Selective separation of phosphate and fluoride from semiconductor wastewater
B. Warmadewanthi and J. C. Liu

ABSTRACT
Hydrofluoric acid (HF) and phosphoric acid (H₃PO₄) are widely used in semiconductor industry for etching and rinsing purposes. Consequently, significant amount of wastewater containing phosphate and fluoride is generated. Selective separation of phosphate and fluoride from the semiconductor wastewater, containing 936 mg/L of fluoride, 118 mg/L of phosphate, 640 mg/L of sulfate, and 26.7 mg/L of ammonia, was studied. Chemical precipitation and flotation reactions were utilized in the two-stage treatment processes. The first-stage reaction involved the addition of magnesium chloride (MgCl₂) to induce selective precipitation of magnesium phosphate. The optimal condition was pH 10 and molar ratio, \([\text{Mg}^2⁺/\text{PO}_4^{3⁻}]\), of 3:1, and 66.2% of phosphate was removed and recovered as bobierrite (Mg₃(PO₄)₂·8H₂O). No reaction was found between MgCl₂ and fluoride. Calcium chloride (CaCl₂) was used in the second-stage reaction to induce precipitation of calcium fluoride and calcium phosphate. The optimum molar ratio, \([\text{Ca}^2⁺/\text{F}⁻]\), was 0.7 at pH 10, and residual fluoride concentration of 10.7 mg/L and phosphate concentration of lower than 0.5 mg/L was obtained. Thermodynamic equilibrium was modeled with PHREEQC and compared with experimental results. Sodium dodecylsulfate (SDS) was an effective collector for subsequent solid–liquid removal via dispersed air flotation (DiAF). The study demonstrated that phosphate can be selectively recovered from the wastewater. Potential benefits include recovery of phosphate for reuse, lower required dosage of calcium for fluoride removal, and less amount of CaF₂ sludge.

Key words | flotation, fluoride, phosphate, precipitation, semiconductor, wastewater

INTRODUCTION
Various types of acids are widely used in production processes in semiconductor manufacturing for etching and rinsing purposes. Consequently, significant amount of wastewater containing fluoride (F⁻), phosphate (PO₄³⁻), sulfate (SO₄²⁻), and nitrate (NO₃⁻) is generated. Semiconductor manufacturers usually segregate their wastewater since the presence of mixed anions will affect efficiency of treatment processes. Precipitation processes by the addition of calcium salts, such as calcium chloride (CaCl₂) is mainly used by semiconductor manufacturer to remove fluoride from wastewater (Huang & Liu 1999; Chang & Liu 2007). Presence of phosphate and sulfate will compete for calcium ion and hinder the removal of fluoride (Huang & Liu 1999; Chuang et al. 2002). Experimental results in electronic wastewater also show inhibitory effect of phosphate ion on fluoride removal not only through competition of calcium but also through differential reaction kinetics that calcium salt forms calcium phosphate precipitate faster than calcium fluoride under alkaline pH (Yang et al. 2001). Consequently, higher calcium dosage is needed when dealing with fluoride-containing wastewater that contains phosphate and sulfate (Huang & Liu 1999). The removal of phosphate from fluoride-containing wastewater prior to its treatment will make the treatment process simpler; the
dosage of calcium salt required for fluoride removal may
decrease as well. While presence of phosphate can cause
eutrophication in surface water, phosphorus is a non-
renewable resource that will run out in the future. There-
fore, it is also important to recover and reuse phosphorus.

