Multiparticle Dissolution Kinetics of Carbon in Iron–Carbon–Sulphur Melts

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The derivation of a model of the dissolution of carbon particles following their injection into an iron bath is presented. The model is based on the dissolution of single particles in complete contact with the liquid iron and predicts the change in bath carbon concentration under continuous injection conditions. The model takes into account rate limitation by mass transport, chemical or mixed control.

The model predictions are shown to be consistent with the results of laboratory studies of the injection of high purity graphite into iron when mass transport limitations dominate. This is so for both pure iron/carbon alloys and those containing up to 1.0% dissolved sulfur. If a carbon source such as petroleum coke is substituted for graphite the experimental results deviate from the model predictions. This experimental result suggests that factors other than mass transport can be significant in limiting the rate of dissolution of non-graphitic carbon into liquid iron.

The experimental and industrial implications of the model are discussed and future plans for extension of the model are presented.

KEY WORDS: ironmaking; carbon dissolution; powder dissolution; carburizing.

1. Introduction

The dissolution of particulate carbon, in the form of char or coal in iron/carbon melts, is an important sub-process in steel recarburization, iron bath coal gasification and ferrous direct smelting. In all these processes it is desirable to achieve the maximum possible rate of dissolution to increase the efficiency of the processes and avoid possible losses of the particulate carbon by carry over and oxidation by air burn in the case of open systems or by infiltrate air in closed reactor systems. Efficient dissolution of the carbon content of injected coal is particularly important in recently developed ferrous bath smelting processes such as HIs melt.^{1,2)}

Laboratory studies of the dissolution of fine carbon injected into iron melts are being conducted at the CSIRO, Division of Mineral and Process Engineering as a part of direct smelting research programs. Some details of work on the dissolution of injected graphite particles and the modelling of single particle dissolution kinetics have been presented in a previous publication.³⁾ This paper presents an extension of the dissolution model covering the multiparticle injection of carbon into Fe/C/S melts.

2. Previous Work

In contrast to the large amount of published work on the decarburization of iron/carbon alloys, relatively

few details have been published on graphite and coal dissolution mechanisms and kinetics in molten iron.

Past laboratory studies of graphite dissolution have concentrated on stationary rod,^{4–7)} rotating rod^{5,8–11)} or revolving disc¹²⁾ geometries in order to estimate mass transfer rates from available generalized mass transfer correlations. It is generally agreed in the past work that the rate of graphite solution in iron melts is controlled by mass transfer in which diffusion of carbon in the liquid boundary layer is rate limiting. It is also generally agreed that sulfur in molten iron, even at low levels, depresses the rate of dissolution. Whether the depression is due to chemical or mass transfer limitations is not yet resolved.

As far as the dissolution of particulate carbons in molten iron is concerned, Lehner¹³⁾ injected carbon powder into 6 tonne steel melts and found that mass transport under the conditions used was so fast that carbon dissolution matched the injection rate. Wright and Denholm¹⁴⁾ investigated the dissolution rates of batch additions of particulate graphite, petroleum coke and brown coal char to nitrogen-stirred Fe/C, melts. It was found that the rates were mass transfer controlled. Orsten and Oerters⁸⁾ measured the dissolution rates of coke particles blown onto the surface of Fe/C baths. The dissolution rates were analysed using mass transfer control assumptions. In a model of the thermodynamics and kinetics of coal gasification in iron baths, Barin *et al.*¹⁵⁾ also assumed mass transport dissolution rate control of individual char particles in an iron bath.

3. Multiparticle Dissolution Model

3.1. Single Particle Dissolution

The basic assumptions of the model are that the particles are spherical, and remain spherical during dissolution without breakup, and the particles are in complete contact with the iron bath at all times. Carbon loss from pyrolysis reactions and physical blowthrough are not considered although the model is written in such a form that these factors will be taken into account in the next stage of development. Consider a single particle of carbon with initial radius R_0 dissolving in an otherwise uniform bath of liquid iron/carbon alloy as shown in Fig. 1.

