

Interactions between gas flow and reversible chemical reaction in porous media

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Abstract: Taking into consideration the gas compressibility and chemical reaction reversibility, a model was developed to study the interactions between gas flow and chemical reaction in porous media and resolved by the finite volume method on the basis of the gas–solid reaction $aA(g) + bB(s) \rightleftharpoons cC(g) + dD(s)$. The numerical analysis shows that the equilibrium constant is an important factor influencing the process of gas–solid reaction. The stoichiometric coefficients, molar masses of reactant gas, product gas and inert gas are the main factors influencing the density of gas mixture. The equilibrium constant influences the gas flow in porous media obviously when the stoichiometric coefficients satisfy $a/c \neq 1$.

Key words: porous media; compressible gas flow; reversible chemical reaction; interaction

1 Introduction

The process of gas flowing through porous media occurs in a number of important fields including shale gas migration in reservoirs in mining engineering [1], blast furnace gas transport in pileup pellets in metallurgical engineering [2], gas movement in chromatographic column in chemical engineering [3], flue gas cleaning in fixed bed in environmental engineering [4], and so on. The physical and chemical properties of solid skeleton and pore gas are the main factors which affect the gas flow in porous media. QUINTARD et al [5–9] investigated the transport processes in ordered and disordered rigid porous media with single phase flow and in chemically and mechanically heterogeneous porous media with slightly compressible single phase flow in two regions [10–14]. The method they used to solve the heterogeneity of porous media was named volume averaging by WHITAKER [15] latter, which made the foundation of studying the multi-scale spatial average questions in porous media.

When gas flows through porous media under differential pressure, the reactant gas is carried into the reaction region and the product gas is carried out of the reaction region under the condition that the gas and the

solid skeleton can have gas–solid reaction. Because the heterogeneous gas–solid reaction can both consume the reactant gas and solid and produce the product gas and solid, and the gases and solids may have totally different physical and chemical properties before and after the reaction, such as density, molar mass, gas pressure, and solid volume, which makes the process of gas flow through porous media very complicated [16–19]. WHITAKER [20] studied the gas movement in porous media and presented the conservation equations of universal significance. The consumption of reactant gas and the generation of product gas can probably change the physical and chemical properties of gas mixture, which can greatly influence the gas flow in porous media. Similarly, the consumption of reactant solid and the generation of product solid can probably change the permeability of solid skeleton, which also can influence the gas flow in porous media. Conversely, the transport action of gas flow may also change the distributions of reactant gas and product gas in porous media, which will affect the process of gas–solid reaction. When the permeability of solid skeleton changes very slowly or the chemical reaction takes place infinitely fast, the influences of chemical reaction on fluid flow have often been ignored [21, 22]. Also when the assumption of pseudosteady state or overfeed is used, the influences of chemical reaction on gas flow can not be reflected

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[23–25].

The packed bed reactor is a typical porous media of particle packing, in which a series of gas-solid reactions with value of industrial applications happened [26]. NEMEC et al [27, 28] studied the fluid flow in packed bed reactor, but ignored the influence of chemical reaction on fluid flow. Considering that the rapid gas-solid reaction can influence the gas flow in porous media obviously, XU et al [29] and JIANG et al [30] studied the interactions between gas flow and irreversible chemical reaction in a packed bed reactor with synthesis reaction $aA(g)+bB(s)=dD(s)$ and metathesis reaction $aA(g)+bB(s)=cC(g)+dD(s)$. In this work, based on the two published papers, a model was presented to study the interactions between gas–solid reaction and compressible gas flow in porous media with reversible metathesis reaction $aA(g)+bB(s)\rightleftharpoons cC(g)+dD(s)$, for most of chemical reactions are reversible.

2 Physical and mathematical model

The schematic diagram of a packed bed reactor is shown in Fig. 1. The gas mixture, including reactant and inert gases, enters from the inlet, reacts in the inner by $aA(g)+bB(s)\rightleftharpoons cC(g)+dD(s)$ and flows out of the outlet of reactor. That is to say, the reactant gas A in gas mixture reacts with reactant solid B in packed bed reactor; the gaseous product C and solid product D are produced.

The following assumptions are made:

- 1) The packed bed reactor is constructed by spherical particles of equal and constant size;
- 2) All the gases involved are ideal gases in thermodynamics;
- 3) The gas–solid chemical reaction is isothermal, first order and reversible;
- 4) The overall reaction rate of single particle is controlled by the rate of chemical reaction at the interface and can be described by shrinking core model;
- 5) The process of gas flow through porous media is one dimensional and observes Darcy’s Law.

When the gas flows through porous media, the mass conservation equation is

$$\frac{\partial(\varepsilon\rho_g)}{\partial t} + \frac{\partial(\rho_g v)}{\partial x} + M_A R_A - M_C R_C = 0 \quad (1)$$

where ε is the porosity of packed bed; ρ_g is the gas density; M_A and M_C are the molar masses of gaseous

reactant A and product C ; v is the gas velocity; R_A and R_C are the consumption rate of gaseous reactant A and production rate of gaseous product C .

On the basis of assumption 2), the gas density can be written as

$$\rho_g = (M_A - M_I)C_A + (M_C - M_I)C_C + M_I \frac{P}{RT} \quad (2)$$

where M_I is the molar mass of inert gas I ; C_A and C_C are the concentrations of gaseous reactant A and product C ; P is the gas pressure; R is the ideal gas constant; T is the temperature.

On the basis of assumption 5), the gas velocity can be expressed by

$$v = -\frac{k}{\mu} \frac{\partial P}{\partial x} \quad (3)$$

where μ is the gas dynamics viscosity and the permeability k is given by [31]

$$k = \frac{\varepsilon^3}{150(1-\varepsilon)^2} d_p^2 \quad (4)$$

where d_p is the particle diameter.

