RUN HUANG
XUEWEI LV
CHENG PAN
DONGHAI LI
ENGUANG GUO

College of Materials Science and Engineering, Chongqing University, Chongqing, China

KINETICS OF THE DECOMPOSITION REACTION OF PHOSPHORITE CONCENTRATE

Article Highlights
- The dolomite decomposes and reacts with SiO_2 at 1250 °C
- The mass loss reaction is caused by the decomposition of the dolomite
- The activation energy of the decomposition of the dolomite is 71.6-123.6 kJ/mol
- The mechanism equation agrees with the Valensi Equation and G-B Equation

Abstract

Apatite is a raw material mainly used in phosphate fertilizer, and partly used in yellow phosphorus, red phosphorus, and phosphoric acid in the industry. With the decrease of the high-grade phosphorite lump, the agglomeration process is necessary for the phosphorite concentrate after the beneficiation process. The decomposition behavior and the phase transformation are of vital importance for the agglomeration process of phosphorite. In this study, the thermal kinetic analysis method was used to study the kinetics of the decomposition of phosphorite concentrate. The phosphorite concentrate was heated at various heating rates, and the phases in the heated sample were examined by X-ray diffraction. It was found that the main phases in the phosphorite are fluorapatite $Ca_5(PO_4)_3F$, quartz SiO_2, and dolomite $CaMg(CO_3)_2$. The endothermic DSC peak corresponding to the mass loss caused by the decomposition of dolomite covers from 600-850 °C. The activation energy of the decomposition of dolomite, which increases with the increase in the extent of conversion, is about 71.6-123.6 kJ/mol. The mechanism equation for the decomposition of dolomite agrees with the Valensi Equation and G-B Equation.

Keywords: phosphorite, kinetics, activation energy, reaction mechanism.

Apatite is the main raw material for the preparation of phosphorous fertilizers and inorganic acids in the chemical industry. As the resources of high-grade phosphate mineral decrease worldwide, more attention should be paid to low grade ores, which have relatively low contents of useful components and high contents of concomitant minerals such as carbonates, silicates, etc. The phosphorite is reduced by coke or coal in an electric arc furnace (EAF) to get phosphorus into the gas phase because of the high vapor pressure and, finally, P_4 will precipitate out of the furnace once the temperature decreases. The carbonates and the fluorides are always contained in the

phosphorite minerals, which can decompose during the heating process and consume electric energy. Therefore, a pretreatment process before the EAF process, in which the carbonates and fluorides decompose, was suggested for reducing the electric energy. On the other hand, as the high-grade phosphorite lump resources are declining, the low-grade phosphorite needs to be upgraded through the milling and beneficiation process. In this case, the agglomeration process is necessary for the phosphorite concentrate. Based on decomposition and agglomeration, a "sintering process" was suggested for the phosphorite concentrate [1-3]. Although the iron ore sintering process has been well known and controlled now, phosphorite sintering has been less studied and differs from the typical sintering process (high decomposition ratio). The decomposition behavior and the phase transformation of phosphorite [4-6], which refers to the phase transformation and the kinetics of

Correspondence: X. Lv, College of Materials Science and Engineering, Chongqing University, Chongqing, 400044, China.
E-mail: lvxuewei@163.com

the decomposition, is of vital importance for the sintering of phosphorite. Although the agglomeration process like sintering and pelletizing has been used to supply the excellent material of the EAF process, the kinetics of the decomposition of the phosphorite have been studied less. Thermal analysis techniques, including thermogravimetry (TG) and differential scanning calorimetry (DSC), are very useful methods for studying the mechanism and kinetics of the reactions, especially for the decomposition reaction. Therefore, the thermal kinetic analysis (TKA) method was used to investigate the kinetics of the decomposition of phosphorite in this study.

EXPERIMENTAL

The DSC and TG measurements were carried out with using a Netzch STA 449C thermal analyzer. The material used in the measurements was phosphate from Leshan, China, which was concentrated by grinding and flotation. The particle size of all the powder of phosphorite concentrate used in this experiment was smaller than 74 µm, and the particle size distribution was measured using a Malvern MS 2000 laser diffractometer in the measuring range 0.02-2000 µm. The maximum heating temperature was fixed at 1300 °C, and the heating rates were 15, 20, 25 and 30 °C/min. Before each experiment, the phosphorite concentrate powder was completely dried at 110 °C for 240 min, and then loaded in the Pt crucible in argon atmosphere. In order to know the change in phase composition during the heating process, the samples of phosphorite powder were pelletized and calcined at the fixed temperature for two hours. The samples calcinated at various temperatures were examined with XRD analysis, which was carried out using D/MAX 3C (CuKα).

