Analysis of Reaction Rate between Solid Carbon and Molten Iron by Mathematical Models

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The factors affecting the carbon dissolution rate into liquid iron and the interdependency between these rate influencing factors were discussed with aid of a kinetic model. These rate influencing factors include temperature, carbon structure, interfacial active elements, metal composition, liquid agitation, wettability between solid and liquid, solid particle size, ash in carbonaceous materials and side reactions.

Experiments were carried out on carbon dissolution from graphite and coke into liquid Fe–C alloy using resistance or induction furnaces at 1 573–1 873 K. The kinetic parameters describing carbon dissolution rate were obtained from the comparison of observed carbon dissolution rates and model calculations. The dissolution rates at higher temperatures or in an induction furnace were found more rapid than those at lower temperatures or in a resistance furnace. The mass transfer in liquid was found to be the major limiting step for the carbon dissolution process.

KEY WORDS: ironmaking; coke; coal; kinetics; dissolution.

1. Introduction

The iron making process is an iron oxide reduction and heating-melting process. High speed reduction and low temperature melting are most important processes for improving the efficiency of the process.¹⁾ Since reaction rates strongly depend on temperature, to maintain high productivity of blast furnace, the major reactions in the process must occur at high speed at lower temperature.

Carburisation of the iron is one of the major reactions in the blast furnace process. It is clear that the high speed carburisation can not be expected through gas. And without further increasing temperature, high speed carburisation can not be expected through the solid contact either. In a coke packed bed, the melting of reduced iron occurs at the contacting points between coke and reduced iron. At high temperatures, liquid iron is initially generated by carburisation at these points because melting temperature of iron is lowered by carbon pickup. And then the iron melts through simultaneous carbon dissolution into liquid iron and carburisation of solid iron by the liquid iron. Therefore, high speed melting of reduced iron is achieved *via* carbon dissolution in a blast furnace.

The dissolution of carbon into liquid iron was traditionally considered to be limited by the mass transfer in liquid iron.^{2–8)} This was mainly evidenced by the strong dependency of the dissolution rate on the liquid agitation and weak dependency of the rate on the temperature and sulfur in liquid. In the recent series of researches, the dissociation reaction at the interface was suggested to be important for the carbonaceous materials with less ordered atomic struc-

ture.^{9–17)} This was mainly evidenced by the strong dependency of the dissolution rate on the crystallite size of carbonaceous materials and sulfur in the liquid.

Lack of agreement on the carbon dissolution mechanism among these investigations requires a kinetic treatment of the dissolution rates with both possible limiting mechanisms, *i.e.*, the interfacial dissociation reaction and the mass transfer. The primary objectives of this study were to further develop the understanding of the carbon dissolution mechanism. Discussion on the factors that influence the carbon dissolution rate was carried out based on the model that includes the interfacial dissociation reaction and mass transfer processes. The kinetics of carbon dissolution was discussed with experimental observations.

2. Model Development and Discussions

2.1. Elementary Steps of Carbon Dissolution

When a solid carbon material contacts with liquid iron at high temperature, the dissolution of carbon from the solid into liquid iron occurs. The overall dissolution reaction is

where, $C_{(\text{solid})}$ is carbon in solid structure, and $[C]$ is carbon in liquid, mass%.

The equilibrium relation of this reaction is

$$K_r = \left(\frac{a_C}{a_{\text{solid}}} \right)_{\text{EQ}} \quad \text{or} \quad \frac{a_C^{\text{Sat}}}{a_{\text{solid}}} \dots\dots\dots(2)$$

where K_r is the equilibrium constant for the reaction (1).

a_{solid} , a_{C} and $a_{\text{C}}^{\text{Sat}}$ are the carbon activities of solid carbon, liquid and liquid saturated (or in equilibrium) with the solid carbon, respectively.

The dissolution occurs through two consecutive steps; the first step is the dissociation of carbon atoms from solid structure into interstitial positions of iron atoms at the liquid side of the interface as expressed by Eq. (3),

where $[C]^*$ is the carbon content at the liquid side of the interface, mass%.

