



Influence of calcium hydroxide on the fate of perfluorooctanesulfonate under thermal conditions

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ABSTRACT

To explore the potential fate and transport of perfluorochemicals in the thermal treatment of sludge, perfluorooctanesulfonate (PFOS), a perfluorochemical species commonly dominant in wastewater sludge, was mixed with hydrated lime (Ca(OH)₂) to quantitatively observe their interaction under different temperatures. The phase compositions of the mixtures after the reactions were qualitatively identified and quantitatively determined using X-ray diffraction technique. The results of the thermogravimetry and differential scanning calorimetry analyses indicate that PFOS gasified directly during the thermal treatment process when the temperature was increased to around 425 °C. However, the formation of CaF₂ at 350 °C suggests that the presence of Ca(OH)₂ in the mixture can lead to the decomposition of PFOS at 350 °C, which is lower than the decomposition temperature of PFOS alone (425 °C). The increase of temperature promoted a solid state reaction between PFOS and Ca(OH)₂, and also enhanced the interaction between the gaseous products of PFOS and CaO (or Ca(OH)₂). The preferred Ca/F molar ratio to achieve fluorine stabilization by Ca(OH)₂ was above 1:1 in the experiment involving 400 °C and 600 °C treatment. It also showed that equilibrium efficiency is achieved within 5 min at 400 °C and within 1 min above 600 °C.

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1. Introduction

Perfluorochemicals (PFCs) are pollutants that have been widely used in a variety of industrial processes and commercial products, including polymer additives, surfactants, fire-fighting foams, pesticides, and lubricants [1]. Given the wide distribution and bioaccumulation of PFCs in the environment, their fate and transport in wastewater treatment plants have recently attracted attention. Studies have shown that PFCs can be strongly sorbed by sludge. Higgins et al. [2] reported that the total PFC concentration in digested sludge reached 3390 µg/kg. As wastewater sludge can host environmental PFCs, the fate and transport of PFCs can be influenced by the processes used to treat sludge. As a major strategy in solid waste management, landfills are commonly used to dispose waste sludge. However, many recent studies have confirmed the significant environmental impact of disposing PFC-bearing waste in landfills. For example, Kallenborn et al. [3] reported that the total concentration of perfluorinated alkylated substances (PFAS) in Norwegian landfill effluent was 1537 ng/L; Busch et al. [4] reported that total PFC concentration could reach 13,000 ng/L in landfill leachate from Northern Germany; and Huset et al. [5] showed that the

perfluorobutanesulfonate (PFBS) concentration in landfill leachate from the United States were as high as 2300 ng/L.

Incineration is another strategy for solid waste treatment, and it is effective in breaking the robust halogen–carbon bonds in solid waste compounds [6,7]. However, very few studies have explored the fate and transport of PFCs during the thermal treatment (such as incineration) of waste sludge. Halogen carbons (such as PFCs) may be destroyed during incineration by releasing gaseous products if they do not interact with other materials during this process [8,9]. These gas-phase perfluorocarbons (such as CF₄, C₂F₆) form during the thermal decomposition of solid PFCs [10], and unfortunately the release of such gaseous perfluorocarbons may further pollute the atmospheric environment. For example, the global warming potential of CF₄ is 6500 times that of CO₂ and its atmospheric lifespan is 50,000 years [11]. Therefore, the strong global warming effect and the environmental persistence of gas-phase perfluorocarbons hamper effort for the development of sustainable solutions to remove PFCs from our environment.

As calcium-based chemicals (such as CaO, Ca(OH)₂, and CaCO₃) are commonly used in sludge conditioning [12], the potential reaction between PFCs and these calcium-rich compounds, such as the formation of calcium fluoride, under thermal conditions should be investigated in detail. During conditioning and stabilization, a large amount of lime is added into the sludge to raise its pH or to reduce levels of odor-causing microorganisms and pathogens. Lime is also effective in dechlorinating solid-phase persistent organic

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pollutants (such as pentachlorophenol, polychlorinated biphenyls, and hexachlorobenzene) during combustion [13–15]. Therefore, this study investigated the effect of hydrated lime ($\text{Ca}(\text{OH})_2$) on the fate and transport of PFCs under thermal conditions.

