Numerical study of magnesium (Mg) production by the Pidgeon process: Impact of heat transfer on Mg reduction process

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ABSTRACT

In this paper, a magnesium (Mg) reduction model considering both heat transfer and chemical reaction kinetics was firstly developed. The reduction model was carried out on a single retort to investigate the impact of different constant heating temperature on the magnesium reduction process in the retort. And then, the reduction model was incorporated into the conventional coal combustion model to describe the process of magnesium production in a coal-fired furnace. The comprehensive model was solved according to the actual industrial operation. The characteristics of magnesium production in the coal-fired furnace, such as thermal-flow field around the retorts in the furnace, the distribution of magnesium reduction extent in the retorts and the total extent of magnesium reduction with time were in detail studied. Especially, the impact of external thermal-flow around the retorts on the extent of magnesium reduction was investigated and discussed.

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1. Introduction

Magnesium is considered as a very promising material that has potential to low weight in automotive and aerospace industries. The world demand for magnesium is increasing by about 10% per year [1–4]. The primary magnesium is at present mainly produced by the Pidgeon process in China which is now the largest magnesium production and exporting country. The Pidgeon process has advantages of producing high purity magnesium as well as simple operation and low investment cost. It is also anticipated to be the main technique for producing high purity magnesium in future. However, the Pidgeon process in China is of intensive energy use and intensive labor operation [5]. Recent years, new technologies had been exploring and simulation as a tool can provide a good knowledge of heat and mass transfer occurred in the process of magnesium production and optimize the new design.

The Pidgeon process is a thermal reduction process that extracts magnesium from calcined dolomite (MgO·CaO) under a vacuum pressure of ~10 Pa and a temperature of 1100–1200 °C by the ferrosilicon (FeSi) as a reducing agent. A small quantity of calcium fluoride (CaF₂) is added as a mineralization agent which can promote the magnesium reduction [6]. The overall reaction of magnesium reduction can be described as follows,

\[
2(MgO)_{(s)} + (FeSi)_{(s)} + CaF₂ \xrightarrow{10 Pa, 1100–1200 °C} 2Mg_{(g)} + 2CaO + SiO₂_{(g)} + Fe₃O₄_{(s)}
\]

It is a solid-state endothermic reaction.

Fig. 1(a) and (b) shows the schematic structure of a retort and cross section of a refractory brick coal-fired furnace with the retorts [7]. In industrial, the raw materials of calcined dolomite, ferrosilicon and calcium fluoride are in advance mixed in a specific ratio and briquetted. The produced briquettes are charged into the retorts which are horizontally placed in the upper and lower rows with a staggered layout in the furnace. The retorts are vacuumed by a pump and heated by high temperature flue gas of around 1200 °C from the coal combustion chambers, which are arranged symmetrically on two sides of the furnace. Magnesium reduction process is carried out in the retorts and the yield magnesium vapor is condensed in crystalline form on the section of retort wall with a water cooling jacket.

The extraction of magnesium by the Pidgeon process was investigated by many authors through experiment, analysis or calculation. It seems that the process was intensively studied through the experiment [6,8–13]. The mathematical model of describing the magnesium reduction process is relatively less, Liu and Xu [14] analyzed in detail the heat transfer of briquette packed layer and calculated the temperature distribution in the retort, but they did not take the reaction into account. Further, Xie et al. [15] treated the reaction heat in reduction process as a constant and Yu [16] treated the heat as a temperature-dependent function. Wynnnyckj [17] developed an intrinsic-transport model for solid–solid reactions involving a gaseous intermediate. The magnesium reduction process in the retort is in fact controlled by the heat transfer and reaction kinetics. Especially, the heat transfer on the wall surface of retort placed in the furnace involves in the heat conduction, convection and radiation from the high temperature flue gas, which will affect the magnesium reduction process in the retort.
Nomenclature