Let

C_s = the saturation carbon concentration (weight fraction)

C_i = the concentration of carbon dissolved in the liquid at the interface (weight fraction)

C_b = the carbon concentration in the bulk liquid away from the particle (weight fraction)

ρ_s = the density of the solid (kg m^{-3})

ρ_l = the density of the liquid (kg m^{-3})

$r(t)$ = the radius of the particle at time t (m).

Assuming a first order reaction, the carbon flux at the interface will be given by:

$$n_{c1} = k(C_s - C_i)\rho_l \quad (1)$$

Where

n_{c1} = the carbon flux, $\text{kg m}^{-2} \text{s}^{-1}$.

k = the interfacial rate constant, m s^{-1} .

The rate of external mass transport is given by:

$$n_{c2} = k_m(C_i - C_b)\rho_l \quad (2)$$

Where here

n_{c2} = the carbon flux, $\text{kg m}^{-2} \text{s}^{-1}$.

k_m = the mass transport coefficient, m s^{-1} .

For steady state dissolution

$$n_{c1} = n_{c2} = n_c \quad (3)$$

Elimination of the unknown interfacial concentration between Eqs. (1) and (2) gives:

$$n_c = k_{\text{eff}}\rho_l(C_s - C_b) \quad (4)$$

Fig. 1. Dissolving particle showing concentration distribution.

Where

$$k_{\text{eff}} = \frac{k_m k}{k_m + k} \quad (5)$$

Note that for processes controlled by mass transport in the liquid phase:

$$k_m \ll k$$

and

$$k_{\text{eff}} \simeq k_m$$

When interfacial effects dominate

$$k \ll k_m$$

and

$$k_{\text{eff}} \simeq k$$

To obtain the overall rate of dissolution, the rate of removal of carbon from the particle must be equated to the rate of carbon transport from the liquid, i.e.

$$n_c = \rho_s \frac{dr}{dt} \quad (6)$$

Thus

$$\frac{dr}{dt} = -\frac{\rho_l}{\rho_s} k_{\text{eff}}[C_s - C_b(t)] \quad (7)$$

To proceed further with the solution of Eq. (7) a value is needed for the effective rate constant k_{eff} . While it is not possible to predict the value of the chemical rate coefficient k , which must be inferred from experimental measurement, correlations are available for the estimation of k_m , the mass transport coefficient in solid-liquid systems.

3.2. Estimation of Mass Transport Coefficients

The estimation of mass transfer coefficients for particles suspended in a liquid is a complex problem for which no reliable correlation has been derived, especially in gas stirred systems. However, it is possible to calculate a *minimum* mass transport coefficient, k_m^* , by taking the slip velocity as the terminal velocity of a particle falling, or in the case of iron/carbon systems, rising in the liquid. Rise velocities were calculated using the standard equation for the terminal velocity of particles in a viscous medium:¹⁶⁾

$$u = \left[\frac{4gd_p(\rho_l - \rho_s)}{3\rho_s c} \right]^{1/2} \quad (8)$$

The drag coefficient c depends on velocity and can only be approximated by analytic expressions over limited ranges. This means that Eq. (8) does not have a simple closed solution but must be solved by an iterative algorithm. The data shown in Fig. 2 was generated by numerical solution of Eq. (8) using a Stokes law approximation to c and $\rho_l = 6900 \text{ kg m}^{-3}$ for liquid iron and $\rho_s = 1600 \text{ kg m}^{-3}$ for graphite.

Rise velocities were calculated at three viscosities which cover the range for iron at 1300 to 1600°C and carbon concentrations of 2% to saturation. Figure 2

Fig. 2.
Dependence of terminal rise velocity on particle size.

shows that for particles of 200 to 1000 μm the rise velocities range from 0.02 to 0.20 m s^{-1} which are significant compared to upward plume velocities of 0.7 to 0.8 m s^{-1} and downward wall velocities of 0.05 to 0.07 m s^{-1} derived in previous work for a 1 kg capacity bottom stirred reactor.^{3,17)} However, the rise velocities rapidly decrease with decreasing particle size. At particle sizes less than 100 μm , the rise velocities ($< 0.006 \text{ m s}^{-1}$) become insignificant compared to the bulk movement of the bath and the small particles can be considered to have negligible slip velocity.