One of the main methods for recovery of phosphate is
continued precipitation by using metallic salts, such as
aluminium, iron and calcium. Calcium is the most common
chemical compound utilized that leads to the formation of
hydroxyapatite (Ca₅(PO₄)₃OH) (de-Bashan & Bashan
2004). However, semiconductor wastewater contains high
concentration of fluoride, which has high reactivity with
calcium, and the calcium phosphate sludge cannot be
obtained in pure state for possible reuse as a fertilizer; and
the presence of phosphate may decrease the recovery factor
of CaF₂ for many industrial purposes as well (Aldaco et al.
2005). Aluminium reacts with phosphate and the optimum
pH for precipitation reactions is 5 to 6 (Georgantas &
Grigoropoulou 2007). However, aluminium also reacts with
fluoride to form a mineral known as cryolite (NaAlF₆),
knowing that sodium ion exists in semiconductor waste-
water (Aldaco et al. 2005). Iron salts can be used as
precipitation reagents to remove phosphate and form a
mineral known as strengite (FePO₄·2H₂O). However, iron
phosphate is not bio-available, and Grzmil & Wronkowski
(2006) have indicated that precipitation of iron phosphate is
not possible when in the presence of fluoride. Magnesium
salts could be the alternative precipitation reagent for
selective removal and recovery of phosphate from fluor-
ide-containing wastewater. Many researchers have already
investigated the recovery of phosphate and ammonium
from anaerobic digester effluent using magnesium salt to
form struvite (MgNH₄PO₄·6H₂O). Reactions of struvite are
influenced by pH, seeding, and concentration. The other
possible species of magnesium phosphate precipitates, all
could potentially be reused as fertilizer or raw materials for
fertilizer plant, include newberyite (MgHPO₄·3H₂O),
obbierrite ((Mg₃(PO₄)₂·8H₂O), and trimagnesium phos-
phate ((Mg₂₃(PO₄)₂·22H₂O) (Mamais et al. 1994; Mustovo
et al. 1999; Le Corre et al. 2007). Chimenos et al. (2006) have
demonstrated that bobierrite can be recovered from
anodizing wastewater containing phosphates and sulfates.

Another limitation associated with CaF₂ precipitation is
sludge/water separation process. Aluminium salts or
organic polymers are required as flocculants in assisting
the sedimentation process since CaF₂ precipitates are too
fine to settle (Chang & Liu 2007). Previous studies show
that flotation process can be used as an alternative for
separating CaF₂ precipitates from wastewater (Huang &
Liu 1999; Chuang et al. 2002). Precipitate flotation involves
the precipitation of the ionized species prior to its flotation
and it is an effective method for separation of solid from
dilute wastewater. The addition of a collector is usually
needed before the gas is introduced into the solution to
increase the collective efficiency of the bubbles (Huang &
Liu 1999; Chuang et al. 2002). Previous research indicates
that sodium dodecylsulfate (SDS) is suitable in DiAF
process as a frother and a collector (Huang & Liu 1999).

It is aimed in the current study to develop a two-stage
treatment process that could selectively separate and
recover phosphate from fluoride-containing semiconductor
wastewater in the first stage, and to effectively remove both
phosphate and fluoride and their sludge from wastewater in
the second-stage reactions. Magnesium chloride (MgCl₂)
was used instead of MgO owing to its high solubility. Effects
of molar ratio, [Mg²⁺]/[PO₄³⁻], and pH for selective
removal of phosphate were investigated using MgCl₂ in
the first-stage reaction, followed by the second-stage
reaction in which CaCl₂ was used to precipitate residual
phosphate and fluoride. The aqueous equilibrium and
effectives of flotation process for separating solid particle
from solution in the second-stage process were examined as
well. Potential benefits of the current study include selective
separation of high-purity magnesium phosphate that can be
reused, lower dosage of calcium required for fluoride
removal, and less amount of CaF₂ sludge generated.

MATERIALS AND METHODS

Wastewater was sampled from a semiconductor manufac-
turer in the Science Park in Hsinchu, Taiwan. The plant,
one of the leading integrated circuit (IC) companies, is
representative of semiconductor manufacturer in Taiwan.
The pH value of wastewater was 7.78 and the turbidity
was 0.64 NTU. The chemical compositions were analyzed
by ion chromatography (Dionex, DI-100) and inductively
coupled plasma–atomic emission spectrometer (ICP-AES,
JY 2000). Samples must be filtered by using 0.2 μm PVDF membrane filter (MFS) before analysis. Major chemical components of wastewater included 936 mg/L of fluoride, 640 mg/L of sulfate, and 118 mg/L of phosphate. The other major contents were 26.7 mg/l of ammonia, 0.24 mg/L of magnesium, 0.64 mg/L of calcium, and lower than 0.05 mg/L of aluminum.