The dissociation reaction rate is the difference between the forward reaction rate and the reverse reaction rate and is given by,

$$J_r = Ak_r \left(a_{\text{solid}} - \frac{a_{\text{C}}^*}{K_r} \right) \dots\dots\dots(4)$$

where J_r is the dissociation reaction rate of carbon, g/s, A is solid-liquid contact area, cm^2 , k_r is rate constant of the dissociation reaction (1), g/s cm^2 , and a_{C}^* is the carbon activity at liquid side of the interface. According to the recent study,⁽¹¹⁾ the dissociation reaction is further divided into dissociation of carbon structure, accumulation of liberated carbon at the interface and adsorption of carbon into interstitial position among iron atoms. Therefore, k_r can be considered as overall rate constant for these processes at the interface.

The second step is the mass transfer of carbon atoms in the interstitial positions of liquid structure at the liquid side of the interface into liquid bulk as expressed by Eq. (5),

It is assumed that a static film of liquid is present at the interface. There is no carbon concentration gradient in the liquid bulk beyond this boundary film, but transport across the static layer is controlled by diffusion. It was also assumed that steady-state conditions exist in the boundary film; thus, Fick's First Law is used to describe the linear variation of the concentration of carbon across the boundary film:

$$J_m = \frac{Ak_m \rho_m}{100} ([C]^* - [C]) \dots\dots\dots(6)$$

where J_m is the mass transfer rate of carbon from the interface into liquid bulk, g/s, k_m is the mass transfer coefficient in the liquid, cm/s , and ρ_m is the density of the liquid, g/ cm^3 .

2.2. Mixed Limiting by Mass Transfer and Interfacial Dissociation

There is no accumulation of carbon at the liquid side of the interface. Thus, the carbon flux down to the bulk must equal to the flux of carbon generated from reaction (3) or J_r ,

$$J_d = J_r = J_m \dots\dots\dots(7)$$

where J_d is the dissolution rate of carbon, g/s.

The interfacial carbon content can be expressed by Eq. (8) from Eqs. (4), (6) and (7),

$$[C]^* = \frac{100k_r a_{\text{solid}} + k_m \rho_m [C]}{k_m \rho_m + 100k_r \frac{f_{\text{C}}^*}{K_r}} \dots\dots\dots(8)$$

where f_{C}^* is the carbon activity coefficient at the liquid side of the interface.

Replacing the interfacial carbon in either Eq. (4) or Eq. (6) with that in Eq. (8), the dissolution rate of carbon is given by,

$$J_d = Ak_t \left(a_{\text{solid}} - \frac{f_{\text{C}}^* [C]}{K_r} \right) \dots\dots\dots(9)$$

where k_t is overall rate constant of carbon dissolution, g/s cm^2 , which is

$$\frac{1}{k_t} = \frac{1}{k_r} + \frac{100f_{\text{C}}^*}{k_m \rho_m K_r} \dots\dots\dots(10)$$

Equation (9) is the carbon dissolution rate equation involving interfacial dissociation reaction and mass transfer processes. The total resistance (R_t), the resistance of dissociation reaction (R_r), and the resistance of mass transfer (R_m) to the carbon dissolution process are given by Eqs. (11), (12) and (13), respectively.

$$R_t = \frac{1}{k_t} = R_r + R_m \dots\dots\dots(11)$$

$$R_r = \frac{1}{k_r} \dots\dots\dots(12)$$

$$R_m = \frac{100f_{\text{C}}^*}{f_m \rho_m K_r} \dots\dots\dots(13)$$

where R_t , R_r and R_m have a unit of $\text{cm}^2 \text{ s/g}$.

It is noted that, the resistance of the mass transfer to the carbon dissolution process, R_m , is a function of interfacial carbon activity coefficient, f_{C}^* , which is a dependence of interfacial carbon content ($[C]^*$). This indicates R_m and k_t vary with time during carbon dissolution process. The driving force for the mixed limiting dissolution process is $a_{\text{solid}} - f_{\text{C}}^* [C]/K_r$.