From Fig. 2, over the range of particle size from 10 to 1000 μm , the terminal velocity of graphite particles in iron can be satisfactorily approximated by the simple relationship:

$$u = 0.168 \left(\frac{d}{0.001} \right)^{1.6} \quad \text{.....(9)}$$

The semi-theoretical Frossling (Ranz–Marshall) correlation predicts the Sherwood number, $Sh = k_m^* d / D$, for spherical particles:

$$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3} \quad \text{.....(10)}$$

where, Re : Reynolds number, ud/ν
 Sc : Schmidt number, ν/D
 d : particle diameter (m)
 D : carbon diffusivity ($\text{m}^2 \text{s}^{-1}$)
 ν : kinematic viscosity ($\text{m}^2 \text{s}^{-1}$).

To use Eq. (10) to predict the mass transfer coefficient a value of D , the carbon diffusivity is required. Wanibe *et al.*¹⁸⁾ have presented a summary of estimates of carbon diffusivity in iron by several investigators. Diffusivity data has also been published by McGannon.¹⁹⁾ From these sources the following values have been adopted as representative of the iron–graphite system at temperature of 1450°C.

$$D = 2.5 \times 10^{-8} \text{ m}^2 \text{s}^{-1}, \quad \nu = 8.7 \times 10^{-7} \text{ m}^2 \text{s}^{-1}.$$

Using these values the entries in Table 1 were calculated.

The values of k_m^* in Table 1 are based on the free rise velocities of buoyant particles through an otherwise stagnant liquid. Agitation of the liquid will result in a higher rate of mass transfer. To account for agitation we

Table 1. Dependence of rise velocity and mass transport coefficient on particle size.

d_p (μm)	u (m s^{-1})	k_m^* (m s^{-1})
1	5×10^{-7}	5.01×10^{-2}
10	4.78×10^{-5}	5.17×10^{-3}
100	4.37×10^{-3}	8.38×10^{-4}
1000	0.166	7.24×10^{-4}

can use the following expression proposed by Sano:²⁰⁾

$$Sh = 2 + 0.4 \left(\frac{\varepsilon d_p^4}{\nu^3} \right)^{0.25} (Sc)^{1/3} \quad \text{.....(11)}$$

In Eq. (11),

ε = power input per unit mass of liquid (W kg^{-1})

$= gHQ/V$

g = the gravitational acceleration, 9.807 m s^{-2}

H = the bath depth, m

Q = the gas flow rate, $\text{m}^3 \text{s}^{-1}$

V = the bath volume, m^3 .

So that

$$k_m = \frac{D}{d_p} \left[2 + 0.4 \left(\frac{\varepsilon d_p^4}{\nu^3} \right)^{0.25} \left(\frac{\nu}{D} \right)^{1/3} \right] \quad \text{.....(12)}$$

For the small reactor that has been used for laboratory studies:³⁾

$$H = 0.058 \text{ m}$$

$$Q = 3.333 \times 10^{-5} \text{ to } 1.066 \times 10^{-3} \text{ m}^3 \text{s}^{-1}$$

$$V = 1.449 \times 10^{-4} \text{ m}^3.$$

Mass transport coefficients calculated from the Frossling correlation for quiescent conditions and those for bottom gas injection at rates of 2 to 64 l min^{-1} are plotted against particle size in Fig. 3.

Figure 3 suggests that for particles less than 100 μm , the mass transport coefficients vary inversely with particle size, while for larger particles the mass transport coefficients are approximately independent of particle size. Gas agitation has only a minor effect on the mass transport coefficients for particles less than 10 μm . For larger particles the influence of stirring becomes more significant as particle size increases.

Fig. 3. Dependence of mass transport coefficient on particle size and gas injection rate.

