Supplementary Data

Characterization, Kinetic Using Deconvolution Techniques and Thermodynamic Studied of Synthetic MgHPO$_4$·3H$_2$O

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Kinetic model assumptions

The models are classified based on the mathematic assumptions about the including nucleation, geometric shape, diffusion, and reaction order. The details will be described as follow.

1) Nucleation and growth

Energy fluctuation of crystal due to imperfection (i.e. impurities, surface, edges, dislocations, cracks, and point defection) may overcome the barriers and lead to a new product. There are three assumptions that used to describe the nucleation rates such as instantaneous nucleation, single-step nucleation (expressing the exponential and linear laws), and multi-step nucleation (giving power law). For a single-step nucleation, assumed that the nucleation and nuclei growth occur in a single step. The rate (dN/dt) equation of the nuclei forming at time t (N), as a simple first-order process is expressed by following Eq. (S1)

$$\frac{dN}{dt} = k_N(N_0 - N) \tag{S1}$$

where N_0 is the probable nuclei forming site and k_N is the nucleation rate constant. Integration of Eq. (S1) gives

$$N = N_0(1 - e^{-k_N t}) \tag{S2}$$

Differentiating Eq. (S2) yields the exponential law Eq. (S3).

$$\frac{dN}{dt} = k_N N_0 e^{-k_N t} \tag{S3}$$

From Eq. (S3), when k_N is small, the equation can be written as Eq. (S4) representing the linear law.

$$\frac{dN}{dt} = k_N N_0 \tag{S4}$$

When k_N is very large, Eq. (S4) become instantaneous law (Eq. (S5)).

$$\frac{dN}{dt} = \infty \tag{S5}$$

According to Bagdassarian's expression, the nucleation rate of multi-step are power law (Eq. (S6)).

$$N = \frac{N_0(k_i t)^\beta}{\beta!} = Dt^\beta \tag{S6}$$

where, $D = N_0(k_i)^\beta/\beta!$. Differentiation of Eq. (S6) gives the equation

$$\frac{dN}{dt} = D\beta t^{\beta-1} \tag{S7}$$

Beside the nucleation rates based on several assumptions are shown in Table S1.

Table S1   Mathematical expressions for nucleation rates law [1].

Nucleation rate law	Differential form dN/dT	Integral form
Exponential	$k_N N_0 e^{-k_N t}$	$N_0(1 - e^{-k_N t})$
Linear	$k_N N_0$	$k_N N_0 t$
Instantaneous	∞	N_0
Power	$D\beta t^{\beta-1}$	Dt^β

Nuclei growth rate ($G(x)$) is expressed through the nuclei growth radius $r(t,t_0)$ at time t and if t_0 is the formation time, the rate of nuclei growth can be written as

$$r(t, t_0) = \int_{t_0}^{t} G(x)dx \tag{S8}$$

The nuclei growth radius are considered in terms of nucleus shape factor (σ) and number of growth dimension (λ), which these factors depend on volume occupied by individual nuclei $v(t)$. The volume occupied by a single nucleus can be written as the equation

$$v(t) = \sigma[r(t, t_0)]^\lambda \tag{S9}$$

The combination between the nucleation rate (dN/dt) and the nuclei growth rate ($v(t)$) leading to the total volume occupied by all nuclei, $V(t)$ gives the equation as followed

$$V(t) = \int_0^t v(t)\left(\frac{dN}{dt}\right)_{t=t_0} dt_0 \tag{S10}$$

Substitutions of Eqs. (S8) and (S9) into Eq. (S10) yields

$$V(t) = \int_0^t \sigma\left(\int_{t_0}^t G(x)dx\right)^\lambda \left(\frac{dN}{dt}\right)_{t=t_0} dt_0 \tag{S11}$$

Under various assumptions of the nucleation rate law (such as in Table 2.3), therefore Eq. (S11) can be transformed to be numerous different mathematical mechanism functions as shown in Table S2.

Table S2 Algebraic expressions of kinetic functions $f(\alpha)$ and $g(\alpha)$ and its corresponding mechanism [2].