Theoretical background

Thermal kinetic analysis methods have developed very fast in the recent years, especially, the non-isothermal methods like the iso-conversional method [7-11]. These methods involve triple factors named E, A and $f(\alpha)$ which means activation energy, pre-exponential factor and mechanism function.

$$d\alpha / dT = \left(\frac{1}{\beta}\right) A \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (1)$$

where α, T and β are the extent of conversion, temperature, and heating rate, respectively. The temperature at time t (min) can be written as:

$$T_t = T_0 + \beta t \qquad (2)$$

Separating variables, and taking the temperature integral of Eq. (1), which can be called the Flynn-Wall-Ozawa (FWO) [12] method gives:

$$\lg \beta = \lg\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT} \qquad (3)$$

where $G(\alpha)$ is the integral expression of the mechanism function of the kinetics. Therefore, the method of FWO is a kind of integration. In addition, the differential method can also be used to solve Eq. (1), which leads to the expression:

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = \frac{d\alpha}{dt}\left[\frac{E\frac{dT}{dt}}{RT^2} - An(1-\alpha)^{n-1}\exp\left(-\frac{E}{RT}\right)\right] \qquad (4)$$

where n and α are related by the mechanism function as follows:

$$f(\alpha) = (1-\alpha)^n \qquad (5)$$

where $f(\alpha)$ is the differential expression of the mechanism function. The left hand side of Eq. (4) equals zero when $T = T_p$, which means the temperature when the reaction rate gets the highest value. Then, the right hand side of Eq. (4) can be rewritten as:

$$\frac{E\frac{dT}{dt}}{RT_p^2} = An(1-\alpha_p)^{n-1}\exp\left(-\frac{E}{RT_p}\right) \qquad (6)$$

Kissinger [13] assumed that the part of $n(1-\alpha_p)^{n-1}$, whose approximate value is 1, has no relation to β. Therefore, Eq. (6) was simplified as follows:

$$\frac{E\beta}{RT_p^2} = A\exp\left(-\frac{E}{RT_p}\right) \qquad (7)$$

Taking logarithm of the two sides of the equation according to the KAS (Kissinger-Akahira-Sunose) method [13], gives:

$$\ln\left(\frac{\beta_i}{RT_{pi}^2}\right) = \ln\frac{AR}{E} - \frac{E}{RT_{pi}} \qquad (8)$$

where T_{pi} and β_i are the temperatures at the highest reaction rate and heating rate, respectively.

Starink [14] recently reviewed the methods of KAS and FWO [12], and gave a universal form of the equation of temperature integral:

$$\ln\left(\frac{\beta}{T^{1.8}}\right) = -\frac{1.0037E}{RT} + Constant \qquad (9)$$

Hu, Gao and Zhang [15] (HuGZ) got another equation for the integral type of the kinetic equation as:

$$\ln\left(\beta\Big/T^{1.882}\right) = \left\{\ln\left[\frac{AE}{RG(\alpha)}\right] + 3.985 - 1.882\ln E\right\} - \frac{1.002E}{RT}$$ (10)

Eq. (1) can also be re-written as:

$$\beta\frac{d\alpha}{dT} = \exp\left(-\frac{E}{RT}\right)Af(\alpha)$$ (11)

Taking the logarithm of the two sides of Eq. (11), the Friedman-Reich-Levi method can be derived [16]:

$$\ln\left(\beta\frac{d\alpha}{dT}\right) = \ln\left[Af(\alpha)\right] - \frac{E}{RT}$$ (12)

Coats and Redfern [17] showed an equation as:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = G(\alpha) = \frac{ART^2}{E\beta}\exp\left(-\frac{E}{RT}\right)$$ (13)

