Mineralization Behavior of Fluorine in Perfluorooctanesulfonate (PFOS) during Thermal Treatment of Lime-Conditioned Wastewater Sludge

Supporting Information

Including 3 tables and 15 figures in 23 pages

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Table S1. Quality of the Rietveld refinement analysis for quantifying the phase compositions of the products heated at 400 °C, 600 °C, and 900 °C for 1, 3, 5, 10 and 15 minutes in the ST sludge + $Ca(OH)_2$+ PFOS system with a Ca/F molar ratio of 2:1 (Figure S9). The values indicate the pattern factors (R_p, R_{wp} and R_{exp}) and the goodness-of-fit (*GOF*).

Temperature (°C)	Time (min)	Quality of Refinement Analysis			
		R_P (%)	R_{WP} (%)	R_{exp} (%)	*GOF*
400	1	4.94	6.42	4.08	1.57
	3	4.41	5.68	3.98	1.43
	5	4.69	6.08	4.04	1.50
	10	4.92	6.42	4.03	1.59
	15	4.70	6.11	4.03	1.52
600	1	5.48	7.28	4.22	1.73
	3	4.82	6.50	4.00	1.62
	5	4.46	5.77	3.94	1.46
	10	5.19	7.19	3.87	1.86
	15	4.56	6.10	3.90	1.57
900	1	4.77	6.38	4.00	1.59
	3	5.10	6.79	3.99	1.70
	5	5.37	7.15	3.94	1.82
	10	5.11	6.83	3.99	1.71
	15	5.30	6.98	4.15	1.68

Note:

(a) $R_P = \frac{\sum |Y_i(obs) - Y_i(calc)|}{\sum Y_i(obs)}$, $R_{WP} = \left\{ \frac{\sum \omega_i [Y_i(obs) - Y_i(calc)]^2}{\sum \omega_i [Y_i(obs)]^2} \right\}^{1/2}$, $R_{exp} = \left\{ \frac{\sum M - P}{\sum \omega_i [Y_i(obs)]^2} \right\}^{1/2}$ and

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

where $Y_{i(obs)}$ and $Y_{i(calc)}$ are the observed and calculated data, respectively, at data point m; M is the number of data points; P is the number of parameters; i is the corresponding data point; ω_i is the weighting given to data point m. The counting statistics is given by $\omega_i = 1/\delta(Y_{i(obs)})^2$, where $\delta(Y_{i(obs)})$ is the error in $Y_{i(obs)}$.

(b) The goodness of fit (chi^2) equals one in an ideal refinement, although, practically, the background and the peak profile mismatch lead to GOF > 1. It is generally considered that the chi^2 value between 1.0 and 2.9 is satisfactory[1]. The quality of the Rietveld refinement work in this study was reflected by the *GOF* ranging from 1.38 to 1.92 for all XRD patterns analyzed in this study.

[1] Fansuri, H.; Zhang, D. K.; French, D.; Elcombe, M.; Studer, A. An X-ray and neutron diffraction study of the structure of α-$Bi_2Mo_3O_{12}$ as a catalyst for partial oxidation of propylene to acrolein. *In Proceedings of the CHEMECA symposium*. **2004**, 234.

Table S2. Quality of the Rietveld refinement analysis for quantifying the phase compositions of the products heated from 300-900 °C for 15 minutes in ST sludge + $Ca(OH)_2$+ PFOS system with a Ca/F molar ratio of 2/1 (Figure S10). The values indicate the pattern factors (R_p, R_{wp} and R_{exp}) and the goodness-of-fit (*GOF*).

Temperature	Quality of Refinement Analysis			
(°C)	R_P (%)	R_{WP} (%)	R_{exp} (%)	*GOF*
300	6.01	8.05	5.21	1.55
400	5.57	7.35	5.33	1.38
500	5.16	6.93	4.48	1.54
600	4.98	6.66	3.99	1.67
700	5.06	6.71	3.94	1.70
800	5.45	7.27	4.97	1.46
900	5.71	7.63	5.27	1.45

Table S3. Quality of the Rietveld refinement analysis for quantifying the phase compositions of the products heated at 400 °C and 900 °C for 15 minutes in ST sludge + $Ca(OH)_2$+ PFOS system with different Ca/F molar ratios (1/2, 1/1, 2/1, 4/1 and 8/1) (Figure S11). The values indicate the pattern factors (R_p, R_{wp} and R_{exp}) and the goodness-of-fit (*GOF*).

Temperature (°C)	Ca/F	Quality of Refinement Analysis			
		R_P (%)	R_{WP} (%)	R_{exp} (%)	*GOF*
400	1/2	5.36	6.89	4.16	1.66
	1/1	5.57	7.44	4.10	1.81
	2/1	5.48	7.28	4.22	1.73
	4/1	5.08	6.60	4.08	1.62
	8/1	5.53	7.29	4.24	1.72
900	1/2	6.01	7.98	4.16	1.92
	1/1	5.55	7.30	4.16	1.75
	2/1	4.39	5.72	4.05	1.41
	4/1	4.79	6.32	3.93	1.61
	8/1	5.25	6.88	4.05	1.70

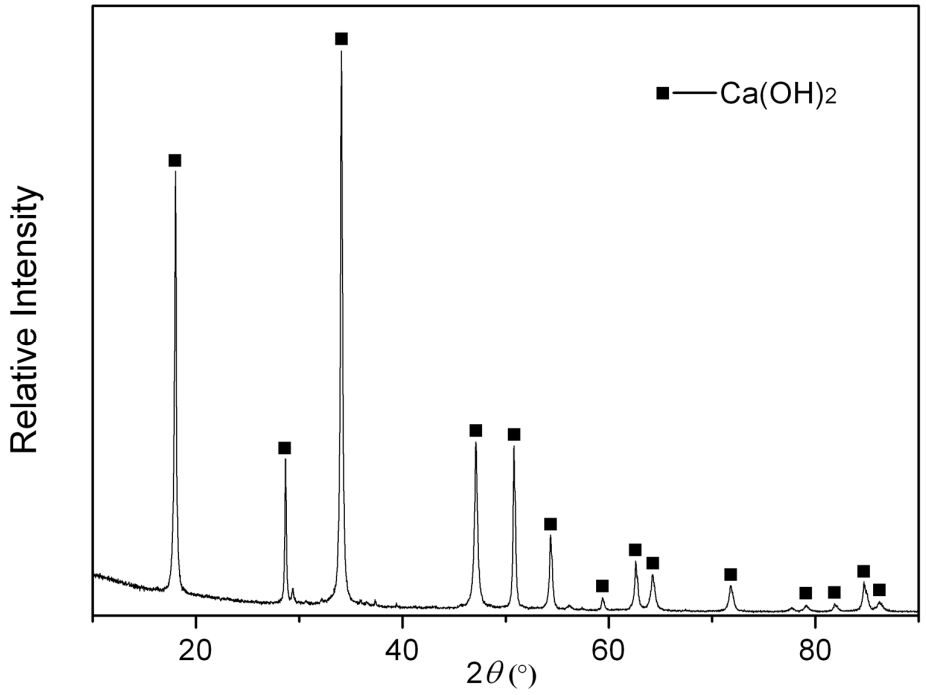


Figure S1. Confirmation of the mineral phase by the XRD pattern of $Ca(OH)_2$ reagent used in this study.

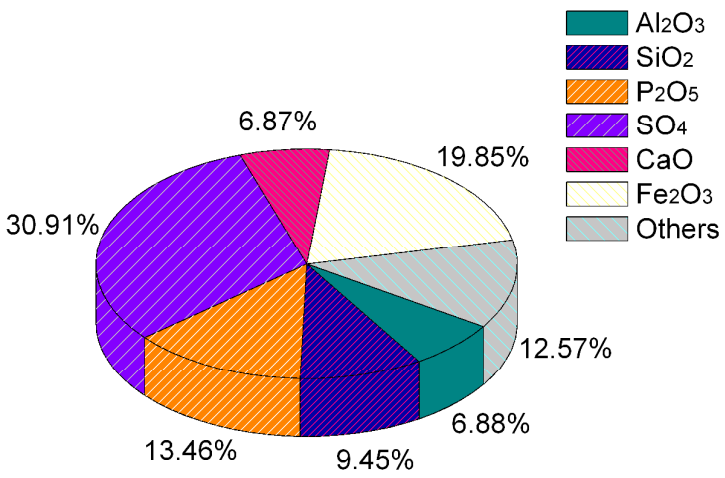


Figure S2. X-ray fluorescence (XRF) result showing the elemental compositions (expressed by their oxide forms) of the dry Shatin WWTP sludge used in this study.

