Conceptual design of a new SF$_6$ abatement technology using a multi-bed series reactor for the production of valuable chemicals free of toxic wastes

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Introduction

With strict environmental regulations and efforts to reduce global warming, perfluorinated compounds (PFCs) such as CF$_4$ [1–3], CHF$_3$ [4, 5], C$_2$F$_6$ [6, 7], C$_3$F$_8$ [8], and SF$_6$ [9–19], which are commonly used as etching and cleaning gases in the semiconductor manufacturing, have globally attracted significant attention because they are toxic chemicals and potential contributors to the global warming as greenhouse gases (GHGs) [2, 3, 9, 20, 21]. PFCs have relatively high global warming potential (GWP) ranging from 6,500 to 23,900 compared to conventional CO$_2$ with a GWP value of 1 [21–23] and among them, SF$_6$ with a GWP value of 23,900 has been identified as the strongest due to its intensive absorption of infrared radiation and long atmospheric lifetime [10–12, 19, 20, 24, 25]. Nowadays, many efforts have been paid to reducing these PFCs and various methods like alternative chemicals, capture/recovery/recycle systems, process optimization, and...
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Abatement systems are being sought [3, 12, 26]. In particular, abatement technology in a catalytic reactor system using various catalysts is actively under development as the most practical PFCs reduction technology [2, 3, 12, 14, 18].

As for SF₆ reductions, there are four technologies under consideration; (1) decomposition using plasma, (2) adsorption with inorganic materials, (3) separation via gas hydrate formation, and (4) catalytic decomposition [13, 14]. Among them, SF₆ abatement technology employing catalytic decomposition is preferred because of high activity for SF₆ decomposition with some catalysts, high efficiency due to a lower energy requirement, and fewer corrosive and toxic byproducts [3, 13, 27]. A lot of studies for SF₆ abatement employing catalytic decomposition have been reported. Kashiwagi et al. [16] studied catalytic activity reporting that metal phosphates are more active for the hydrolysis of SF₆ and alkaline earth phosphates are less active. They also pointed out that the catalytic activity of metal fluorides is significantly lower than the one of metal phosphate such as AlPO₄ and CePO₄ suggesting that preventing the fluorination of catalysts is necessary to keep the catalytic activity. Park et al. [18] used AlPO₄/γ-alumina catalysts in order to decompose SF₆ and their catalytic activity was investigated and showed that the stability of the catalyst was enhanced using a phosphoric acid impregnated γ-alumina. Zhang et al. [19] found that kirschsteinite-dominant stainless steel slag (SSS) has higher activity than conventional pure metal oxides catalysts such as Fe₂O₃ and CaO and waste material SSS could be an effective abatement reagent of SF₆.

Figure 1A shows a schematic diagram of a conventional SF₆ abatement system consisting of a catalytic reactor for SF₆ hydrolysis (eq. 1) and a scrubber [28–30] for a post-treatment of the produced HF and SO₃. Because these
toxic chemicals are inevitably produced by hydrolysis, a post-treatment like a scrubber to securely treat toxic HF and SO$_3$ is required thus leading to additional capital and operating costs.

$$\text{SF}_6 + 3\text{H}_2\text{O} \rightleftharpoons \text{SO}_3 + 6\text{HF} \quad (1)$$

Moreover, frequent damage and replacement of a scrubber due to corrosive nature of HF result in unavoidable maintenance costs. To overcome these limitations that a conventional system currently has, a new reactor system of employing multi-bed series reactors containing a catalyst bed for hydrolysis reaction and an adsorbent bed using CaO to react with HF and produce CaF$_2$ (eq. 2) was proposed as a new CF$_4$ abatement technology [2, 3, 31] and this proposed system successfully eliminated the use of a scrubber thus saving capital and operating costs significantly.

$$\text{CaO} + 2\text{HF} \rightleftharpoons \text{CaF}_2 + \text{H}_2\text{O} \quad (2)$$

Moreover, produced CaF$_2$ exhibits excellent characteristics such as low reflectivity and high transparency and can be used in various applications such as lenses, window, prism, and electrochemical fields for solid electrolyte in galvanic cells [32–34]. The simultaneous removal of produced HF during reaction by adsorption with CaO resulted in improved product yields driven by equilibrium shift (Le Chatelier’s principle) [35–37] and it provided an additional benefit of lowered operating temperature for the same amount of CaF$_2$ production via sorption-enhanced hydrolysis leading to a reduced operating temperature [31, 38]. Therefore, a multi-bed series reactor proved a very useful concept for simultaneous CF$_4$ abatement and utilization method free of toxic wastes.