As a predominant PFC compound commonly found in wastewater sludge, perfluorooctanesulfonate (PFOS: $\text{C}_8\text{F}_{17}\text{SO}_3\text{K}$) was selected to represent PFC pollutants, and the thermal reaction between PFOS and $\text{Ca}(\text{OH})_2$ was investigated through the characterization of their reaction products. Operational parameters of the thermal treatment process, such as the retention time, temperature, and Ca/F molar ratio, were also studied to observe their influence on the composition of product phases. To the best of our knowledge, this is the first time that a quantitative X-ray diffraction (XRD) analysis based on the Rietveld refinement method was used to indicate the fluorine incorporation efficiency during the thermal treatment of PFCs. The results of this study predict the fate and transport of sludge PFCs under thermal treatment processes, and describe the fixation of gas-phase perfluorocarbons after sludge thermal treatment.

2. Materials and methods

2.1. Chemicals and sample preparation

PFOS and $\text{Ca}(\text{OH})_2$ powders were purchased from Sigma-Aldrich, and the mineral phase of $\text{Ca}(\text{OH})_2$ was confirmed by XRD method. After homogenization using mortar and pestle, the powder mixture samples (2–5 g) were transferred to an alumina crucible and combusted in a muffle furnace that has been preheated at temperatures between 300 and 900 °C. The period of thermal treatment ranged between 1 and 30 min. After the thermal treatment, the samples were air-quenched, weighted, and ground (particle size less than 10 μm) before XRD analysis.

2.2. Thermogravimetry and differential scanning calorimetry analyses

Thermogravimetry (TG) analysis was carried out with a Q50 TGA (TA Instruments, USA) with an initial PFOS of around 8.65 mg. Using a heating rate of 20 °C/min, the thermogravimetry of the PFOS compound was tested from room temperature to 700 °C under nitrogen purging. Differential scanning calorimetry (DSC) was performed using a DSC-7 analyzer (Perkin Elmer, USA) with an initial PFOS of around 4.60 mg. Measurement was carried out from 275 to 465 °C at a heating rate of 10 °C/min under nitrogen purging.

2.3. XRD analysis

The phase transformation during heat treatments was monitored using powder XRD technique. The XRD patterns of each powder sample were collected on a D8 Advance Diffractometer (Bruker AXS) equipped with a Cu X-ray tube and a LynxEye detector operated at 40 kV and 40 mA. The system was calibrated for the line position by Standard Reference Material 660a (lanthanum hexaboride, LaB_6), which was obtained from the U.S. National Institute of Standard and Technology. Scans were collected from 10° to 130° 2θ -angle, with a step width of $2\theta = 0.02^\circ$ and a sampling time of 0.3 s per step.

Qualitative phase identification was conducted by matching powder XRD patterns with those retrieved from the standard powder diffraction database of the International Centre for Diffraction Data (ICDD PDF-2 Release 2008). The crystalline phases found in all products include CaF_2 (PDF#70-2049), CaO (PDF#77-2376), CaCO_3 (PDF#86-0174), and $\text{Ca}(\text{OH})_2$ (PDF#84-1263). Quantitative analysis of the phase compositions was performed using TOPAS (version 4.0) for XRD data. TOPAS uses a whole pattern fitting function via the

Table 1

Decrease in mass of PFOS during thermal treatments at 300, 350, and 400 °C for 30 min.

Temperature (°C)	Initial weight (g)	Residue weight (g)
300	0.50	0.49
350	0.50	0.48
400	0.50	0.49

Rietveld method to match the observed diffraction pattern to determine the weight percentage of crystalline phases in a sample [16]. To evaluate the quality of matching results, the refinement analysis of each pattern generates the pattern factor (R_p), the weighted pattern factor (R_{wp}), the expected pattern factor (R_{exp}), and the goodness of fit (GOF) value, which are defined by the following equations:

$$R_p = \frac{\sum |Y_i(\text{obs}) - Y_i(\text{calc})|}{\sum Y_i(\text{obs})} \quad (1)$$

$$R_{wp} = \left\{ \frac{\sum \omega_i [Y_i(\text{obs}) - Y_i(\text{calc})]^2}{\sum \omega_i [Y_i(\text{obs})]^2} \right\}^{1/2} \quad (2)$$