The mass transfer equation of gaseous reactant A is

$$\frac{\partial(\varepsilon C_A)}{\partial t} = \frac{\partial}{\partial x} (D_{Ae} \frac{\partial C_A}{\partial x}) - \frac{\partial}{\partial x} (v C_A) - R_A \quad (5)$$

where D_{Ae} is the effective diffusivity of gaseous reactant A in packed bed.

The mass transfer equation of gaseous product C is

$$\frac{\partial(\varepsilon C_C)}{\partial t} = \frac{\partial}{\partial x} (D_{Ce} \frac{\partial C_C}{\partial x}) - \frac{\partial}{\partial x} (v C_C) + R_C \quad (6)$$

where D_{Ce} is the effective diffusivity of gaseous product C .

According to assumptions 3) and 4), the consumption and production rates of A and C are given respectively by [32]

$$R_A = \frac{3(1-\varepsilon)r_c^2}{r_s^3} k_r (C_A - \frac{C_C}{K}) \quad (7)$$

and

$$R_C = \frac{c}{a} R_A \quad (8)$$

where r_c is the radius of unreacted core; r_s is the particle radius; k_r is the reaction rate constant at interface; K is

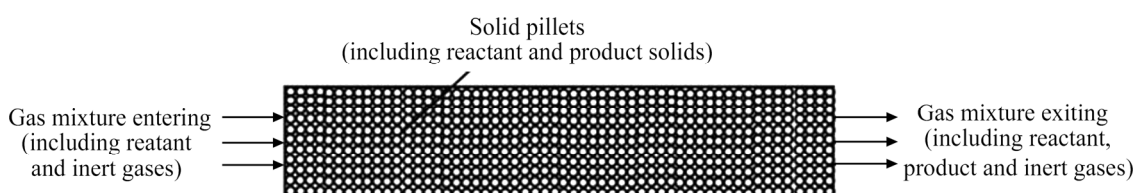


Fig. 1 Schematic diagram of a packed bed reactor

the equilibrium constant of reaction system; a and c are the stoichiometric coefficients for gaseous reactant A and product C.

The radius of unreacted core is calculated by

$$r_c = r_s - \frac{bM_B}{a\rho_B} k_r \int_0^t (C_A - \frac{C_C}{K}) dt \quad (9)$$

where b is the stoichiometric coefficient for solid reactant B; M_B is the molar mass of solid reactant B; ρ_B is the density of solid reactant B.

Equations (1)–(9) describe the interactions between compressible flow and reversible chemical reaction in porous media completely. It can be seen evidently that the chemical reaction has effects on gas flow by consuming gaseous reactant and producing gaseous product. At the same time, the gas flow has effects on the chemical reaction by the way of carrying gaseous reactant and product. So the compressible gas flow and reversible chemical reaction in porous media are coupled with each other and have interactions indeed.

3 Numerical method

The initial and boundary conditions to be applied may be written as follows:

$$P(x, 0) = P_L \quad (10)$$

$$C_A(x, 0) = 0 \quad (11)$$

$$C_C(x, 0) = 0 \quad (12)$$

$$r_c(0) = r_s \quad (13)$$

$$P(0, t) = P_0 \quad (14)$$

$$C_A(0, t) = C_{A0} \quad (15)$$

$$C_C(0, t) = 0 \quad (16)$$

$$P(L, t) = P_L \quad (17)$$

$$\left. \frac{\partial C_A}{\partial x} \right|_{x=L} = 0 \quad (18)$$

$$\left. \frac{\partial C_C}{\partial x} \right|_{x=L} = 0 \quad (19)$$

The finite volume method (FVM) was used to obtain the numerical solution of mathematical model with initial and boundary conditions presented above. In the process of discretization, the fully implicit scheme for equations, the central difference scheme for diffusion terms, the QUICK scheme for convection terms and the additional source term method for boundary conditions are used to ensure the calculation accuracy [33, 34]. The nonlinear equations and the coupled equations are solved by iterative method. The sequence of calculation steps is as follows:

1) At initial time, the molar concentrations of

reactant gas A and product gas C, gas mixture pressure and radius of unreacted core are given by $C_A^{(0)}$, $C_C^{(0)}$, $P^{(0)}$ and $r_c(0) = r_s$ according to the initial conditions.

2) At the first time level $t = \Delta t$, the molar concentrations of reactant and product gases are supposed as $[C_A^{(1)}]^{(1)}$ and $[C_C^{(1)}]^{(1)}$, respectively. Then the radius of unreacted core $[r_c^{(1)}]^{(1)}$ is obtained by solving Eq. (9) combined with the initial conditions (11)–(13).

3) Using the molar concentrations of gaseous reactant $[C_A^{(1)}]^{(1)}$ and product $[C_C^{(1)}]^{(1)}$ and the radius of unreacted core $[r_c^{(1)}]^{(1)}$, combining Eqs. (2)–(4), (7) and (8) with initial condition (10) and boundary conditions (14) and (17), we can solve Eq. (1) and obtain the pressure of gas mixture $[P^{(1)}]^{(1)}$. It is especially noted that the mass conservation equation of gas mixture itself is a nonlinear equation about pressure, so the iteration is also needed when solving the single Eq. (1) by numerical method and here the detailed process is omitted.

4) Substituting the pressure of gas mixture $[P^{(1)}]^{(1)}$ into Eq. (3), we can obtain the gas seepage velocity $[v^{(1)}]^{(1)}$.

5) Using the radius of unreacted core $[r_c^{(1)}]^{(1)}$, gas seepage velocity $[v^{(1)}]^{(1)}$, gas product concentration $[C_C^{(1)}]^{(1)}$, combining Eq. (7) with initial condition (11) and boundary conditions (15) and (18), we can solve Eq. (5) and obtain the molar concentration of reactant gas A $[C_A^{(1)}]^{(2)}$. The mass transfer equation of reactant gas A (5) itself is also a nonlinear equation about C_A , so the iteration is also needed in it, and here the detailed process is omitted.