In the first-stage reaction, MgCl₂ (Showa, Japan) was added for precipitation of phosphate. In this experiment 1,000 ml of wastewater and measured amount of MgCl₂ with fixed molar ratio was stirred at 200 rpm for 40 minutes. Sodium hydroxide (NaOH, 1 M) and nitric acid (HNO₃, 1 M) were used for the adjustment of pH. Sample was taken at certain interval. Precipitate was allowed to settle for 15 min before it was separated from solution. In the consecutive second-stage reaction, CaCl₂ (Acros) was added as precipitation reagent to the supernatant of treated wastewater from the first-stage reaction with different molar ratio of calcium to fluoride, [Ca²⁺]/[F⁻]. These solutions were stirred at 100 rpm for 3 min, 20 rpm for 30 min before subject to flotation process for separating solid from solution. Measured amount of SDS was added to 500 ml of suspension. Dispersed air flotation (DiAF) equipment utilized in the experiment was similar with previous study (Huang & Liu 1999). An acrylic flotation column with volume of 500 mL was used. A lipped side arm at 5 cm from top of column serves as the foam discharge port. Bubble was generated by passing nitrogen gas through flow meter (Aalborg), humidifier (Duran), and a sparger (Merck) with pore size about 10–16 μm, at the bottom of column.

Residual soluble fluoride was measured by ion selective electrode method (Cole Palmer). To avoid very fine particles of CaF₂ from interference, samples were filtered by membrane filter (MFS) with pore size of 0.2 μm before analysis. For residual phosphate, samples were filtered by membrane filter (MFS) with pore size of 0.45 μm first and then measured by ion chromatography (Dionex, DI-100). All measurements were triplicated and the average value was taken. Turbidity was measured by a turbidity meter (Orbeco-Hellige 956–10) and zeta potential was measured by a zeta meter (Zetamaster). Suspension sample for zeta potential measurement was sonicated for 5 min to break up aggregates before injected to the cell for analysis (Lee & Liu 2000). PHREEQC was used for modeling of magnesium, calcium, phosphate, and fluoride speciation. This model is developed by the US Geology Survey to predict the equilibrium concentration and speciation of selected ions in solution. This model allows user to create personal thermodynamic database in which the possible solid phases are included with their characteristic values of solubility product (Ksp) and stoichiometric coefficient. The equilibrium concentrations of dissolved and precipitated ionic species can be calculated based upon the input of concentration, pH, temperature, and ionic strength. Modeled results would reveal equilibrium as predicted by thermodynamics and assist in assessing probable reaction path and products in the wastewater. Theoretical predictions were compared with experimental results to delineate if there is any discrepancy. The thermodynamic database considered in PHREEQC modeling can be found in Table 1.

RESULTS AND DISCUSSION

First-stage reaction

Excess concentration of magnesium in the solution is important to induce effective precipitation of magnesium phosphate. Only 41.3% of phosphate was removed at pH 10 when at the stoichiometric molar ratio, [Mg²⁺]/[PO₄³⁻], of 3:2 (Table 2). Higher removal efficiency was found as molar ratio increased. Experimental results showed slightly lower