Comparing Eq. (13) with Eq. (1), the following equation can be given:

$$G(\alpha) = \frac{RT^2}{E\beta}\frac{d\alpha}{dt}\frac{1}{f(\alpha)}$$ (14)

When α equals to 0.5, Eq. (14) can be transformed as:

$$G(0.5) = \frac{RT_{0.5}^2}{E\beta}\left(\frac{d\alpha}{dt}\right)_{0.5}\frac{1}{f(0.5)}$$ (15)

where $T_{0.5}$ and $d\alpha/dt$ are the temperature and reaction rate, respectively, when extent of conversion equals to 0.5. When Eq. (14) divided by Eq. (15), the expression of $y(\alpha)$ can be written as:

$$y(\alpha) = \left(\frac{T}{T_{0.5}}\right)^2\frac{\left(\dfrac{d\alpha}{dt}\right)}{\left(\dfrac{d\alpha}{dt}\right)_{0.5}} = \frac{f(\alpha)G(\alpha)}{f(0.5)G(0.5)}$$ (16)

The kinetic mechanism equation $f(\alpha)$ and $G(\alpha)$ frequently used or the standard "$y(\alpha)$-α" curves can be found for determining the reaction progress by comparing the experimental curves with the theoretical curves.

RESULTS AND DISCUSSION

The chemical composition of the phosphorite concentrate obtained by wet chemical analysis is shown in Table 1. The main phases in the phosphorite concentrate are fluorapatite $Ca_5(PO_4)_3F$, quartz SiO_2 and dolomite $CaMg(CO_3)_2$, which are the same as given in literature [18]. The medium particle size ($d(0.5)$) was about 83.3 μm (more details were shown in our previous study [19]).

The TG and DSC curves at various heating rates (Figure 1) show that the total mass loss of the sample is about 5.4% when the temperature reaches 1300 °C.

Table 1. Chemical composition of phosphorite concetrate

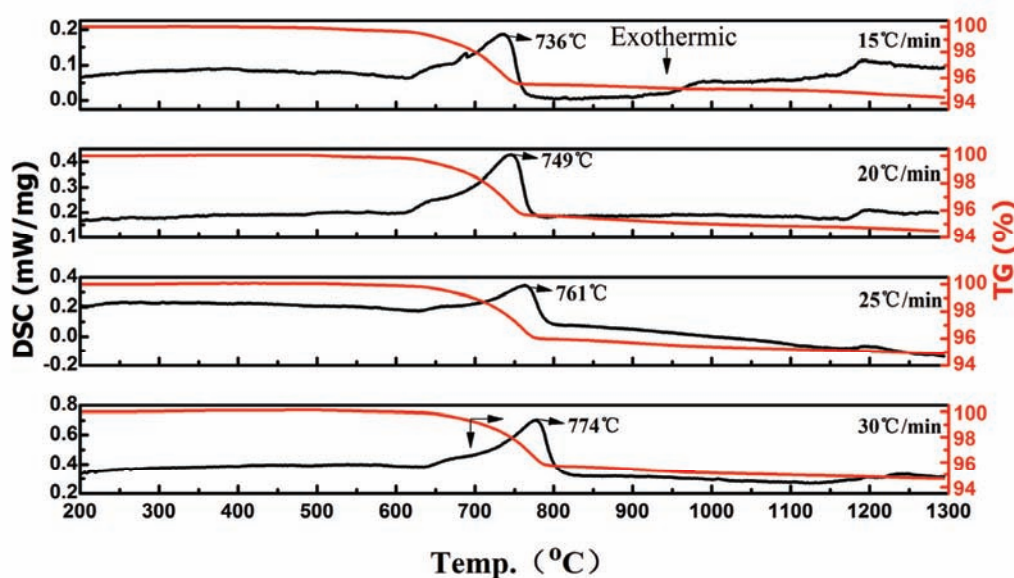| Component	SiO2	Fe2O3	Al2O3	CaO	MgO	P2O5	F
Content, mass%	16.99	0.56	1.35	45.07	2.26	31.2	2.85

Figure 1. TG and DSC pattern at various heating rates.