6) Using the radius of unreacted core $[r_c^{(1)}]^{(1)}$, gas seepage velocity $[v^{(1)}]^{(1)}$, gas reactant concentration $[C_A^{(1)}]^{(1)}$, combining Eqs. (7) and (8) with initial condition (12) and boundary conditions (16) and (19), we can solve the mass transfer equation of product gas C (6) and obtain the molar concentration of product gas C $[C_C^{(1)}]^{(2)}$. The mass transfer equation of product gas C (6) itself is also a nonlinear equation about C_C , so the iteration is also needed in it, and here the detailed process is omitted.

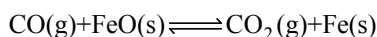
7) Comparing the differences between $[C_A^{(1)}]^{(1)}$ and $[C_A^{(1)}]^{(2)}$, $[C_C^{(1)}]^{(1)}$ and $[C_C^{(1)}]^{(2)}$, steps 2)–6) will be repeated, until the two differences meet the precision requirements simultaneously. Then we can obtain the radius of unreacted core $r_c^{(1)} = [r_c^{(1)}]^{(i)}$, the pressure of gas mixture $P^{(1)} = [P^{(1)}]^{(i)}$, gas seepage velocity $v^{(1)} = [v^{(1)}]^{(i)}$, the molar concentrations of gas reactant $C_A^{(1)} = [C_A^{(1)}]^{(i)}$ and gas product $C_C^{(1)} = [C_C^{(1)}]^{(i)}$ at the first time level $t = \Delta t$.

When we calculate the pressure of gas mixture $P^{(n+1)}$, the molar concentrations of reactant gas

$C_A^{(n+1)}$ and product gas $C_C^{(n+1)}$, the radius of unreacted core $r_c^{(n+1)}$ at the next time level $t = t_{n+1}$, the pressure of gas mixture $P^{(n)}$, the molar concentrations of reactant gas $C_A^{(n)}$ and product gas $C_C^{(n)}$, the radius of unreacted core $r_c^{(n)}$ at the current time level $t = t_n$ will be taken as the initial variables. Then steps 2)–7) are repeated until the convergence values are reached. By doing this process repeatedly, we can obtain the pressure of gas mixture $P(x, t)$, the gas seepage velocity $v(x, t)$, the molar concentrations of gaseous reactant $C_A(x, t)$ and product $C_C(x, t)$, the radius of unreacted core $r_c(x, t)$ at any given time and location.

4 Results and discussion

Considering that the reduction of iron ore is an important process in metallurgical industry [35, 36], the interactions between the compressible flow and reversible chemical reaction are analyzed based on the following gas-solid reaction



The equilibrium constant, which depends on the temperature T , can be expressed as [37]

$$K = \exp\left(\frac{5450 - 5.87T}{1.987T}\right) \quad (20)$$

The reaction rate constant is written as [38]

$$k_r = 0.096 \exp\left(-\frac{3460}{T}\right) \quad (21)$$

In the process of numerical simulation, the following parameters are used:

$M_I=0.028$ kg/mol, $M_A=0.028$ kg/mol, $M_C=0.044$ kg/mol, $M_B=0.072$ kg/mol, $\rho_B=5.7118 \times 10^3$ kg/m³, $r_s=0.005$ m, $T=1173$ K, $L=5$ m, $P_0=1.05 \times 10^5$ Pa, $P_L=1.0 \times 10^5$ Pa, $\varepsilon=0.32$, $C_{A0}=5.0$ mol/m³, $t=3600$ s.

The effective diffusivities can be expressed as [39]

$$D_{Ae} = D_{Am} \frac{\varepsilon}{\tau} \quad (22)$$

and

$$D_{Ce} = D_{Cm} \frac{\varepsilon}{\tau} \quad (23)$$

where the tortuosity factor of the packed bed is

$$\tau = 1/\varepsilon \quad (24)$$

The diffusivities of gaseous reactant and product in gas mixture are given by [40]

$$D_{Am} = \frac{1 - X_A}{\frac{X_C}{D_{AC}} + \frac{X_I}{D_{AI}}} \quad (25)$$

$$D_{Cm} = \frac{1 - X_C}{\frac{X_A}{D_{CA}} + \frac{X_I}{D_{CI}}} \quad (26)$$

where the ordinary diffusivities of gas pair A–C, A–I and C–I are expressed as [41]

$$D_{AC} = \frac{(1 \times 10^{-7})T^{1.75}}{P(v_A^{1/3} + v_C^{1/3})} \sqrt{\frac{1}{M_A} + \frac{1}{M_C}} \quad (27)$$

$$D_{AI} = \frac{(1 \times 10^{-7})T^{1.75}}{P(v_A^{1/3} + v_I^{1/3})} \sqrt{\frac{1}{M_A} + \frac{1}{M_I}} \quad (28)$$

$$D_{CI} = \frac{(1 \times 10^{-7})T^{1.75}}{P(v_C^{1/3} + v_I^{1/3})} \sqrt{\frac{1}{M_C} + \frac{1}{M_I}} \quad (29)$$

where the v_A , v_C and v_I are diffusion volumes of gaseous reactant A, product gas C and inert gas I, their values are $v_{CO}=18.9$, $v_{CO_2} = 26.9$ and $v_{N_2} = 17.9$.

The solid conversion of elementary volume can be defined as

$$X = [1 - (\frac{r_c}{r_s})^3] \times 100\% \quad (30)$$

The profiles of gas pressure, velocity, gas concentrations and solid conversion are given in Fig. 2. Note that the gas pressure, the reactant gas concentration and the solid conversion decrease along packed bed, although the gas velocity increases and the concentration of product gas increases at first and then decreases.