No.	Mechanism	Name of the kinetic function	$f(\alpha)$	$g(\alpha)$	Rate-determining mechanism
I. Chemical process or mechanism non-invoking equations					
1.	$F_{1/3}$	One-third order	$(3/2)(1-\alpha)^{1/3}$	$1-(1-\alpha)^{2/3}$	Chemical reaction
2.	$F_{3/4}$	Three-quarters order	$4(1-\alpha)^{3/4}$	$1-(1-\alpha)^{1/4}$	Chemical reaction
3.	$F_{3/2}$	One and a half order	$2(1-\alpha)^{3/2}$	$(1-\alpha)^{-1/2}-1$	Chemical reaction
4.	F_2	Second order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$	Chemical reaction
5.	F_3	Third order	$(1/2)(1-\alpha)^3$	$(1-\alpha)^{-2}-1$	Chemical reaction
II. Acceleratory rate equations					
6.	$P_{3/2}$	Mampel power law	$(2/3)\,\alpha^{-1/2}$	$\alpha^{3/2}$	Nucleation
7.	$P_{1/2}$	Mampel power law	$2\alpha^{1/2}$	$\alpha^{1/2}$	Nucleation
8.	$P_{1/3}$	Mampel power law	$3\alpha^{2/3}$	$\alpha^{1/3}$	Nucleation
9.	$P_{1/4}$	Mampel power law	$4\alpha^{3/4}$	$\alpha^{1/4}$	Nucleation
10.	E1	Exponential law	α	$\ln\alpha$	Nucleation
III. Sigmoidal rate equations or random nucleation and subsequent growth					
11.	A_1, F_1	Avrami–Erofeev eq.	$(1-\alpha)$	$-\ln(1-\alpha)$	Assumed random nucleation and its subsequent growth, n = 1
12.	$A_{3/2}$	Avrami–Erofeev eq.	$(3/2)(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$	Assumed random nucleation and its subsequent growth, n = 1/2
13.	A_2	Avrami–Erofeev eq.	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$	Assumed random nucleation and its subsequent growth, n = 2
14.	A_3	Avrami–Erofeev eq.	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$	Assumed random nucleation and its subsequent growth, n = 3
15.	A_4	Avrami–Erofeev eq.	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$	Assumed random nucleation and its subsequent growth, n = 4
16.	A_u	Prout-Tomkins eq.	$\ln[\alpha/(1-\alpha)]$	$\alpha(1-\alpha)$	Branching nuclei

Table S2 Algebraic expressions of kinetic functions $f(\alpha)$ and $g(\alpha)$ and its corresponding mechanism [2] (cont.).

No.	Mechanism	Name of the kinetic function	$f(\alpha)$	$g(\alpha)$	Rate-determining mechanism
IV. Deceleratory rate equations IV.I Phase boundary reaction					
17.	R_1, F_0, P_1	Power law	$(1-\alpha)^0$	α	Contracting disk
18.	$R_2, F_{1/2}$	Power law	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$	Contracting cylinder (cylindrical symmetry)
19.	$R_3, F_{2/3}$	Power law	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$	Contracting sphere (spherical symmetry)
IV.II Based on the diffusion mechanism					
20.	D_1	Parabola low	$1/2\alpha$	α^2	One-dimensional diffusion
21.	D_2	Valensi eq.	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$	Two-dimension diffusion
22.	D_3	Jander eq.	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion, spherical symmetry
23.	D_4	Ginstling–Brounstein eq.	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$	$1-2\alpha/3-(1-\alpha)^{2/3}$	Three-dimensional diffusion, cylindrical symmetry
24.	D_5	Zhuravlev, Lesokin, Tempelman eq.	$(3/2)(1-\alpha)^{4/3}[(1-\alpha)^{-1/3}-1]^{-1}$	$[(1-\alpha)^{-1/3}-1]^2$	Three-dimensional diffusion
25.	D_6	anti-Jander eq.	$(3/2)(1+\alpha)^{2/3}[(1+\alpha)^{1/3}-1]^{-1}$	$[(1+\alpha)^{1/3}-1]^2$	Three-dimensional diffusion
26.	D_7	anti-Ginstling-Brounstein eq.	$(3/2)(1+\alpha)^{-1/3}-1]^{-1}$	$1+2\alpha/3-(1+\alpha)^{2/3}$	Three-dimensional diffusion
27.	D_8	anti-Zhuravlev, Lesokin, Tempelman eq.	$(3/2)(1+\alpha)^{4/3}[(1+\alpha)^{-1/3}-1]^{-1}$	$[(1+\alpha)^{-1/3}-1]^2$	Three-dimensional diffusion
V. Another kinetics equations with unjustified mechanism					
28.	G_1		$1-(1-\alpha)^2$	$1/2(1-\alpha)$	
29.	G_2		$1-(1-\alpha)^3$	$1/3(1-\alpha)^2$	
30.	G_3		$1-(1-\alpha)^4$	$1/4(1-\alpha)^3$	
31.	G_4		$[-\ln(1-\alpha)]^2$	$1/2(1-\alpha)[-\ln(1-\alpha)]^{-1}$	
32.	G_5		$[-\ln(1-\alpha)]^3$	$1/3(1-\alpha)[-\ln(1-\alpha)]^{-2}$	
33.	G_6		$[-\ln(1-\alpha)]^4$	$1/4(1-\alpha)[-\ln(1-\alpha)]^{-3}$	
34.	G_7		$[1-(1-\alpha)^{1/2}]^{1/2}$	$4\{(1-\alpha)[1-(1-\alpha)]^{1/2}\}^{1/2}$	
35.	G_8		$[1-(1-\alpha)^{1/3}]^{1/2}$	$6\{(1-\alpha)^{2/3}[1-(1-\alpha)]^{1/3}\}^{1/2}$	