2.3. Mass Transfer Limiting

When the carbon dissolution is limited by mass transfer, i.e., $R_m \gg R_r$, the equilibrium of the reaction (1) is achieved at the interface because the rate of interfacial dissociation reaction is much faster than that of the mass transfer. If the interfacial contents of other alloying elements are equal to their bulk counterparts, interfacial values of carbon are able to be obtained from equilibrium relation of reaction (1) as,

$$[C]^* = [C]^{\text{Sat}}, f_{\text{C}}^* = f_{\text{C}}^{\text{Sat}}, \text{ and } a_{\text{C}}^* = a_{\text{C}}^{\text{Sat}} \dots\dots\dots(14)$$

where $f_{\text{C}}^{\text{Sat}}$ is carbon activity coefficient in the liquid when carbon reaches saturation.

Replacing the interfacial values in Eq. (9) with those in Eq. (14) and ignoring R_r , the dissolution rate equation becomes,

$$J_d = \frac{Ak_m \rho_m}{100M_{\text{C}}} ([C]^{\text{Sat}} - [C]) \dots\dots\dots(15)$$

Equation (15) describes the dissolution rate that is limited by the liquid phase mass transfer. The driving force for the dissolution process is $[C]^{\text{Sat}} - [C]$. The rate is dictated by mass transfer coefficient, k_m and carbon saturation content,

the former varies with temperature, liquid composition, liquid phase agitation and the latter with temperature, liquid composition and solid structure. Eq. (15) or its integrated form as given in Eq. (16) is frequently used to describe the dissolution rate if liquid phase mass transfer limits the dissolution rate.

$$\ln \frac{([C]^{\text{Sat}} - [C])}{([C]^{\text{Sat}} - [C]_0)} = \frac{Ak_m}{V_m} t \quad (16)$$

where t is the time period over which the dissolution occurs, s, V_m is volume of liquid iron, cm^3 , and $[C]_0$ is the initial carbon content in the liquid, mass%.

2.4. Limiting by Interfacial Dissociation

When the dissolution is limited by the dissociation reaction at the interface, *i.e.*, $R_r \gg R_m$, the equilibrium of the mass transfer shown in Eq. (5) is achieved because interfacial dissociation is much slower than the mass transfer process. Interfacial values are equal to their bulk values as,

$$[C]^* = [C], f_C^* = f_C \text{ and } a_C^* = a_C \quad (17)$$

where f_C is the carbon activity coefficient in the bulk of the liquid.

Replacing the interfacial values in Eq. (9) with bulk values in Eq. (17) and ignoring R_m , the dissolution rate becomes,

$$J_d = Ak_r \left(a_{\text{solid}} - \frac{a_C}{K_r} \right) \quad (18)$$

Equation (18) describes the dissolution rate limited by the interfacial dissociation reaction. The driving force for the process is $a_{\text{solid}} - a_C/K_r$. Since activity of pure solid is usually unity, $a_{\text{solid}} = 1$, the rate is dictated by dissociation reaction rate constant, carbon activity, and equilibrium constant for the reaction (1). The dissociation rate constant varies with temperature, structure of solid and interfacial active elements. The carbon activity varies with temperature and liquid composition, and the equilibrium constant varies with temperature and solid structure. Carbon with different structures has different free energy changes for reaction (1) at standard state and thus has different values of K_r at a given temperature. Using equilibrium relation in Eq. (2), a

hypothetic solid activity ($a_{\text{solid(EQ)}}$) in equilibrium with carbon in the liquid bulk can be obtained as

$$a_{\text{solid(EQ)}} = a_C/K_r \quad (19)$$

This hypothetic solid activity can be thought as “solid carbon potential of the liquid”. With this relation, the Eq. (18) becomes

$$J_d = Ak_r (a_{\text{solid}} - a_{\text{solid(EQ)}}) \quad (20)$$

The driving force is $a_{\text{solid}} - a_{\text{solid(EQ)}}$, which is the difference between solid activity and a solid activity in equilibrium with carbon in the liquid bulk.