$$R_{exp} = \left\{ \frac{\sum M - P}{\sum \omega_i [Y_i(\text{obs})]^2} \right\}^{1/2} \quad (3)$$

$$\text{GOF} = \chi^2 = \frac{R_{wp}}{R_{exp}} = \left\{ \frac{\sum \omega_i [Y_i(\text{obs}) - Y_i(\text{calc})]^2}{M - P} \right\}^{1/2} \quad (4)$$

where $Y_i(\text{obs})$ and $Y_i(\text{calc})$ are the observed and calculated data, respectively, at data point m ; M is the number of data points; P is the number of parameters; and ω_i is the weighting given to data point m . The counting statistics are given by $\omega_i = 1/\delta(Y_i(\text{obs}))^2$, where $\delta(Y_i(\text{obs}))$ is the error in $Y_i(\text{obs})$. The R_{wp}/R_{exp} ratio or the GOF value will be equal to 1 in an ideal refinement. However, in an actual situation, the background and peak profile mismatch lead to a GOF of >1. A GOF value between 1.0 and 2.9 is generally considered satisfactory [17].

3. Results and discussion

3.1. Thermal reaction of PFOS and $\text{Ca}(\text{OH})_2$

The single-step degradation of PFOS was observed at around 425 °C, and it indicated that the gasification temperature for PFOS is around 425 °C (Fig. 1a). Similar studies on fluorochemicals have detected the decomposition products of polytetrafluoroethylene (PTFE) at temperature reaching 480 °C [9]. To determine whether PFOS may undergo any further reaction or phase transformation in the sludge before gasification, it was further tested using a DSC analyzer. The results show that the first endothermic peak of PFOS was also observed at around 425 °C (Fig. 1b), which indicated that no major reaction or phase transformation had occurred before its gasification temperature. The results of the TG and DSC analyses indicate that PFOS will gasify directly under N_2 purging when the temperature reaches 425 °C.

Prolonged heating (30 min) for PFOS (Fig. 2a) and PFOS + $\text{Ca}(\text{OH})_2$ (Fig. 2b) samples were conducted at 300, 350, and 400 °C in air, and the major crystalline phases in the products were identified by XRD technique (Fig. 2). The mass of the PFOS sample did not decrease (Table 1) and no phase change for PFOS compound was observed (Fig. 2a) when the heating temperature was below 400 °C for 30 min. To our knowledge, this is the first work reporting the diffraction peaks of PFOS and its stable range is also consistent with the TG and DSC results, which further confirms that PFOS does not decompose below 425 °C. Similarly,