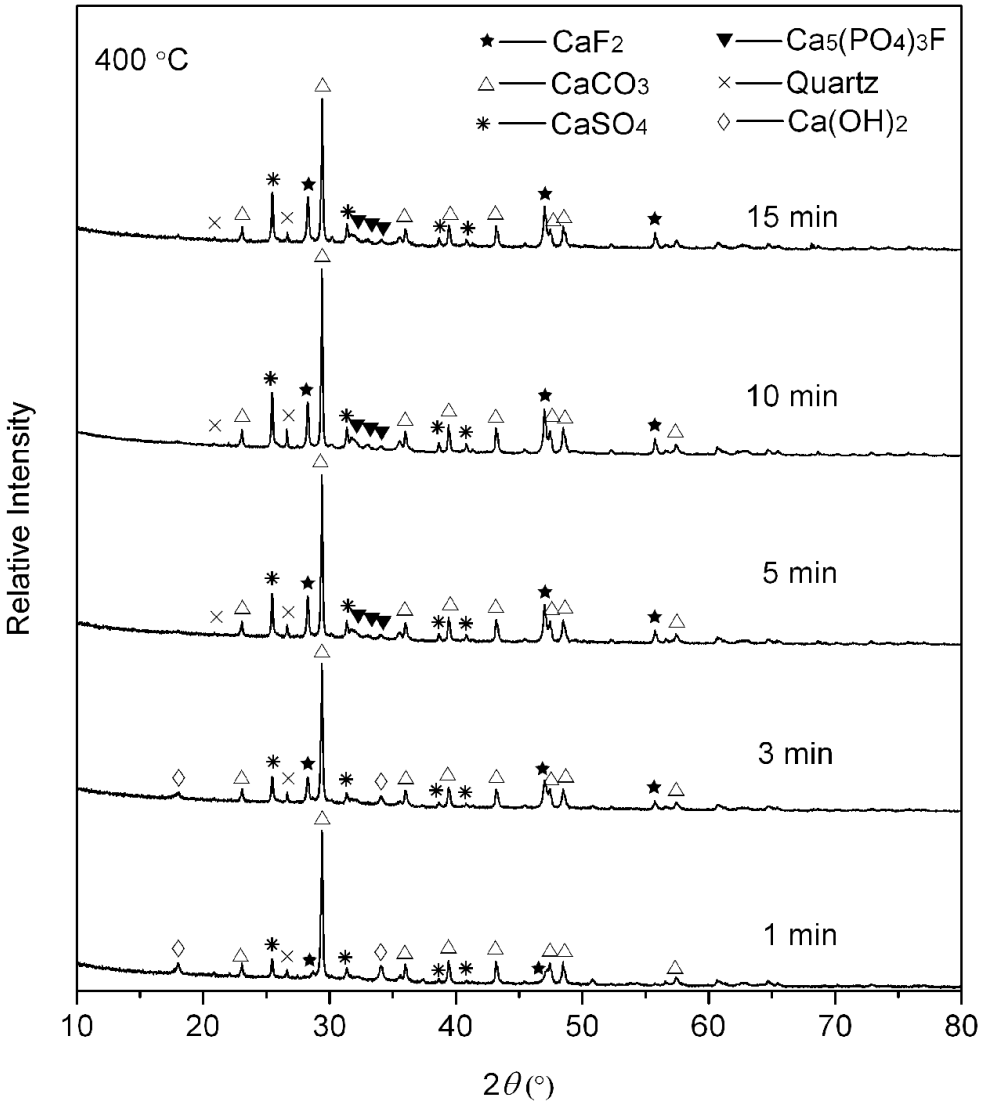


Figure S3. The XRD results of Sludge + $Ca(OH)_2$+ PFOS samples (Ca/F molar ratio of 2/1) heated at 400 °C for different treatment times.

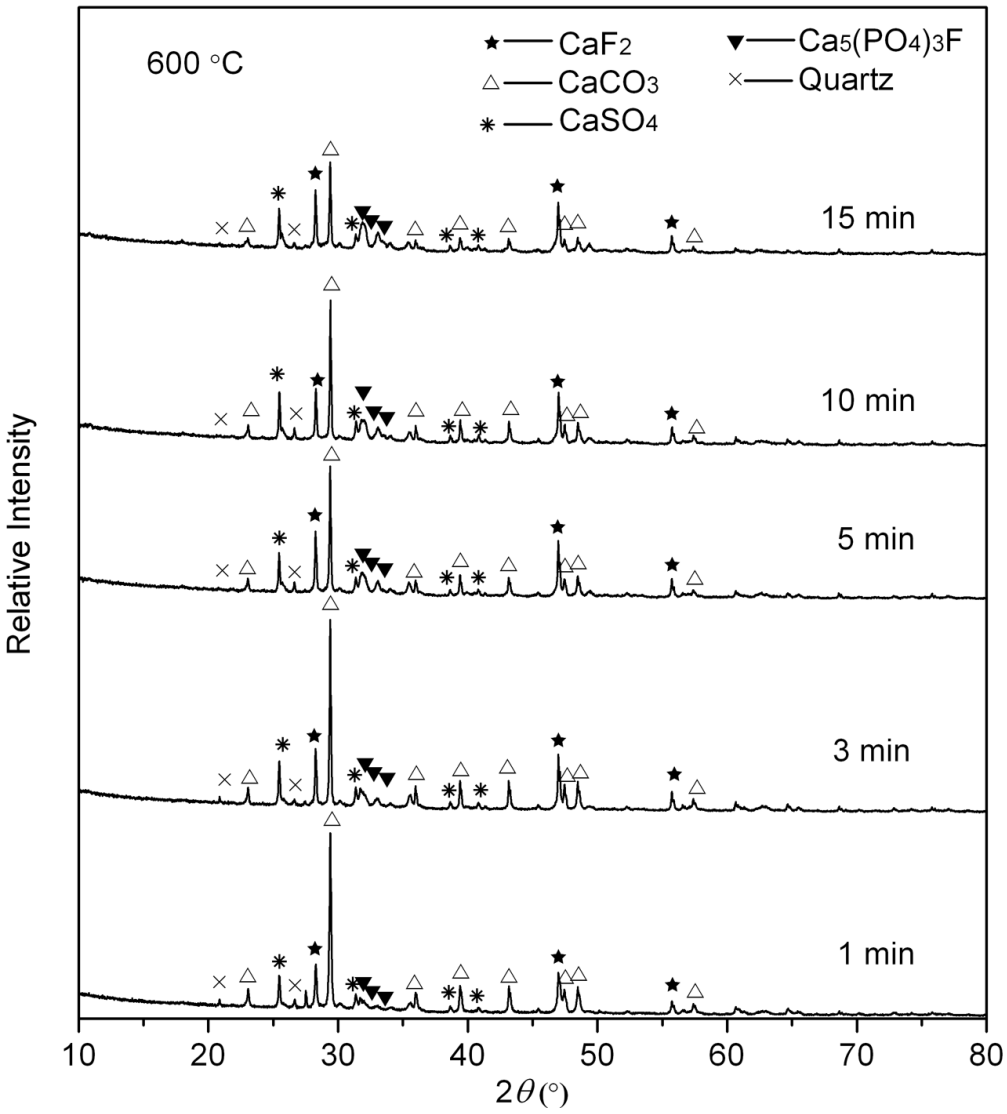


Figure S4. The XRD results of Sludge + $Ca(OH)_2$+ PFOS samples (Ca/F molar ratio of 2/1) heated at 600 °C for different treatment times.

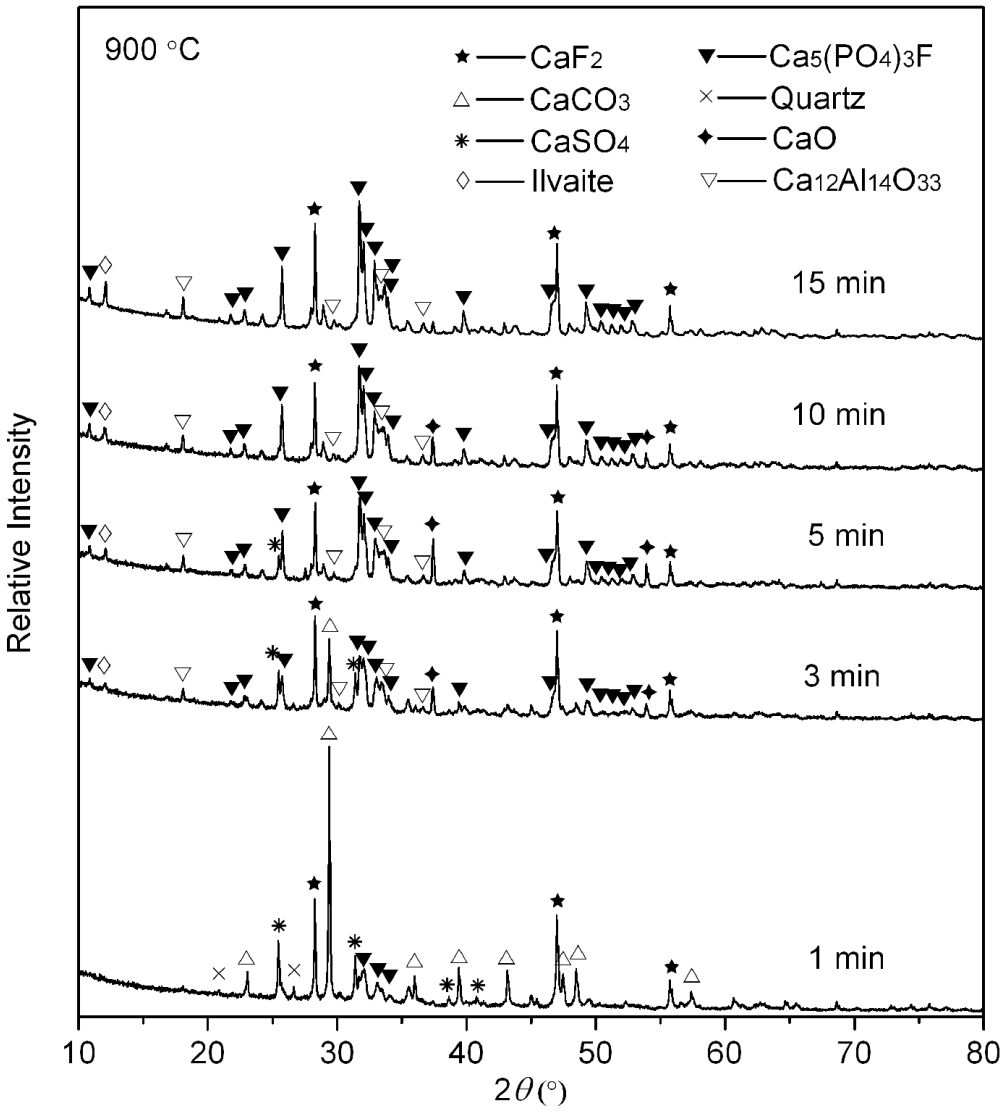


Figure S5. The XRD results of Sludge + $Ca(OH)_2$+ PFOS samples (Ca/F molar ratio of 2/1) heated at 900 °C for different treatment times.

