The Effect of the Liquid Fe–C Phase on the Kinetics in the Carburization of Iron by CO at 1 523 K

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In order to evaluate the effect of liquid Fe–C alloy produced during the carburization on the kinetics of iron carburization, the rates of carburization of iron by CO–Ar gas mixtures have been measured gravimetrically at 1 523 K and the growing rates of the liquid Fe–C layer thickness are also measured. The measurements were made under conditions for which the gas phase mass transfer was negligible. It is found that the weight gains due to the carburization reaction are almost proportional to \( t^{2/3} \) within experimental scatters. For all runs except that of 1% CO, the liquid phase is observed after the carburization time of 300 s. The liquid phase thickness is found to be almost constant for the first 3.6 ks. After 3.6 ks, the liquid phase thickness starts to increase almost linearly with time. The mechanism to maintain the constant thickness is briefly discussed. The carburization reaction rate is calculated based on the well established decarburization rates and the chemical reaction rates, it is confirmed that the rate-controlling step of the carburization reaction of iron with CO gas at 1 523 K is the chemical reaction \( CO + O_{ad} \rightarrow CO_2 \) at the surface after the liquid Fe–C phase is produced.

KEY WORDS: carburization; liquid-solid interface; liquid Fe–C phase, melting point; ironmaking.

1. Introduction

Carburization process of iron by CO gas is of essential importance for the ironmaking process in the blast furnace and scrap melting. A considerable attention has been devoted to the kinetics and reaction mechanisms of the carburization process. Most of studies have been mainly devoted to the measurements of the carburization rate of solid iron and its chemical reaction mechanism.\(^1\)–\(^4\) It is well known that the carburization reaction was consisted of elementary reactions involving absorbed species,

\[
\begin{align*}
CO \rightarrow C_{ad} + O_{ad} & \quad \text{(1)} \\
CO + O_{ad} \rightarrow CO_2 & \quad \text{(2)}
\end{align*}
\]

and the reaction (2) was found to be rate determining step.\(^1\)–\(^4\) Most of carburization experiments for the solid iron have been carried out for the thin film or thin wire of iron to avoid the contribution of the diffusion process in the solid samples. For the liquid state carburization, the experiments were carried out by jetting CO gas onto the surface of the inductively heated and stirred molten iron in the crucible\(^5\) or strongly stirred levitated iron sphere\(^5\) to minimize the mass transfer restriction in the liquid phase. In the actual processes, there will be always with the effect of mass transport process, since the charged iron is generally not the shape of film or wire. So it is very important to evaluate the mass transfer contribution in the carburization process from a practical view point.

Most of carburization experiments with the solid iron with CO gas have been carried out at less than 1 426 K (eutectic temperature of Fe–C system) while with molten iron at more than 1 810 K\(^6\) (melting point of iron\(^6\)). The carburization reaction of iron with CO gas between 1 426 K and 1 810 K have not been well studied. In this experimental condition, the liquid phase is not existed for an initial reaction stage, however, liquid Fe–C alloy phase is consequently produced at the reacting surface with proceeding of the reaction since the melting point of Fe–C alloy is decreased with increasing of the carbon content in iron. After the development of the liquid Fe–C phase, the carbon is transferred through this liquid Fe–C phase to the solid Fe–C matrix and the liquid-solid interface will be moved to the solid iron side with time. Namely the amount of the liquid phase will increase with time. In this carburization process, the role of the liquid phase for the total carburization process gas has not been well understood despite of its practical importance.

In the present study, the carburization rates with various CO–Ar gas mixtures have been measured gravimetrically at 1 523 K and the growing rates of the liquid Fe–C layer are also measured in order to investigate the role of the liquid Fe–C alloy phase on the carburization reaction of iron with CO gas.
2. Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 1. An iron plate (20×20×5 mm) was buried in Al₂O₃ powder contained in an alumina crucible (30×40 mm) and heated by a SiC furnace. The alumina reaction tube (ID 60 mm) was fitted with water-cooled O-ring sealed brass caps. The reacting CO–Ar gas mixture was jetted onto the surface of the metal. A 4-mm bore alumina tube held 10 mm above the metal surface was used to introduce the reacting gas. The end position of the gas inlet tube was adjusted to keep the center of reacting tube by using the Al₂O₃ adjusting ring. The Ar–CO gas mixtures were prepared by mixing the high purity gases, after drying, by passing through columns of magnesium percolate and, for CO, by passing ascarite. Flow rates were controlled by mass flow controllers. All the experiments were carried out at 1 523 K. High purity iron was used for specimen preparation. The typical impurity content of this material (in wt pct) is: O, 0.04, C, 0.02, Al, 0.007, S, 0.002. The specimen was prepared by surface grinding and metallographically polishing the upper surface.