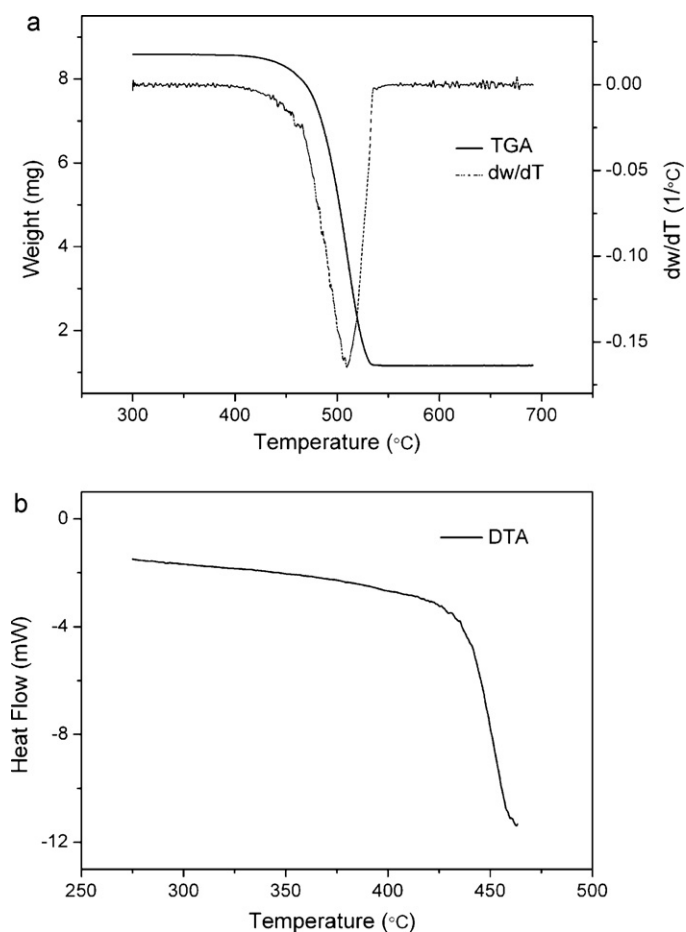


Fig. 1. The results of the (a) thermogravimetry (TG) analysis and (b) differential scanning calorimetry (DSC) analysis for PFOS. Solid PFOS gasified directly when the thermal treatment temperature was above 425 °C.

no diffraction peaks other than those of the starting materials (i.e., PFOS and $\text{Ca}(\text{OH})_2$) were detected at 300 °C (Fig. 2b). However, a significant formation of CaF_2 was observed at temperatures 350 and 400 °C, which indicates the effective solid state interaction between $\text{Ca}(\text{OH})_2$ and PFOS. The formation of CaF_2 at these two temperatures suggest that $\text{Ca}(\text{OH})_2$ triggered the decomposition of PFOS at a temperature lower than its gasification temperature (425 °C). Yang and Pittman [13] pointed out that the key mechanism in the reaction between chlorinated organic molecules and $\text{Ca}(\text{OH})_2$ was the displacement of chloride with hydroxide. In their process, the displaced chlorine mineralizes to calcium chloride, which then led to the combustion or pyrolysis of the remaining organic residues. Therefore, the decomposition of PFOS may similarly start from the replacement of fluoride in PFOS by hydroxide, and the remaining organic residues were further decomposed into gaseous products. Furthermore, the increasing intensity of CaF_2 when temperature was increased from 350 to 400 °C indicates that the yield of CaF_2 also increases with elevated temperature.

3.2. Treatment temperature and Ca/F molar ratio

The results discussed in the previous section showed that increasing temperature may promote the yield of CaF_2 ; therefore, the influence of treatment temperature on the formation of CaF_2 was further quantitatively evaluated. The Rietveld refinement technique was used to determine the relative weight percentages of the crystalline phases in the systems using TOPAS V 4.0. Using the result

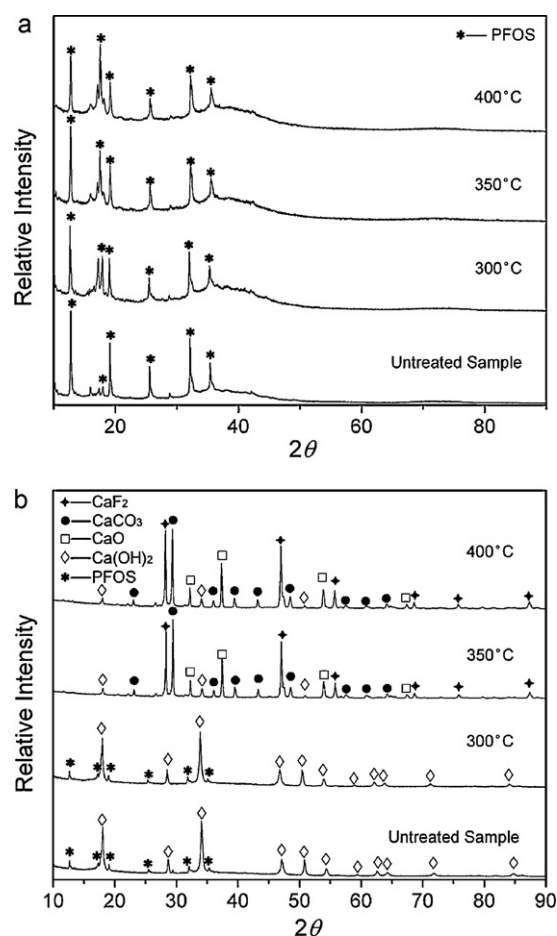


Fig. 2. The XRD results of (a) PFOS and (b) PFOS + $\text{Ca}(\text{OH})_2$ treated at 300 °C, 350 °C, and 400 °C for 30 min. The results indicate that PFOS was not decomposed at these three temperatures even under prolonged heating. The $\text{Ca}(\text{OH})_2$ facilitated the decomposition of PFOS at 350 and 400 °C, which were lower than the decomposition temperature of PFOS alone (425 °C).