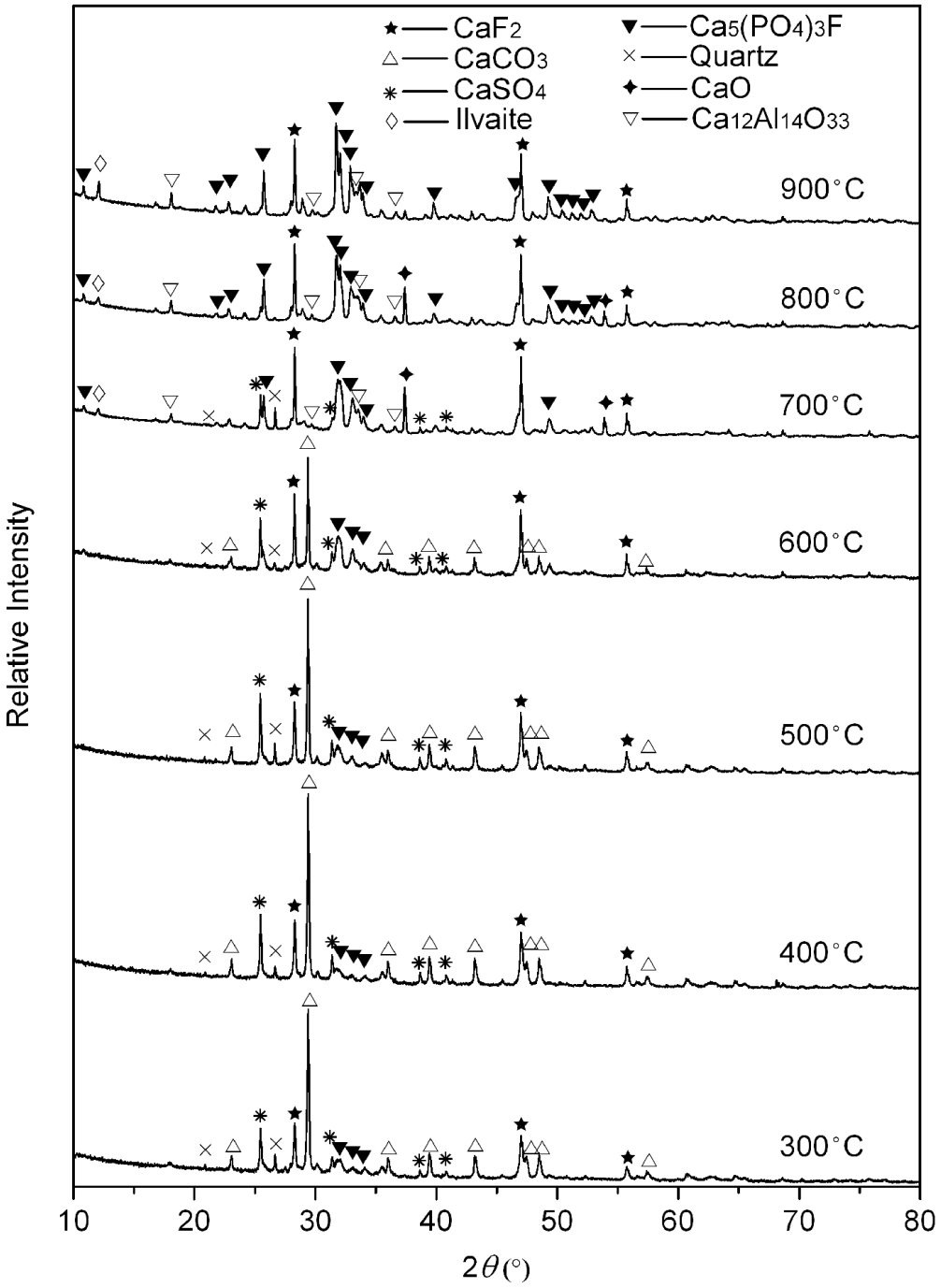


Figure S6. The XRD results of Sludge + $Ca(OH)_2$+ PFOS samples (Ca/F molar ratio of 2:1) heated at temperatures between 300 °C and 900 °C for 15 min.

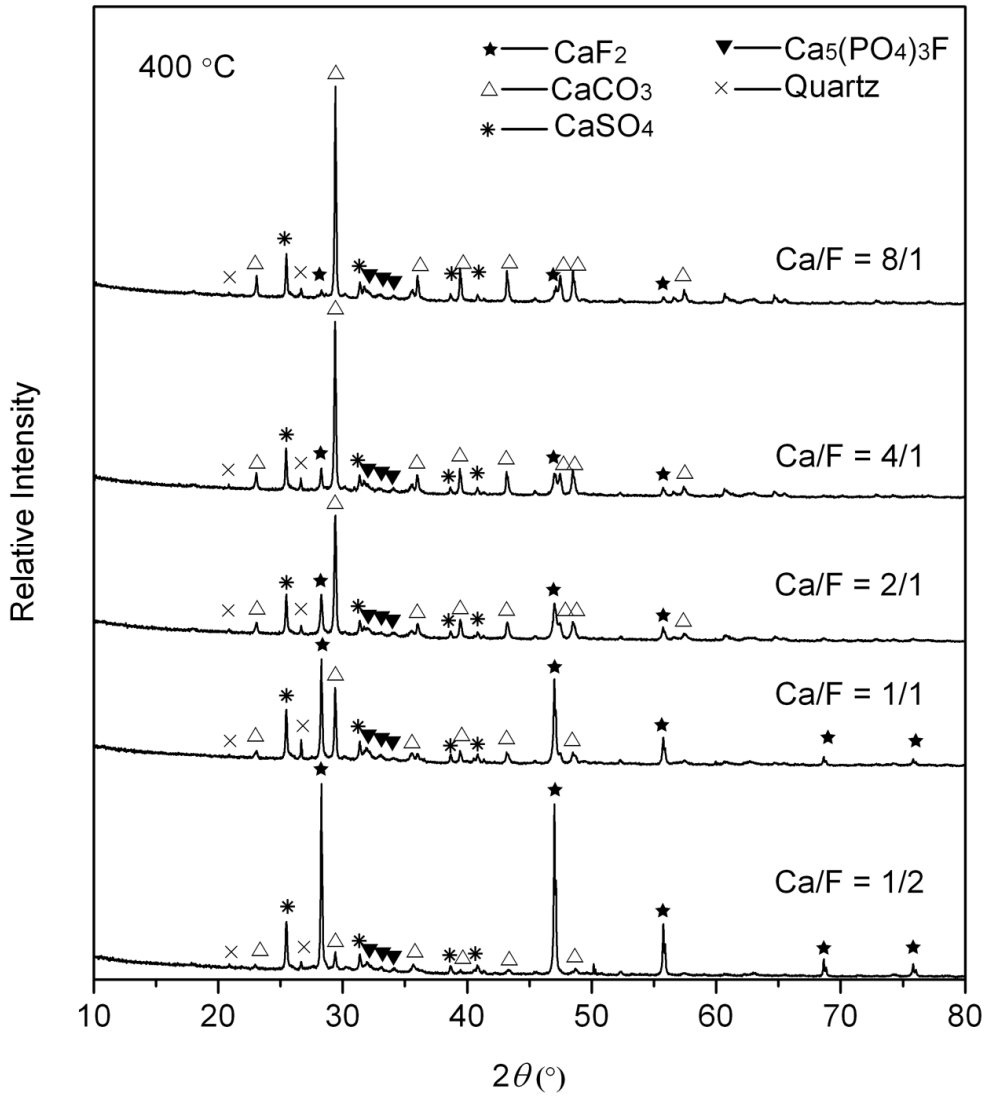


Figure S7. The XRD results of Sludge + $Ca(OH)_2$+ PFOS samples heated at 400 °C with different Ca/F molar ratios for 15 min.