For this reaction, the ratio of stoichiometric coefficients for gaseous reactant to product is 1, i.e., $c/a=1$. That is to say, the volume consumption rate of gaseous reactant is equal to the volume production rate of gaseous product. So the chemical reaction has no effect on the gas pressure [30]. Then, the chemical reaction has no effect on the gas velocity as the pressure and velocity satisfy Darcy's Law. In this case, the profiles of gas pressure and velocity both show characteristics of compressible gas flow through porous media without chemical reaction, i.e., the pressure gradient decreases linearly and the velocity increases linearly from the inlet to the outlet of the packed bed, as shown in Figs. 2(a) and (b).

As shown in Figs. 2(c) and (d), in the vicinity of the reactor inlet, the gaseous reactant is consumed and its concentration decreases for gas-solid reaction, but in the same region, the product gas concentration increases greatly. It is significantly different from irreversible chemical reaction that in the region without chemical reaction, where the solid conversion is zero, the gaseous reactant concentration is nonzero. That is to say, in this region, the gas-solid reaction has not happened for the reversibility, although there is an amount of gaseous reactant, and the reactant solid and gas are in contact with each other. For the irreversible reaction, the

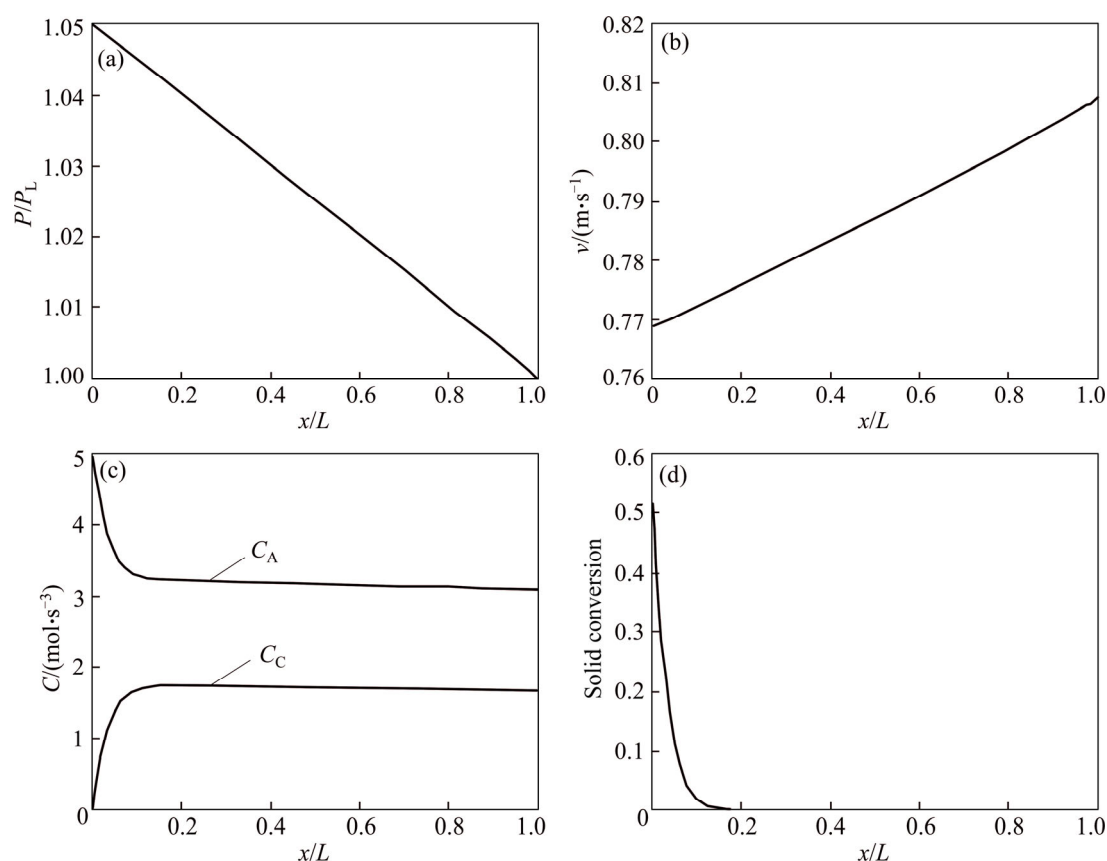


Fig. 2 Profiles of gas pressure, velocity, concentrations and solid conversion: (a) Gas pressure; (b) Gas velocity; (c) Reactant and product gases concentrations; (d) Solid conversion

gas–solid reaction will happen, so long as the reactant solid and gas are in contact with each other. But for reversible reaction, the gas–solid reaction will happen, when not only they are in contact with each other but also the concentration ratio of product gas to reactant gas is below the equilibrium constant in ambient. So the product gas concentration is also an important factor affecting the process of reversible gas–solid reaction

In the region where gas–solid reaction reaches equilibrium, the overall chemical reaction stops and the reactant gas and product gas concentrations both decrease gradually with the decrease of the distance from reactor outlet, but the concentration ratio of reactant gas to product gas keeps unchanged. Since the reactant gas concentration decreases gradually and the product gas concentration increases gradually with the increase of the distance from reactor inlet, the concentration ratio of product to reactant increases gradually. At a location in the reactor where the concentration ratio is equal to equilibrium constant, the reaction stops. In the region behind this location, the reaction can not happen and the ratio keeps constant, i.e., in the region where the solid conversion is zero, the ratio is equal to equilibrium constant K . Considering that the gas pressure decreases gradually with the decrease of the distance from reactor outlet, the reactant gas and product gas concentrations

will decrease inevitably under the condition of constant temperature.