Power Law (P) Models:

When the nucleation rate follows the power law (Table S1) and nuclei growth is assumed to be constant ($G(x) = k_G$). The Eq. (S11) can be written as

$$V(t) = \int_0^t \sigma(k_G(t - t_0))^\lambda (D\beta t_0^{\beta-1})dt_0 \qquad (S12)$$

Integrating Eq. (S12) gives

$$V(t) = \sigma k_G^\lambda D\beta t^{\beta+\lambda}(1 - \frac{\lambda\beta}{\beta+1} + \frac{\lambda(\lambda-1)}{2!} \cdot \frac{\beta}{\beta+2} \dots), \lambda \leq 3$$

where, $n = \beta + \lambda$. The equation change to be

$$V(t) = \sigma k_G^\lambda D' t^n \qquad (S13)$$

where, $D' = D\beta(1-\lambda\beta/(\beta+1))+\lambda(\lambda-1)/2!\cdot\beta/(\beta+2)$. $V(t)$ is directly proportional to the degree of conversion α

$$\alpha = V(t) \cdot C \qquad (S14)$$

C is a constant, $C = 1/V_0$ and V_0 is an initial volume. Substituting Eq. (S14) into (S13) leads to Eq. (S15) after the new rearrangement.

$$\alpha = (kt)^n$$

or
$$kt = \alpha^{1/n} \qquad (S15)$$

where $k = (\sigma k_G^\lambda CD')^{1/n}$ as the rate constant. Eq. (S15) represent the power law (P) models as various n-orders. The P models is the acceleratory, which assume that nuclei growth is constant without restrictions.

Avrami-Erofeyev (A) Models:

The nuclei growth restrictions always occur in solid state decomposition. There are two restriction types found on nuclei growth such as (i) coalescence: loss of reaction interface by overlapping of nuclei and (ii) ingestion: elimination of nucleation site, ingestion site dosed not produce the product called "phantom nuclei". At time t, the total number of possible nuclei forming sits (N_0) can be expressed by

$$N_0 = N(t) + N_1(t) + N_2(t)$$

where, $N(t)$ is the number of nuclei activated, $N_1(t)$ is the actual number of nuclei, and $N_2(t)$ is the number of nuclei ingested. Therefore, the actual number of nuclei equal to

$$N_1(t) = N_0 - N(t) - N_2(t) \tag{S16}$$

Based on Eq. (S12), substituting the nucleation rate by exponential law gives

$$V(t) = \int_0^t \sigma(k_G(t - t_0))^\lambda (k_N N_0 e^{-k_N t}) dt \tag{S17}$$

Eq. (S17) is impossible to solve. Avrami [1] has proposed the extended conversion fraction α_E, which include the effect of restrictions (the overlapping of nucleation and ingestion of the nucleation) as following the equation

$$d\alpha_E = \frac{1}{(1-\alpha)}.d\alpha \tag{S18}$$

integrating Eq. (S18) yields

$$\alpha_E = \int_0^\infty \frac{1}{(1-\alpha)} d\alpha = -\ln(1 - \alpha) \tag{S19}$$

According to Eq. (S15), which neglect the restricted nucleation, instead α by α_E, the equation change to be

$$(kt)^n = -\ln(1 - \alpha)$$
$$kt = [-ln(1 - \alpha)]^{1/n} \tag{S20}$$

Eq. (2.36) agree with the research reported by Johnson, Mehl, Avrami, Erofeyev, and Kholmogorov [**Error! Bookmark not defined.**], therefore the A models with different n-order may be called the JMAEK models.