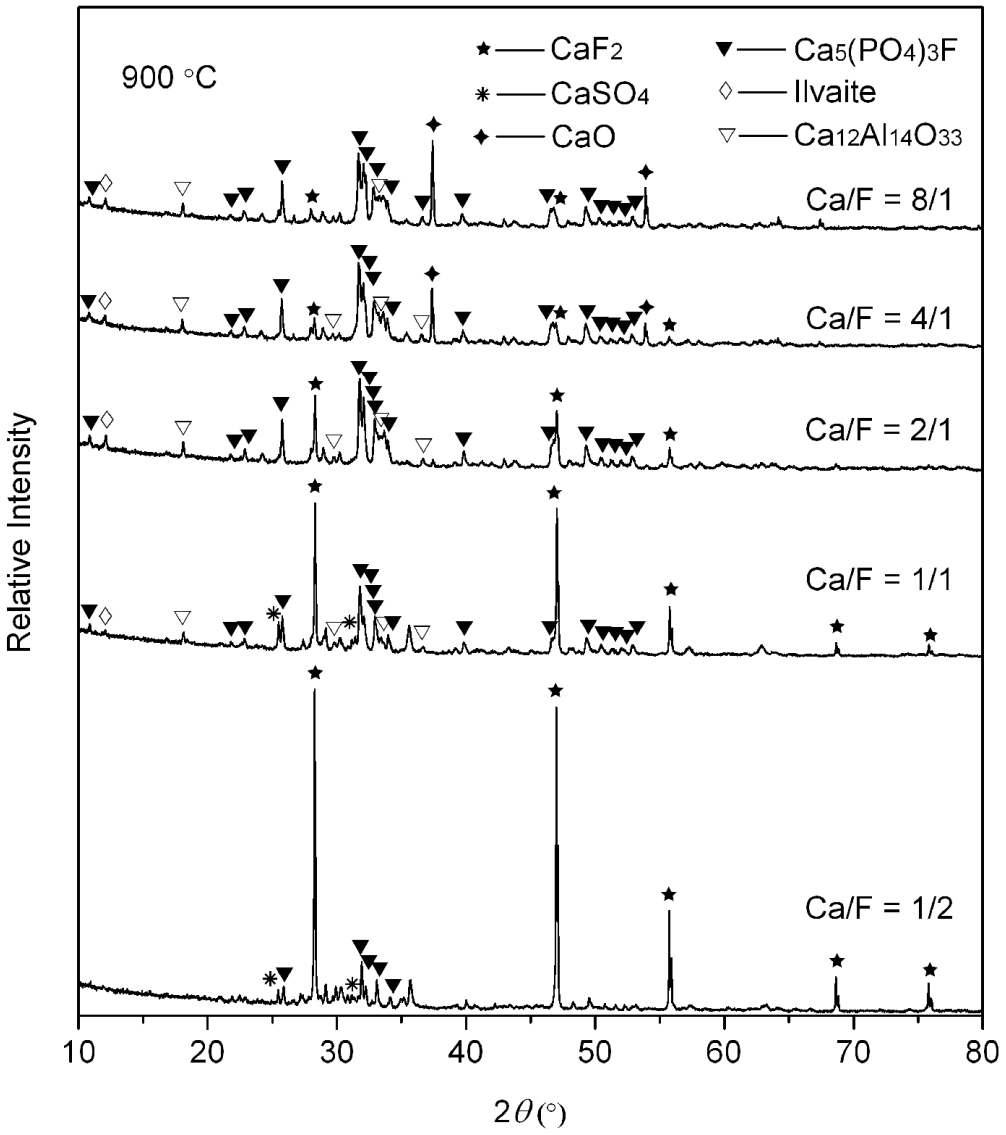
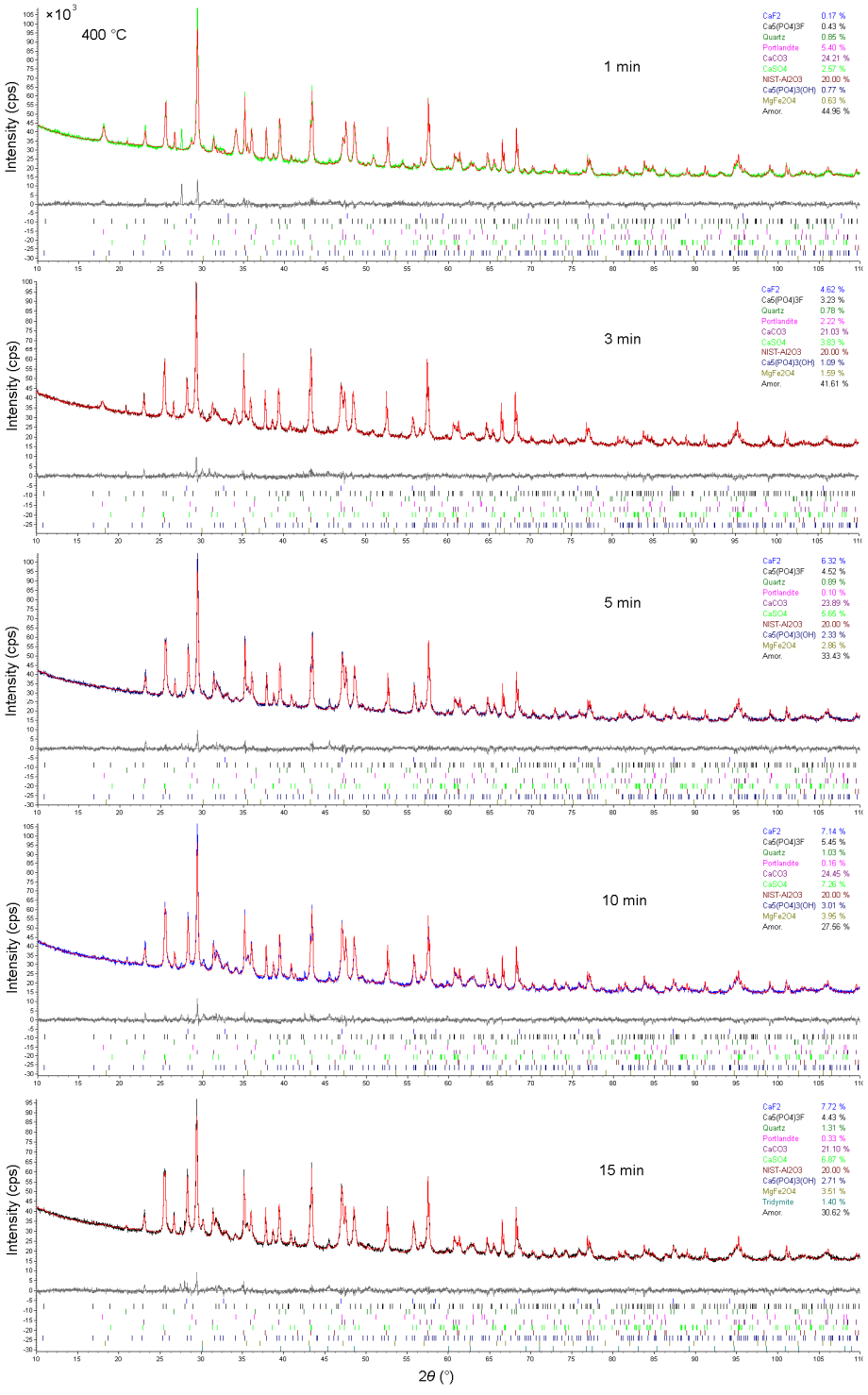
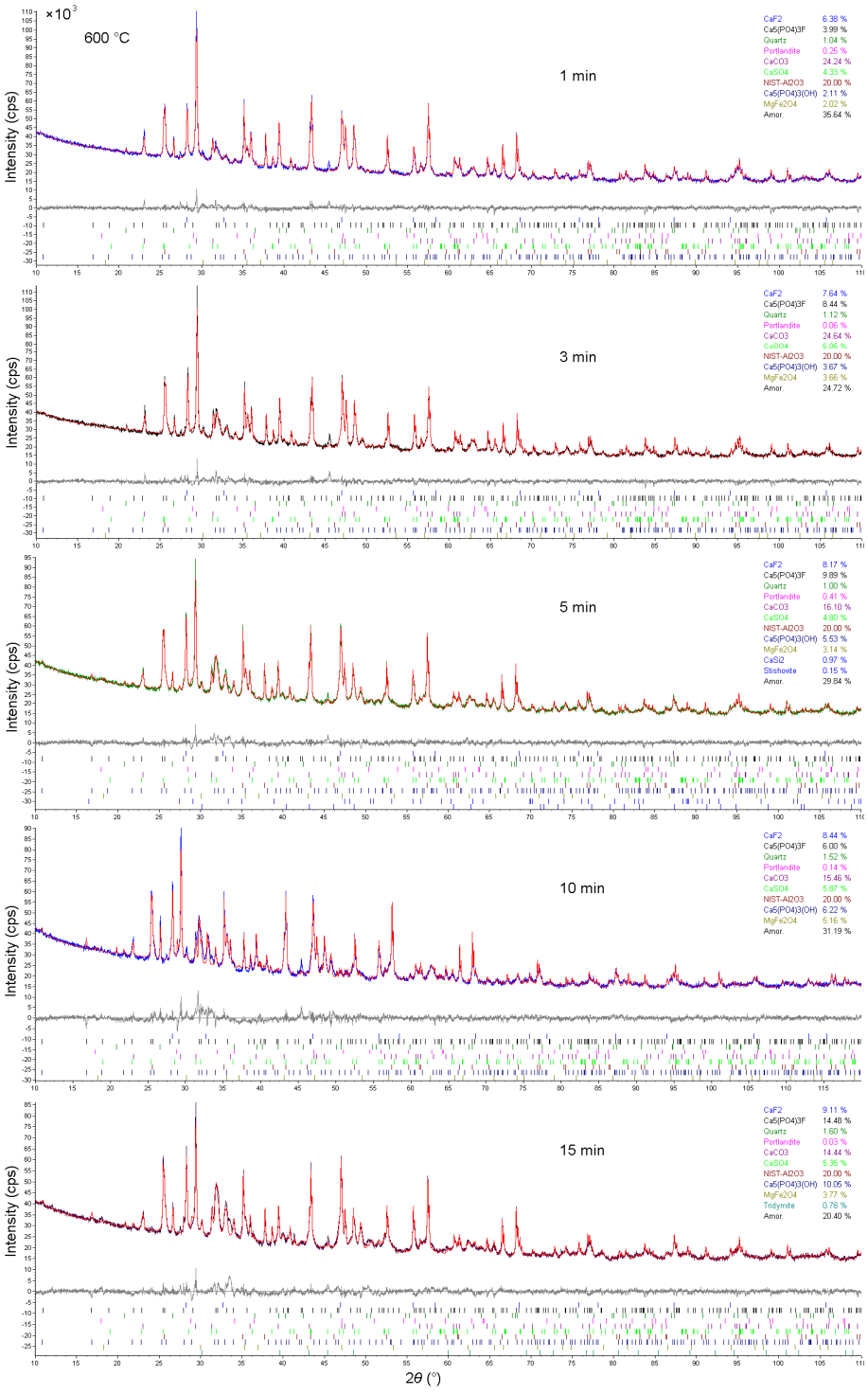


Figure S8. The XRD results of Sludge + $Ca(OH)_2$+ PFOS samples heated at 900 °C with different Ca/F molar ratios for 15 min.