| Minerals and their solubility products included in PHREEQC modeling at 25°C |
|-----------------------------|-----------------|
| First-stage reactions       |                 |
| Struvite (MgNH₄PO₄·6H₂O)    | 13.15           |
| Newberyite (MgHPO₄·3H₂O)    | 5.8             |
| Bobierrite (Mg₃(PO₄)₂·8H₂O)| 25.2            |
| Trimagnesium phosphate (Mg₅(PO₄)₂·22H₂O) | 23.1 |
| Brucite (Mg(OH)₂)           | −11.6           |
| Second-stage reactions      |                 |
| Fluorite (CaF₂)             | 10.5            |
| Hydroxyapatite (Ca₅(PO₄)₂·OH) | 44.33         |
| Fluorapatite (Ca₅(PO₄)₃·F)  | 59              |
| Monetite (CaHPO₄)           | 19.27           |
| Brushite (CaHPO₄·2H₂O)      | 18.99           |
| Portlandite (Ca(OH)₂)       | −22.80          |
removal efficiency than predictions from PHREEQC. It was noted that molar ratio did not affect residual concentration of fluoride, and it proved that there was no reaction between MgCl₂ and fluoride. Bobierrite is predicted to be the most stable solid species formed in the system. This was in accordance with experimental results. Bobierrite can potentially be recovered as raw materials for fertilizer plant (Chimenos et al. 2006). Although higher percentage of phosphate could be removed at higher molar ratio, the ratio was kept at 3:1 for further experiments.

Effects of pH on precipitation reactions are shown in Table 3. Increasing pH from 8 to 10 would raise removal efficiency of phosphate from 46.5% to 66.2%. However, the removal efficiency decreased as pH increased from 10 to 12. It was because of the competition between hydroxyl ion and phosphate ion, and the formation of brucite (Mg(OH)₂) at pH 11 and 12, as supported by model prediction. For further experiments, molar ratio, [Mg₂⁺]/[PO₄³⁻], was kept at 3:1 and pH at 10. Again it was evident that MgCl₂ did not react with fluoride to form precipitate. It is in agreement with previous study that magnesium is favorable to form magnesium phosphate precipitate rather than MgF₂ under alkaline pH (Battistoni et al. 2006). This justified that MgCl₂ can be used as a selective precipitation reagent for phosphate from the semiconductor wastewater that contains fluoride. Assuming that the wastewater flow rate is 1,000 m³ per day and phosphate concentration is 118 mg/L, 66.2% selective removal of phosphate results in total of 107 kg (dry weight) of bobierrite recovered daily that can be reused as fertilizer. This is significant improvement considering that a mixture of calcium fluoride and calcium phosphate, that finds reuse purpose only as raw material in cement, would be generated if calcium is used for non-selective removal of both fluoride and phosphate.

**Second-stage reactions**

Calcium chloride was added to the treated effluent from the first-stage in the second-stage reaction to form precipitates with phosphate and fluoride. Excess concentration of calcium was needed to ensure residual fluoride concentration below effluent standard (15 mg/L) (Figure 1). From experimental results and model predictions, further increase of molar ratio, [Ca²⁺]:[F⁻], beyond 0.7 had insignificant effect on removal efficiency. The molar ratio was chosen as 0.7, and residual soluble fluoride concentration was

<table>
<thead>
<tr>
<th>pH</th>
<th>Model prediction Residual P mol/L (% removal)</th>
<th>Experimental result Residual P mol/L (% removal)</th>
<th>Model prediction Residual F (mol/L)</th>
<th>Experimental result Residual F (mol/L)</th>
<th>Solid phase (moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>8.85 × 10⁻⁴ (28.6%)</td>
<td>6.63 × 10⁻⁴ (46.5%)</td>
<td>4.94 × 10⁻²</td>
<td>4.92 × 10⁻⁴</td>
<td>Bobierrite (1.79 × 10⁻⁴)</td>
</tr>
<tr>
<td>9</td>
<td>4.34 × 10⁻⁴ (65.0%)</td>
<td>5.14 × 10⁻⁴ (58.5%)</td>
<td>4.94 × 10⁻²</td>
<td>4.92 × 10⁻⁴</td>
<td>Bobierrite (4.05 × 10⁻⁴)</td>
</tr>
<tr>
<td>10</td>
<td>2.50 × 10⁻⁴ (79.8%)</td>
<td>4.20 × 10⁻⁴ (66.2%)</td>
<td>4.94 × 10⁻²</td>
<td>4.93 × 10⁻²</td>
<td>Bobierrite (4.97 × 10⁻⁴)</td>
</tr>
<tr>
<td>11</td>
<td>6.42 × 10⁻⁴ (48.2%)</td>
<td>6.18 × 10⁻⁴ (50.2%)</td>
<td>4.94 × 10⁻²</td>
<td>4.92 × 10⁻²</td>
<td>Bobierrite (3.01 × 10⁻⁴)</td>
</tr>
<tr>
<td>12</td>
<td>1.24 × 10⁻³ (0.0%)</td>
<td>6.83 × 10⁻⁴ (44.9%)</td>
<td>4.94 × 10⁻²</td>
<td>4.92 × 10⁻²</td>
<td>Brucite (2.16 × 10⁻³)</td>
</tr>
</tbody>
</table>
10.7 mg/L at pH 10. It was noted that all phosphate was removed and residual phosphate concentration was all below 0.5 mg/L. This revealed that calcium reacts with both phosphate and fluoride under alkaline pH.