The pre-weighted (about 20×10⁻¹ kg) sample was slowly brought to temperature under flowing purified Ar. The inlet tube was adjusted to the appropriate height and then the reaction gas, which had been preset, was introduced over the sample. Experiments were terminated by switching back to argon and the sample was pulled down to the lower part of the furnace and allowing to cool to room temperature. The weight gain of carbon during an experiment was determined by measuring the total weight gain of the sample. The sample was sectioned and the liquid phase thickness is determined by the optical microscope and SEM.

3. Results

The initial results for the rate of carburization as a function of the flow rate of CO gas at 1 523 K are presented in Fig. 2 with the expected values for gas mass-transfer control calculated from the well established correlation of Taniguchi et al. The details of the calculation for mass transfer control are presented in the appendix. Clearly, the effects of gas mass-transfer restriction at high flow rates would be negligible. In the studied range of CO pressures the reaction rate were independent of the total gas flow for the carburization in CO–Ar at flow velocities between 6.66 to 13.33×10⁻⁶ m³/s.

The weight gains of iron in CO–Ar mixtures ranging from 1 to 100 % CO with total flow rate of 11.66×10⁻⁶ m³/s as a function of time at 1 523 K are shown in Fig. 3. All these weight gains are replotted logarithmically as a function of time in Fig. 4, and where the lines are drawn with a slope of 2/3. From Fig.4, It can be said that the weight gains are reasonably proportional to t²/₃ within experimental scatters except one result. This exception will be due to the unexpected experimental error. Thus the weight gain (Wg) is experimentally expressed by following equation.

\[ Wg = k_{app} p_{CO} t^{2/3} \] ..............................(3)

where \( k_{app} \) is the experimental rate constant and \( p_{CO} \) is the partial pressure of CO gas. Calculated weight gain curves based on the Eq. (3) are also presented by solid lines in Fig. 3.

For all runs except that of 1 % and 20 % of \( p_{CO} \), the liquid phase was always observed after the carburization time of 5 min. For runs with \( p_{CO} \) of 20 %, the liquid phase was not
thickness was about 40 μm for 100% CO gas. After about 3.6 ks, the liquid phase thickness starts to increase with time. The nearly constant thickness of liquid layer means that the supply rate and removal rate of carbon at the liquid-solid interface is approximately equal for the first 3.6 ks of the reaction time.

4. Discussion

Carburization process of iron with CO gas at 1523 K in the present study can be divided into following steps. (1) gas phase mass-transfer, (2) chemical reaction at the liquid iron surface, (3) carbon diffusion in the liquid phase, (4) carbon diffusion in the solid phase. As we already mentioned, the gas phase mass-transfer step is not the rate controlling step in the present experimental conditions. The step of carbon diffusion in the solid phase also cannot be the rate-limiting process, because if the carbon diffusion process in the solid phase is slow, the carbon will accumulate at the liquid-solid interface and then the liquid phase is simply produced due to the carbon accumulation. Namely the diffusion process in the solid phase has essential no effects with the total carburization rate once the liquid phase is produced; Slow solid phase diffusion process is replaced by the liquid phase production.

4.1. Diffusion Rate of Carbon in the Liquid Fe–C

As shown in Fig. 5, the liquid layer thickness is nearly constant for the first 3.6 ks. It means that the carburization process is apparently under steady state condition. Under steady state condition, the carbon diffusion rate, \( J_0 \) (kg/m²s), in the liquid phase can be presented by

\[
J_0 = D_L \frac{\partial C_i}{\partial x} = D_L (C_S - C_i) / \delta_L \quad \ldots \ldots \ldots \ldots \ldots (4)
\]

where \( D_L \) is the chemical diffusivity, \( C_S \) and \( C_i \) are the carbon concentration in kg/m³ at the liquid surface and at the liquid–solid interface respectively and \( \delta_L \) is the liquid phase thickness.