×10^3
400 °C
1 min
CaF2 0.17 %
Ca5(PO4)3F 0.43 %
Quartz 0.85 %
Portlandite 5.40 %
CaCO3 24.21 %
CaSO4 2.57 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 0.77 %
MgFe2O4 0.63 %
Amor. 44.96 %
3 min
CaF2 4.62 %
Ca5(PO4)3F 3.23 %
Quartz 0.78 %
Portlandite 2.22 %
CaCO3 21.03 %
CaSO4 3.83 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 1.09 %
MgFe2O4 1.59 %
Amor. 41.61 %
5 min
CaF2 6.32 %
Ca5(PO4)3F 4.52 %
Quartz 0.99 %
Portlandite 0.10 %
CaCO3 23.88 %
CaSO4 5.65 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 2.33 %
MgFe2O4 2.86 %
Amor. 33.43 %
10 min
CaF2 7.14 %
Ca5(PO4)3F 5.45 %
Quartz 1.03 %
Portlandite 0.16 %
CaCO3 24.45 %
CaSO4 7.26 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 3.01 %
MgFe2O4 3.95 %
Amor. 27.56 %
15 min
CaF2 7.72 %
Ca5(PO4)3F 4.43 %
Quartz 1.31 %
Portlandite 0.33 %
CaCO3 21.10 %
CaSO4 6.87 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 2.71 %
MgFe2O4 3.51 %
Tridymite 1.40 %
Amor. 30.62 %
Intensity (cps)
2θ (°)


×10^3
600 °C
1 min
CaF2 6.38 %
Ca5(PO4)3F 3.99 %
Quartz 1.04 %
Portlandite 0.25 %
CaCO3 24.24 %
CaSO4 4.33 %
NIST-AO3 20.00 %
Ca5(PO4)3(OH) 2.11 %
MgFe2O4 2.02 %
Amor. 35.64 %
3 min
CaF2 7.64 %
Ca5(PO4)3F 8.44 %
Quartz 1.12 %
Portlandite 0.06 %
CaCO3 24.64 %
CaSO4 6.05 %
NIST-AO3 20.00 %
Ca5(PO4)3(OH) 3.67 %
MgFe2O4 3.66 %
Amor. 24.72 %
5 min
CaF2 8.17 %
Ca5(PO4)3F 9.89 %
Quartz 1.00 %
Portlandite 0.41 %
CaCO3 16.10 %
CaSO4 4.80 %
NIST-AO3 20.00 %
Ca5(PO4)3(OH) 5.53 %
MgFe2O4 3.14 %
CaSi2 0.97 %
Stishovite 0.15 %
Amor. 29.84 %
10 min
CaF2 8.44 %
Ca5(PO4)3F 6.00 %
Quartz 1.52 %
Portlandite 0.14 %
CaCO3 15.46 %
CaSO4 5.87 %
NIST-AO3 20.00 %
Ca5(PO4)3(OH) 6.22 %
MgFe2O4 5.16 %
Amor. 31.19 %
15 min
CaF2 9.11 %
Ca5(PO4)3F 14.48 %
Quartz 1.60 %
Portlandite 0.03 %
CaCO3 14.44 %
CaSO4 5.35 %
NIST-AO3 20.00 %
Ca5(PO4)3(OH) 10.05 %
MgFe2O4 3.77 %
Tridymite 0.78 %
Amor. 20.40 %
Intensity (cps)
2θ (°)

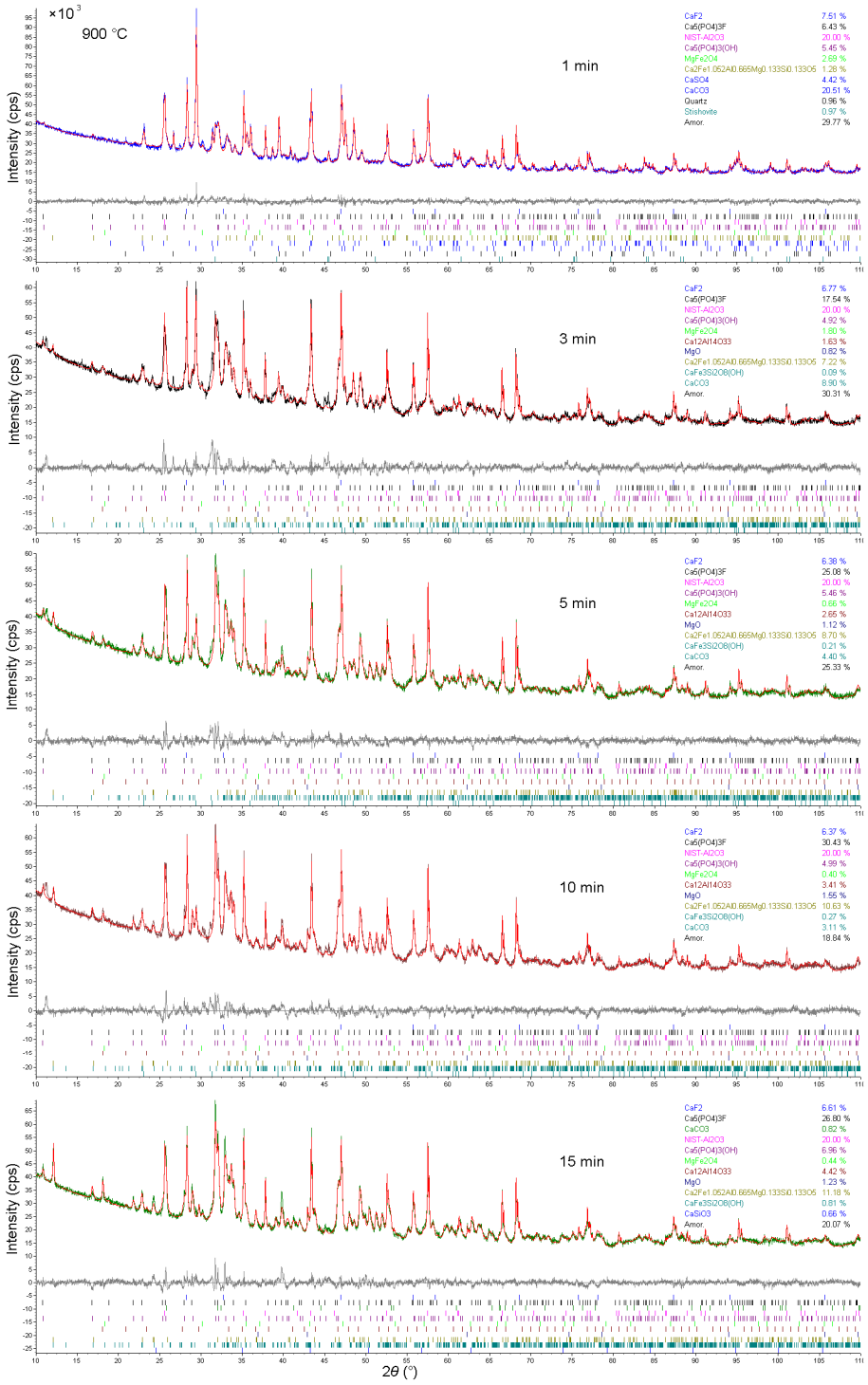
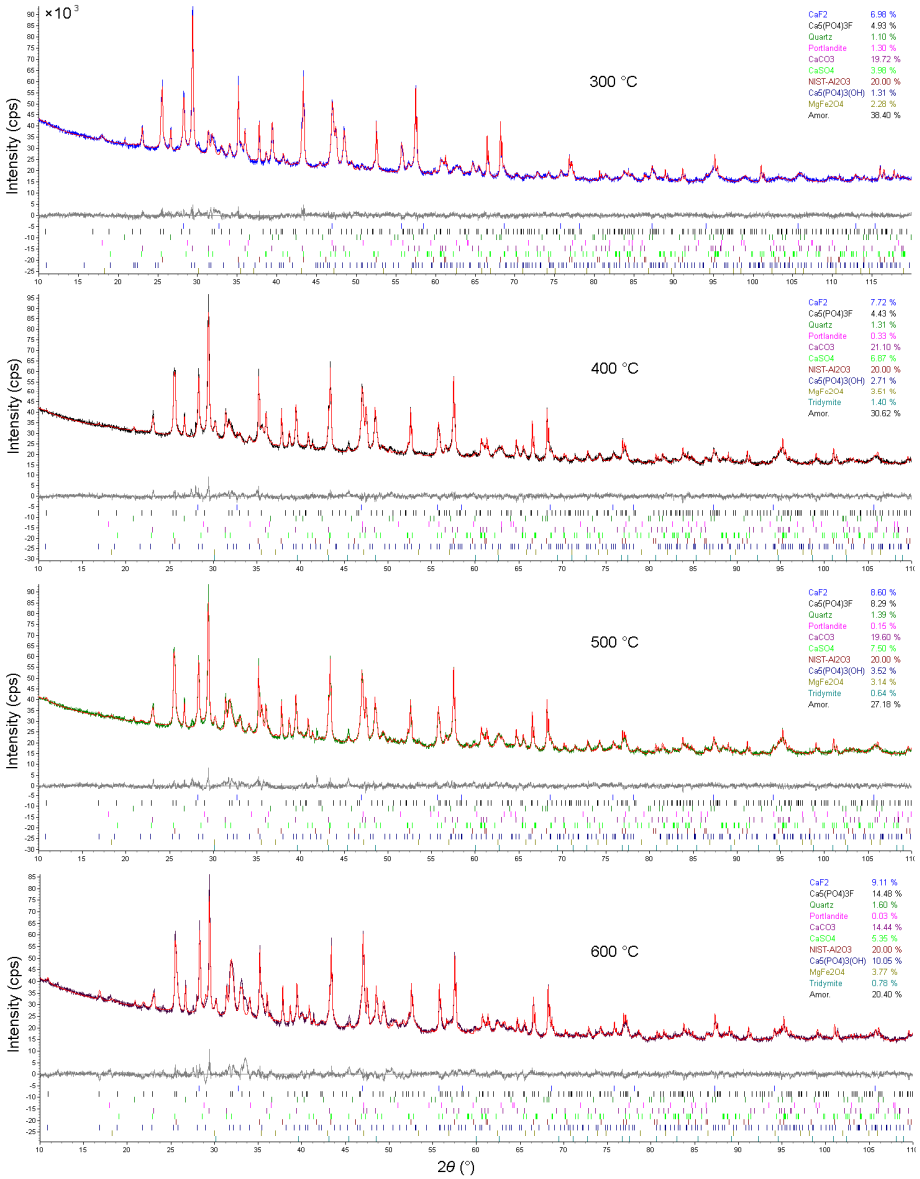