**Alphabets**

- \( A_p \): projected area of particle, \( \text{m}^2 \)
- \( d_p \): equivalent absorption coefficient of particles in cell, \( \text{m}^{-1} \)
- \( d_g \): gas absorption coefficient, \( \text{m}^{-1} \)
- \( C_1, C_2, C_d \): model constants, 1.44, 1.92, 2.0
- \( C_p, C_{pb} \): specific capacity of gas phase, \( \text{J kg}^{-1} \text{K}^{-1} \)
- \( c_p \): specific capacity of coal particle, \( \text{J Kg}^{-1} \text{K}^{-1} \)
- \( d_p \): diameter of particle, \( \text{m} \)
- \( E \): apparent activation energy, \( \text{J mol}^{-1} \)
- \( E_p \): equivalent emission of particles in cell, \( \text{m}^{-1} \)
- \( F_{di}, F_{gi} \): drag force and gravity, \( N \)
- \( f \): Favre mean mixture fraction
- \( f^{\text{r}} \): Favre mean mixture variance fraction
- \( G \): incident radiation in \( P - 1 \) radiation model, \( \text{W m}^{-2} \)
- \( G_k \): generation of turbulence kinetic energy due to the mean velocity gradients
- \( g_i \): acceleration of gravity, \( \text{m s}^{-2} \)
- \( H \): Favre mean total enthalpy, \( \text{J kg}^{-1} \)
- \( h \): convective heat transfer coefficient between particle and gas phase, \( \text{W m}^{-2} \text{K}^{-1} \)
- \( k \): kinetics reaction constant, \( \text{s}^{-1} \)
- \( k_0 \): proportional coefficient, \( \text{s}^{-1} \)
- \( M \): maximum magnesium production per unit volume, \( \text{kg m}^{-3} \)
- \( m_p \): mass of coal particle, \( \text{kg} \)
- \( N_u \): Nusselt number
- \( P \): the static pressure, \( \text{Pa} \)
- \( Pr \): Prandtl number
- \( Q_{\text{Conv}} \): convective heat transferred between particle and gas phase, \( \text{J s}^{-1} \)
- \( Q_{\text{Comb}} \): combustion heat of coal, \( \text{J s}^{-1} \)
- \( Q_{\text{rad}} \): radiative heat transferred between particle and gas phase, \( \text{J s}^{-1} \)
- \( q_m \): radiation flux, \( \text{W m}^{-2} \)
- \( R \): universal gas constant, \( \text{J K}^{-1} \text{mol}^{-1} \)
- \( R_{ei} \): Reynolds number based on the particle diameter and the relative velocity
- \( S_p \): surface area of particle, \( \text{m}^2 \)
- \( S_{1} \): magnesium reduction reaction heat, \( \text{W m}^{-3} \)
- \( S_{m} \): generalized source term
- \( S_{\text{sp}} \): source term of interaction between particle and gas phase
- \( T_g \): temperature of gas, \( \text{K} \)
- \( T_B \): reaction temperature of briquette, \( \text{K} \)
- \( t \): reaction time, \( \text{s} \)
- \( u_i \): instantaneous gas velocity, \( \text{m s}^{-1} \)
- \( u_t \): time-mean velocity of gas phase, \( \text{m s}^{-1} \)
- \( u_p \): fluctuating velocity of gas phase, \( \text{m s}^{-1} \)
- \( x_i \): coordinate, \( \text{m} \)
- \( \Delta H \): heat of coal combustion, \( \text{J kg}^{-1} \)
- \( \Delta M \): mass change for each particle, \( \text{kg} \)
- \( \Delta t \): integration time step between particle and gas phase, \( \text{s} \)