The decomposition reaction is endothermic and the endothermic DSC peak covers the range 600-850 °C. As the heating rate increases, the mass loss and the endothermic peak shift to higher temperatures. Characteristic parameters of decomposition reaction and the endothermic DSC peak with various heating rate were extracted and listed in Table 2. The onset, mid, and end temperature of the mass loss increased with the increase in heating rate. On the other hand, the total mass loss percentage of the reaction also increased with the increase of heating rate. However, when the heating rate was higher than 25 °C/min, the total of mass loss percentage increased only slightly. The relationship between the extent of conversion and the temperature at various heating rates is shown in Figure 2. It indicates that the start temperature of

the decomposition reaction becomes higher with increasing heating rate. From the data in Figure 2 and the model shown by Eqs. (3)-(12), the activation energy of the decomposition reaction can be calculated and the results are plotted in Figure 3.

Table 2. Characteristic parameters of decomposition reaction at various heating rates

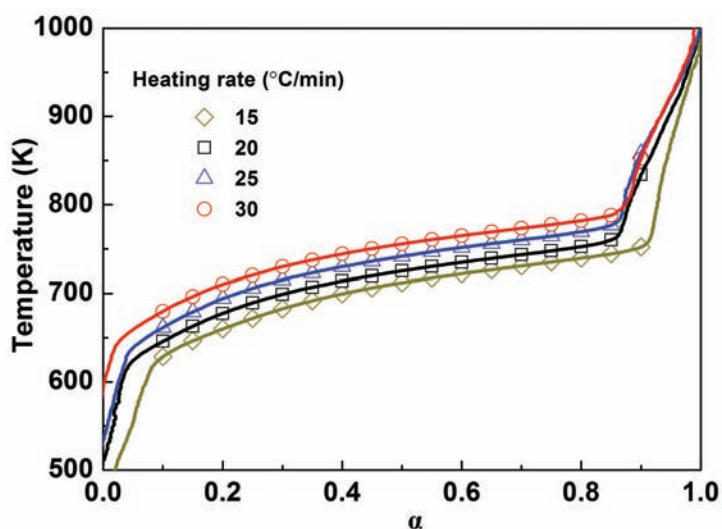| Parameter	Heating rate, °C/min			
	15	20	25	30
Onset temperature, °C	687	702	707	719
Mid temperture, °C	736	745	764	776
End temperature, °C	748	758	774	788
Mass loss, %	4.48	4.53	4.67	4.69
Area, J/g	33.77	39.07	48.66	51.45

Figure 2. Relationship between extent of conversion and temperature.
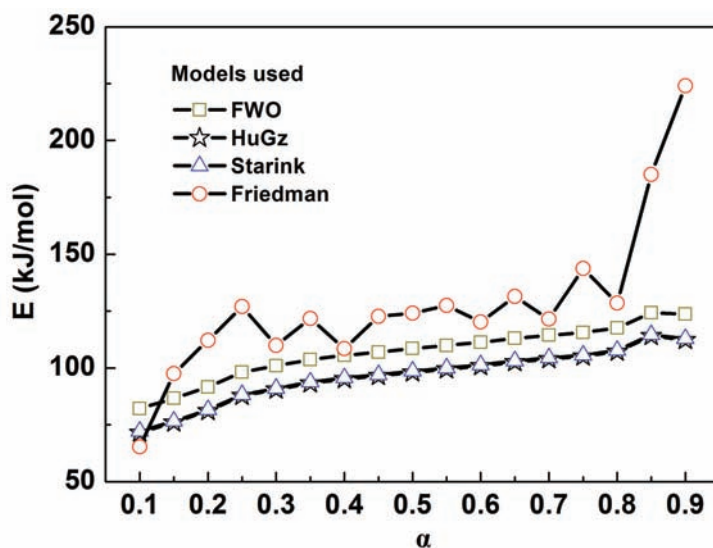

Figure 3. Activation energy versus extent of conversion.

The results show that the activation energy calculated by the Friedman model fluctuates with the extent of conversion; however, the results from models like FWO, HuGZ and Starink show relatively constant values of activation energy with the extent of conversion, and the activation energy increases slightly with reaction progress. The correlation coefficients of the model fitting are shown in Figure 4. The correlation coefficients calculated by the model of Friedman change greatly from 0.95 to 0.99. The correlation coefficients calculated by other models are relatively constant. However, the correlation coefficients calculated by FWO, HuGZ and Starink models are very low when the extent of conversion is 0.9, only about 0.5, and the correlation coefficient calculated by model of Friedman is higher than other models when the extent of conversion is 0.9. The probable reason for this phenomenon is that as the curves of extent of conversion with the temperature get close to each other, the influence of the measuring error on the calculation becomes great. Therefore, the activation energy calculated by the FWO, HuGZ and Starink models are credible only when the extent of conversion is less than 0.9. The activation energy varies from 71.6 to 123.6 kJ/mol.

