2$ in the 105°C treated synthetic CaF$_2$ was performed following the ASTM E1506-08 standard test method for the analysis of acid-grade calcium fluoride, while the waste H$_2$SO$_4$ concentration were measured complying with CNS 997, a method of test for sulfuric acid.

2.2 HF Analysis

Productivity of hydrogen fluoride can be acquired by the generated hydrogen fluoride divided by theoretical hydrogen fluoride and subsequently multiplying by 100% as shown in Eq. 2.

$$\text{Productivity of hydrogen fluoride} = \frac{\text{Generated HF}}{\text{Theoretical HF}} \times 100\%$$ (2)

Based on the stoichiometry, CaF$_2$ during the reaction in this study could be identified as the limiting reagent and used for the prediction of theoretical hydrogen fluoride. In the stoichiometric calculation, once the reaction includes synthetic CaF$_2$, the moles of which should be multiplied by 77.7% because its purity is 77.7%. Generated hydrogen fluoride would be the amount of which measured by fluoride test paper.
3. Results and discussion

3.1 Effect of H$_2$SO$_4$ concentration on HF yield

The effect of the concentration of H$_2$SO$_4$ on the HF yield was studied by reacting commercial CaF$_2$ with different concentrations of H$_2$SO$_4$ as shown in Table 1. The HF produced increased with increasing H$_2$SO$_4$ concentration. The HF productivity were calculated and plotted against H$_2$SO$_4$ concentration, as shown in Figure 1. The HF productivity was observed to increase with increasing H$_2$SO$_4$ concentration. The HF productivities were 13.7%, 16.4%, 17.0%, 19.5% and 20.9% when the H$_2$SO$_4$ concentration used were 40%, 50%, 60%, 70%, and 80%, respectively. Theoretically, an increase in the concentration of reactants increases the reaction rate due to the increased number of collisions of the reactant molecules. However, the trend is not quite clear given that the total volume (H$_2$SO$_4$ + H$_2$O) was also a variable. Therefore, experiments were carried to determine the effect of this total volume on HF productivity.

| CaF$_2$ (g) | Total Vol. (mL) | H$_2$SO$_4$ conc. (v/v%) | HF produced (g) |
|------------|----------------|--------------------------|-----------------|
| 10         | 98             | 40                       | 0.70            |
| 10         | 78             | 50                       | 0.84            |
| 10         | 65             | 60                       | 0.87            |
| 10         | 56             | 70                       | 1.00            |
| 10         | 50             | 80                       | 1.07            |

Figure 1. HF productivity against H$_2$SO$_4$ concentration.

3.2 Effect of Total volume/CaF$_2$ ratio and drying temperature of synthetic CaF$_2$ on HF yield

The waste H$_2$SO$_4$ concentration from the semiconductor company was found to be 70%, therefore, 70% H$_2$SO$_4$ was chosen to study the effect of the total volume/CaF$_2$ ratio on the HF yield. Total volume/CaF$_2$ ratio is defined as the total volume of H$_2$SO$_4$ solution (ml, H$_2$SO$_4$ + H$_2$O) over the weight of pure CaF$_2$ (g). The HF produced from the various total volume/CaF$_2$ ratios is given in Table 2 and the total volume was the only variable in the reactions. The increase in the total volume/CaF$_2$ ratio led to the increase in HF produced. This is because in a well-mixed environment, a larger volume might ensure that there is lesser agglomeration of CaF$_2$ particles. Also, CaSO$_4$ produced as a byproduct will precipitate and settle in the reactor which might hinder the reaction by covering the CaF$_2$, especially in lower volume.
The synthetic CaF$_2$ which is produced via coagulation needed to be dried before it is used in the production of HF. This is because the product of the coagulation process usually contains a lot of water. Therefore, experiments were carried to study the effect of the synthetic CaF$_2$ drying temperature on HF. Table 3 presents the parameters and the HF produced during those reactions. The HF produced in the reactions involving the 105 °C-dried synthetic CaF$_2$ were higher than the 600 °C-dried synthetic CaF$_2$ ones. This is because the robust heat treatment (600 °C) solidifies the structure of synthetic CaF$_2$, having an effect on not only the moisture content, but also its physical characteristics including surface area, density and compressive strength [11]. The solid structure and relatively lower surface area impact the reaction of CaF$_2$ with H$_2$SO$_4$ which led to the observed lower HF production. Also, the 105 °C-dried synthetic CaF$_2$ was in slurry form which could enhance the mixing of the reactants and improve the reaction. The results from these experiments also support the effect of the Total volume/CaF$_2$ on the HF productions. The HF productivity of the abovementioned reactions were calculated and plotted against the respective Total volume/CaF$_2$ ratio as shown in Figure 2. The HF productivity was highest when 105 °C-dried synthetic CaF$_2$ was used, then followed by commercial CaF$_2$ and finally 600 °C-dried synthetic CaF$_2$. The 105 °C-dried synthetic CaF$_2$ had a higher yield than commercial CaF$_2$ probably because it was in slurry form and will have better mixing properties than solid form.

**Table 2. HF production using commercial CaF$_2$ and varying total volume of 70% H$_2$SO$_4$**

| CaF$_2$ (g) | Total Vol. (mL) | H$_2$SO$_4$ conc. (v/v%) | HF produced (g) |
|------------|----------------|--------------------------|-----------------|
| 10         | 200            | 70                       | 1.6             |
|            | 112            | 53                       | 1.2             |

**Table 3. HF production using dried synthetic CaF$_2$ and varying total volume of 70% H$_2$SO$_4$**

| 105 °C CaF$_2$ (g) | Total Vol. (mL) | H$_2$SO$_4$ conc. (v/v%) | HF produced (g) |
|--------------------|----------------|--------------------------|-----------------|
| 10                 | 200            | 70                       | 1.8             |
|                    | 112            | 53                       | 1.4             |

| 600 °C CaF$_2$ (g) | Total Vol. (mL) | H$_2$SO$_4$ conc. (v/v%) | HF produced (g) |
|--------------------|----------------|--------------------------|-----------------|
| 10                 | 200            | 70                       | 0.25            |
|                    | 112            | 56                       | 0.16            |
|                    | 56             |                          | 0.01            |
4 Conclusion
The impact of H$_2$SO$_4$ concentration, total volume/CaF$_2$ ratio, and drying temperature of synthetic CaF$_2$ on HF productivity were investigated in this study. The HF yield increased with increasing H$_2$SO$_4$ concentration and total volume/CaF$_2$ ratio. A reaction carried out using 105 ºC-dried synthetic CaF$_2$ had a higher HF productivity than 600 ºC-dried synthetic CaF$_2$.

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