KnE Engineering

Knowledge E
Engaging minds

Conference Paper

Study of Decarbonization Processes During Siderite Ore Roasting

Boris Yur'ev and Vyacheslav Dudko

Ural Federal University, Ekaterinburg, Russia

Abstract

The dissociation process of powdered and lumpy siderite ore in the helium, carbon dioxide and air atmospheres is studied with the use of OD-102 derivatograph. The dependences of dissociation degrees and rates from the temperature are received through thermograms processing. The kinetic equations of powders dissociation from the siderite ore are obtained with the help of complex method. It is determined that found regularities also remain unchanged for the lumpy materials. However, the temperature intervals of decomposition will be different. The received results may be used for optimization of thermal conditions of siderite ore burning in the shaft furnaces which heating causes the decomposition of carbonates within iron-bearing minerals, as well as further endothermic effects. They are necessary to compare the material and heat balances of roasting process, which provide an opportunity to properly determine the fuel-consumption rate and work out recommendations for its lowering. Moreover, they are necessary to optimize the design and operating parameters of thermal treatment of siderite ore in the shaft furnaces, which ensure the obtaining of roasted siderite ore in accordance with the requirements applicable to the quality of raw materials during the blast-furnace production. Furthermore, they may be used when working out the methods of reducing roasting and further receiving of metalized iron product rich in iron.

Keywords: derivatograph, dissociation process, siderite ore, shaft furnace, roasting, kinetic equations, carbonates, temperature, dissociation degree and rate, heating rate, gas phase, helium, air, carbon dioxide

Corresponding Author:
Boris Yur'ev
yurev-b@mail.ru

1. Introduction

The reactions proceeding during the heating of siderite ore in the different gas environments are specified in works [1–8]. These works analyze the processes of dissociation of finely dispersed siderite ore in the kinetic area. The chemical regularities of roasting of the lumpy polycrystalline ores to which the siderite ore also belongs will differ due

to the various mass transfer conditions. The information on this issue is insufficient to date.

Resulting from the use of roasted lumpy Bakal siderite ore in the blast furnaces, the issues on both the rate of decarbonization processes and giving the definite mechanical properties to the roasted prills that ensure the minimal smalls formation during transportation and loading to the shaft furnace are thrown into sharp relief. In order to solve this problem, it is necessary to combine the macro- and micrographical investigations with the kinetic and phase analyses.

As the dissociation of lumpy siderite ores in the shaft furnaces flows in the conditions of continuous temperature increase and changeable gas-phase composition, the goal of this work was to envisage this process in the non-isothermal conditions, as well as various gas environments.

2. Experimental Research of Decarbonization Processes

In this article the dissociation kinetics of powdered (0–0.05 mm) and lumpy (12×12×12 mm) Bakal siderite ore was studied with the help of Hungarian OD-102 derivatograph with the power unit of increased output that allows increasing of maximal heating temperature to 1,220°C. The tests were carried out in the gas environments (He, CO_2, air) which composition was controlled through sampling of operating space. The chemical composition of average ore sample was the following one (% wt): 33.98 Fe; 40.60 FeO; 3.47 Fe_2O_3; 1.27 CaO; 8.94 SiO_2; 1.30 Al_2O_3; 9.32 MgO; 1.39 MnO; 0.31 S_{gen}; 33.24 RSL.

The powdered ore was studied in the beginning. The dependences of dissociation degree and rate on the temperature were obtained through processing the thermograms received in the helium, carbon dioxide and air atmospheres. The typical dependences (e.g., heating in the air atmosphere) are shown in Figure 1. The dissociation of mineral is described by the single differentially thermographic curve without divided temperature intervals of ferrous carbonate, magnesium and manganese decomposition. The temperatures of reaction beginning and end at 10°C/min heating rate were changed due to the composition of gas environment. The lowest thermal resistance was marked in the neutral atmosphere (Table 1).