Alternatively, a hypothetic carbon content in equilibrium with solid and an instantaneous f_C can be defined from equilibrium relation for reaction (1) as,

$$[C]_{\text{EQ}} = K_r a_{\text{solid}}/f_C \quad (21)$$

$[C]_{\text{EQ}}$ can be thought as “liquid carbon potential of the solid with an instantaneous f_C ”. With this relation, the Eq. (18) becomes,

$$J_d = Ak'_r ([C]_{\text{EQ}} - [C]) \quad (22)$$

where k'_r is apparent reaction rate constant, expressed by,

$$k'_r = \frac{f_C}{K_r} k_r \quad (23)$$

The driving force is then $[C]_{\text{EQ}} - [C]$, which is the difference between bulk carbon content and the carbon content in equilibrium with solid and the instantaneous f_C . It is noted that (22) has a similar form as Eq. (15) for mass transfer limiting process. However, k'_r and $[C]_{\text{EQ}}$ in Eq. (22) are not constant since they vary with instantaneous f_C . This will forbid Eq. (22) to be integrated into similar form as Eq. (16) because f_C varies with carbon content, and the carbon content varies with dissolution time.

2.5. Rate Influencing Factors

2.5.1. Kinetic and Thermodynamic Parameters vs. Their Influencing Factors

Table 1 summarized the dissolution rate equations for the carbon dissolution process for three cases. Case (A), Case (B) and Case (C) represent the rate is limited by the mass transfer, interfacial dissociation reaction, and by the

Table 1. Limiting step(s), rate equation, and kinetic and thermodynamic parameters for carbon dissolution.

Case	Limiting step(s)	Rate equation	Parameters				
			A	k_m	k_r	K_r	$[C]^{\text{Sat}}$
(A)	Mass transfer	$J_d = \frac{Ak_m \rho_m}{100} ([C]^{\text{Sat}} - [C])$ or $\ln \frac{([C]^{\text{Sat}} - [C])}{([C]^{\text{Sat}} - [C]_0)} = \frac{Ak_m}{V_m} t$	Y	Y	N	N	Y
(B)	Interfacial reaction	$J_d = Ak_r \left(a_{\text{solid}} - \frac{a_C}{K_r} \right)$	Y	N	Y	Y	N
(C)	Mass transfer & interfacial reaction	$J_d = \frac{A \left(a_{\text{solid}} - \frac{f_C^* [C]}{K_r} \right)}{\frac{1}{k_r} + \frac{100 f_C^*}{k_m \rho_m K_r}}$	Y	Y	Y	Y	N

Y: Involves

N: Not involve

both of them, respectively. The parameters involved in the carbon dissolution rate of each case were also summarised in the Table. For all cases, the dissolution rate is strongly influenced by the contact area A . The dissolution rates for Case (A) and Case (C) vary with k_m , those for Case (B) and Case (C) vary with k_r and K_r , and that for Case (A) varies with carbon saturation content, $[C]^{Sat}$. The interdependency between $[C]^{Sat}$ and K_r can be obtained from Eq. (2) as,

$$[C]^{Sat} = \frac{a_{solid} K_r}{f_C^{Sat}} \dots\dots\dots (24)$$

$[C]^{Sat}$ depends on temperature and alloying elements in the liquid, while K_r solely depends on temperature for a given solid.

Table 2 shows the influencing factors on parameters that directly dictate the dissolution rate. The interdependencies between these factors are summarised in **Table 3**. As can be seen in Tables 1 through 3, a thorough thought must be given when investigating the dissolution process of impure carbon materials such as coke, coal or natural graphite. Efforts should be made to isolate the rate influencing factor of interest; otherwise its influence could be masked by the uncontrollable variation of other rate influencing factor(s). The rate influencing factors in Table 3 and the interdependencies between them are discussed in the following sections.

Table 2. Rate influencing factors for carbon dissolution.