**Greeks**

- \( \rho \): gas density, \( \text{kg m}^{-3} \)
- \( \rho_b \): effective density of the charged briquettes, \( \text{kg m}^{-3} \)
- \( \alpha \): extent of magnesium reduction
- \( \psi \): thermal energy needed per unit mass of magnesium production, \( \text{J kg}^{-1} \)
- \( \kappa \): turbulent kinetic energy, \( \text{m}^2 \text{s}^{-2} \)
- \( \varepsilon \): dissipation rate of turbulent kinetic energy, \( \text{m}^2 \text{s}^{-3} \)
- \( \sigma_p \): emissivity of particle
- \( \phi \): generalized dependent variable
- \( \Gamma \): generalized diffusion coefficient
- \( \Gamma_{r} \): radiation parameter related to the absorption and scattering coefficients
- \( \mu \): molecular viscosity, \( \text{kg m}^{-1} \text{s}^{-1} \)
- \( \mu_t \): turbulent viscosity, \( \text{kg m}^{-1} \text{s}^{-1} \)
- \( \lambda \): molecular thermal conductivity, \( \text{W m}^{-1} \text{K}^{-1} \)
- \( \lambda_t \): turbulent thermal conductivity, \( \text{W m}^{-1} \text{K}^{-1} \)
- \( \lambda_b \): effective thermal conductivity of the charged briquettes, \( \text{W m}^{-1} \text{K}^{-1} \)
- \( \sigma \): Stefan-Boltzmann constant, \( 5.67 \times 10^{-8} \text{W m}^{-2} \text{K}^{-4} \)
- \( \sigma_t \): model constant, 0.85
- \( \sigma_{n, c} \): turbulent Prandtl number for \( \kappa \) and \( \varepsilon \) equations in realizable \( \kappa-\varepsilon \) model

Therefore, the one objective of this paper is to develop a model considering both the heat transfer and chemical reaction kinetics to describe the magnesium reduction process in the retort, and impact of different constant heating temperature on the magnesium reduction process including the temperature distribution and extent of magnesium reduction (the ratio between the quantity of magnesium reduced compared to the initial quantity of magnesium in the briquette) will be investigated and discussed. Another is to couple the magnesium reduction model with the conventional coal combustion models to describe the magnesium production in the coal-fired furnace, and impact of thermal-flow field in the coal-fired furnace on the magnesium reduction process in the retorts will be investigated and discussed.

2. Model description and solution method

The processes occurred in magnesium production in the coal-fired furnace include: (1) magnesium reduction process in the retorts, (2) coal combustion and gas turbulent flow, and (3) radiative heat transfer between the high temperature gas and the retorts wall. The models of describing different processes were individually developed and numerical details were presented below.

2.1. Magnesium reduction model in the retort

2.1.1. Kinetically modified shrinking non-reacted core model

The overall reaction in magnesium reduction process was described as Eq. (1). It is a solid-state endothermic reaction under vacuum and at high temperature.

Experimental analysis on a briquette indicates that the magnesium reduction is a gradual process advancing from exterior of the briquette to interior [18]. At one time instant, the reduction reaction occurs only in a thin region of the briquette, and the outside of the thin region is fully reacted while the inside of the region is not reacted. Since the thickness of the region is far smaller than the briquette radius, the reaction can be considered to occur at the interface with a constant temperature and the shrinking non-reacted core model can be used to describe the magnesium reduction process. The expressions of the model are:

\[
\frac{dx}{dt} = k(1 - x)^{2/3}
\]

\[
\alpha = 1 - \left(1 - \frac{k t}{3}ight)^{3/2}
\]
where \(a\) is the extent of magnesium reduction, \(t\) is the reaction time (s) and \(k\) is the kinetics reaction constant determined by the Arrhenius equation (s\(^{-1}\)),

\[
k = k_0 \exp \left(-\frac{E}{RT_b}\right)
\]

where \(k_0\) is the proportional coefficient equals to 0.10184 \([19]\) (s\(^{-1}\)), \(R\) is the universal gas constant (J mol\(^{-1}\) K\(^{-1}\)), \(E\) is the apparent activation energy (J mol\(^{-1}\)) and \(T_b\) is the reaction temperature of briquette (K).

As we know, the component and temperature of the briquette will vary as the magnesium reduction reaction proceeds, resulting in different apparent activation energy \(E\) at different time. In the present study, we derived the apparent activation energy \(E\) from reversing calculating the reduction rate \(a\) with the experimental data.

Combining Eqs. (2) and (4) obtained the expression of the apparent activation energy \(E\) as follows,

\[
E = \frac{RT_b}{k_0 t} \ln \left(\frac{1 - \sqrt{1 - a}}{a}\right)
\]

The experimental data of reduction rate \(a\) at different times and temperatures was obtained from Xu and Yuan \([18]\) and the calculated apparent activation energy was illustrated with symbols in Fig. 2. It will be a complicated equation if the apparent activation energy was directly correlated to both time and temperature. Two simplifications were made:

(1) The apparent activation energy at a fixed time was linearly averaged with temperature because the variation of the apparent activation energy with time was far larger than that with temperature, i.e., the variation of the apparent activation energy with temperature was neglected.