From the above analysis of Fig. 2, it can be seen that the gaseous reactant is carried into the interior of the reactor by the gas flow, which provides a necessary condition for reaction, when the reversible gas–solid reaction happens in porous media. The reaction takes place first in the region near the reactor inlet. On the one hand, it consumes gaseous reactant. On the other hand, it produces gaseous product. Under the carrying action of gas flow, the gaseous product migrates from the inlet to the outlet of the reactor. In the region with reaction, the gaseous reactant is consumed, so its concentration decreases gradually. In contrast, the gaseous product is produced and its concentration increases gradually. It can be seen from Fig. 2, in the region with higher solid conversion, the gaseous reactant concentration is more concentrated and the gaseous product concentration is less concentrated. In contrast, in the region with lower solid conversion, the concentration of the gaseous reactant is less concentrated and the gaseous product concentration is more concentrated. This effect accelerates the solid conversion in the region with higher solid conversion, but inhibits it in the region with lower solid conversion simultaneously.

For the packed bed with reversible gas–solid

reaction $aA(g)+bB(s)\rightleftharpoons cC(g)+dD(s)$, the reaction in the back of the reactor is sure to be affected by the gaseous product produced by the reaction in the front of the reactor and carried by the gas flow to the outlet of the reactor, which is bad for making full use of the reactor. So it is necessary to find a way to weaken or eliminate the negative effect.

Although the chemical reaction has no effect on the gas pressure and flow for the reaction system $CO(g)+FeO(s)\rightleftharpoons CO_2(g)+Fe(s)$, i.e., the chemical reaction may be ignored when we calculate the gas pressure and velocity, we can see from Fig. 3 that the chemical reaction leads to a marked change of gas density. As shown in curve 1, the density increases significantly in the region with remarkable gas–solid reaction. By comparing curves 1 and 2, we can see that the gas density, taking into account the mass-change and density-change caused by reaction, is higher than that ignoring the factor, along the entire length of the reactor except the inlet.

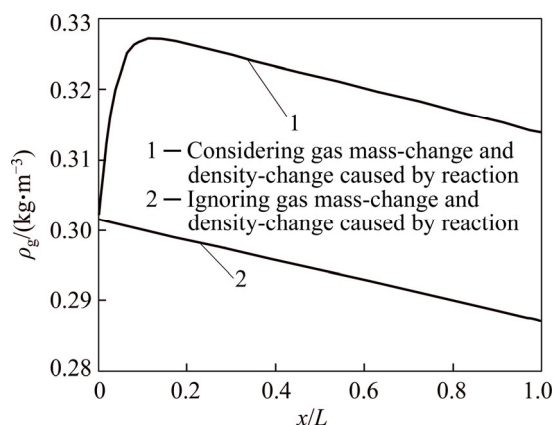


Fig. 3 Profiles of gas density

In the process of studying compressible gas flow, if the effect of reaction on density is ignored, the gas is only inert gas. So the gas density can be expressed as

$$\rho_g = M_1 \frac{P}{RT} \tag{31}$$

By this time, we can see that the gas density is in proportion to the pressure and it is easy to understand that the density decreases gradually along the reactor (curve 2).

For the inert gas used here is N_2 , we can have

$$M_A - M_1 = 0 \tag{32}$$

Substituting Eq. (32) into Eq. (2) yields

$$\rho_g = (M_C - M_1)C_C + M_1 \frac{P}{RT} \tag{33}$$

Comparing Eq. (33) with Eq. (31), we can see that because $M_C - M_1 = 0.016 \text{ kg/mol} > 0$ and the gaseous product concentration $C_C \geq 0$, $(M_C - M_1)C_C \geq 0$ is obvious.

This is why the gas density taking into account the density-change caused by reaction is higher.

Moreover, the phenomenon that the gas density is higher induced by reaction can be interpreted from another angle. Equation (1) can be rewritten as

$$\frac{\partial(\varepsilon\rho_g)}{\partial t} = -\frac{\partial(\rho_g v)}{\partial x} - M_A R_A + M_C R_C \tag{34}$$

Based on Eq. (8), the stoichiometric coefficients satisfy $a=c$ in this case, which makes the consumption rate of the gaseous reactant equal to the production rate of gaseous product, $R_A=R_C$, and Eq. (34) can be rewritten as

$$\frac{\partial(\varepsilon\rho_g)}{\partial t} = -\frac{\partial(\rho_g v)}{\partial x} + (M_C - M_A)R_A \tag{35}$$

Because $M_C - M_A = 0.016 \text{ kg/mol} > 0$ and $R_A \geq 0$, $(M_C - M_A)R_A \geq 0$ is obvious, i.e., the chemical reaction takes the role of source term for gas density which makes the density increased.

Through the analysis of Eq. (35), we can also see that the change of gas density is determined by the molar masses of gaseous reactant and product if their consumption and production rates are equal. When the molar mass of gaseous product is larger than the gaseous reactant, the gas density will increase due to the chemical reaction. Conversely, when the molar mass of gaseous product is smaller than the gaseous reactant, the gas density will decrease. When their molar masses are equal, the gas density will not change with chemical reaction. Put in another way, it can be described that for the gas mixture when one kind of gas is replaced with another gas for equal mole or equal volume, the density of gas mixture will increase if the light gas is replaced by the heavy gas. If the heavy gas is replaced by the light gas, the density of gas mixture will decrease. If the two gases are of the same mass, the density of gas mixture will not change.

The above conclusions can be expanded to the condition that the stoichiometric coefficients of reactant gas and product gas are unequal. Substituting Eq. (8) into Eq. (1) yields

$$\frac{\partial(\varepsilon\rho_g)}{\partial t} = -\frac{\partial(\rho_g v)}{\partial x} + (cM_C - aM_A) \frac{R_A}{a} \tag{36}$$

It can be seen from Eq. (36) that:

When $cM_C - aM_A > 0$, the gas density will increase;

When $cM_C - aM_A < 0$, the gas density will decrease;

When $cM_C - aM_A = 0$, the gas density does not change.