Influencing factors	Carbon dissolution parameters				
	A	k_m	k_r	K_r	$[C]^{Sat}$
Temperature	N	S	G	G	G
Solid structure	N	N	U	S	S
Adsorption blockage	N	N	G	N	N
Alloying elements	N	S	N	N	G
Liquid agitation	N	G	N	N	N
Liquid-solid wettability	M	N	U	N	N
Particle size of solid	M	N	N	N	N
Ash in coke	G	N	N	N	N
Side reactions	N	U	U	N	N

G: greatly influence
S: slightly influence
M: may influence
U: unclear
N: no influence (may indirectly influence)

Table 3. Interdependency between influencing factors.

	Temperature	Solid structure	Adsorption blockage	Alloying elements	Liquid agitation	Liquid-solid wettability	Particle size of solid	Ash	Side reactions
Temperature		Y	Y	N	N	Y	N	N	Y
Solid structure	Y		U	N	N	Y	N	N	N
Adsorption blockage	Y	U		Y	N	Y	N	N	Y
Alloying elements	N	N	Y		N	Y	N	N	Y
Liquid agitation	N	N	N	N		N	N	N	Y
Liquid-solid wettability	Y	Y	Y	Y	N		U	Y	U
Particle size of solid	N	N	N	N	N	U		N	N
Ash	N	N	N	N	N	Y	N		Y
Side reactions	Y	N	Y	Y	Y	U	N	Y	

Y: Interdependence
N: No or weak interdependence
U: Unclear

tions.

2.5.2. Temperature

Temperature will not directly affect the contact area, but temperature may indirectly, through affect wettability between solid carbon and liquid, viscosity and fusion of the ash to affect the contact area. Temperature has a stronger impact on the k_r than on k_m because chemical reaction usually has larger activation energy. K_r and $[C]^{Sat}$ are functions of temperature. Temperature also affects k_r through affecting interfacial adsorption blockage and solid carbon structure. As will be discussed later, some side reactions are sensitive to the temperature, which will in turn affect the carbon dissolution rate.

2.5.3. Solid Structure

Structure of solid may affect k_r , K_r and $[C]^{Sat}$. This is because k_r describes the dissociation reaction rate of carbon atoms from solid lattice into the interstitial positions surrounded by iron atoms in the liquid. The dissociation process includes the ruptures of atomic bonds between carbon atoms in solid, and atomic bonding type and the bonding strength are determined by the solid structure. K_r is related to the free energy change of reaction (1) which depends on the solid structure. Graphite, natural graphite, various cokes and coal, and diamond are carbon of different structure, and they have different K_r at a given temperature. $[C]^{Sat}$ is the equilibrium carbon content with the solid and varies with K_r and thus with solid structure. The interfacial tension between solid and liquid varies with the solid structure, this indicates the adsorption blockage by interfacial active elements and the wettability between liquid and solid may be affected by the solid structure.

2.5.4. Adsorption Blockage

Interfacial active elements in the liquid, such as sulfur, will occupy the reaction sites to reduce k_r . The investigation on the sulfur effect¹⁸⁾ suggested that the dissolution rate was controlled by both mass transport and phase boundary reactions when sulfur was present in the liquid. The fraction of interfacial reaction sites occupied by the interfacial active elements is the temperature dependency which is quantitatively described by Gibbs–Lunngmir adsorption isotherm. The liquid composition will affect the fraction of the occupied sites by affecting activity of the interfacial active elements in the liquid. The better wetting can be expected between liquid and solid with increasing interfacial active elements in the liquid because the interfacial tension between liquid and solid decreases. The rate of side reactions that are limited by the reaction at interface, for example reductions of silica²⁰⁾ or titania²¹⁾ in ash by dissolved carbon in the liquid, are very sensitive to the interfacial adsorption blockage.

2.5.5. Alloying Elements

Elements present in the liquid, such as Si, Mn and S, affect the activity coefficient of carbon in liquid and therefore the carbon saturation content. Alloying element will also affect k_m through affecting diffusivity of carbon in liquid and viscosity of the liquid. For example, the addition of 0.2 mass% sulfur can decrease the mass transport coefficient.

cient for the dissolution of graphite by approximately 20%,²²⁾ and diffusivity of carbon in liquid is decreased by addition of silicon in the melt.³⁾ Wettability between liquid and solid would vary with metal composition because the interfacial tension between the two phases is influenced largely by the liquid compositions.¹⁹⁾ As will be discussed later, the side reactions are influenced by the liquid compositions.