of the quantitative XRD analysis, a transformation ratio (TR) index can be used to indicate the fluorine mineralization efficiency:

$$\text{TR}(\%) = \frac{2 \times (\text{wt. of } \text{CaF}_2 / \text{MW of } \text{CaF}_2)}{17 \times (\text{wt. of PFOS} / \text{MW of PFOS})} \times 100\% \quad (5)$$

where MW means molecular weight. A TR of 100% means a complete transformation of fluorine into CaF_2 phase is achieved, whereas 0% means no CaF_2 incorporation occurred.

The fluorine transformation ratios of heating PFOS + $\text{Ca}(\text{OH})_2$ mixture over the temperature range of 300–900 °C for 30 min are summarized in Fig. 3. As the temperature of the heat treatment increased, the TR of fluorine increased gradually from around 60% to 90% within the temperature range of 350–900 °C. The potential mechanism of yielding CaF_2 is likely a solid state reaction between PFOS and $\text{Ca}(\text{OH})_2$, or a gas–solid reaction between the PFOS decomposition products and $\text{Ca}(\text{OH})_2$. For the solid state interaction, the reaction efficiency is closely associated with the effective contact between the reactants [18], and the increase in temperature may further facilitate the diffusion process of fluoride into the Ca-containing reactant [19]. For the gas–solid reaction, gaseous $\text{CF}_2=\text{CF}_2$ could react with $\text{Ca}(\text{OH})_2$ to form CaF_2 [20], and such C_1 or C_2 perfluorocarbons (e.g., CF_4 , C_2F_4 and C_2F_6) were observed when heating PFOS at temperature above 500 °C [21]. This indicates that the gaseous products of PFOS might be captured by the surrounding $\text{Ca}(\text{OH})_2$ in the thermal treatment experiments of this study. In addition, Lee and Choi [22] observed the significant

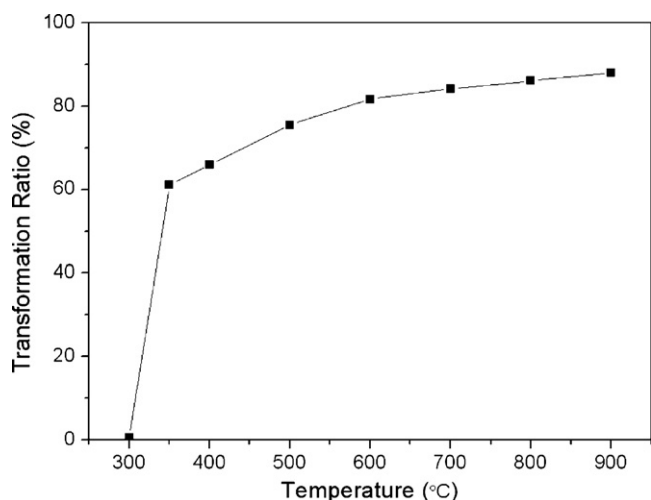


Fig. 3. The effect of temperature on fluorine transformation efficiency. Transformation ratio (TR) values were plotted for PFOS + Ca(OH)₂ samples with Ca/F molar ratio of 1:1 heated at the corresponding temperatures for 30 min.

interaction between CF₄ and CaO, and they showed that the formation of CaF₂ was enhanced with high temperature. As a high temperature phase of Ca(OH)₂, CaO may also react strongly with the gaseous products of PFOS with an increase in temperature.

The effects of the Ca/F molar ratio on the fluoride TR at 400 °C and 600 °C are illustrated in Fig. 4, which clearly shows that an increase in Ca/F molar ratio effectively enhances the transformation of fluorine into CaF₂. When the thermal treatment was tested at 600 °C, strong decomposition of PFOS into gaseous products should have occurred rapidly. A higher Ca(OH)₂ content in the system presumably provides a higher gas–solid contact frequency to react with the highly mobile decomposition products. Fig. 4 shows a substantial enhancement of fluorine mineralization efficiency from 57% to 85% at 600 °C, when the Ca/F molar ratio in the starting material was increased from 0.5:1 to 1:1. A similar experiment tested at 400 °C also shows the substantial high TR occurred when Ca/F molar ratios was higher than 1:1. The maximum fluoride TR values were generally achieved by samples with Ca/F molar ratios between 1:1 and 1.5:1, and such result also indicates a minimum Ca/F molar ratio of 1:1 for the effective fluorine transformation at 400 °C and 600 °C.