(2) The apparent activation energy was unchanged when the time is beyond the experimental time where the reaction time was relatively short.

Consequently, the averaged activation energy \(E\) was correlated as follows,

\[
E = \begin{cases} 66691.31 & t \leq 900s \\ 64605.507 + 2.478t - 1.844 \times 10^{-4}t^2 + 6.251 \times 10^{-7}t^3 & 900 < t \leq 12600s \\ 79065.39 & t > 12600s \end{cases}
\]

2.1.2. Reaction heat

The magnesium reduction process in industrial production is carried out under a vacuum pressure of \(~10\) Pa and temperature of 1100–1200 °C (1373–1473 K). In fact, the onset temperature of reaction (1) is 1158 K at 10 Pa according to the calculated correlation by Halmann et al \([20]\). But this calculation is for stoichiometric reaction. Considering non-stoichiometric mixture, the onset temperature was determined to be 1223 K. Therefore, the magnesium reduction reaction heat was calculated in two stages:

(1) 300 K (the charging temperature) \(~1223\) K, the briquettes is only heated up, there is no reaction occurred. It is just a heat conduction process. The reaction heat is zero.

(2) 1223 K–1473 K, the magnesium reduction reaction will begin and the reaction rate increases with increase of temperature.
The expression of reaction heat was given as follows,

\[ S_r = \begin{cases} 
0 & T < 1223 \text{ K} \\
-M \psi \frac{dT}{dt} & 1223 \text{ K} \leq T \leq 1473 \text{ K} 
\end{cases} \]  

(7)

where, \( M \) is the maximum magnesium production per unit volume (kg m\(^{-3}\)), \( \psi \) is the thermal energy needed per unit mass of magnesium production (J kg\(^{-1}\)).

2.1.3. Control equation

Two assumptions were made to establish the transportation equation governing the magnesium reduction process in the retort,

(1) Briquettes charged into the retort were considered as solid, and the effective values of the thermophysical properties were adopted, which were listed in Table 1.

(2) The heat conduction in axial direction and heat radiation at the end of the retort were neglected due to a large aspect ratio of height to diameter of the retort.

Accordingly, the magnesium reduction process in the retort was simplified as a two-dimensional (2-D), unsteady process with inner heat source, and the control equation was expressed in the Cartesian coordinate as follows,

\[ \frac{\partial}{\partial t} (\rhoSc_{pb}T_p) = \frac{\partial}{\partial \xi} \left( \lambda \frac{\partial T_p}{\partial \xi} \right) + S_r \]  

(8)

where \( \rho, c_{pb}, \lambda_p \) and \( T_p \) are the effective density (kg m\(^{-3}\)), effective specific heat capacity (J kg\(^{-1}\) K\(^{-1}\)), effective thermal conductivity (W m\(^{-1}\) K\(^{-1}\)) and temperature of the charged briquettes (K), respectively. \( S_r \) is the reaction heat of magnesium reduction calculated by Eq. (7) (W m\(^{-3}\)), and added to Eq. (8) as a source term via the user-defined function (UDF).

2.2. Coal combustion and gas turbulence flow

The conventional gas-particle turbulent flow and combustion model [21] were used to simulate the coal combustion occurred in the furnace. Generally, the coal particle was modeled as a discrete phase in a Lagrangian reference frame and the gas turbulent flow was modeled in an Eulerian reference frame. The coal combustion was modeled using the simplified probability density function (PDF) model [21], and the gas turbulence was modeled by the standard k-\( \varepsilon \) model.