2.5.6. Liquid Agitation

Liquid agitation increases k_m through reducing the boundary layer thickness in liquid, and thus diffusion distance. The rate of side reactions that are limited by mass transfer process, for example, reaction of sulfur, phosphorus and manganese between ash and liquid,²³⁾ are sensitive to the liquid agitation.

2.5.7. Liquid Solid Wettability

Wettability between solid carbon and liquid affects the contact area when porous or small particles of solid are in contact with the liquid. This is because good wetting will allow liquid to penetrate into pores of the solid or interstitial space between particles to increase the contact area. Good wetting means higher work of adherence (strength of bonds between two media) that may help to “tear off” carbon atoms from solid lattice and this may give a higher k_r . The factors that affect the interfacial tension between solid and liquid will affect the wettability, since wettability between two phases is the result of the balance of interfacial tension forces at the interface; these factors include temperature, solid structure, interfacial active elements and metal composition. The wettability may decrease when small solid particles are in contact with the liquid because “lotus” phenomenon (A phenomenon of non wetting of liquid on a rough solid surface) may occur. The wettability may dramatically increase by dynamic low interfacial tension due to the side reactions. Side reactions will change metal composition including interfacial active element contents to change the wetting character.

2.5.8. Solid Particle Size

Carbon particle size will affect the contact area particularly during powder injection process such pulverized coal injection (PCI). The wetting character could be affected by the particle size as mentioned before.

2.5.9. Ash

Ash in carbonaceous materials would accumulate at the interface and become physical barriers at the interface, which will reduce contact area available for further carbon dissolution. The “strength” of the barrier depends on the interfacial and physical properties of ash, such as viscosity, fusion temperature, and interfacial tension between ash and iron or solid carbon. These properties depend on temperature and the ash composition and the latter is strongly affected by the side reactions. Coke ash accumulation at the interface will change wetting character since a portion of liquid/solid interface area will be replaced by ash.

2.5.10. Side Reactions

Ash components provide reactant for most of side reac-

tions occurring at the interface. The side reactions will not directly affect the carbon dissolution rate, but they will indirectly affect carbon dissolution rate by the reaction with dissolved carbon or by changing compositions of the liquid and the ash. The major component in ash is silica, and the silica reduction will occur when fused ash contacts the liquid through the reaction:

This reaction will take a portion of carbon away from liquid, increase silicon in the liquid, and reduce silica in the ash. The former will cause confusion when observing the carbon dissolution rate, the second will cause the carbon saturation content to change with time during the dissolution process, and Eq. (15), for example, will not be able to be integrated, and the last will decrease the viscosity of the ash.

Sulfur usually presents in carbonaceous materials, either in carbon structure or in ash phase. The sulfur pickup from coke or coal occurs during carbon dissolution. The rate of sulfur pickup due to carbon dissolution is considered to be in proportion to the carbon dissolution rate and sulfur/carbon ratio in coke. The sulfur pickup will change carbon saturation content and k_r by sulfur adsorption blockage during carbon dissolution process. When fluxing materials such as CaO present in the system, following reaction will occur to consume dissolved carbon and the product of this reaction, CaS, may remain at the interface to reduce contact area.

CO generated from side reactions, as seen in reaction (25) and reaction (26) may contribute to the liquid phase agitation to increase k_m .⁸⁾ On the other hand, the gas bubbles could be jammed at the interface to reduce the area available for carbon dissolution.