3.3. Solution of the Single Particle Dissolution Equation for Mass Transport Control

Direct substitution of Eq. (12), the value of mass transport coefficient according to Sano into Eq. (7), assuming that $k_{\text{eff}} \approx k_m$, results in a non-linear equation with variable coefficients. The equation in its full form can be solved numerically.

$$\frac{dr}{dt} = -\frac{\rho_l}{\rho_s} \frac{D}{2r} \left[2 + 0.8 \left(\frac{gr^4}{\nu^3} \right)^{0.25} \left(\frac{\nu}{D} \right)^{1/3} \right] \times [C_s - C_b(t)] \quad (13)$$

The radius of a dissolving particle predicted by Eq. (13) was found by numerical simulation using simple Euler integration. As a check on the accuracy of the numerical solution of Eq. (13) analytical solutions can be found for the asymptotic approximations for the mass transport coefficient.

In the case of large particles k_m is approximately independent of particle size and if $C_b(t)$ can be considered to be constant during the dissolution of a single particle then:

$$\int dr = \int -\frac{\rho_l}{\rho_s} k_m [C_s - C_b] dt \quad (14)$$

So that

$$r = R_0 - \frac{\rho_l}{\rho_s} k_m [C_s - C_b] t \quad (15)$$

Equation (15) is a closed solution for the radius of a dissolving carbon particle based on the assumption of a constant value of k . It should be noted that a particle disappears completely after a time given by

$$t_{dl} = \frac{\rho_s}{\rho_l} \frac{R_0}{k_m [C_s - C_b]} \quad (16)$$

Where t_{dl} is the time for complete dissolution of particles sufficiently large for the value of mass transport coefficient to be replaced by a constant value. Note that this solution is also valid for cases in which the particle dissolves under chemical or mixed control if k_m is replaced by k or k_{eff} respectively.

In the case of small particles the mass transport coefficient can be approximated by

$$k_m = k_{m0} \frac{R_0}{r} \quad (17)$$

Where k_{m0} is the value of k_m for particles of a radius R_0 chosen to be sufficiently small that a simple inverse relationship can be applied to k_m and r . From Fig. 3 it would seem that this approximation can be applied for particles of diameter smaller than $50 \mu\text{m}$. For such small particles:

$$\int dr = \int -\frac{\rho_l}{\rho_s} k_{m0} \frac{R_0}{r} [C_s - C_b] dt \quad (18)$$

Noting as before that if C_b is substantially constant during the dissolution of one particle we solve Eq. (18) to get the following expression for r .

$$r = R_0 \left(1 - \frac{2\alpha t}{R_0} \right)^{1/2} \quad (19)$$

Once again the particle disappears after a dissolution time given by

$$t_{ds} = \frac{\rho_s}{\rho_l} \frac{R_0}{2k_{m0} [C_s - C_b(t)]} = \frac{t_{dl}}{2} \quad (20)$$

Where the subscript s indicates that the dissolution time applies to small particles.

3.3.1. Equation Solutions

Figure 4 shows a plot of the dissolution trajectory for a graphite particle of $100 \mu\text{m}$ initial diameter dissolving in a 1 kg iron bath containing 2% C at 1450°C with a carrier gas flow of 4 l min^{-1} under mass transport control. It should be noted that the prediction based on the full Sano correlation is bounded by the two asymptotic approximations.

To illustrate the dependence of dissolution on particle size and agitation of the liquid, Fig. 5 was prepared using data from the numerical solution. The important conclusions from these calculations are that wetted particles less than about $50 \mu\text{m}$ can be considered as a part of the liquid and agitation has an insignificant

Fig. 4.
Predicted dissolution trajectories a particle of 100 μm initial size.

Fig. 5.
Dependence of particle dissolution time on the rate of gas injection into the laboratory scale vessel. Bath carbon content 0.2%.

effect on the dissolution rate of such small particles. For particles of size less than 50 μm , dissolution times are of the order of a fraction of a second in the absence of chemical rate control.

