

Table 2. Reaction models employed to fit the empirical data (adapted from Khawam and Flanagan, 2005b).

Model	Integral Rate law $g(\alpha) = kt$
Nucleation and Growth	
Power-law (P2)	$\alpha^{\left(\frac{1}{2}\right)}$
Power-law (P3)	$\alpha^{\left(\frac{1}{3}\right)}$
Power-law (P4)	$\alpha^{\left(\frac{1}{4}\right)}$
Avrami Erofeev (A2)	$[-\ln(1-\alpha)]^{\frac{1}{2}}$
Avrami Erofeev (A3)	$[-\ln(1-\alpha)]^{\frac{1}{3}}$
Avrami Erofeev (A4)	$[-\ln(1-\alpha)]^{\frac{1}{4}}$
Avrami Erofeev (An)	$[-\ln(1-\alpha)]^{\frac{1}{n}}$
Prout-Tompkins (B1)	$\ln\left[\frac{\alpha}{1-\alpha}\right]$
Geometrical contraction	
Contracting area (cylinder) (R2)	$[1-(1-\alpha)^{1/2}]$
Contracting volume (sphere) (R3)	$[1-(1-\alpha)^{1/3}]$
Diffusion	
1-D diffusion (D1)	α^2
2-D diffusion (D2)	$[(1-\alpha)\ln(1-\alpha)] + \alpha$
3-D diffusion (D3)	$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2$
Ginstling-Brounshtein (D4)	$1-\left(\frac{2\alpha}{3}\right)-(1-\alpha)^{2/3}$
Reaction-order	
Zero-order (F0)	α
First-order (F1)	$-\ln(1-\alpha)$
Second-order (F2)	$(1-\alpha)^{-1} - 1$
Third-order (F3)	$0.5\left((1-\alpha)^{-2} - 1\right)$

Table 3. Results of the hydrothermal experiments including, the initial mass of the samples, its mass change (%) after reaction, the porosity (%) calculated from the expected against actual mass change, the percentage of fluorite in each sample, and the overall rate at which fluorite formed in each experiment.

T (°C)	Reaction time (h)	m_{initial} (mg)	m_{decrease} (%)	pH_{final}	Porosity (%)	CaF_2 (%)	Reaction rate ($\text{mg}_{\text{CaF}_2}/\text{h}$)
60	1	76	1.7	8.1	16.2	7	7
60	2	76	3.3	8.2	17.6	15	7
60	3	73	4.0	8.3	18.2	17	6
60	4	73	5.1	8.3	19.1	21	5
60	8	73	6.3	8.4	20.1	28	4
60	16	76	9.3	8.6	22.7	45	3
60	24	76	11.7	8.7	24.7	59	2
60	32	76	13.2	8.7	26.0	67	2
60	48	76	15.9	8.8	28.3	86	2
80	1	76	2.9	8.1	17.2	13	13
80	2	76	5.2	8.4	19.2	20	10
80	4	76	6.7	8.5	20.5	30	7
80	8	71	10.4	8.6	23.7	49	6
80	16	76	13.4	8.7	26.2	66	4
80	24	76	16.3	8.8	28.7	87	4
100	1	76	5.5	8.4	19.5	25	25
100	2	76	9.0	8.5	22.4	40	20
100	3	73	11.0	8.6	24.2	51	17
100	4	68	12.6	8.6	25.5	58	15
140	1	74	10.0	8.5	23.3	46	46
140	2	75	13.7	8.7	26.4	64	32
140	3	76	16.6	8.8	29.0	84	28

Table 4. Calculated kinetic parameters (pre-exponential factor, A , and activation energy, E_a) using the model-fitting method for the isothermal experiments performed in this study.

Model	A (min^{-1})	E_a (kJ/mol)	r^2
P2	4.88×10^1	34	0.9721
P3	2.46×10^1	33	0.9637
P4	1.58×10^1	32	0.9590
A2	3.65×10^2	38	0.9911 ^b
A3	1.67×10^2	37	0.9860
A4	1.01×10^2	36	0.9824
An ^d	7.29×10^4	40	0.9925 ^b
B1	6.88×10^2	36	0.9814
R2	2.99×10^2	39	0.9952 ^b
R3 ^d	2.86×10^2	40	0.9949
D1 ^{c,d}	7.32×10^2	41	0.9968 ^b
D2	8.06×10^2	42	0.9897
D3	3.96×10^2	43	0.9732
D4	2.38×10^2	43	0.9848
F0	1.88×10^2	37	0.9895
F1 ^d	1.69×10^3	41	0.9906 ^b
F2	8.60×10^3	43	0.9530
F3	2.37×10^4	42	0.9073

a) Correlation coefficient $g(\alpha)$ vs t (min).

b) Equivalent models based on goodness of fit.

c) Model selected based on model-fitting method.

d) Models that E_a resulted to be equal to the E_a calculated with the model-free method (41(1) kJ/mol).