2.) Geometrical Contraction (R) Models

Based on assumption that the nucleation occur rapidly on the surface and the rate of decomposition is controlled by the reaction progresses toward from into center of crystal. The radius at time t (r) can be derive as

$$r = r_0 - kt \tag{S21}$$

where, r_0 is the radius of at time t_0 and k is the rate constant. The mathematical models are different depending on crystalline shape.

The contracting cylinder (contracting area) or R$_2$ model:

The volume of cylindrical structure equal to $h\pi r^2$, where h is the cylindrical height and r^2 is the cylindrical radius. The volume of n molecules is $nh\pi r^2$. From the description of the conversion fraction α ($\alpha = \frac{m_i - m_t}{m_i - m_f}$), which assume that $m_f = 0$, hence

$$\alpha = \frac{m_0 - m_t}{m_0} \tag{S22}$$

when, weight = volume $\times$ density (ρ), therefore α can be expressed as follow.

$$\alpha = \frac{n\rho h\pi r_0^2 - n\rho h\pi r^2}{n\rho h\pi r_0^2}$$

$$\alpha = \left(1 - \frac{r^2}{r_0^2}\right) \tag{S23}$$

substituting Eq. (S221) into Eq. (S22) followed by the arrangement yields

$$\alpha = 1 - \left(\frac{r_0 - kt}{r_0}\right)^2$$

$$1 - \alpha = \left(1 - \frac{k}{r_0}t\right)^2 \qquad \text{(S24)}$$

If $k/r_0 = k_0$, Eq. (S24) will be changed to Eq. (S25), which represents the contracting cylinder (contracting area) or R_2 models as followed

$$1 - (1 - \alpha)^{1/2} = k_0 t \qquad \text{(S25)}$$

The contracting sphere/cube (contracting volume) R_3 or model:

For n number of spherical or cubical shape of crystalline solid, the volume equal to $n4h\pi r^3/3$ and the weight can be written as

$$\text{weight} = \frac{4}{3}n\rho\pi r^3 \qquad \text{(S26)}$$

The conversion fraction in Eq. (2.38) can be expressed as

$$\alpha = \frac{\frac{4}{3}n\rho\pi r_0^3 - \frac{4}{3}n\rho\pi r^3}{\frac{4}{3}n\rho\pi r_0^3}$$

$$\alpha = \left(1 - \frac{r^3}{r_0^3}\right) \qquad \text{(S27)}$$

Substitution of r from Eq. (S21), the Eq. (S27) will be in the form of Eq. (S28)

$$\alpha = 1 - \left(\frac{r_0 - kt}{r_0}\right)^3$$

$$1 - \alpha = \left(1 - \frac{k}{r_0}t\right)^3 \qquad \text{(S28)}$$

If $k/r_0 = k_0$, the Eq. (S28) will be changed to the contracting sphere/cube (contracting volume) or R_3 model as shown in Eq. (S29).

$$1 - (1 - \alpha)^{1/3} = k_0 t \qquad \text{(S29)}$$

3.) Diffusion (D) Models

Homogeneous solid-state reaction, which occurs between crystal lattices or with molecules that permeate into lattices, where motion is restricted and is dependent on lattices defect. The reaction rate is controlled by the lattice movement from the reaction interface. Therefore, the rate of diffusion-controlled reactions decreases proportionally with the thickness of the product barrier.