That is to say, the gas density, which will increase, decrease or remain, is determined by the relationship

between the masses of the two gases, when replacing a mol reactant gas with c mol product gas. If the mass of the substitute gas is more than that of the substituted gas, the density of gas mixture will increase. If the mass of the substitute gas is less than that of the substituted gas, the density of gas mixture will decrease. If the mass of the substitute gas is equal to that of the substituted gas, the density of gas mixture will be unchanged.

Based on the above research conclusions, we can analyze qualitatively the effects of the chemical reaction system on the gas density by observing the chemical equations, not by doing any complex calculations.

For the gas–solid reaction $aA(g)+bB(s)=cC(g)+dD(s)$, we can see from Fig. 3 that the chemical reaction has no effect on gas pressure and velocity, when the stoichiometric coefficients satisfy $a=c$, but leads to obvious changes of gas density. Consequently, for this type of gas–solid reaction, we also need to take full consideration of the changes of density and mass of gas mixture induced by chemical reaction.

Figure 4 shows the effects of molar mass of inert gas on the density of gas mixture. It can be seen that the density of gas mixture always increases with the increase of the molar mass of inert gas, whether or not the changes of mass and density of gas mixture due to reaction having been considered.

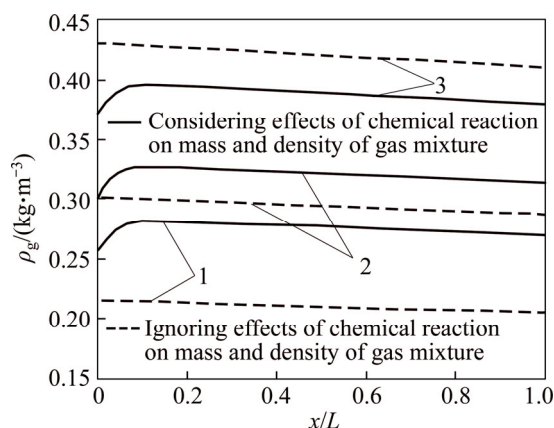


Fig. 4 Effects of inert gas molar mass on gas mixture density (1—Inert gas of Ne, $M_I=0.020$ kg/mol; 2—Inert gas of N_2 , $M_I=0.028$ kg/mol; 3—Inert gas of Ar, $M_I=0.040$ kg/mol)

Taking account of the changes of mass and density of gas mixture induced by chemical reaction, according to Eq. (2), the gas density can be written as

$$\rho_g = M_A C_A + M_C C_C + M_I \left(\frac{P}{RT} - C_A - C_C \right) \quad (37)$$

Based on the above analysis, we can know that, for this case, the molar mass of inert gas has no effect on the gas pressure and velocity, and also on the concentration of gaseous reactant and product. So in Eq. (37), the three terms $M_A C_A$, $M_C C_C$ and $P/RT - C_A - C_C$ are unchanged

with the molar mass of inert gas. Quite obviously, when the molar mass of inert gas increases, the term $M_I(P/RT - C_A - C_C)$ increases and therefore the density of gas mixture increases.

When ignoring the effects of the chemical reaction on the mass and density of gas mixture, the expression of gas density is Eq. (31). For this case, the gas pressure is unaffected by the molar mass of inert gas when the effects of the chemical reaction on the mass and density of gas mixture are ignored. So the density of gas mixture increasing with the increase of the molar mass of inert gas is obvious, as shown in Fig. 4 with the dotted lines.

In the same way, when taking account of the effects of the chemical reaction on the mass and density of gas mixture, based on assumption 2), the gas density also can be written as

$$\rho_g = M_A C_A + M_C C_C + M_I C_I \quad (38)$$

For this case, when the effects of chemical reaction on the mass and density of gas mixture are taken into consideration, the gas pressure is also unaffected by the inert gas molar mass. In addition, considering that the relationship between pressure and velocity can be described by Darcy's law, the gas velocity is also unchanged with the inert gas molar mass. So the molar concentrations of reactant gas C_A and product gas C_C are also unaffected by the inert gas molar mass. Hence, based on Eq. (38), it is easy to get that the density of gas mixture will increase with the increase of the inert gas molar mass, as shown in Fig. 4 with the solid lines, when the effects of the chemical reaction on the mass and density of gas mixture are taken into consideration.

We can also see from Fig. 4 that when the inert gas is Ne ($M_I=0.020$ kg/mol) and N_2 ($M_I=0.028$ kg/mol), respectively, the density of gas mixture is higher considering the effects of chemical reaction on the mass and density of gas mixture. By contrast, when the inert gas is Ar ($M_I=0.040$ kg/mol), the density of gas mixture is higher ignoring the effects of chemical reaction on the mass and density of gas mixture.

For this case, the gas pressure is not changed whether or not considering the effects of the chemical reaction on the mass and density of gas mixture. According to Eqs. (2) and (31), the differences about density are determined by the relationships between the molar masses of reactant gas A, product gas C and inert gas I.

When Ne is used for the inert gas, $M_I=0.020$ kg/mol, there are $M_A - M_I = 0.008$ kg/mol > 0 and $M_C - M_I = 0.024$ kg/mol > 0 . Obviously, the gas density is higher considering the changes of gas mass and density caused by chemical reaction, as shown in Fig. 4 with curve 1.

When N_2 is used for the inert gas, $M_I=0.028$ kg/mol,

there are $M_A - M_I = 0$ kg/mol and $M_C - M_I = 0.016$ kg/mol > 0. Obviously, the gas density is still higher considering the changes of gas mass and density caused by chemical reaction, as shown in Fig. 4 with curve 2.