The phase composition of the phosphorite after decomposition is shown in Figure 5. It can be seen that dolomite $CaMg(CO_3)_2$ decomposes with increasing temperature, the diffraction peak of dolomite disappears at 700 °C, and the CaO and MgO are formed.
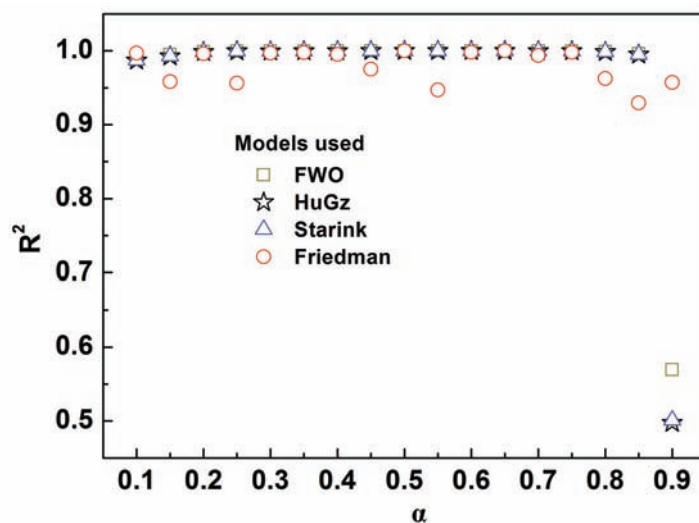

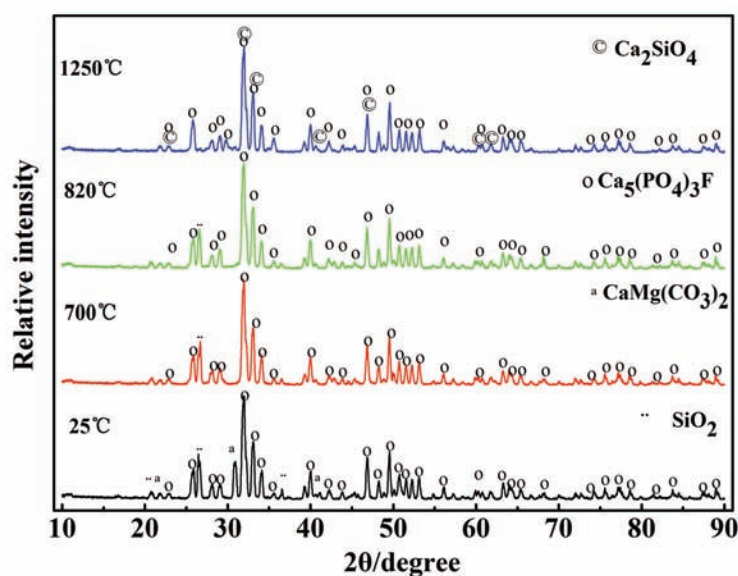Figure 4. Correlation coefficient versus extent of conversion.

Figure 5. The mineral phases of phosphorite heated at various temperatures.

With increasing the temperature, the SiO_2 reacts with the new CaO/MgO phase, and the silicate is formed at 1250 °C.

According to the method suggested by Malek [20], the $y(\alpha)$ *vs.* α curve can be used to determine the reaction mechanism function $f(\alpha)$. The results (Figure 6) show that the $y(\alpha)$ vs. α curve obtained from the experiments agrees with the standard Valensi equation [21] and G-B (Ginstling-Brounshtein) equation [22], which can be expressed as:

2) The mass loss caused by the decomposition of dolomite is endothermic and the endothermic peak covers the range of 600–850 °C.

3) The activation energy of the decomposition of dolomite is about 71.6-123.6 kJ/mol, and increases with increasing extent of conversion.