If carbon diffusion rate in the liquid phase is assumed to be the rate-limiting process, the carbon concentration at the surface \( C_s \) can be reasonably assumed to be carbon saturated concentration (4.5 mass% at 1523 K) of 0.33×10⁻³ kg/m³ at 1523 K and \( C_i \) is the carbon concentration at the solid–liquid interface of about 0.116×10⁻¹ kg/m³, calculated from the carbon concentration (1.6 mass%) at the solidus line in Fe–C system at 1523 K. Unfortunately, the diffusivity of carbon in liquid Fe–C alloy are not well established.⁹–¹¹ Reported \( D_L \) at 1523 K is about 1.0×10⁻⁸ to 2.2×10⁻⁸ m²/s and the lowest \( D_L \) of 1.0×10⁻⁸ m²/s was adapted in the present calculation. Tentatively the value of 100 μm is used for that of \( \delta_L \) as a lowest diffusion rate. By substituting these values, the carbon diffusion rate \( (J_0) \) in the liquid phase is given by about 7×10⁻⁵ kg/m²s.

Differentiate the Eq. (3) with time, the experimental carburization rate can be expressed by

\[
\text{Rate} = \frac{dW_g}{dt} = (2/3) k_{app} p_{CO} \rho_{CO}^{1/3} \quad \ldots \ldots \ldots \ldots \ldots (5)
\]

The calculated carbon diffusion rate in the liquid phase and experimental carburization rates with several partial pressures of CO gas a function of time from 0.3 to 3.6 ks are presented in Fig. 6. As a reacting surface, the sample’s
nominal surface area of 4 cm\(^2\) is used. The calculate diffusion rate in the liquid phase is about 10\(^4\) order larger than the experimental result, even the lowest \(D_o\) was used to calculate. It means that the carbon diffusion in the liquid phase cannot be the rate-limiting process at least for the first 3.6 ks. The calculated diffusion rate doesn’t depend on time, since the calculation was carried out by assuming the steady state. In actual situation, the surface concentration and the liquid phase thickness can change slightly with time. But these slight changes will not affect the fundamental view of the calculated result that the liquid phase diffusion rate is much larger than the experimental ones.

### 4.2 Chemical Reaction at the Surface of Liquid Fe–C Alloy

It was reported that the rate of the carburization reaction of solid iron with CO was decreased with the carbon concentration\(^1\)\(^2\). Unfortunately the effect of the carbon concentration on the carburization rate of liquid iron was not well examined. But it will be assumed that the rate in the liquid phase has the same tendency with carbon, or the carburization rate at the liquid phase or carbon supply rate also will decrease with the carbon concentration. In the carburization process of iron, once the liquid phase is produced, the surface carbon concentration suddenly increases from around 1.6 to 3.4 mass%. After that, the carburization reaction is carried out at the surface with high carbon concentration of more than 3.4 mass%. Thus the carburization reaction rate will drastically decrease since the activity of carbon \(a_C\) significantly increases with slight increase of carbon concentration over 3.4 mass%.

If the rate determining step for the carburization is taken to be given by the reaction (2),\(^1\)\(^3\) we may express the reaction rate \((V)\) as

\[ V=k_p\theta_0-k'_p\theta_0(1-\theta_0-\theta_s) \] ..........................(6)

where \(\theta_0\) and \(\theta_s\) are the fractional coverage by oxygen and sulfur respectively. \(k_p\) and \(k'_p\) represent forward and reverse rate constant, respectively. We may assume the equilibrium between chemisorbed oxygen and dissolved oxygen, then a general equilibrium absorption isotherm of the form is:

\[ \theta_0/(1-\theta_0-\theta_s)=K_O(p_{CO}/p_{CO}) \] ..........................(7)

\[ \theta_s/(1-\theta_0-\theta_s)=K_S'a_s \] ..........................(7')

where \(K_O\) is the absorption coefficient for oxygen with respect to the oxygen activity expressed by \(p_{CO}/p_{CO}\). \(K_S\)' is the absorption coefficient for sulfur and \(a_s\) is the sulfur activity with a standard state of 1 mass% S in carbon saturated iron. If microscopic reversibility\(^1\)\(^2\) holds,

\[ k_{pcO}\theta_0=k'_p\theta_0(1-\theta_0-\theta_s) \] ..........................(8)

it follows from Eq. (7) and

\[ k'_p/k_p=K_O \] ..........................(9)