When Ar is used for the inert gas, $M_I = 0.040$ kg/mol. Considering that the molar concentrations of reactant gas and product gas always satisfy $C_C \leq KC_A$, so combined with Eq. (2), the density of gas mixture satisfies the following inequality (39), when the changes of mass and density of gas mixture produced by chemical reaction are taken into account.

$$\rho_g \leq (M_A - M_I)C_A + (M_C - M_I)KC_A + M_I \frac{P}{RT} \quad (39)$$

As can be seen from inequality (39), the size of the gas density in two cases is determined by the positive or negative of the expression $(M_A - M_I) + (M_C - M_I)K$. Substituting the value of M_A , M_C , M_I and K into the expression yields $(M_A - M_I) + (M_C - M_I)K < 0$. So the gas density is higher when ignoring the changes of mass and density of gas mixture produced by chemical reaction, which are shown in Fig. 4 with curves 3.

Extending the discussion above, we can get the following results:

When $M_I < M_A$ and $M_I < M_C$, the gas density is lower than the truth value, ignoring the changes of mass and density of gas mixture produced by chemical reaction;

When $M_I > M_A$ and $M_I > M_C$, the gas density is higher than the truth value, ignoring the changes of mass and density of gas mixture produced by chemical reaction;

When $M_A < M_I < M_C$ or $M_C < M_I < M_A$, the final result that the gas density is lower than, higher than or equal to the truth value, is determined by the molar mass of reactant gas M_A , product gas M_C , inert gas M_I and the equilibrium constant K , ignoring the changes of mass and density of gas mixture produced by chemical reaction.

It can be seen from the discussions of Fig. 4 that the molar mass of inert gas has clearly influenced the density of gas mixture. The bigger the molar mass of the inert gas, the higher the density of the gas mixture. When the molar mass of inert gas changes, whether or not considering the changes of the mass and density of gas mixture produced by chemical reaction will lead to the changes of the gas mixture density not only quantitative but also qualitative.

The influences of the equilibrium constant K on the molar concentrations of reactant and product gases, the gas density and solid conversion are shown in Fig. 5. It is seen that with the increase of the equilibrium constant K , the concentration of reactant gas decreases; the concentration of product gas increases; the gas density increases and the solid conversion increases.

Based on the definition of equilibrium constant for reversible chemical reaction, we can know that the

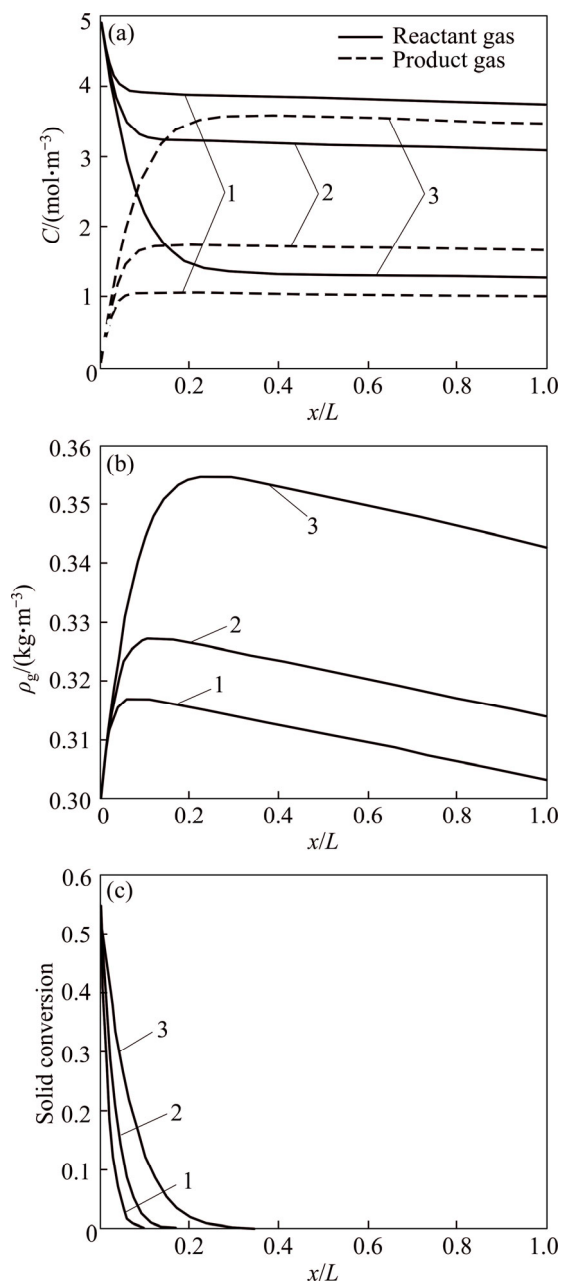


Fig. 5 Effects of equilibrium constant K on gas concentration, gas density and solid conversion: (a) Molar concentrations of reactant and product gases; (b) Gas density; (c) Solid conversion

equilibrium constant is the ratio of the product of equilibrium concentration power for reaction resultants to reactants. The larger the equilibrium constant is, the more completely the chemical reaction takes place. For this case, the equilibrium constant is equal to the concentration ratio of product gas to reactant gas, i.e., $K = C_C / C_A$, based on assumption 3). So with the increase of the equilibrium constant, the gas–solid reaction will take place more completely; more reactant gas will be consumed and more product gas will be produced. This will lead to the reactant gas concentration decreasing, the product gas concentration increasing and solid

conversion increasing. For this reaction system, the lighter reactant gas CO is replaced by the heavier product gas CO₂, so the chemical reaction will lead to the increase of the density of gas mixture inevitably, and with further reaction taking place, the range of gas density increasing will increase.

It can be seen from the analysis of Fig. 5 that the equilibrium constant is a very important factor influencing the process of the reversible gas–solid reaction. Increasing the equilibrium constant will promote the positive reaction.

When $a/c \neq 1$, the effects of equilibrium constant K on gas velocity are shown in Fig. 6 for a hypothetical reaction system $aA(g) + bB(s) \rightleftharpoons cC(g) + dD(s)$. As can be seen from Fig. 6(a), when $a/c = 2/3$, the gas velocity decreases near the inlet of the packed bed, but increases near the outlet with the increase of equilibrium constant K . In contrast, when $a/c = 3/2$, the gas velocity increases near the inlet, but decreases near the outlet with the increase of equilibrium constant K , as shown in Fig. 6(b).