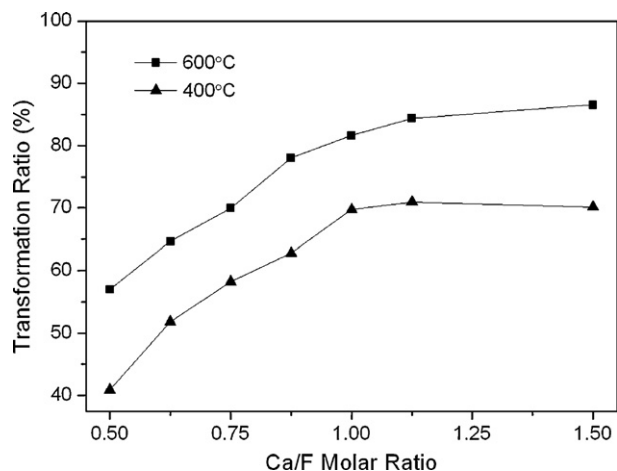


Fig. 4. The effect of Ca/F molar ratio on the formation efficiency of CaF₂. Transformation ratio (TR) values were plotted for PFOS + Ca(OH)₂ samples with different Ca/F molar ratios heated at 400 °C and 600 °C for 30 min.

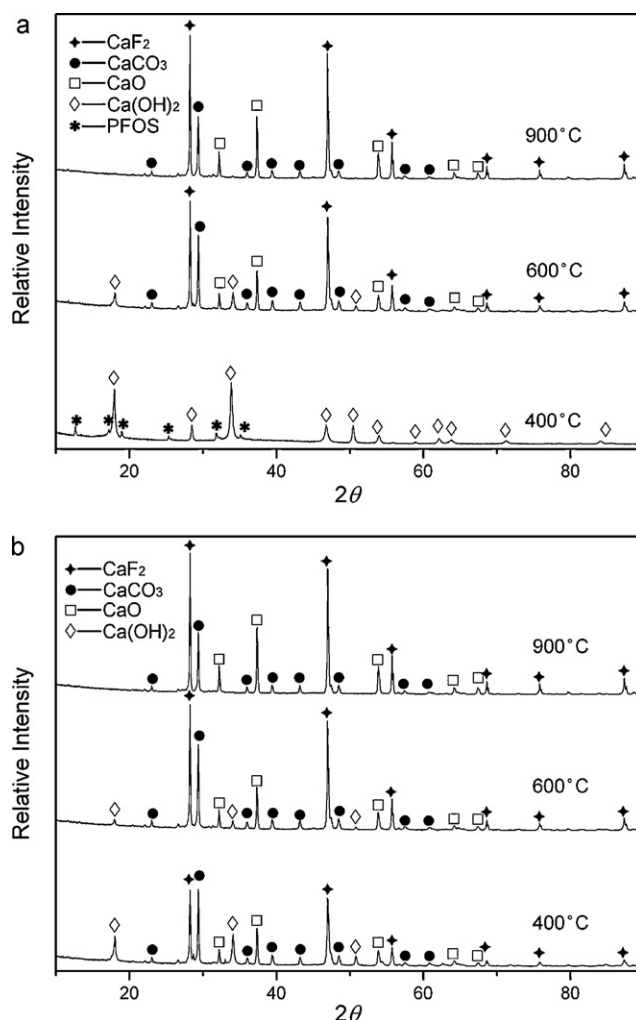


Fig. 5. The XRD results of PFOS + Ca(OH)₂ samples (Ca/F molar ratio of 1:1) heated at 400, 600, and 900 °C for (a) 2 min and (b) 5 min.