2.2.1. Coal particle model

In the Lagrangian reference frame, the coal particles move mainly under the drag force and gravity, and other forces were omitted. They were meanwhile dispersed by the gas turbulence. The control equation was,

\[ \frac{d(m_pu_p)}{dt} = \frac{1}{2} C_D \rho (u_i - u_p)|u_i - u_p|A_p + m_pg \]  

(9)

where \( m_p \) is the mass of coal particle which is composed of volatile, char and ash (kg), \( \rho_p \) is the particle projected area \((-m^2\)), \( u_i \) is the particle velocity \((-m/s\)), \( C_D \) is the drag coefficient given by Morsi and Alexander [22], \( \rho \) is the gas density defined by using the ideal gas law \((\text{kg m}^{-3}\)), \( g \) is the acceleration of gravity \((-m/s^2\)), \( u_i \) is the instantaneous gas velocity which is decomposed into time mean component \( \bar{u}_i \) and fluctuating one \( \bar{u}_i' \) to account for the effects of turbulence on the particle dispersion \((-m/s\)). The time mean component is determined by the following gas control equation and the fluctuating one by the stochastic tracking method [23]. In the stochastic method, the particle interacts with a succession of discrete stylized fluid phase turbulent eddies. Each eddy is characterized by a Gaussian distributed velocity fluctuation and a time scale or the lifetime of eddy. And the interaction is determined over the smaller of the eddy lifetime and the particle eddy crossing time.

The mass of coal particles changed continuously during motion, and the particles were heated, combusted with gases and were irradiated from the high temperature gas. The exchange of mass and momentum between phases in cell were respectively calculated by,

\[ \sum_{i} \Delta m_{pi} \]  

(10)

\[ \sum_{i} (F_{di} + F_{gi}) \Delta m_{pi} \Delta t \]  

(11)

where, \( \Delta m_{pi} \) is the mass change of each particle (kg), \( F_{di} \) and \( F_{gi} \) are the drag force and gravity \((N)\), respectively. \( \Delta t \) is the integration time step, which are in advance defined in Eq. (9) \((s)\).

The total heat transfer equation for the particles was expressed as,

\[ \frac{dm_p c_p T_p}{dt} = Q_{\text{Conv}} + Q_{\text{Comb}} + Q_{\text{Rad}} \]  

(12)

where, \( c_p \) is the specific heat capacity of particle \((\text{J kg}^{-1} \text{ K}^{-1})\), \( T_p \) is the temperature of particle \((K)\), \( Q_{\text{Conv}}, Q_{\text{Comb}} \) and \( Q_{\text{Rad}} \) are the convective, combustion and radiative heat transferred between particle and gas phase \((\text{J s}^{-1})\), which were respectively calculated by,

\[ Q_{\text{Conv}} = hS_p(T_p - T_g) \]  

(13)

\[ Q_{\text{Comb}} = \frac{dm_p}{dt} \Delta H \]  

(14)

\[ Q_{\text{Rad}} = \varepsilon_{sp} \sigma \left( \frac{T_p^4}{T_g^4} - 1 \right), \quad \theta_R = \left( \frac{G}{4\sigma} \right)^{1/4} \]  

(15)

where, \( S_p \) is the surface area of particle \((-m^2)\), \( T_p \) is the gas temperature derived from the gas energy equation \((K)\), \( h \) is the convective heat transfer coefficient calculated from the Ranz–Marshall correlation [24] \((\text{W m}^{-2} \text{K}^{-1})\),

\[ Nu = \frac{h d_p}{\lambda} = 2.0 + 0.6 \text{Re}_{d_p}^{1/2} \text{Pr}^{1/3} \]  

(16)

where, \( d_p \) is the diameter of particle which was assumed to remain constant while the density of particle is allowed to change during reactions \((-m)\), \( \lambda \) is the thermal conductivity of the gas phase \((\text{W m}^{-1} \text{ K}^{-1})\), \( Nu \) is the Nusselt number, \( Re_{d_p} \) is the Reynolds number based on the particle diameter and the relative velocity, \( Pr \) is the Prandtl number of the gas phase.