The precipitates were then separated from aqueous phase via flotation using SDS as collector. Flotation time was kept at 10 min and the nitrogen gas flow rate was at 100 ml/min. The effect of SDS concentration on flotation reaction can be seen in Figure 2. It has been indicated that surface of fluorite (CaF$_2$) is positively charged under pH 2 to 12 (Huang & Liu 1999). Model prediction shows that fluorite was predominant species with a small fraction of fluorapatite (Ca$_5$(PO$_4$)$_3$F) in solid phase (Figure 3). Fluorapatite surface is negative at pH 4 and above (Chairat et al. 2007). There has been no study on zeta potential of mixed precipitates of fluorite and fluorapatite. However, it was found that the mixed precipitates had zeta potential of 7.5 mV at pH of 10 ± 0.1. The zeta potential decreased when concentration of SDS increased. It was therefore reasonable to assume that the anionic collector became adsorbed on precipitates surfaces via electrostatic attraction, similar to the case on fluorite surfaces (Chuang et al. 2002). Concentration of SDS also affected the effectiveness of separation process in flotation. It was found that residual turbidity decreased rapidly to 4.70 NTU when SDS concentration was 75 mg/L. There were two roles that SDS played. Firstly, SDS was a collector whose adsorption on the surface of fluoride and fluorapatite precipitates rendered their surfaces more hydrophobic, and the attachment of gas was facilitated. Secondly, SDS produced stable and sufficient foam as a frother to maintain the precipitates on the top of solution and to prevent redispersion thereof (Medina et al. 2005).

PHREEQC model predicts that pH value is not a significant factor on fluoride removal under pH range 8 to
This has been confirmed that pH does not significantly affect fluoride removal efficiency under alkaline pH when using calcium salt (Chang & Liu 2007). However, experimental results revealed that the lowest residual fluoride concentration was found at pH 10. It slightly increased when pH dropped to 8. It was probably because of the interference of residual phosphate in the treated effluent from first-stage reaction. The presence of phosphate would decrease amount of free calcium ion in the solution and higher than stoichiometric amount of calcium is required to ensure effective removal of fluoride (Huang & Liu 1999; Chuang et al. 2002). The residual fluoride significantly increased as pH was raised to 11 and 12. It was due to the formation of portlandite (Ca(OH)₂) precipitates under high pH (Huang & Liu 1999). This is confirmed in the model predictions from PHREEQC (Figure 3). Concerning the possible interference of sulfate (640 mg/L), it was predicted that sulfate exists as a free ligand ([SO₄²⁻]), or a soluble complex with calcium ion (CaSO₄). Experimental results showed that only limited amount (4.3–7.3%) of sulfate was removed as affected by molar ratio when at pH 10 (Table 4). Similarly, it was found that only insignificant amount (3.8–7.3%) of sulfate was removed as affected by pH when at molar ratio of 3:1 (Table 5). This demonstrated that sulfate did not involve in reaction with calcium as predicted by model. Results of this experiment also revealed that calcium salt tended to react with phosphate preferentially than fluoride at alkaline pH. The phosphate concentration in treated effluent of the second-stage reaction was all below 0.5 mg/L under all pH range. Grzmil & Wronkowski (2006) also claim that phosphate precipitation is more favorable when pH increases to alkaline conditions. Depending on pH,