Thus \(k_p\) can be estimated from Eq. (9) since the value of \(k'_p\) (mol cm\(^{-2}\) s\(^{-1}\) atm\(^{-1}\)) and \(K_O\) have been already established and given by\(^1\)\(^3\)\(^-\)\(^5\)\(^1\)\(^5\)

\[ \log(K_O)=2.910/T+0.47 \] ..........................(10)

\[ \log(k'_p)=-5.080/T-0.21 \] ..........................(11)

The evaluated \(k_p\) is about 1.2\(\times\)10\(^{-2}\) mol/m\(^2\) s\(^{-1}\) atm at 1 523 K.

The adsorption coefficient \(K_O\)' with respect to a standard state for the dissolved oxygen of the 1 mass% ideal solution may be readily deduced to given by

\[ \log(K_O)'=11.370/T-4.09 \] ..........................(12)

Under high carbon concentration (small \(\theta_0\), the carburization rate can be expressed by using the evaluated rate constant \(k_p\),

\[ \text{Rate}=k_p\theta_0 \]

\[ =k_p\theta_0(K_O'a_0/(1+K_O'a_O+K_S'a_s)) \] ..........................(13)

where \(a_O\) is the oxygen activity with respect to a standard state for the dissolved oxygen of the 1 mass% ideal solution. The adsorption coefficient \(K_S\)' with respect to a standard state for the dissolved sulfur of the 1 mass% ideal solution is given by\(^1\)\(^3\)\(^-\)\(^5\)\(^1\)\(^5\)

\[ \log(K_S)'=3.600/T+0.57 \] ..........................(14)

Limited studies suggested that relationship (14) were applicable from carbon saturation down to at least 3 mass% of carbon.\(^1\)\(^0\) In the present study, the carbon concentration of the liquid phase is more than 3 mass%. Therefore, the relation (14) was used to evaluate the effect of absorbed sulfur. As already mentioned, the reaction (2) is the rate-controlling step for the carburization of iron with CO and other steps are at virtual equilibrium, the reaction

\[ O+2C=CO \] ..........................(15)

will be also in equilibrium. Then, the oxygen activity \(a_O\) can be evaluated from the carbon activity with the appropriate thermodynamic data.\(^5\)\(^6\)-\(^8\) Since the chemical reaction is assumed to be the rate limiting, the liquid phase diffusion rate can be very fast compared with the chemical reaction rate. Therefore, the carbon concentration at the liquid surface will be close to that at the liquid-solid interface of 3.4 mass% at 1 523 K. Thus \(a_O\) can be calculated by assuming the carbon surface concentration of 3.4 mass% as a first approximation. Substituting all these values into Eq. (13), this
constant diffusivity yields assuming unidirectional diffusion into a semi-infinite medium from the appropriate solution to Fick’s second law by diffusion in the solid phase for the initial stage may be calculated at the surface.

The reaction rates using the evaluated rate constant are shown as closed squares in Fig. 7 and the empirical carburization rates by Eq. (5) for CO 100 % are also shown as closed circles. There is a reasonable quantitative agreement (within the factor of 2) between the calculated carburization rate and the experimental result. If we take into account the gradual increase of the surface carbon concentration for the calculation, the calculated reaction rate will become much closer to the experimental one. Compared the experimental carburization rate with the chemical reaction rate and the carbon diffusion rate in the liquid phase, the carburization process in the present study is most likely to be controlled by the chemical reaction of (2).

4.3. Constant Liquid Phase Thickness

The constant liquid phase thickness for the first 3.6 ks must be related to the balance between the supply rate and removal rate of carbon at the liquid–solid interface. Since the liquid phase diffusion rate of Fe–C alloy is likely to be significantly fast compared with the surface reaction rate, the carbon supply rate at the solid–liquid interface will be essentially the same to the chemical reaction rate at the surface. Therefore the carbon supply rate at the solid–liquid interface can be assumed to be equal to the chemical reaction rate at the surface.