Even though HF is produced from hydrolysis of both CF$_4$ and SF$_6$, SO$_3$ is additionally obtained from SF$_6$ hydrolysis (eq. 1), whereas CO$_2$ is produced from CF$_4$ hydrolysis (CF$_4$ + 2H$_2$O $\rightarrow$ CO$_2$ + 4HF). This produced SO$_3$, regarded as a pollutant, can be further converted to CaSO$_4$, a valuable chemical, by reacting with lime (CaO) as shown in equation (3).

$$\text{CaO} + \text{SO}_3 \rightleftharpoons \text{CaSO}_4 \quad (3)$$

Upon addition of water, CaSO$_4$ is transformed into CaSO$_4$$\cdot$$2\text{H}_2\text{O}$ called as gypsum and can be used for a wide variety of applications such as plaster, physical conditioner, and concrete industries [39–41]. By introducing CaO in SF$_6$ abatement technology, both CaF$_2$ and CaSO$_4$, valuable chemicals, can be obtained with the elimination of toxic wastes such as HF and SO$_3$. Therefore, with some aforementioned benefits, previously reported multi-bed series reactors concept employing sorption-enhanced reaction due to equilibrium shift by Le Chatelier’s principle [2, 3, 31] was extended for SF$_6$ in this paper as a simultaneous SF$_6$ abatement and utilization process with no toxic wastes produced as shown in Figure 1B. To investigate the effect of number of beds in multi-bed series reactors, a single-bed reactor (SR-1), a two-bed series reactor (SR-2), and a three-bed series reactor (SR-3) were considered and process simulation studies using Aspen HYSYS® were carried out to assess the feasibility of employing this new concept for a new SF$_6$ abatement technology in terms of CaF$_2$ and CaSO$_4$ production, operating temperature, natural gas usage, and CO$_2$ emissions.

**Methods**

**Process simulation using Aspen HYSYS®**

Commercial process simulators such as Aspen HYSYS® (Aspen Technology, Inc., Bedford, MA, USA) [2, 3, 42–47], Aspen Plus® (Aspen Technology, Inc., Bedford, MA, USA) [48–50], UniSim® Design Suite (Honeywell International Inc., Morris Plains, NJ, USA) [51, 52], and CHEMCAD (Chemstations, Inc., Houston, TX, USA) [53, 54] have been widely used to simulate the proposed processes of interest and obtain the useful process design guidelines and optimized conditions based on material and energy balances of the overall systems. Among them, Aspen HYSYS® was chosen for this study as the most suitable process simulator for the proposed processes to simulate based on experimental data for SF$_6$ hydrolysis over alumina-based catalysts as presented in Figure 2. Brunauer, Emmett, and Teller (BET) surface area of the alumina-catalyst was 175 m$^2$ g$^{-1}$ and a catalyst amount of 30 mL was used in the experiment with a gas hourly space velocity (GHSV) of 2000 h$^{-1}$. In addition, the Peng–Robinson fluid property package was opted as an appropriate equation of state and a steady-state condition was assumed. Since thermodynamic properties of

![Figure 2. Experimental data for SF$_6$ conversion by hydrolysis.](image-url)
some components (SF$_6$, SO$_3$, CaO, CaF$_2$, and CaSO$_4$) are not in the component library of Aspen HYSYS$^\text{®}$, hypothetical components were created using some important thermodynamic properties of each component like molecular weight, normal boiling point, and ideal liquid density [44–46, 55, 56]. In particular, thermodynamic properties for the utilized adsorbent, CaO with molecular weight of 56.08 g mol$^{-1}$, normal boiling point of 3123 K, and ideal liquid density of 3,340 kg m$^{-3}$ were used in this study.