4) The mechanism equation for the decomposition of dolomite agrees with the Valensi equation and G-B equation.
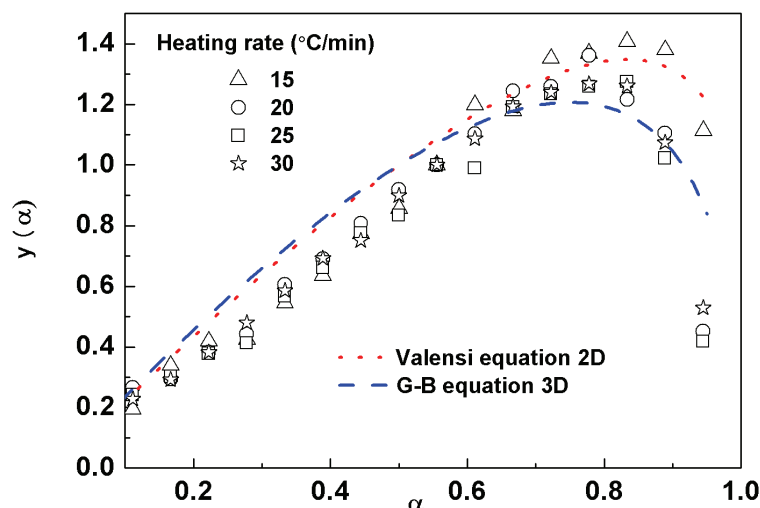

Figure 6. Relationship between $y(\alpha)$ and α.

$$f(\alpha) = \left[-\ln(1-\alpha)\right]^{-1} \qquad (17)$$

$$f(\alpha) = \frac{3}{2}\left[(1-\alpha)^{-\frac{1}{3}} - 1\right]^{-1} \qquad (18)$$

Equation (17) is the Valensi equation, which indicates a two-dimensional diffusion model of the cylinder symmetry. Equation (18) is the G-B model, which indicates a three-dimensional diffusion model of the cylinder symmetry. Both of these equations describe the deceleration α *vs.* t curves.

CONCLUSIONS

The kinetics of the processes with phosphorite concentrate during heating was clarified in the present study. The conclusions can be summarized as follows:

1) The main phases in the phosphorite are fluorapatite $Ca_5(PO_4)_3F$, quartz SiO_2 and dolomite $CaMg(CO_3)_2$. Dolomite decomposes and reacts with SiO_2 to form a new phase Ca_2SiO_4 at 1250 °C.

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RUN HUANG
XUEWEI LV
CHENG PAN
DONGHAI LI
ENGUANG GUO

College of Materials Science and Engineering, Chongqing University, Chongqing, China

NAUČNI RAD

KINETIKA REAKCIJE DEKOMPOZICIJE FOSFORITNOG KONCENTRATA

Apatit je sirovina koja se uglavnom koristi kao sastavna komponenta fosfatnog đubriva ili u obliku žutog i crvenog fosfora, kao i fosforne kiseline u industriji. Sa smanjenjem grumena fosforita visokog stepena čistoće, neophodan je proces aglomeracije fosforitnog koncentrata nakon procesa oplemenjivanja. Ponašanje za vreme razlaganja i fazne transformacije su od vitalnog značaja za proces aglomeracije fosforita. U ovom radu, korišćena je metoda termičke kinetičke analiza za proučavanje kinetike razlaganje koncentrata fosforita. Koncentrat fosforita je zagrevan različitim brzinama zagrevanja, a faze u zagrevanom uzorku su analizirane pomoću rendgenske difrakcione metode. Nađeno je da su glavne faze u fosforitu fluoroapatit, $Ca_5(PO_4)_3F$, kvarc, SiO_2, i dolomit, $CaMg(CO_3)_2$. Endotermni DSC pik odgovara gubitku mase nastalom razlaganjem dolomita u intervalu od 600 do 850 °C. Energija aktivacije razlaganja dolomita, koja se povećava sa povećanjem stepena konverzije je oko 71,6 do 123,6 kJ/mol. Jednačina mehanizma razlaganje dolomita je u saglasnosti sa Valensi-evom i G-B jednačinom.

Ključne reči: fosforit, kinetika, energija aktivacije, reakcioni mehanizam.