Figure S9. Graphical plots of the refinement results for the products heated at 400 °C, 600 °C, and 900 °C for 1, 3, 5, 10 and 15 minutes in the ST sludge + $Ca(OH)_2$+ PFOS system with a Ca/F molar ratio of 2/1 (color line = experimental XRD patterns, red line = calculated XRD patterns, and blue line = differences between the experimental and calculated patterns). Vertical bars with different colors indicate the Bragg positions of the corresponding phases. The observed goodness of fit (chi^2) values are provided in Table S1.


×10 3
300 °C
CaF2 6.98 %
Ca5(PO4)3F 4.93 %
Quartz 1.10 %
Portlandite 1.30 %
CaCO3 19.72 %
CaSO4 3.98 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 1.31 %
MgFe2O4 2.28 %
Amor. 38.40 %
400 °C
CaF2 7.72 %
Ca5(PO4)3F 4.43 %
Quartz 1.31 %
Portlandite 0.33 %
CaCO3 21.10 %
CaSO4 6.97 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 2.71 %
MgFe2O4 3.61 %
Tridymite 1.40 %
Amor. 30.62 %
500 °C
CaF2 8.60 %
Ca5(PO4)3F 8.29 %
Quartz 1.39 %
Portlandite 0.15 %
CaCO3 19.60 %
CaSO4 7.50 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 3.52 %
MgFe2O4 3.14 %
Tridymite 0.64 %
Amor. 27.18 %
600 °C
CaF2 9.11 %
Ca5(PO4)3F 14.48 %
Quartz 1.60 %
Portlandite 0.03 %
CaCO3 14.44 %
CaSO4 5.35 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 10.05 %
MgFe2O4 3.77 %
Tridymite 0.78 %
Amor. 20.40 %
Intensity (cps)
2θ (°)

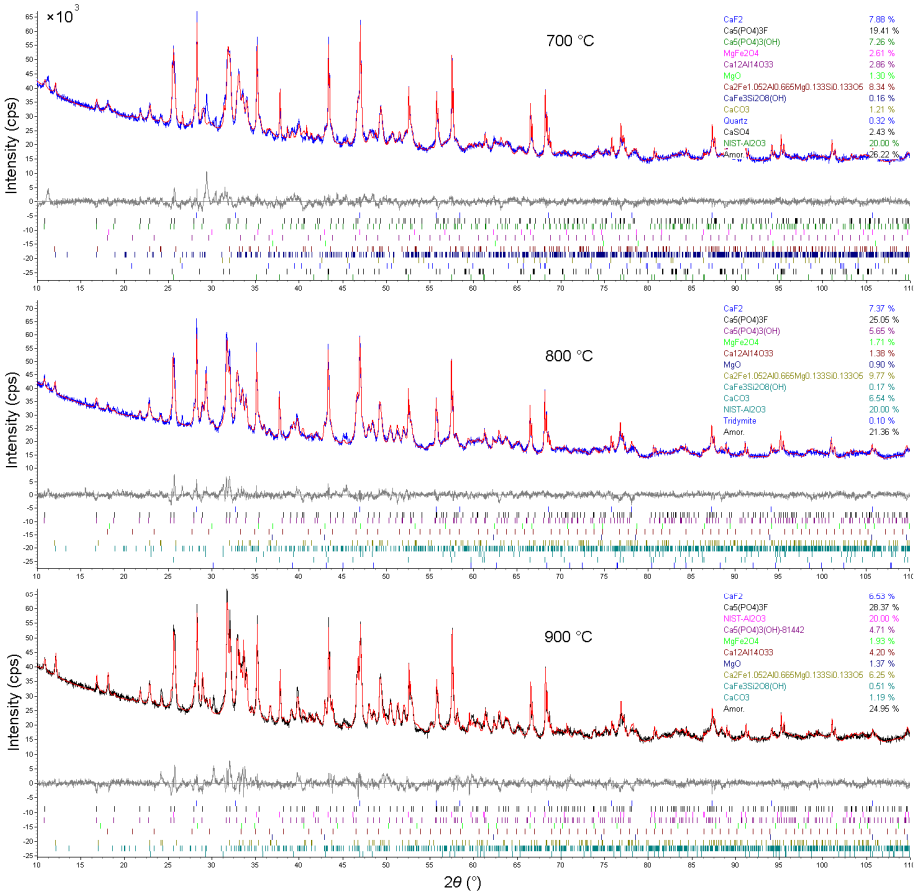
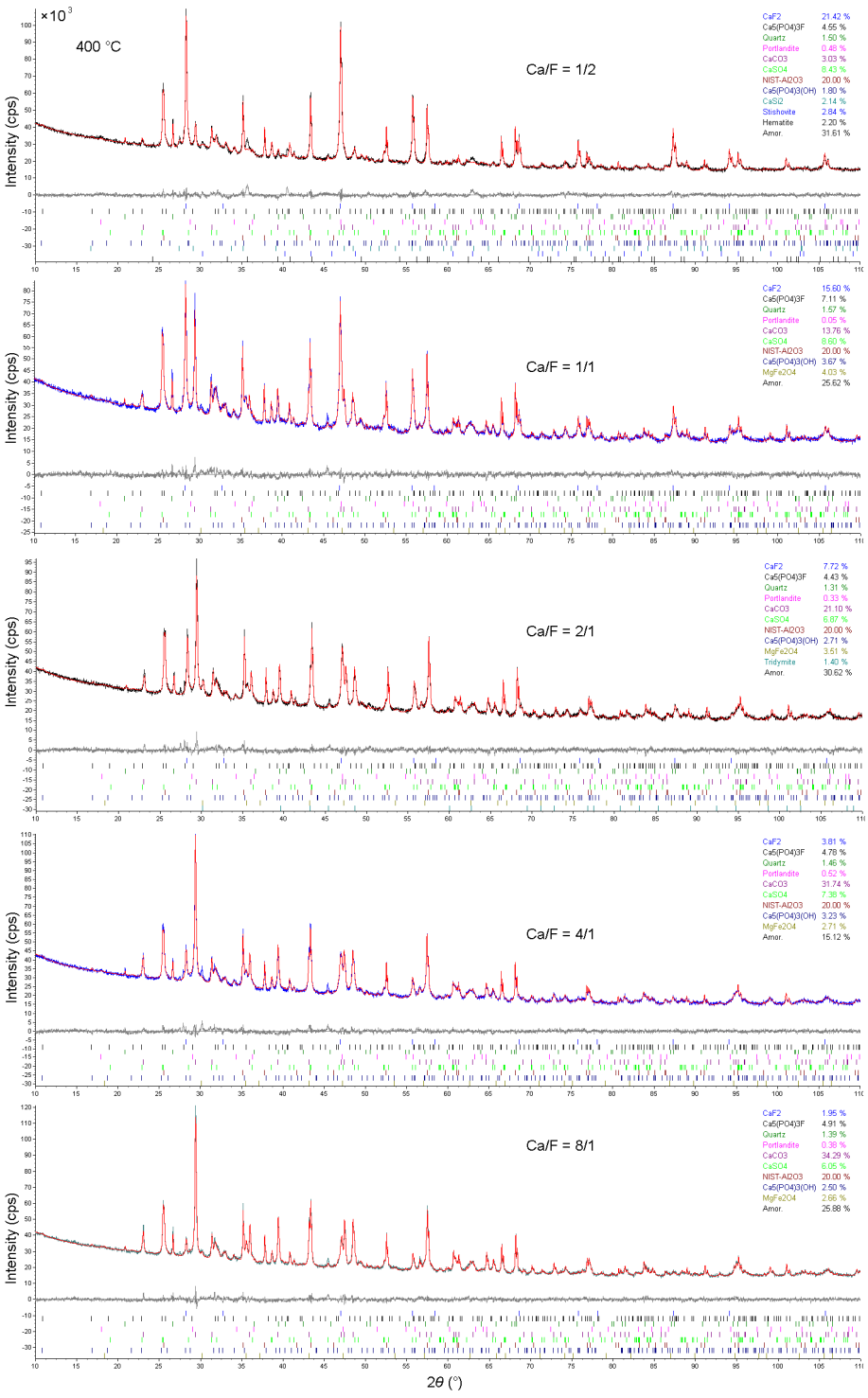


Figure S10. Graphical plots of the refinement results for the products heated from 300-900 °C for 15 minutes in the ST sludge + $Ca(OH)_2$+ PFOS system with a Ca/F molar ratio of 2/1 (color line = experimental XRD patterns, red line = calculated XRD patterns, and blue line = differences between the experimental and calculated patterns). Vertical bars with different colors indicate the Bragg positions of the corresponding phases. The observed goodness of fit (chi^2) values are provided in Table S2.