2.2.2. Gas turbulence flow model

The control equations for the gas turbulence flow were written in a generalized form in the Cartesian coordinate as follows,

\[ \frac{\partial}{\partial t} (\rho \phi) + \frac{\partial}{\partial x_i} (\rho \phi u_i) = \frac{\partial}{\partial x_i} \left( \Gamma \frac{\partial \phi}{\partial x_i} \right) + S_\phi + S_{\text{sp}} \]  

(17)

where \( \phi \) represents any quantity of mass, velocity components, gas enthalpy, turbulent kinetic energy and its dissipation rate, mixture

<p>| Table 1 Effective thermophysical properties of the charged briquettes in the retort. |
|----------------------------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg m(^{-3}))</td>
<td>1150</td>
</tr>
<tr>
<td>Specific heat capacity (J kg(^{-1}) K(^{-1}))</td>
<td>1100</td>
</tr>
<tr>
<td>Thermal conductivity (W m(^{-1}) K(^{-1}))</td>
<td>1.3</td>
</tr>
</tbody>
</table>
fraction and its variance, $\Gamma$ is a generalized diffusion coefficient, $S_{\epsilon}$ is the source term and $S_{\epsilon q}$ an additional source term representing the interaction between coal particle and gas phase. Values or expressions of these variables are listed in Table 2.

### 2.3. Radiative heat transfer

The P-1 radiation model was used to model the radiative heat transfer between coal particles, gas phase and retort walls [25]. In this model, the radiation flux $q_r$ was calculated by,

$$q_r = -\Gamma_r \frac{\partial G}{\partial \xi}$$

where $\Gamma_r$ is a radiation parameter related to the absorption and scattering coefficients, $G$ is the incident radiation determined by the following transport equation (W m$^{-2}$).

$$\frac{\partial}{\partial \xi} \left( \Gamma_r \frac{\partial G}{\partial \xi} \right) - (q_g + q_p)G + 4\pi \left( a_g \sigma T^4 + q_r + q_b \right) = 0$$

where $q_g$ is the equivalent emission coefficient of the particles in cell (m$^{-1}$) and $a_g$ is the equivalent absorption coefficient in cell (m$^{-1}$). $q_p$ is the gas absorption coefficient calculated by the Weighted-Sum-of-Gray-Gases Model (WSGGM) [26] (m$^{-1}$). The emissivity of the furnace wall and retort wall are set to 0.4 and 0.8, respectively.

### 2.4. Simulation procedure and solution method

The magnesium reduction model developed in Section 2.2 was firstly carried out on a single retort without taking the external thermal-flow into account. As we know, the heating temperature on the wall of the retort placed in the furnace is usually not so steady and falls into a certain range. Therefore, the wall of retort was given the condition of constant heating temperature of 1423 K, 1448 K, 1473 K and 1498 K to investigate the impact of different heating temperature on the magnesium reduction process in the retort. The initial temperature of reactant was set to 300 K. In addition, a quarter of the whole geometry was taken as the computational domain due to the symmetry of the geometrical structure and calculation conditions, which was indicated by dashed line. The computational domain was discretized by the unstructured grids and the grids near the external wall of retorts were refined where there were a larger gas velocity and thermal gradient.

The simulation procedure was divided into two steps according to the actual industrial operation. The retorts are firstly heated up to 1150–1200 °C before the briquettes are charged into. Therefore, a steady state process was firstly solved to obtain an initial condition of the gas temperature around the retort region being about 1200 °C by adjusting the flowrates of coal and air. In this process, we assumed that the retorts were charged with the briquettes but the magnesium reduction process was not considered, i.e. the source term $S_{\epsilon}$ equals to zero in control Eq. (8). The time-dependent term was also omitted. Such deal would not affect the calculation results. Once the steady state process reached, the reaction heat $q_r$ was added as source term via a user-defined function (UDF) and temperature of the briquettes in the retorts were simultaneously initialized to be the charging temperature, 300 K. The unsteady process was solved by the time-marching method [27]. The time step was set to 60 s, and interphase coupling iterations were performed to get a convergent solution at each time step.

### 3. Results and discussion

#### 3.1. Comparison with the experimental data

The extent of magnesium reduction in a single retort under the constant heating temperature of 1473 K was compared with the experimental data in publication [7,28]. Fig. 4 shows the comparison results. The model results are in general agreement with the experimental data at low extent of magnesium reduction, but about 8–10% higher than the experimental data at higher extent. In addition, the larger the extent is, the larger is the deviation. Considering the model limitation for higher magnesium reduction extent and the experimental uncertainties, the magnesium reduction model results are acceptable, and the model is reasonable and feasible.