3.4. Continuous Injection Simulation

To simulate industrial scale injection of particulate carbon into liquid iron in the laboratory, large numbers of particles are injected continuously. If we make the following assumptions then results already obtained which describe the dissolution of single particles can be applied to the behaviour of large populations of particles.

- (1) Dissolution is controlled by mass transport. In later work this restriction will be relaxed.
- (2) Particles are in complete contact with the bath at all times during dissolution *i.e.* no blowthrough or floating of particles on the bath surface.
- (3) The dissolution of a single particle makes only a small relative contribution to the total bath carbon concentration.
- (4) The bath carbon concentration can be considered constant during the dissolution time of any one particle.
- (5) Large numbers of particles are injected at a

constant average rate with individual particles arriving at random and unrelated times.

- (6) All particles have the same initial size.

(7) Statistical properties of particles, such as mean sizes, are the same if determined across the population of particles or on a time basis during the entire lifetime of one particle. In the formal language of statistics the mean properties are ergodic with respect to time and ensembles of particles.

Assumptions 1 to 4 have already been made in the course of the derivation of the single particle results. The additional assumptions allow us to represent the behaviour of large numbers of particles in terms of population averages.

Consider now the total mass of carbon in contact with and wetted by the bath M_w . The wetted carbon will be subject to continuous addition from the injected carbon and a continuous loss through dissolution. If $\dot{M}_i$ (kg s^{-1}) is the rate at which carbon is injected into the bath then the mass balance equation can be written

$$\dot{M}_w = \dot{M}_i - \dot{M}_{bc} \quad \text{.....(21)}$$

Where M_{bc} is the total amount of carbon dissolved in the bath.

Now as a result of the random nature of their arrival,

the particles comprising M_w will have a size distribution ranging from R_0 down to zero. The mean particle mass can be found in terms of a time average from

$$\bar{M}_p = \frac{1}{t_d} \int_0^{t_d} m_p dt \quad (22)$$

Where m_p is the mass of the dissolving particle at time t .

The decrease of particle size as a function of time has been studied at some length in a previous section. In addition to the full solution of the non-linear dissolution equation, two approximations were developed which represent the behaviour of particles in the limiting cases of large and small particles. In the case of large particles, r is a linear function of time *i.e.*

$$r = R_0 \left(1 - \frac{t}{t_{dl}} \right) \quad (23)$$

As

$$m_p = \rho_s \frac{4\pi}{3} r^3 \quad (24)$$

Eq. (22) becomes

$$\bar{M}_p = \frac{M_{p0}}{t_d} \int_0^{t_d} \left(1 - \frac{t}{t_{dl}} \right)^3 dt \quad (25)$$

Where $M_{p0} = (4\pi/3)\rho_s R_0^3$ is the initial particle mass.

The integral in Eq. (25) can be evaluated to give

$$\bar{M}_p = \frac{M_{p0}}{4} \quad (26)$$

For small particles the increase in mass transport coefficient with decreasing particle size becomes significant. By re-arranging Eq. (19) we get as an expression for r

$$r = R_0 \left(1 - \frac{t}{t_{ds}} \right)^{1/2} \quad (27)$$

The expression for the time average particle mass corresponding to Eq. (25) is thus

$$\bar{M}_p = \frac{M_{p0}}{t_{ds}} \int_0^{t_{ds}} \left(1 - \frac{t}{t_{ds}} \right)^{3/2} dt \quad (28)$$

This can be reduced to

$$\bar{M}_p = \frac{2M_{p0}}{5} \quad (29)$$

The actual size *vs.* time dissolution profile of a particle of arbitrary initial size will lie within the bounds defined by the two cases considered above. From this it can be concluded that the mean particle mass for a population of particles will lie between the limits

$$\frac{1}{4} M_{p0} < \bar{M}_p < \frac{2}{5} M_{p0} \quad (30)$$

The number of wetted particles is

$$N_{pw} = \frac{M_w}{M_p} \quad (31)$$

The mean rate of mass loss from the wetted carbon due to the dissolution of one particle is