3. Experimental

Several experiments were carried out on carbon dissolution using stationary immersion method to compare the model calculations. About 100 g of iron-carbon alloy was first melted in an alumina crucible (ID=30 mm, height=50 mm) in resistance or induction furnaces under an argon atmosphere. After the experimental temperature was attained, the graphite or coke cylinder (diameter=13 mm, height=20 mm) was immersed into the liquid Fe-C alloy to start the carbon dissolution process. Before being immersed, the solid carbon was heated to the experimental temperature near the melt surface for several minutes to ensure the constant of temperature during the carbon dissolution. The solid sample was immersed for a predetermined time period and was withdrawn from the melt. Some metal samples (1–3 g) for carbon analyses were withdrawn before and after the immersion. The contact area for each immersed sample was calculated from the average dimensions of the solid cylinder before and after its immersion, and the contact area of each run was determined from the average areas of all samples immersed in the run. To keep the solid sample size or contact area constant, the above procedure was repeated using a new solid sample to create a carbon content versus time relationship. **Table 4** summarises the

Table 4. Experimental conditions.

Run	Temperature K	[C] mass%	Liquid weight, g	Contact area, cm ²
1573R*	1573	3.00	101.6	8.12
1673R*	1673	2.40	103.9	7.77
1773R*	1773	2.58	100.5	7.71
1873I**	1873	1.57	99.5	9.18

* Resistance furnace and graphite were used

** Induction furnace and coke were used

experimental conditions. The experimental conditions differed mainly in the temperature and melting furnace.

4. Results and Discussions

The variations of carbon in the liquid with time of all runs are shown in Fig. 1. It was found that the carbon dissolution rate at higher temperatures and with induction furnace were faster than those at lower temperatures and with resistance furnace.

Equation (9) for carbon dissolution where dissociation reaction and mass transfer are involved was used to analyse the observed rates. Equilibrium constant for reaction (1), K_r , for graphite, and activity interaction parameter of carbon, e_C^c , as a function of temperature²⁴⁾ were used in the model calculation. A numerical method is used for obtaining the theoretical carbon contents that best fits observed carbon contents by adjusting the kinetic parameters, which are then determined.

Since both k_m and k_r may dictate the dissolution rate, these kinetic parameters will not be able to be identified if both of them are unknown. For example, the results of run 1573R can be fitted well by Case (A) using $k_m = 0.00186$ cm/s and $k_r > 0.50$ g/s cm², or by Case (B) using $k_r = 0.00027$ g/s cm² and $k_m > 0.0571$ cm/s, or by Case (C) using $k_m = 0.00286$ cm/s and $k_r = 0.001$ g/s cm². The variations of carbon content calculated from the model using these three sets of kinetic parameters for run 1573R were essentially same and they are represented by the solid line in Fig. 1. All cases showed good agreement. The fraction of resistances of each limiting step to the carbon dissolution process was calculated from following equations,

$$FR_m = 100 \times \left(\frac{R_m}{R_m + R_r} \right) \dots \dots \dots (27)$$

$$FR_r = 100 \times \left(\frac{R_r}{R_m + R_r} \right) \dots \dots \dots (28)$$

where, FR_m and FR_r are fraction of resistances of mass transfer and interfacial reaction processes, respectively, to the dissolution process, %.

In Case (A), the dissolution process is limited by mass transfer since $FR_m > 99\%$ and the dissolution rate is independent of k_r when $k_r > 0.50$ g/s cm²; in Case (B), the process is limited by interfacial dissociation reaction since $FR_r > 99\%$ and the dissolution rate is independent of k_m when $k_m > 0.0571$ cm/s; in Case (C), the process is evenly limited by the both since $FR_r \approx FR_m \approx 50\%$ and the dissolution rate varies with both k_m and k_r . The variation of [C]

Fig. 1. Variations of carbon in the liquid with time.

calculated from three cases are essentially same and fits the observed results well.

The results of runs 1673R and 1773R were treated in the same manner for Case (A) and Case (B). A set of k_m was obtained when mass transfer limiting is assumed for dissolution at different temperatures. They are

	1 573 K	1 673 K	1 773 K
k_m (cm/s)	0.00186	0.00257	0.00286

Similarly, a set of k_r was obtained when interfacial reaction limiting is assumed for the dissolution at different temperatures. There are

	1 573 K	1 673 K	1 773 K
k_r (g/s cm ²)	0.00027	0.00040	0.00050

The solid, dashed and dash-dot lines in Fig. 1 show the results of the model using these parameters for run 1573R, 1673R and 1773R, respectively. The calculated results based on the different assumptions were essentially same and were represented by the same line for each run in the figure. All runs showed good agreement with both assumptions.