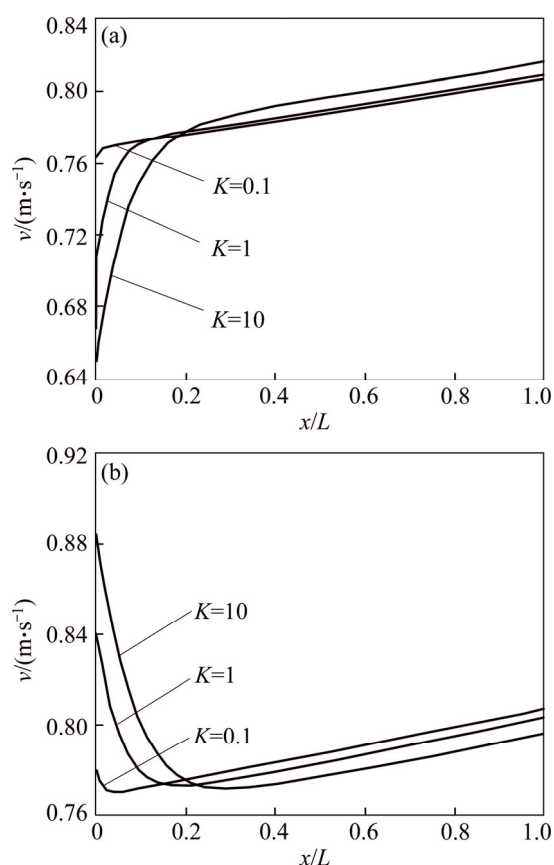


Fig. 6 Effects of equilibrium constant K on gas velocity: (a) $a/c = 2/3$; (b) $a/c = 3/2$

Because the interactions between gas–solid chemical reaction and gas flow in porous media are taken into account, based on the conclusions received in previous study [30], the chemical reaction will give rise to the increase of the gas pressure and make the velocity profile lower at the inlet and higher at the outlet of the packed

bed, when $a/c = 2/3$, i. e., the reactant gas consumes per 2 mol and the product gas will produce 3 mol. With the increase of equilibrium constant K , the overall reaction rate increases. Therefore, the influence of chemical reaction on gas flow becomes more obviously and also the increase of gas pressure caused by chemical reaction becomes more significant. With the boundary conditions that the inlet and outlet pressure keep constant, the gas pressure difference will decrease near the inlet and increase near the outlet inevitably, which will lead to the gas velocity decrease near the inlet and increase near the outlet.

Similarly, when $a/c = 3/2$, i. e., the reactant gas consumes per 3 mol and the product gas will produce 2 mol, the chemical reaction will give rise to the decrease of the gas pressure and make the velocity profile higher at the inlet and lower at the outlet of the packed bed. With the increase of equilibrium constant K , the overall reaction rate increases and the decrease of the gas pressure caused by chemical reaction becomes more significantly. Near the inlet of the packed bed, the chemical reaction takes place firstly, so the biggest drop of gas pressure is in here. Under the condition of constant inlet pressure and outlet pressure, the gas velocity increases near the inlet and decreases near the outlet inevitably.

Through the analysis of Fig. 6, we can see that the equilibrium constant K affects the seepage velocity of the gas mixture obviously for the reversible gas–solid reaction with $a/c \neq 1$. The seepage velocity will decrease near the inlet and increase near the outlet with the increase of the equilibrium constant for the reaction system with $a/c < 1$. But for the reaction system with $a/c > 1$, the seepage velocity will increase near the inlet and decrease near the outlet with the increase of the equilibrium constant.

5 Conclusions

1) It is significantly different from the irreversible reaction, the reversible reaction may also terminate although the reactant gas concentration is not zero, which depends on the equilibrium constant K of the gas–solid chemical reaction system.

2) For a gas–solid reaction system with $a/c = 1$, the chemical reaction has no effect on the gas pressure and velocity, but it affects the gas density notably. Whether or not considering the changes of gas mass and density, the density of gas mixture obtained is quite different, not only quantitatively, but also qualitatively.

3) For a gas–solid reaction system $aA(g) + bB(s) \rightleftharpoons cC(g) + dD(s)$, if $cM_C - aM_A > 0$, the chemical reaction will give rise to the increase of the gas density. If $cM_C - aM_A < 0$, the chemical reaction will give rise to the

decrease of the gas density. If $cM_C - aM_A = 0$, the chemical reaction will have no effect on the gas density.

4) The molar mass of the inert gas has significant effect on the gas density, the bigger the molar mass of the inert gas, the bigger the gas density.

5) For a reaction system, which will give rise to the increase of gas density, with the molar mass of inert gas changing, the gas density obtained considering the changes of gas mass and density induced by chemical reaction is not always higher than that not considering the effect of chemical reaction.

6) For the reaction system $\text{CO(g)} + \text{FeO(s)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{Fe(s)}$, increasing the equilibrium constant K will lead to the decrease of reactant gas concentration and the increases of product gas concentration and gas density.

7) For the reaction system $a\text{A(g)} + b\text{B(s)} \rightleftharpoons c\text{C(g)} + d\text{D(s)}$, when $a/c \neq 1$, the equilibrium constant K has evident influences on the gas velocity profile. For the reaction system with $a/c < 1$, the increase of the equilibrium constant will give rise to the decrease of the gas velocity near the inlet of the packed bed and the increase of the gas velocity near the outlet. But for the reaction system with $a/c > 1$, the increase of the equilibrium constant will give rise to the increase of the gas velocity near the inlet of the packed bed and the decrease of the gas velocity near the outlet.

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