$$\bar{\dot{m}}_p = \frac{1}{t_d} \int_0^{t_d} \frac{dm_p}{dt} dt \quad (32)$$

But the integral on the right side of Eq. (32) represents the total mass of the particle so that

$$\int_0^{t_d} \frac{dm_p}{dt} dt = M_{p0} \quad (33)$$

Then

$$\bar{\dot{m}}_p = \frac{M_{p0}}{t_d} \quad (34)$$

It should be noted that Eq. (34) holds irrespective of the actual profile of dissolution within the time interval t_d . Now the total rate of carbon gained by the bath as a result of dissolution is the product of the number of wet particles and the mean rate of dissolution from one particle.

$$\dot{M}_{bc} = N_{pw} \bar{\dot{m}}_p \quad (35)$$

Using the result for the case of constant mass transfer coefficient

$$\dot{M}_{bc} = \frac{4M_w}{M_{p0}} \frac{M_{p0}}{t_{dl}} \quad (36)$$

$$\dot{M}_{bc} = \frac{4M_w}{t_{dl}} \quad (37)$$

But t_{dl} is known as a function of initial radius and bath carbon concentration. By substituting from Eq. (16) we get

$$\dot{M}_{bc} = 4M_w \frac{k_m \rho_l}{R_0 \rho_s} [C_s - C_b(t)] \quad (38)$$

$$\dot{M}_{bc} = \frac{M_w}{\tau} [C_s - C_b(t)] \quad (39)$$

Where the time constant τ is given by

$$\tau = \frac{R_0 \rho_s}{4k_m \rho_l} \quad (40)$$

By a similar process using the appropriate average particle size and noting that $t_{dl} = 2t_{ds}$, the value of τ for small particles can be evaluated as

$$\tau = \frac{1}{2} \times \frac{2}{5} \frac{R_0 \rho_s}{k_m \rho_l} \quad (41)$$

So that τ must lie between the limits

$$0.2 \frac{R_0 \rho_s}{k_m \rho_l} > \tau > 0.25 \frac{R_0 \rho_s}{k_m \rho_l} \quad (42)$$

The difference between these limits on τ are likely to be less than the uncertainty in the estimate of particle size and shape or mass transport coefficient in any practical situation. The significance of this is that the actual detail of the dissolution profile of individual particles is of little consequence so far as the observable

behaviour of a population of particles is concerned. It should be noted that the initial size of particles is most important as it determines the value of the mass transport coefficient k_m in expression 42 as well as appearing explicitly in the limits for τ .

As the bath carbon concentration is related to the bath iron mass by the simple relationship

$$C_b = \frac{M_{bc}}{M_{bc} + M_{iron}} \quad \dots\dots\dots(43)$$

Then

$$\dot{M}_{bc} = \frac{M_w}{\tau} \left[C_s - \frac{M_{bc}}{M_{bc} + M_{iron}} \right] \quad \dots\dots\dots(44)$$

Equation (44) together with Eq. (21), the mass balance equation, describe the situation in which carbon is continuously injected into an iron bath. As these equations contain products and quotients of the dependent variables simple analytic solution is not possible. For this reason these equations were solved by numerical integration. As was done in the case of the single particle dissolution equation a simple Euler algorithm was used.

Two computer programs were written to numerically simulate the continuous injection of particles. In the first program the rate of carbon dissolution from the total mass of wetted carbon is calculated using Eq. (44). The second version incorporated a more detailed simulation of the dissolution process by taking into account the size distribution of the wetted carbon particles. This version does not depend on the assumptions which underlie the analytical treatment of multi-particle injection. The modelling of the particle size distribution involves a considerable increase in computation but yields as a by-product, information on the size distribution of the dissolving particles. If desired, this model could be extended to accept the size distribution of the injected particles. Because of its independence of the assumptions made to derive Eq. (44) the model incorporating the size distribution can be used as a validity check for this derivation and the assumptions on which it is based. This is illustrated by Fig. 6 which is a