**Single-bed reactor (SR-1)**

Figure 3 presents a process flow diagram (PFD) for a SR-1 using Aspen HYSYS$^\text{®}$ consisting of conversion reactors modeled for SF$_6$ hydrolysis (Reaction 1), HF conversion to CaF$_2$ (Reaction 2), and SO$_3$ conversion to CaSO$_4$ (Reaction 3). For SF$_6$ hydrolysis (Reaction 1), experimental conversion data obtained from Korea Institute of Energy Research (KIER) were used for this simulation. For conceptual studies of employing adsorbent (CaO) to convert HF to CaF$_2$ and SO$_3$ to CaSO$_4$, complete conversions were assumed for both reactions (Reactions 2 and 3). Use of conversion reactors in this study can be considered enough to obtain some preliminary results as conceptual design, but kinetics should be sought to fully represent various reactions involved. A mixture stream containing 5 sccm of SF$_6$ with a SF$_6$-H$_2$O molar ratio of 1:19.5 and air as balance was used as a feed and sent to a conversion reactor (Conv.1) for SF$_6$ hydrolysis at 873-973 K. The operating pressure was 1 atm. Next, a produced HF was converted to CaF$_2$ in a conversion reactor denoted as Conv.2 and a produced SO$_3$ was changed into CaSO$_4$ in a conversion reactor denoted as Conv.3. A heat was required for SR-1 because reactions involved are endothermic and it was assumed that a required heat was supplied by burning a natural gas boiler with an excess O$_2$ of 20%.

**Two-bed series reactor (SR-2) and three-bed series reactor (SR-3)**

Sorption-enhanced hydrolysis to improve product yields and lower operating temperature simultaneously [2, 3, 31] was applied for SF$_6$ abatement by introducing multi-bed series reactors (SR-2 and SR-3). Figure 4 shows PFDs for a SR-2 and a SR-3 showing multiple conversion reactors connected in series and all reaction conditions were same as the ones used for SR-1.
Figure 4. Process flow diagram for (A) a two-bed series reactor (SR-2) and (B) a three-bed series reactor (SR-3).
Results and Discussion

Comparative studies for SR-1, SR-2, and SR-3

As a new simultaneous SF$_6$ abatement and utilization technology, SR-1, SR-2, and SR-3 were proposed and elimination of a postscrubber was possible from the introduction of these SR-1, SR-2, and SR-3 leading to savings in capital and operating costs. In addition, a continuous removal of HF from SF$_6$ hydrolysis through reactions with CaO to be converted to CaF$_2$ and CaSO$_4$ can result in improved product yields and reduced operating temperature possibly due to sorption-enhanced hydrolysis.

Figure 5A shows the amount of CaF$_2$ produced from SR-1, SR-2, and SR-3 at operating temperatures from 823 to 973 K. First, the highest amount of CaF$_2$ production was obtained from SR-3 followed by SR-2 and SR-1 clearly demonstrating the positive effect of using multi-bed series reactors. This trend was applied to all temperatures studied and the effect was dominant at lower operating temperatures with slight at higher operating temperatures. As for CaSO$_4$, similar trends of improved CaSO$_4$ production in multi-bed reactors (SR-3 > SR-2 > SR-1) at all temperatures studied were observed as shown in Figure 5B. For both CaF$_2$ and CaSO$_4$, it is believed that sorption-enhanced hydrolysis shifts reaction equilibrium via continuous removal of the produced HF and SO$_3$ and thus results in improved production by Le Chatelier’s principle [31, 38]. These improved CaF$_2$ and CaSO$_4$ production in multi-bed series reactors compared to a SR-1 also provides additional benefit of lowered operating temperatures for the same amount of CaF$_2$ and CaSO$_4$ production. For CaF$_2$ production of 6.60 × 10$^{-4}$ mol min$^{-1}$ and CaSO$_4$ production of 2.20 × 10$^{-4}$ mol min$^{-1}$ at 973 K in SR-1, respective operating temperatures of 916 and 888 K were obtained in SR-2 and SR-3 clearly indicating the positive effect of multi-bed series reactors.

Further analysis to investigate the effect of multi-bed series reactors was performed for SR-1 at 923 and 873 K
as shown in Table 1. Similarly, for the same amount of CaF₂ and CaSO₄ production, reduced operating temperatures were observed in SR-2 and SR-3 also confirming the benefit of multi-bed series reactors compared to a SR-1. In addition, more significant reductions in operating temperatures were found in multi-bed series reactor for higher operating temperatures in SR-1 with the highest reduction of 85 K observed in SR-3 for an operating temperature in SR-1 of 973 K.