×10^3
400 °C
Ca/F = 1/2
CaF2 21.42 %
Ca5(PO4)3F 4.55 %
Quartz 1.50 %
Portlandite 0.48 %
CaCO3 3.03 %
CaSO4 8.43 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 1.80 %
CaSi2 2.14 %
Stishovite 2.84 %
Hematite 2.20 %
Amor. 31.61 %
Ca/F = 1/1
CaF2 15.60 %
Ca5(PO4)3F 7.11 %
Quartz 1.57 %
Portlandite 0.05 %
CaCO3 13.76 %
CaSO4 8.60 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 3.67 %
MgFe2O4 4.03 %
Amor. 25.62 %
Ca/F = 2/1
CaF2 7.72 %
Ca5(PO4)3F 4.43 %
Quartz 1.31 %
Portlandite 0.33 %
CaCO3 21.10 %
CaSO4 6.87 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 2.71 %
MgFe2O4 3.51 %
Tridymite 1.40 %
Amor. 30.62 %
Ca/F = 4/1
CaF2 3.81 %
Ca5(PO4)3F 4.78 %
Quartz 1.46 %
Portlandite 0.52 %
CaCO3 31.74 %
CaSO4 7.36 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 3.23 %
MgFe2O4 2.71 %
Amor. 15.12 %
Ca/F = 8/1
CaF2 1.95 %
Ca5(PO4)3F 4.91 %
Quartz 1.39 %
Portlandite 0.36 %
CaCO3 34.29 %
CaSO4 6.05 %
NIST-Al2O3 20.00 %
Ca5(PO4)3(OH) 2.50 %
MgFe2O4 2.66 %
Amor. 25.88 %
Intensity (cps)
2θ (°)

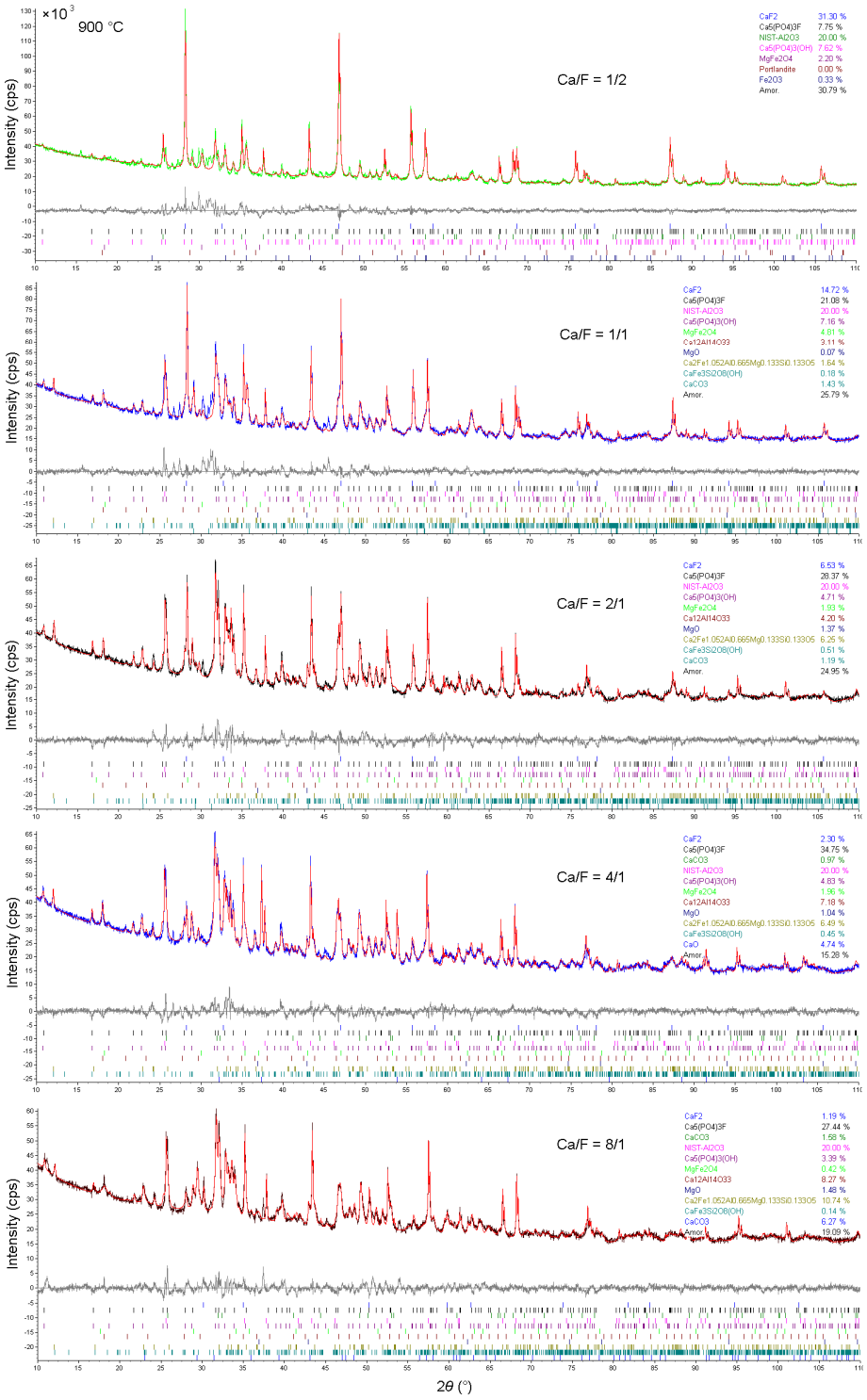


Figure S11. Graphical plots of the refinement results for the products heated at 400 °C and 900 °C for 15 minutes in the ST sludge + $Ca(OH)_2$+ PFOS system with different Ca/F molar ratios (1/2, 1/1, 2/1, 4/1 and 8/1) (color line = experimental XRD patterns, red line = calculated XRD patterns, and blue line = differences between the experimental and calculated patterns). Vertical bars with different colors indicate the Bragg positions of the corresponding phases. The observed goodness of fit (chi^2) values are provided in Table S3.

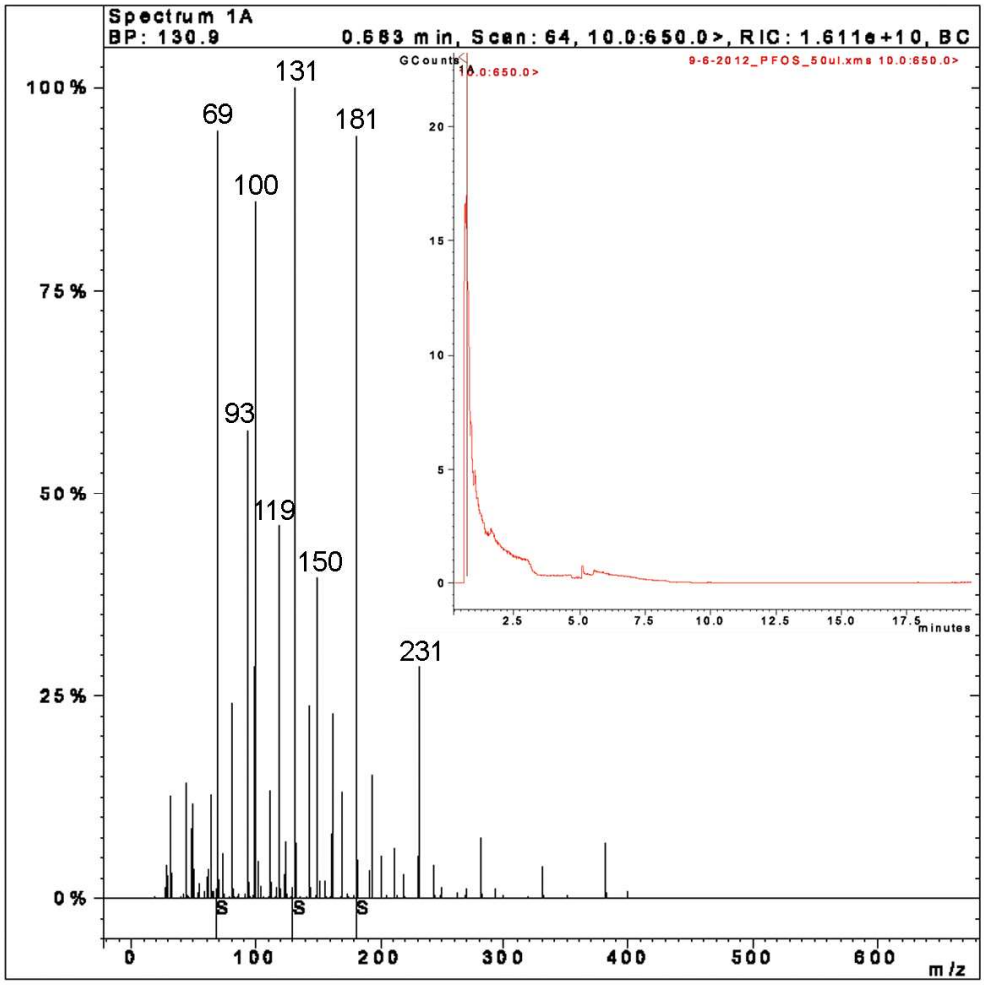


Figure S12. Full-scan mass spectrum of gas products derived from thermally treating PFOS at 600 °C.