As a first approximation, the carbon gain due to the diffusion in the solid phase for the initial stage may be calculated from the appropriate solution to Fick’s second law by assuming unidirectional diffusion into a semi-infinite medium with constant surface concentration of 1.6 mass% and constant diffusivity yields

$$W = (2/\pi)^{1/2}(D_s \rho)^{1/2}(C_s - C_0)S \quad \quad \quad (16)$$

and the corresponding diffusion rate is by

$$dW/dt = (D_s / \pi)^{1/2}t^{-1/2} (C_s - C_0)S \quad \quad \quad (17)$$

where $D_s$ is the chemical diffusivity, $t$ is the time in seconds, $C_0$ and $C_s$ are the concentration in kg/m$^3$ initially and at the surface ($0.116 \times 10^3$ kg/m$^3$) respectively and $W$ (kg) is the total weight gain of carbon which has entered the semi-infinite medium and $S$ is the cross-sectional area of $4 \times 10^{-4}$ m$^2$. The diffusivity of carbon in solid Fe–C alloy also are not well established.$^{19-21}$ Reported $D_s$ at 1523 K is about $2.8 \times 10^{-10}$ to $6.0 \times 10^{-9}$ m$^2$/s and the lowest $D_s$ of $2.8 \times 10^{-10}$ m$^2$/s was tentatively adapted in the present study. In this calculation, the initial concentration of carbon in the solid phase is assumed to be zero. However, the carbon is actually existed in the solid phase after the liquid phase has been developed.

The effect of the initial carbon distribution in the solid phase is approximately compensated by adjusting the starting time. Since the liquid phase thickness is almost constant as shown in Fig. 5. The initial weight gain just before the liquid phase formation can be almost equal to the carbon content in the liquid phase of constant thickness and is about 5.0 mg and 2.5 mg for $p_{CO}$ of 100 % and 50 % respectively. From the Eq. (16), the time needed to gain these initial carbon weights, $t_i$, can be easily calculated and $t_i$ is adapted as a starting time of carburization reaction with the liquid phase layer. The values of $t_i$ for $p_{CO}$ of 100 % and 50 % are about 72 s and 40 s respectively. The diffusion process before $t_i$ can be neglected since it reflects the process without the liquid phase.

The diffusion rate in the solid phase based on Eq. (17) and the calculated chemical reaction rate with 100 % CO at the liquid surface are shown in Fig. 8. It is shown that the diffusion rate and the chemical reaction rate are reasonably close each other. However, the diffusion rate especially for the initial stage is relatively faster than the chemical reaction rate. The same situation will be occur for the reaction with 50 % CO because the chemical reaction rate is much slower than that with 100 % CO. The diffusion rate may be much larger since the calculation is carried out by using the lowest $D_s$. From the calculated result, it can be suggested that the carbon removal rate at the liquid–solid interface surpasses the carbon supply rate for the carburization of iron at the initial stage and the liquid–solid interface may shift towards to the liquid phase side and then the liquid phase thickness will be decreased, although the experimental results showed the almost constant thickness.

The concept of the mechanism to maintain the near constant thickness of liquid phase even though the removal rate

Fig. 7. Comparison of the chemical reaction rate at the surface and the experimental carburization rates. Closed circles are experimental results and closed squares are calculated chemical reaction rates.

Fig. 8. Comparison of the chemical reaction rate at the surface and the carbon diffusion rate in the solid phase.
Since the reaction rate is almost constant due to the near constant carbon concentration at the surface, finally the reaction flux at solid phase side of the interface will decrease. Due to the decrease of concentration gradient in the solid will decrease since the carbon supplied from the liquid phase to the solid side by carburization reaction of iron with high carbon content, some amount of carbon must be removed from the interface. As shown in Fig. 5, the thickness of the liquid phase is apparently fluctuated. This fluctuation may reflect the proposed mechanism, but unfortunately the experimental scatters are too large to confirm the supposed oscillation.

Based on the same assumption for calculating the solid–liquid interface, some amount of carbon must be removed from the interface. Therefore the sudden increase of the liquid phase thickness with time after 3.6 ks may reach to another end. Accordingly, the proposed mechanism to maintain the constant liquid phase thickness during the carburization of Fe with CO gas appears to be fully consistent with all the results.