Natural gas amount required in a boiler and CO₂ emissions from a boiler were obtained from process simulation studies and multi-bed series reactors were proved to be positive for reductions in them. The calculation of reductions in natural gas amount and CO₂ emissions for SR-2 and SR-3 compared to SR-1 revealed more reductions in SR-3 than SR-2 and interestingly more reductions were obtained at higher SR-1 temperature. Based on process simulation results obtained here, comprehensive techno-economic analysis (TEA) can be very meaningful in future research to evaluate the feasibility of using a multi-bed series reactor for SF₆ abatement technology in both technical and economic aspects when this conceptual design is implemented more in detail [47].

Comparative studies of $T_{\text{Reduction}}$ for SR-1, SR-2, and SR-3

To investigate the trend of reduced operating temperatures in multi-bed series reactors, $T_{\text{Reduction}} = \frac{T_{\text{SR1}} - T_{\text{SR2,3}}}{T_{\text{SR1}}} \times 100$ (%) was introduced as a measure to present temperature reductions in SR-2 and SR-3 compared to SR-1. As depicted in Figure 6A and B, a clear trend of increased $T_{\text{Reduction}}$ with increased CaF₂ or CaSO₄ production was observed for both SR-2 and SR-3. In evaluating the effect of number of catalysts and adsorbent beds, it was found that SR-3 with higher $T_{\text{Reduction}}$ performed better than SR-2 for the same amount of CaF₂ or CaSO₄ production.

Conclusively, it is recommended that employing multi-bed series reactors is beneficial in terms of higher CaF₂ or CaSO₄ production and reduced operating temperature with better performance in SR-3 than SR-2.

Conclusions

Conceptual design studies have been carried out to assess the feasibility of using multi-bed series reactors as a simultaneous SF₆ abatement and utilization technology. Multi-bed series reactors are composed of a series of alumina-based catalysts and CaO adsorbent beds and valuable chemicals such as CaF₂ and CaSO₄ were produced from this new technology in addition to successful reduction in SF₆, a greenhouse gas with high global warming potential (GWP).

From process simulation works using Aspen HYSYS®, the performance of multi-bed series reactors (a two-bed series reactor, SR-2 and a three-bed series reactor, SR-3) was compared to that of a single-bed reactor (SR-1) in terms of CaF₂ and CaSO₄ production and operating temperature. It was found that more CaF₂ and CaSO₄ were produced in multi-bed series reactors compared to a SR-1 (SR-3 > SR-2 > SR-1) because of sorption-enhanced hydrolysis confirming the positive effect of

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**Figure 6.** Comparison of temperature reduction ($T_{\text{Reduction}}$) with the same amount of (A) CaF₂ and (B) CaSO₄ for a two-bed series reactor (SR-2) and a three-bed series reactor (SR-3) compared to a single-bed reactor (SR-1).
using multi-bed series reactors. Moreover, the effect was more significant at lower operating temperatures.

To produce the same amount of CaF$_2$ and CaSO$_4$ production, lower operating temperatures were obtained in multi-bed series reactors ($T_{SR1} > T_{SR2} > T_{SR3}$) leading to reduction in natural gas amount required (4.5–9.3%) and CO$_2$ emissions (3.9–8.9%) compared to a SR-1. Conclusively, employing multi-bed series reactors as a new SF$_6$ abatement technology proved a cost-effective concept to both produce more CaF$_2$ and CaSO$_4$ and abate SF$_6$ effectively.

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**Conflict of Interest**

None declared.

**Nomenclature**

- PFCs: Perfluorinated compounds
- GHGs: Greenhouse gases
- GWP: Global warming potential
- SSS: Stainless steel slag
- SR-1: Single-bed reactor
- SR-2: Two-bed series reactor
- SR-3: Three-bed series reactor
- BET: Brunauer, Emmett, and Teller
- GHSV: Gas hourly space velocity
- PDF: Process flow diagram
- KIER: Korea Institute of Energy Research
- NG: Natural gas
- TEA: Techno-economic analysis

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