comparison of the predictions of the lumped size model based on Eq. (44) and the size distribution model. The two models predict rates of carbon dissolution which are indistinguishable. **Figure 6** was based on a value of mass transport coefficient of 10^{-4} m s^{-1} . This low value is unrepresentative of graphite dissolution in pure iron under mass transport control. It was selected together with a large particle size of 1 mm to facilitate comparison of the dissolution rate predicted by the two models. It also serves as a point of comparison for the simulations of more realistic situations presented in the next section. Although in Fig. 6, the trajectory corresponding to immediate dissolution of the total injected carbon terminates at the level of carbon saturation of the liquid, the simulation represents the physical situation in which carbon injection proceeds at a uniform rate beyond this level.

4. Experimental

Full details of the apparatus, material used and experimental procedure have been described in a previous paper.³⁾ Briefly, the various carbon sources were crushed and $-355 + 106 \mu\text{m}$ size fractions were prepared by dry screening (Alpine air screening system). The particulate carbon was bottom injected into a 1 kg Fe/C bath at 1450°C using nitrogen as a carrier gas. Bath samples were taken from the bath at fixed intervals throughout the injection period and later analysed for dissolved carbon.

5. Results

The dissolution model predicts increase of bath carbon content as a function of time resulting from the continuous injection of carbon into an iron bath. **Figure 7** compares the calculated and measured rates of graphite dissolution at injection rates of 3.4 and 7.2 g min^{-1} . From the plots it is impossible to detect any disagreement between the high rate of dissolution predicted on the basis of theory and the experimental measurements. There are no adjustable parameters in the model as the mass transport coefficient was deter-

Fig. 6.
Carbon dissolution rates predicted by lumped and distributed particle size models.

Fig. 7.
Comparison of experimental and model results for two injection rates.

Fig. 8.
Comparison of experimental and model results for injection into an iron bath containing sulfur.

Fig. 9.
Model and experimentally determined dissolution profiles for petroleum, coke injected into an iron bath of low sulfur content ($S=0.02\%$, equivalent carbon injection rate $=3.9\text{ g min}^{-1}$).

mined by the Sano correlation. For a carrier gas flow of 4 l min^{-1} this gives a value of $\approx 10^{-3}\text{ m s}^{-1}$.

High rates of graphite dissolution were observed even if the iron baths contained sulfur. Figure 8 compares calculated and measured dissolution rates for the injection of graphite at 4 g min^{-1} into a bath containing 1.0% sulfur. The fractional carbon concentration takes into account the lowering of the carbon saturation level

at the sulfur concentration (5.02% at zero $[S]$ to 4.62% at 1.0% $[S]$). The initial slope of the carbon uptake line is unchanged and little difference in the breakway from the total carbon injection line can be distinguished. It has been estimated in other work²¹⁾ that the addition of 0.12% sulfur can decrease the mass transport coefficient for the dissolution of graphite by approximately 20% . Further increases have pro-

Fig. 10.

Model and experimentally determined dissolution profiles for petroleum coke injected into an iron bath of high sulfur content ($S=0.4\%$, equivalent carbon injection rate $= 3.9 \text{ g min}^{-1}$).

gressively less effect. A reduction of this magnitude leads to an imperceptible change of the shape of the simulated injection curves because of the already high values of the mass transport coefficients.

If non-graphitic forms of carbon such as petroleum coke are injected instead of graphite there is a detectable reduction in the effective rate coefficient (k_{eff}). This is illustrated by Fig. 9 which shows a carbon dissolution trajectory calculated by the model superimposed on experimental data. In this case the effective rate coefficient was found by an iterative procedure which minimised the square error between the model and experimental data.

The effective rate coefficient is depressed further if the bath sulfur content is increased. This is shown by Fig. 10. As well as a reduction of effective rate coefficient, adding sulfur to the bath leads to a profile of carbon accumulation which cannot be closely fitted by the model for any value of k_{eff} . This suggests that the influence of bath sulfur extends beyond a reduction in the effective rate coefficient k_{eff} as defined by Eq. (5). The implication is that bath sulfur impedes carbon dissolution through mechanisms which have not been incorporated in the model.