To find out the process mechanism and obtain the kinetic parameters of decomposition at the non-isothermal heating, the complex method based on the assumption that non-isothermal reaction in the infinitely small time range may be regarded as
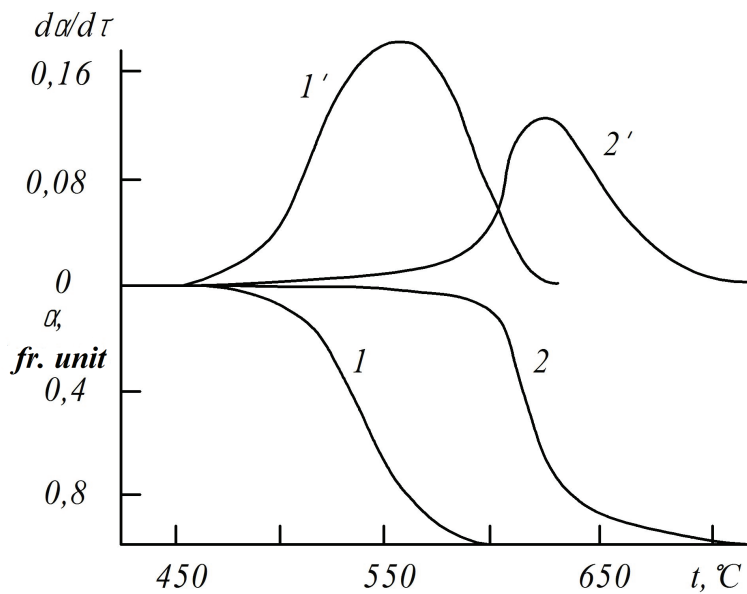
Figure 1: Dependence of decomposition degree (α) and change rate of decomposition degree in the air at the speed of 10°C/min: 1, 1′ – siderite ore powder and Al_2O_3 at the ratio of 1:1; 2, 2′ – prill of siderite ore with the size of 12×12×12 mm.

TABLE 1: Dependence of powdered ore dissociation temperatures on the composition of gas environment.

Atmosphere	Dissociation onset temperature, °C	Dissociation finishing temperature, °C
He	360	600
Air	450	630
CO_2	450	620

isothermal one was used. Thereafter, [9] give the generalized kinetic equation for the infinitely small time range:

$$d\alpha/d\tau = A \exp(-E/RT) f(\alpha),\qquad(1)$$

where α – process timing extent; τ – time; E – activation energy; R – universal gas constant; T – absolute temperature; f(α) – function of conversion degree which form is determined by the process mechanism.

Taking integral of equation (1) at the constant heating rate $dT/d\tau = a$, we obtain:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{a} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT.\qquad(2)$$

Setting

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha), \quad \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT = p(T),$$

equation (2) can be written as:

$$g(\alpha) = \frac{A}{a} p(T). \tag{3}$$

Integrating $p(T)$ by parts, we transform the equation (3) as follows:

$$g(\alpha) = \frac{A}{a}\frac{E}{R} p`(T), \tag{4}$$

where

$$p`(T) = \left\{ E_0\left(\frac{E}{RT}\right) - E_0\left(\frac{E}{RT_0}\right) - \left[-E_i\left(-\frac{E}{RT}\right)\right] + \left[-E_i\left(\frac{E}{RT_0}\right)\right] \right\},$$

E_0 and $(-E_i)$ – integral exponents which values are tabulated in the reference book [11].

Taking the logarithms of equation (4), we obtain:

$$\lg g(\alpha) = \lg A - \lg a + \lg(E/RT) + \lg p`(T). \tag{5}$$

If $E \geq 84$ kJ/mol $\lg p'(T)$ will be proportional to T^{-1} and equation (3) can be written as follows:

$$\lg g(\alpha) = \lg A - \lg a + \lg(E/R) + K_0 T^{-1}, \tag{6}$$

where K_0 – proportionality factor.

If the formula for g(α) function is obtained, the linear connection of $\lg g(\alpha) - T^{-1}$ coordinates will be observed in case of experiment correspondence and made assumptions.

To primarily estimate the magnitude of activation energy, we used Freeman-Carrol method [6] due to which the following equation is true for the majority of solid-phase processes

$$\frac{(E/2,3R)\Delta T^{-1}}{\Delta \lg W_3} = -n + \frac{\Delta \lg(dW/d\tau)}{\Delta \lg W_3}, \tag{7}$$

where $W_3 = W_c - W$; W_c – maximal weight loss during dissociation; W – weight loss up to τ time; n – apparent orders of reaction.