#### 3.2. Magnesium reduction process in a single retort

##### 3.2.1. Temperature characteristics

Fig. 5(a) and (b) show the temperature distributions in the retort and temperature profiles in radial direction at fixed times of 30 min, 2 h, 6 h and 12 h. In general, the temperature gradient is large in radial direction at the beginning of time, and decreases with time due to the continuous heat conduction. The briquettes close the retort wall are quickly heated up to 1469 K, and the temperature at the center region of retort increases from 300 K to 1167 K during the first 2 h. However the temperature at the center region increases only by around 200 K in the following 10 h. It can be expected that the heat conducted is at the time almost provided for reaction. Fig. 6 compares the temperature profile of the...
magnesium reduction process with that of a just heat conduction process in the first 3 hours. In Fig. 6, a suffix “-ns” was added to the time in legend which represents the results of the just heat conduction process. The two curves are almost coincident at 30 min and show an increasing larger deviation with increase of time after 30 min. The deviation reaches about 180 K at 3 h. Especially, the temperature profiles of the just heat conduction process is always higher than that of magnesium reduction process.

It can be expected that the heat conducted from the retort wall was used for two processes: rising reactants temperature and magnesium reduction reaction. The former process is dominant at the initial heat and the latter is dominant in the following time. The inconsistency of temperature profile between the just heat conduction and magnesium reduction process indicates that the magnesium reduction process in the retort is controlled by both heat conduction and reaction kinetics. Improving the heat conduction rate is a main factor of improving the extent of magnesium reduction.

3.2.2. Extent of magnesium reduction

The heat conduction affects the temperature distributions in the retort. The impact of different heating temperature on the extent of magnesium reduction was then investigated.

Fig. 7 shows the curves of the extent of magnesium reduction with time. At the beginning, the extent of magnesium reduction is low but increases quickly. It can be explained that the reactants close to the wall of retort are firstly heated up and react, but the reaction region is relatively small. However, the heat conduction is at the time dominating and the conduction rate is high. The reaction region is quickly expanded due to the rapid rise of reactants temperature, resulting in a rapid increase of magnesium reduction.
extent. At the final stage of reduction, the reduction extent increases slowly because of the decreasing heat conduction rate and consumption of the reactants. Compared to the curves of magnesium reduction extent at different heating temperatures, it can be found that the magnesium reduction extent increases with the increase of heating temperature although they all show a similar trend. The higher heating temperature improves the heat conduction rate and reaction temperature that will accelerate the magnesium reduction reaction of the briquettes. It can be concluded that the heating temperature has a large impact on extent of the magnesium reduction in the retort.

3.3. Magnesium production in the coal-fired furnace

3.3.1. Flow field and temperature characteristics in the furnace

The flow field and gas temperature characteristics in the retort region were firstly obtained through the steady state calculation. Fig. 8 shows the flow field in the furnace. The high temperature flue-gas is introduced into the furnace from the combustion chamber, flows around the retorts and then flows out via the outlet. Recirculation zones are formed in the furnace corner adjacent to the flue gas inlet and in between the retorts. In addition, there is

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**Fig. 6.** Comparison of temperature of the reduction process with that of a pure heat conduction process.

**Fig. 7.** Curves of extent of magnesium reduction with time at the constant heating temperature.

**Fig. 8.** Flow field in the coal-fired furnace in the steady state process.

**Fig. 9.** Temperature characteristics in the coal-fired furnace in the steady state process: (a) variation in temperature along the Lines-x1&x2. (b) Variation in temperature along the Lines-y1&y2.
a large difference of velocity magnitude around the retorts. The velocity in the recirculation zone is much smaller.

Investigation of temperature characteristics in the retort region was made by illustrating the variation in temperature along several typical lines, which is shown in Fig. 9(a) and (b). Line-x1 and line-x2 are defined as horizontal lines passing through the circle center of retort 2 and that of retorts 1 and 3, respectively, while Line-y1 and line-y2 are defined as vertical lines passing through the circle center of retort 2 and that of retort 1, respectively.