6. Discussion

The application of the model to the experimental results for the injection and dissolution of particulate graphite in Fe/C melts has confirmed the supposition in past work that the rates are controlled by mass transfer limitations. The mass transfer coefficient is high and under these conditions the dissolution rates are so fast that relatively large variations in the feedrate, particle size, bath sulfur concentration and gas stirring rate have only a minor effect under the experimental conditions studied.

This is not always the case, as has been demonstrated in the case of petroleum coke injection where k_{eff} is reduced by an order of magnitude by the presence of sulfur in the bath. Similar experimental results have been obtained for other partially graphitised forms of carbon such high rank coals, and chars derived from

Table 2. Comparison of effective rate constants determined by matching the dissolution model to experimental results.

Carbon source	$k_{\text{eff}} \text{ (m s}^{-1}\text{)}$	
	Sulfur $< 0.01\%$	Sulfur $= 0.4\%$
Graphite [†]	7×10^{-4}	6×10^{-4}
Non graphitic [†]	6×10^{-4}	1×10^{-4}
Graphite	1×10^{-3}	1×10^{-3}
Anthracite	2×10^{-3}	2×10^{-3}
Petroleum Coke	$3 \times 10^{-5}^*$	6×10^{-6}
Jarrah Char	2×10^{-5}	6×10^{-7}
Brown Coal Char	1×10^{-5}	6×10^{-6}

[†] Results by Shigeno *et al.*

* Bath sulfur $\approx 0.03\%$ due to pickup from the coke

coal and wood. The results are consistent with the work of Shigeno, Tokuda and Ohtani⁹⁾ (see Table 2) who found that the apparent mass transport coefficient of non-graphitic carbon dissolving in iron is lower than that of graphite. In the same study, it was found that the dissolution rate of non-graphitic carbons was more sensitive than graphite to sulfur in the liquid phase. The petroleum coke used for these injection tests was 98% pure carbon and apart from the small impurity content, differed from graphite only in inter-atomic structure. This supports the conclusion of Shigeno *et al.* that the crystalline structure of carbon influences its dissolution rate.

A limitation of the model in its present state is that it is based on the assumption that all injected particles enter the bath liquid. It does not take into account loss of carbon from volatiles, physical blowthrough or dissolution of floating carbon. For this reason the entries in Table 2 corresponding to 0.4% bath sulfur should be interpreted with caution. At this sulfur level the model cannot be made to fit the experimental data. This suggests that at least one of the assumptions on which the model is based is in error. Sulfur is a surface active agent in liquid iron and may impede carbon dissolution by inhibiting the entry of carbon bearing particles into liquid iron by changing the wetting characteristics of the gas-liquid interface.

The extension of the model to include factors such as coal volatility, dissolution of floating char, char/iron wetting characteristics and coal/char structures is the topic of continuing work.

7. Conclusions

(1) A mathematical model describing the change in bath carbon concentration during the continuous injection of particulate carbon has been developed.

(2) The model shows that dissolution times for individual particles under mass transport control in baths of carbon concentrations less than about 4% are very short. This results in predictions over ranges of practical interest that feedrate, particle size and gas stirring rates have little effect on the overall rates of bath takeover of injected carbon.

(3) The model predictions are consistent with experimental measurements of the dissolution rates of graphite injected into an iron bath when mass transport limitations dominate.

(4) When non-graphitic carbon is injected into liquid iron of low sulfur content the rate of dissolution is slower. The overall behaviour is consistent with a model in which dissolution rate is limited by a combination of liquid side mass transfer and interfacial effects.

(5) The dissolution of non-graphitic carbon injected into liquid iron of high sulfur content departs from the predictions of a mass transport based model. This suggests that the rate of carbon accumulation is limited by factors other than mass transport from solid to liquid.

(6) The initial model forms the foundation for further development leading to the production of a comprehensive predictive and analytical tool for iron bath coal injection/dissolution.

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