To represent the equation (7), the thermographic and differentially thermographic curves were divided into 8–10 parts. ΔT^{-1}, ΔlgW, Δlg(dW/dτ) values were determined by means of the end and initial temperature values, weight loss and rate of weight loss for each of such parts. The dependences in $\Delta T^{-1}/\Delta \lg W_3 - \Delta \lg(dW)/\Delta \lg W_3$ coordinates were built. The value of activation energy was determined according to the slope ratio, and n value – due to $\Delta \lg(dW/d\tau)/\Delta \lg W_3$– intercept.

The processing of experimental data showed that dependences in $\Delta T^{-1}/\Delta \lg W_3 - \Delta \lg(dW/d\tau)/\Delta \lg W_3$ coordinates are near linear in all used atmospheres during disso-ciation process. E and n parameters of studied atmospheres were practically indis-cernible corresponding to 125 kJ/mol and 0.5, respectively. Independence of activation energy from the type of used atmosphere and its value for the immediate dissociation reaction ($E = 130 - 140$kJ/mol) $FeCO_3 = FeO + CO_2$, testifies that crystal-chemical transformation in the course of carbonate lattice rearrangement into the wurtzite is a rate-limiting step in all cases. The further oxidation reaction of FeO and Fe_3O_4 proceeds quickly and don't have the catalytic effect on the decarbonization. These conclusions are also proved by the analysis of equation (6) which feasibility check for different g(α) functions is carried out according to the model kinetic equations of topochemical reactions with the reactant gas taken from the work [9].

The linear relationship $\lg g(\alpha) - T^{-1}$ for all three atmospheres is closely fulfilled only in case when

$$g(\alpha) = A_3 = [-\ln(1 - \alpha)]^{1/3}. \tag{8}$$

The equation (8) received by the author [6] on the hypothesis that the crystal-chemical act consisting in the accidental nucleus formation is a process, which deter-mines the reaction rate on the interphase boundary of solid reagent and reaction product. Notably, the new phase is formed not only by the emergence of nucleating centers of equal size, but also due to the growth of existing ones.

Therefore, the connection of powdered ore dissociation degree with the time and temperature in the non-isothermal heating mode is described by means of equation (3) when $g(\alpha) = [-\ln(1-\alpha)]^{1/3}$. It is necessary to know not only E value, but also parameter A for the practical application of formula (3). It can be easily found out by means of

equation (5), through building the dependences in $\frac{1}{3}\lg[-\ln(1-\alpha)]-\lg p`(T)$ coordinates due to the experimental data or when determining $\frac{1}{3}\lg[-\ln(1-\alpha)]$ intercept b, that is,

$$b = \lg A - \lg a + \lg(E/R). \tag{9}$$

In order to specify the values of activation energy that was determined previously according to Freeman–Carrol equation, let's consider the equation (5). It shows that alga(α) is proportional to lgp'(T), and the gradient of corresponding right line is to be equal to 1. This condition is met in case of the certain value of activation energy. The found E values for helium, carbon dioxide and air atmospheres are 42, 42 and 63 kJ/mol, respectively. Knowing the values of activation energy and heating rate applied during testing it is possible to find A parameter in the equation (9).

The kinetic equations of powders dissociation in different gas environments are represented as follows:

helium atmosphere

$$[-\ln(1-\alpha)]^{1/3} = (0,5/w)10^6 p`(T),$$

$$p`(T) = -0,5 \cdot 10^{-5} + E_0(x) - [-E_i(-x)] \text{ for } x = 5035T^{-1};$$

carbon dioxide atmosphere

$$[-\ln(1-\alpha)]^{1/3} = (0,6/w)10^6 p`(T),$$

$$p`(T) = -0,131 \cdot 10^{-4} + E_0(x) - [-E_i(-x)] \text{ for } x = 5035T^{-1};$$

air atmosphere

$$[-\ln(1-\alpha)]^{1/3} = (1,6/w)10^7 p`(T),$$

$$p`(T) = -0,01 \cdot 10^{-5} + E_0(x) - [-E_i(-x)] \text{ for } x = 7553T^{-1},$$

where α – dissociation degree, fry unit.; w – heating rate, °C/min; T – temperature, K; $E_0(x)$ and $E_i(-x)$ – integral exponents.