The activation energy calculated for k_m is $E(k_m) = 50.3$ kJ/mol and for k_r is $E(k_r) = 71.7$ kJ/mol. The $E(k_m)$ has a low value that is within a reasonable range of the activation energy for a mass transfer process, but $E(k_r)$ is obviously too low for a reaction process. k_m is related to carbon diffusivity by,

$$k_m = D_C / \delta \dots \dots \dots (29)$$

where D_C is self diffusivity of carbon, cm²/s, and δ is boundary layer thickness in liquid, cm.

The activation energy obtained for carbon diffusivity was found to be 62.9 kJ/mol²⁵⁾ in Fe-C melt ($S = 0.005$ – 0.023%) which is close to the activation energy found for k_m in this work. Therefore, Case (A), *i.e.*, the mass transfer in the liquid is considered to be the major limiting step for the carbon dissolution while interfacial dissociation only plays a minor role. This statement is supported by a faster carbon dissolution rate in run 1873I where induction agitation was applied; this is because agitation increases k_m by reducing the boundary layer thickness, while k_r was essentially unaffected by the agitation. The temperature dependence of k_m can be estimated using $E(k_m) = 50.3$ kJ/mol. $k_m =$

Table 5. Kinetic analysis of observed carbon dissolution rates.

Answered by experiments & modeling analysis	Are the		
	mass transfer	interfacial reaction	mass transfer & interfacial reaction
	the rate limiting step(s) for the carbon dissolution?		
Observed rates fit well with modeling	yes	yes	yes
Small activation energy of rate constants	yes	no	unclear
Rate affected by liquid phase agitation	yes	no	unclear
Rate constants agreed with other studies	yes	unclear	unclear
Summary	yes	no	unclear

0.00355 cm/s was estimated at 1 873 K in a resistance furnace. But this k_m value is not large enough to describe the fast dissolution rate observed in run 1 873I in the induction furnace. A higher mass transfer coefficient, $k_m=0.0143$ cm/s, was found to provide the best fitting for the results of run 1 873I as shown by dotted line in Figure. The increase of k_m from 0.00355 cm/s estimated for resistance furnace to 0.0143 cm/s obtained for induction furnace at 1 873 K is readily explained by induction forced convection in the liquid phase. This strongly indicates the importance of mass transfer to the overall dissolution process. Another fact that supports this argument is the mass transfer coefficient, k_m , obtained from this study were of same order with those found by Shibata *et al.*²³⁾ and Mori *et al.*²⁶⁾ for slag-metal reaction. However, there was no evidence to show the dissociation reaction rate for coke is unimportant.

Unfortunately, there is no k_r reported for carbon dissociation reaction rate constant for various cokes, coals or even for graphite. There is a lack of K_r for various carbonaceous materials. Further argument on the extent of the relative resistances, from each of dissociation reaction or mass transfer, to the carbon dissolution process will require a profound knowledge of the interfacial dissociation process. As can be seen in **Table 5**, mass transfer limiting is supported by a number of evidences but there is no evidence to rule out the possibility of the mixed limiting mechanism.

5. Conclusions

A kinetic model was developed for carbon dissolution. The driving force, kinetic and thermodynamic parameters for carbon dissolution when the rate is limited by mass transfer are different with that limited by the dissociation reaction. The rate influencing factors suggested by the model discussion were temperature, solid structure, interfacial active elements, metal composition, liquid agitation, wettability between solid and liquid, solid particle size, ash and side reactions.

Experiments were carried out for the investigation of the limiting step. Resistance or induction furnaces were used to investigate the dissolution rate of graphite and coke at 1 573–1 873 K. It was found that the dissolution rate at higher temperatures and with induction furnace were faster than those at lower temperatures and with resistance furnace, and the mass transfer in the liquid was the major limiting step for the carbon dissolution.

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