Generally, the temperature distribution is uniform with a maximum temperature difference of 5 K because the furnace is relatively small. However, it shows a lower temperature distribution at the recirculation zone.

### 3.3.2. Magnesium reduction process in the retorts

Fig. 10 shows the distribution of magnesium reduction extent in each retort at fixed times of 2 h, 5 h, 8 h and 11 h. In general, the reduction region expands in radial direction from the external layer to the center of the retorts. The briquettes close to the wall of retorts are firstly reduced and the reduction extents increase with time, but the reaction proceeds in a thin layer of briquettes. Note that the briquettes at the center of the retort are almost not reduced during a long time. It can be explained that the heat from the retort wall which is heated by the external thermal flow, is hard to be conducted into the center of retort because the heat is firstly provided for the rising temperature and reaction of the external layer of briquettes. The required heat of the external layer of briquettes decreases with increase of temperature and decrease of reaction rate. When the required heat is small enough, the thin layer is then advanced. Accordingly, the magnesium reduction process in the retort is a gradual process advancing from the external region to the center of the retort, and the reduction reaction occurs in a thin layer of briquettes.

However, unlike the constant heating condition, the extent of magnesium reduction under the thermal-flow heating shows an obvious asymmetry in each retort. Take the retort 3 for an example, the up of retort 3 has a higher reduction extent than the other. The retorts placed in the furnace are under the action of thermal-flow fields. The radiation and convection heat transfer on the wall surface of the retort would affect the temperature of the retort wall, and further affect the heat conduction of the briquettes and reduction process in the retort. We extracted the data of gas velocity along a circle 5 mm away from the wall of the retort 3 and temperature along the wall of the retort 3 to try to explain the asymmetry.

![Fig. 11](image.png)

**Fig. 11.** Curves of gas velocity and temperature along the defined circle: (a) variation in velocity along the circle 5 mm away from the wall of the retort 3. (b) Variation in temperature along the wall of the retort 3.
for the other two retorts. In industry, the new design of furnace guaranteeing the uniform thermal-flow field is therefore required.

3.3.3. The total extent of magnesium reduction

Fig. 12 shows the curve of the total extent of magnesium reduction with time under the thermal-flow heating condition in the furnace. The results at the constant heating condition of 1423 K obtained were also presented for comparison. Generally, the total reduction extent under the thermal-flow heating has a similar trend as that at the constant heating temperature, i.e., increases rapidly at first and then slowly with time. However, the value of reduction extent under the thermal-flow heating is lower about 10% than that at constant heating at fixed times. That is mainly because the wall temperature of the retort is lower than 1423 K during a long time under the thermal-flow heating condition. When the briquettes of room temperature were charged into the retorts, the wall temperature will be quickly cooled from 1473 K to a low temperature. We monitored the variation in temperature of two specified points on the retort wall with time under the thermal-flow heating condition, which is shown in Fig. 13. The retort wall temperature drops sharply from the 1473 K to about 1050 K at point 2 at the beginning time of 0.5 h, and then increase gradually from the low temperature to the onset temperature of magnesium reduction in the next time of 2 h. Such long time temperature rising depletes the reaction rate and prolongs the reduction time. Although the temperature at some places of the wall is higher than 1423 K, the difference of magnesium reduction extent is not be made up.

4. Conclusions

The magnesium reduction process in the retort is controlled by both the heat transfer and reaction kinetics. The impact of heat transfer, including the heat conduction of briquettes in the retorts and the external thermal-flow around the retorts, on the magnesium reduction process in the retorts is significant. The heat conducted from the retort wall is used for rising temperature of briquettes and magnesium reduction reaction. Improving the heat conduction rate can improve the extent of magnesium reduction. The magnesium reduction reaction proceeds in a thin layer of briquettes and the reduction process advances gradually from the external region of the retort to the center. The external thermal-flow results in an obvious asymmetry distribution of magnesium reduction extent in the retort. It is therefore required for new design of furnace to guarantee the uniform thermal-flow field in industry. In addition, the longtime temperature rising of the retort wall when charging the briquettes at room temperature in the coal-fired furnace results in a lower total extent of magnesium reduction than that at the constant heating conditions.

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