5. Concluding Remarks

Generally speaking, the measurements of the carburization rate of solid or liquid iron with CO gas are carried out with the conditions of the low carbon content in the iron. In these cases, the carburization rate is significantly fast, and to make the chemical reaction to be the rate-controlling step, many efforts have been devoted to eliminate the effect of the mass transfer of gas or liquid phase. However, in the present carburization study, the chemical reaction rate is relatively slow and will be the rate-controlling step. This is simply because the carbon content of iron in the present experimental conditions is very high especially after the liquid phase is produced. It means that the carbon penetration depth reaches to about 4 mm closed to the sample thickness of 5 mm. It means that the penetration depth after about 3.6 ks may reach to another end of the sample. Therefore the sudden increase of the liquid phase thickness with time after 3.6 ks just as shown in Fig. 5 may be corresponded to the situation after the penetration depth reaches to another end. Accordingly, the proposed mechanism to maintain the constant liquid phase thickness during the carburization of Fe with CO gas appears to be fully consistent with all the results.
bon concentration. Unfortunately, however, there are few studies on the carburization reaction of iron with high carbon. Further work at high carbon concentration, possibly by studying the carburization rate of liquid iron with high carbon concentration, is needed to provide the quantitative information.

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REFERENCE


Appendix

Mass Transfer Considerations for Gas Phase

Several mass transfer correlations have been proposed for the case of the impinging jet onto the surface of a melt in a crucible. Actually there are no significant differences between them to estimate the mass transfer coefficient. Within the experimental scatter, these correlations are in reasonable accord with the data at the higher Reynolds numbers.

In the present study, the correlation of Taniguchi was used. They obtained the correlation

\[ Sh = 0.40(x_0/d)^{-1.1} \text{Re}^{0.68} \text{Sc}^{1.3} \quad \text{(A-1)} \]

for \((a/d) = C(a/d)_C\) where

\[ (a/d)_C = 0.0046 \text{Re}^{0.68} (x_0/d)^{-1.5} \times \exp[(1.98(d_0/x_0/d)(\exp \text{Sc}/\text{Sc})] \]

and where \(x_0\) is radius of reaction surface, \(d\) is inside diameter of nozzle, \(d_0\) is outer diameter of nozzle and \(a\) is nozzle to surface distance. \(Sh = \text{mD/\delta}, \text{Re} = \text{vDp/\mu}\) and Sc (\(=\text{v}/\mu\)) are Sherwood number, Reynolds number and Schmidt number respectively. With the method of Hirsheldfielder et al. and Wilke were used for the calculation of viscosities and the diffusivity of CO_2. The film temperature is defined as the arithmetic mean of the ingoing gas and the specimen surface temperatures. Applying this approximation to the present study and taking the film temperature to be 908 K, yields, from Eq. (A-1), a mass transfer coefficients \((m)\) of \(4.3 \times 10^{-2} \text{ m s}^{-1}\) at the flow rate of \(5.0 \times 10^{-6} \text{ m}^3/\text{s}\).

The rate of carburization controlled by the counter diffusion of CO_2 and CO is given by

\[ \text{J}_{CO_2} = (m/RT) \ln[(1 + p_{CO_2})/(1 + p_{CO_2}^*]) = (m/RT) \ln[1/(1 + p_{CO_2}^*)] \quad \text{(A-2)} \]

where \(\text{J}_{CO_2}\) is the molar flux of CO_2, \(p_{CO_2}\) is the CO_2 partial pressure in the bulk and \(p_{CO_2}^*\) is that equilibrated with the carbon activity at the surface. The \(p_{CO_2}^*\) over the surface at \(\delta\) is assumed to be zero. The \(p_{CO_2}^*\) will vary with the surface concentration of carbon. Thus the \(\text{J}_{CO_2}\) will be a function of the carbon concentration. \(T\) is defined as the arithmetic mean of the surface and ingoing gas temperatures. The \(p_{CO_2}^*\) for 3.4 mass% C is about 0.0013 atm (132.73 Pa). Substituting the value of \(p_{CO_2}^*\), Eq. (A-2) gives values for the carbon supply rate to the unit area. The estimated rate is \(4.05 \times 10^{-2} \text{ mol/m}^2\text{s}\) at the flow rate of \(5.0 \times 10^{-6} \text{ m}^3/\text{s}\) and is shown to be significantly higher than the measured rate as shown in Fig. 2.