In one-dimensional diffusion through a flat plane as showed in Figure S1. When A and B are reactants, AB is the product, l is the thickness of the interface, and x is the distance from product AB to interface Q.
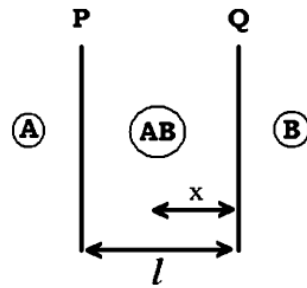
Figure S1   One-dimensional diffusion through a flat plane [1]

According to Figure S1, the mass of B moving across P (unit area) in time dt to form product AB is

$$\frac{dl}{dt} = -D\frac{M_{AB}}{M_B\rho}\frac{dC}{dx} \tag{S30}$$

where, M_{AB} and M_B are the molecular weight of product AB and reactant B, respectively, D is the diffusion coefficient, ρ is the density of product, and C is the concentration. Based on assumption that the concentration of B has a linear relationship with that of AB. $dC/dx|_{x=l} = -(C_2 - C_1)/l$, where C_2 and C_1 are the concentration of B at interfaces P and Q, respectively, Eq. (S30) can be written as

$$\frac{dl}{dt} = D\frac{M_{AB}}{M_B\rho}\frac{(C_2-C_1)}{l} \tag{S31}$$

Integrating Eq. (S31) gives

$$l^2 = 2D \frac{M_{AB}(C_2 - C_1)}{M_B \rho} t \qquad \text{(S32)}$$

when, $k = 2D[M_{AB}(C_2 - C_1)]/M_B\rho$, the equation can be reduced to be

$$l^2 = kt \qquad \text{(S33)}$$

Eq. (2.49) is the parabolic law, which is the simplest rate equation and suitable for an infinity flat plane without the consideration of a shape factor. The conversion fraction α is directly proportional to the product layer l, therefore, Eq. (S33) leads to the one-dimensional diffusion (D$_1$) model as followed

$$\alpha^2 = k't \qquad \text{(S34)}$$

Based on the assumption that the spherical particles (Figure S2) can follow the mathematical equation representing the three-dimensional diffusion (D$_3$) model.
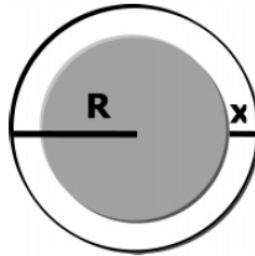
Figure S2   Schematic representation of a spherical reaction [1]

According to Eq. (S22) and the definition of the spherical volume, the conversion fraction is derived to be

$$\alpha = \frac{\frac{4}{3}n\rho\pi R^3 - \frac{4}{3}n\rho\pi(R-x)^3}{\frac{4}{3}n\rho\pi R^3}$$

$$\alpha = 1 - \left(\frac{R-x}{R}\right)^3$$

After the mathematical arrangement, Eq. (S35) is obtained.

$$x = R(1 - (1 - \alpha)^{1/3}) \qquad \text{(S35)}$$

From Eq. (S35), Jander [1] used the parabolic law (Eq. (S34)) to define x and substituted into Eq. (S35). The equation can be written as

$$R^2(1 - (1 - \alpha)^{1/3})^2 = kt \qquad \text{(S36)}$$

when $k' = k/R^2$, Eq. (S36) becomes the D3 (Jander) model and the equation is expressed as

$$(1 - (1 - \alpha)^{1/3})^2 = k't \qquad \text{(S37)}$$

The Jander model (Eq. (S37)) is oversimplified and can used at low x/R values. However, there are many assumptions used to derive various diffusion controlled models.

4.) Reaction order (F) Models

In homogenous kinetics, the reaction order (F) models are the simplest models controlling the mechanism. Under the assumption that the rate is proportional to concentration, conversion fraction of reactants raise to a power, which is the reaction order. The general equation of the reaction order model is

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \qquad \text{(S38)}$$

where, n is the reaction order. At $n = 0$, Eq. (S38) become the zero-order (F0/R1) model as the differential form

$$\frac{d\alpha}{dt} = k \qquad \text{(S39)}$$

which corresponds to the following integral form

$$\alpha = kt \qquad \text{(S40)}$$

If $n = 1$, the first-order (F$_1$) model can be obtained as in Eq. (S41), which is in the differential form.

$$\frac{d\alpha}{dt} = k(1 - \alpha) \qquad \text{(S41)}$$

The integral form is shown in Eq. (2.58)

$$-ln(1 - \alpha) = kt \qquad \text{(S42)}$$

This F$_1$ model shown in Eq. (S42) may be called the Mampel model as a particular case of the A models when $n = 1$.

References

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