![Figure 4](https://iwaponline.com/wst/article-pdf/59/10/2047/435260/2047.pdf)

**Figure 4** | Residual soluble fluoride as affected by pH at molar ratio, ([Ca²⁺]:[F⁻]) of 0.7.

![Figure 5](https://iwaponline.com/wst/article-pdf/59/10/2047/435260/2047.pdf)

**Figure 5** | Zeta potential and residual turbidity as affected by pH.

<table>
<thead>
<tr>
<th>Molar ratio ([Ca²⁺]:[F⁻])</th>
<th>Residual SO₄ (mg/L)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5:1</td>
<td>612.6</td>
<td>4.3</td>
</tr>
<tr>
<td>0.7:1</td>
<td>593.5</td>
<td>7.3</td>
</tr>
<tr>
<td>1:1</td>
<td>605.3</td>
<td>5.4</td>
</tr>
<tr>
<td>2:1</td>
<td>596.6</td>
<td>6.8</td>
</tr>
</tbody>
</table>

**Table 4** | Residual soluble sulfate as affected by molar ratio, ([Ca²⁺]:[F⁻]), at pH 10 = 0.2

<table>
<thead>
<tr>
<th>pH</th>
<th>Residual SO₄ (mg/L)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>614.3</td>
<td>4.0</td>
</tr>
<tr>
<td>10</td>
<td>593.5</td>
<td>7.3</td>
</tr>
<tr>
<td>11</td>
<td>615.8</td>
<td>3.8</td>
</tr>
<tr>
<td>12</td>
<td>613.8</td>
<td>4.1</td>
</tr>
</tbody>
</table>

**Table 5** | Residual soluble sulfate as affected by pH at molar ratio, ([Ca²⁺]:[F⁻]), of 0.7:1

<table>
<thead>
<tr>
<th>pH</th>
<th>Residual SO₄ (mg/L)</th>
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</tr>
</thead>
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<td>8</td>
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<tr>
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<td>613.8</td>
<td>4.1</td>
</tr>
</tbody>
</table>
different interfacial properties and reaction routes may be found in flotation. The pH in the solution also influences the attachment or detachment of collector. The zeta potential as affected by pH (Figure 5) showed that increase of pH shifted zeta potential slightly to positive values. As illustrated from residual turbidity, precipitates were effectively separated from aqueous phase when in pH range of 8 to 10. However, residual turbidity increased when at higher pH, probably caused by decrease of electrostatic attraction between SDS and precipitates as shown by the zeta potential.

CONCLUSIONS

The development of a two-stage treatment process for fluoride-containing semiconductor wastewater was studied. This study demonstrated that selective precipitation of phosphate as bobierrite in the first-stage was feasible by utilizing MgCl₂ as a precipitation reagent. The optimal pH was found at 10 and 66.2% of phosphate was effectively removed and recovered at molar ratio, [Mg²⁺]:[PO₄³⁻], of 3:1. No reaction was found between MgCl₂ and fluoride in this process. Precipitate flotation utilizing calcium chloride (CaCl₂) was assessed in the second-stage reactions. Very effective removal of phosphate and fluoride from aqueous phase was found. Though of high concentration, sulfate did not interfere with the chemical precipitation. The optimum dose for SDS was 75 mg/L at molar ratio, [Ca²⁺]:[F⁻], of 0.7:1 at pH 10 ± 0.1. Total of 107 kg (dry weight) of bobierrite could be recovered daily and be reused as fertilizer from a typical semiconductor manufacturer. Potential benefits of the proposed two-stage process include selective separation of high-purity magnesium phosphate that can be reused, lower dosage of calcium dosage required for fluoride removal, and lower amount of CaF₂ sludge generated.

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