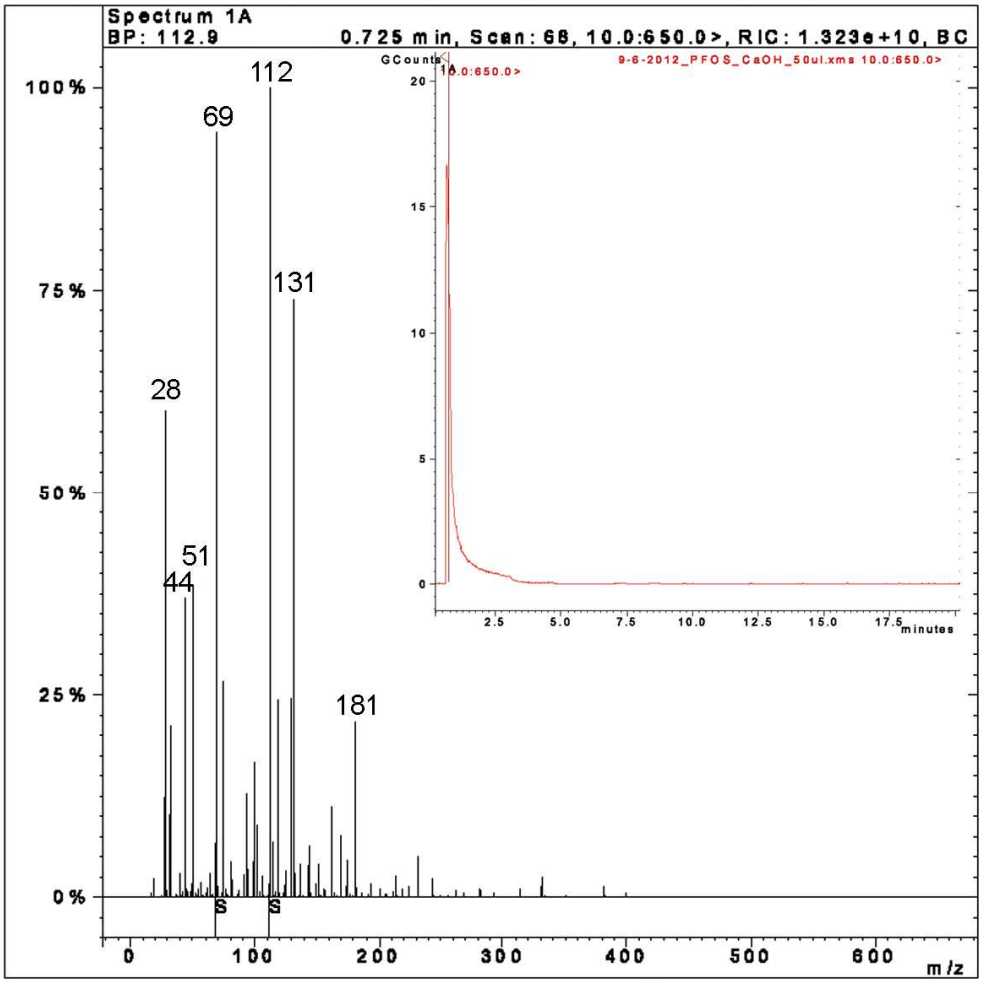


Figure S13. Full-scan mass spectrum of gas products derived from thermally treating PFOS + $Ca(OH)_2$ at 600 °C.

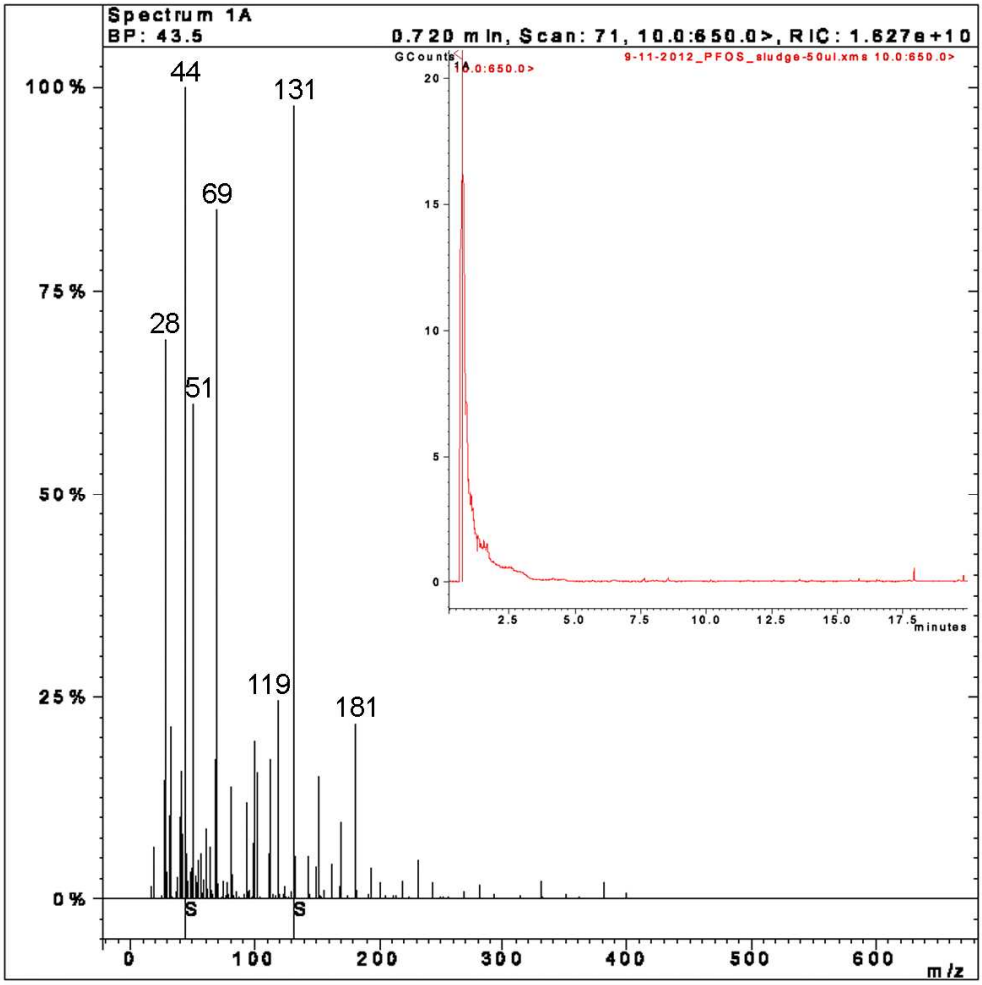


Figure S14. Full-scan mass spectrum of gas products derived from thermally treating PFOS + sludge at 600 °C.

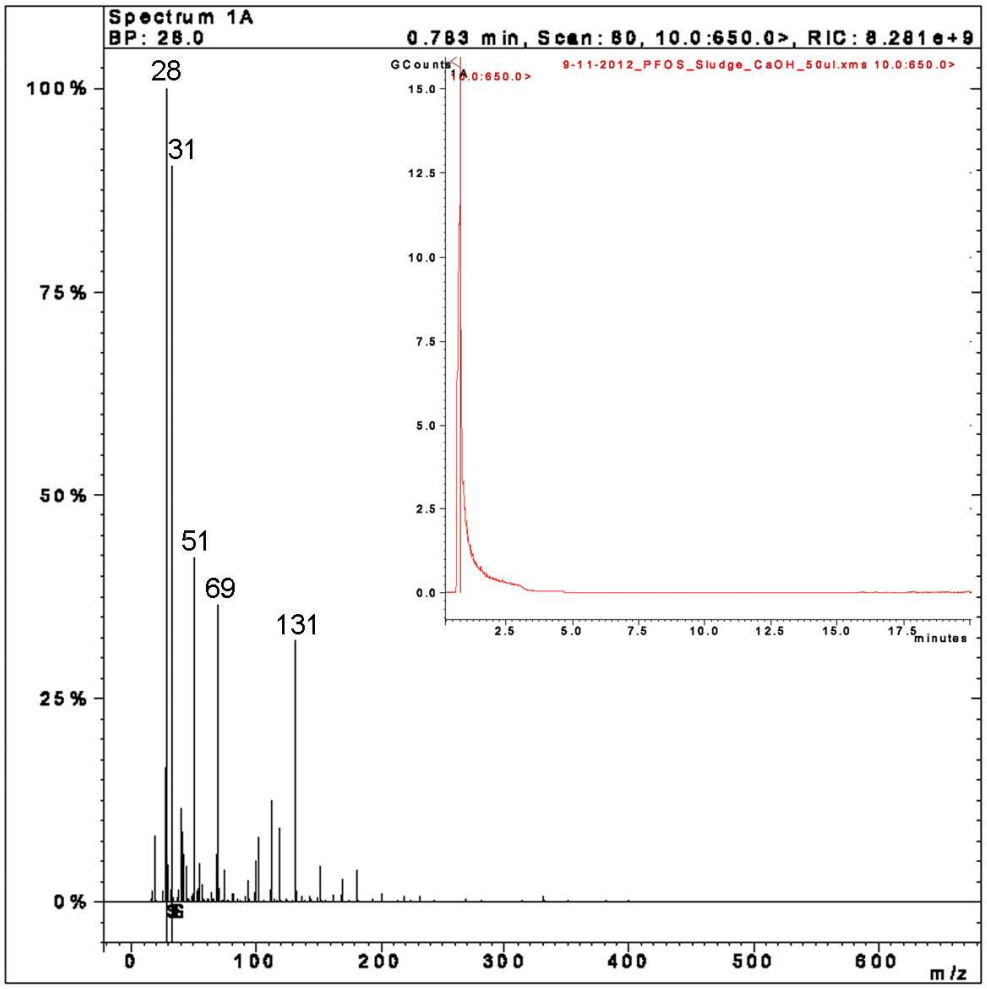


Figure S15. Full-scan mass spectrum of gas products derived from thermally treating PFOS+ $Ca(OH)_2$ + sludge at 600 °C.