3.3. Effect of treatment time

To observe the influence of treatment time on the formation of CaF₂, the PFOS + Ca(OH)₂ mixtures were heated at 400, 600, and 900 °C for different periods. Fig. 5a shows the XRD spectra for heating the PFOS + Ca(OH)₂ mixture for 2 min at 400, 600, and 900 °C. Although CaF₂ formed at 600 and 900 °C, no CaF₂ diffraction peaks were observed at 400 °C. Further extending the treatment to 5 min resulted in a significant growth of CaF₂ in all samples heated at these three temperatures (Fig. 5b). As both heating time and temperature enhance the diffusion process of fluoride to react with the Ca-containing compounds, this reflects the importance of providing sufficient contact frequency to facilitate the mass transfer process for the PFOS + Ca(OH)₂ reaction system, particularly at lower temperature (e.g., 400 °C).

The formation of CaF₂ under the three temperatures (i.e., 400, 600, and 900 °C) were quantified using the XRD data over 1–30 min of treatment time, and Fig. 6 summarizes the results of transformation ratios to indicate the degrees of mineralization of fluorine. At 400 °C, the transformation needed at least 5 min to reach ~60% mineralization of fluorine into the CaF₂ phase, and prolonged heating was only able to enhance mineralization to almost 70%. Hori et al. [23] performed an iron-induced decomposition for perfluorohexanesulfonate (a compound similar to PFOS in structure type) in sub- and supercritical water, and showed that the fluorine transformation ratio was around 47% at 380 °C. Therefore, treatment at

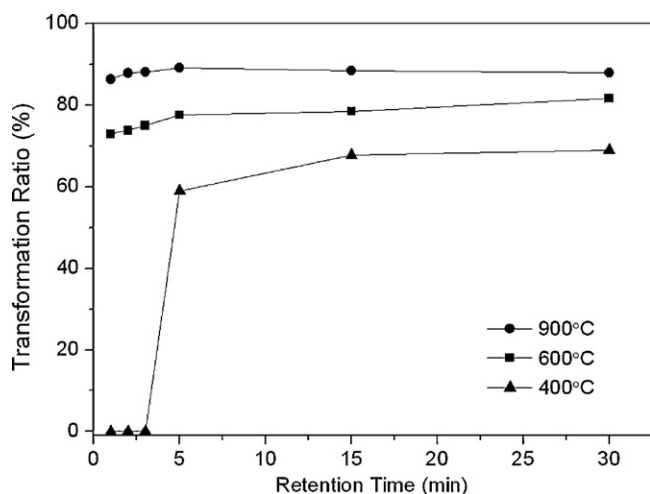


Fig. 6. The formation of CaF_2 at different time period of thermal treatment process. The transformation ratio (TR) values for the PFOS + $\text{Ca}(\text{OH})_2$ samples (Ca/F molar ratio of 1:1) were obtained by heating at 400, 600, and 900 °C with different treatment times.

400 °C shows that the effectiveness of incorporating fluorine into CaF_2 by heating PFCs with a lime-based precursor is comparable, if not superior, to iron-induced decomposition in sub- and supercritical water. At 600 and 900 °C, the formation of CaF_2 was quickly achieved within 1 min, and the transformation ratios were around 80% and 90%, respectively. This clearly indicates that high temperature promotes the incorporation of fluorine into CaF_2 , and a very high degree of fluorine mineralization could be achieved within an extremely short period at treatment temperatures above 600 °C.

4. Conclusions

The results of thermal reaction between PFOS and $\text{Ca}(\text{OH})_2$ indicate that $\text{Ca}(\text{OH})_2$ facilitates the decomposition of PFOS at 350 °C. This effect is initiated by the replacement of fluorine in PFOS by hydroxide, and this process occurs at a temperature lower than that of the decomposition of PFOS alone (425 °C). After a few minutes of thermal treatment at 400, 600, and 900 °C, the fluorine transformation ratios reach 60%, 80%, and 90%, respectively. Therefore, $\text{Ca}(\text{OH})_2$ and other Ca-rich matrices may be effectively used to defluorinate PFCs under thermal conditions. In addition, the strong interaction between PFOS and calcium provides an indication of the fate of PFOS in sludge during a variety of thermal treatment processes. Considering the more complicated system in real wastewater sludge, other factors that may influence this reaction pathway should be further evaluated in future studies.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.06.009.

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