The analysis of reduced equations shows that the significant differences relating to the dissociation rate in the air and carbon dioxide atmospheres are not found.

The obtained regularities of finely dispersed powders dissociation remain unchanged for lumpy materials in many ways. Using thermograms made in the helium, carbon dioxide and air atmospheres it is determined that decarbonization of isomorphous mixture of iron, magnesium and manganese also runs simultaneously. However, the decomposition temperature interval at the heating rate of 10°C/min is increased by 100–150°C (in comparison with powders) as it can be seen from Table 2.

TABLE 2: Dependence of dissociation temperatures of lumpy ore on the gas environment composition.

Atmosphere	Dissociation onset temperature, ^{a}ct	Dissociation finishing temperature, ^{a}ct
He	500	750
Air	520	720
CO_2	530	720

It is necessary to admit that weight lost in the air and CO_2 atmospheres before oxidation start during prill roasting was the same being equal to 35 % wt at 4 and 10°C/min heating rate. The weight loss was greater (37–40%) for helium atmosphere with the similar heating rates.

Thus, the gas-dynamic prop of reaction products evolved in the course of decarbonization complicates the passing of air and CO2 from in the furnace atmosphere into the internal prill regions. Therefore, the reaction is to be considered in both cases as that proceeding in the same atmosphere that is similar to the composition of CO_2 with some CO additives resulting from $3FeO + CO_2 = Fe_3O_4 + CO$ reaction.

3. Summary

The dissociation process of siderite ore of different fineness and in various gas environments was studied by means of derivatographic method. The data on kinetics of carbonates decomposition process in the iron-bearing mineral were obtained, and the kinetic equations connecting the dissociation degree of carbonates with the temperature were developed based on complex method. The received data may be used when optimizing the operating parameters of siderite ore roasting in the shaft furnaces.

References

[1] Yur'ev, B. P. and Melamud, S.G. (1998, June). The study of mechanism and kinetics of bakal siderite ores dissociation during thermal treatment, Izvestiya VUZ. *Radioelektronika*, vol. 41, pp. 3–9.

[2] Xing, B., Chen, T., Qing, C., et al. (1 August 2016). Structural characteristic of natural siderite during thermal treatment, Kuei Suan Jen Hsueh Pao. *Journal of the Chinese Ceramic Society*, vol. 44, pp. 1207–1212.

[3] Alkaç, D. and Atalay, Ü. (July 2008). Kinetics of thermal decomposition of Hekimhan–Deveci siderite ore samples. *International Journal of Mineral Processing*, vol. 87, pp. 120–128.

[4] Leontiev, L. I., Vatolin, N. A., Shavrin, S. V., et al. (1997). *Pyrometallurgical Processing of Complex* Ores, p. 432. M.: Metallurgy.

[5] Yuriev, B. P., Melamud, S. G., Spirin, N. A. (2012). Study of Bakal siderite ores dissociation kinetics. *News of High Educational Institutions. Iron Industry*, no.10, pp. 12–14.

[6] Kubas, Z. and Szatkonicz, M. (1973). Kompleksour badania kinetyki procesu termiczne-gorosktadu rudy Syderytowy. *Zeszyty nauk. AGH*, no. 367, pp. 123–136.

[7] Belousova, M. I. (1962). The study of thermal dissociation of ferrous carbonates of Bakal deposit and product features resulting from this process, in *Collection of Research Papers of Uralmekhanobr Institute* (9th edition), pp. 68–84. Sverdlovsk: Uralmekhanobr.

[8] Goldman, M. M., Ni, L. P., Ardasheva, A. I., et al. (1977). Siderite behavior in the course of roasting. *News of Higher Educational Institutions. Nonferrous metallurgy*, no. 3, pp. 41–44.

[9] Wendland, U. (1978). *Thermal Methods of Analysis*, p. 528. M.: World.