



Full Length Article

Research, development and application of compound-vertical-retort technology for magnesium production

Rongbin Li^a, Shaojun Zhang^{b,*}, Peixu Yang^b, Jinhui Liu^b, Fengqin Liu^{a,*}^a*School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China*^b*School of Material Science and Engineering, Zhengzhou University, Zhengzhou, Henan 450001, China*

Received 1 November 2022; received in revised form 17 May 2023; accepted 24 May 2023

Available online 5 August 2023

Abstract

This paper comprehensively introduces a new magnesium production technology the compound-vertical-retort technology, involving in the related fundamental researches, core equipment development, working flow, and technical characteristics. Scale-up test and an annual 1200-ton-magnesium demonstration-level test was conducted to confirm the rationality, reliability, and advancement of the equipment, system and process design. It is indicated that the new technology solved a series of problems of traditional silicothermic process including adhesion and glaze, short life of retort, low efficiency, high impurity of crystallized magnesium, large heat losses, and poor working environment, making a great technological breakthrough in this field. Representatively, the new well-designed ceramic-lined steel retort serves 2~3 times in life than the normal retorts. The magnesium yield per retort is improved 4~5 times, with purity of >99.8%. The energy consumption in reduction stage is reduced by more than 20%. The mechanical production is fully realized and operating environment is significantly improved.

© 2023 Chongqing University. Publishing services provided by Elsevier B.V. on behalf of KeAi Communications Co. Ltd.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Peer review under responsibility of Chongqing University

Keywords: Silicothermic process; Magnesium; Compound retort; Vertical retort; Mechanization.

1. Introduction

Magnesium (Mg) and Mg alloys are increasingly favored due to their lightest structural metallic property [1] and functional properties used for batteries, hydrogen storage materials and bio-magnesium alloys [2,3]. China has extremely abundant magnesium resource, large-scale primary magnesium industry and high-quality magnesium alloy preparation and processing technology. There are the greatest advantages to develop vigorously the magnesium industry in China. However, the low-level, extensive technology of producing the primary magnesium is slowing down the development of the magnesium industry in recent years.

In industry, the magnesium metal is mainly produced by the silicothermic reduction and electrolysis. Yet, because the

energy consumption, production cost and investment of electrolysis is normally much more than the silicothermic reduction [4], most of electrolysis smelters have been stopped or semi-suspended. Up to now, it is reported that more than 80% of primary magnesium in the world is produced in China [5], which is mainly produced by the Pidgeon process (a horizontal-retort silicothermic process). The Pidgeon process has advantages of saving investment, simple flow and low cost, but its further development is limited due to a number of shortcomings. The Pidgeon process is a batch process that needs highly intensive labor work. As shown in Fig. 1(a) & (b), the horizontal retort makes it difficult to achieve mechanization and automation. Both charging and discharging is completed through manual operation [6]. Still, the magnesium yield for one retort at a time is only 20~30 kg, and the service life of retort is only 2~3 months [7]. The heat efficiency of reducing furnace is low, and the heat released in the high-temperature slag cooling and magnesium crystallization do not be recovered. The slag is not effectively utilized.

* Corresponding authors.

E-mail addresses: zhangs@zzu.edu.cn (S. Zhang), liufq@ustb.edu.cn (F. Liu).

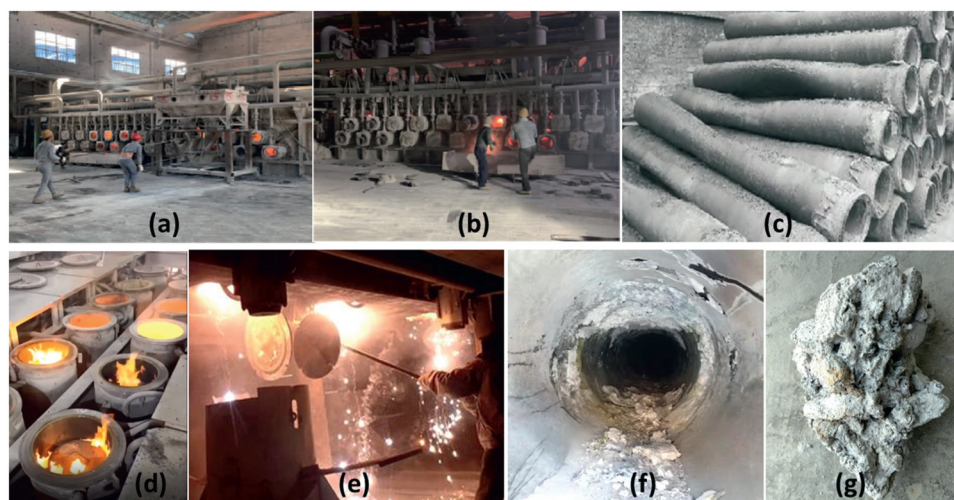


Fig. 1. Situation of production in the Pidgeon process and normal vertical-retort silicothermic process. (a) & (b) charging and discharging in Pidgeon process, (c) the collapsed retort, (d) the chimney effect in the vertical-retort process, (e) manual raking, poking and shoveling to clean the retort, (f) & (g) phenomenon of fusion and slag agglomeration.

Therefore, the innovation and development of magnesium production technologies need to solve the problems of the low production efficiency, high labor intensity, low mechanization, short life of retort, slag disposal, high energy consumption and carbon emissions.

The vertical-retort silicothermic process developed in recent years [8–10] is considered as a more advanced magnesium production technology. Since the retort is designed to install vertically, the mechanical feeding and discharging can be conducted by the gravity. Simultaneously, the magnesium yield per retort can be scaled up through configuring a small-diameter inner cylinder in the larger-diameter retort. Compared with the Pidgeon process, the mechanization, production efficiency and labor productivity have been generally improved. However, actually adhesion and glaze (a phenomenon of fusion and slag agglomeration due to low-melting-point products during the reduction, as shown in Fig. 1(f) and (g)), has not been well solved so that the slag cannot be smoothly discharged by gravity. The frequent manual raking, poking and shoveling to clean the retort, as shown in Fig. 1(e), are need. The burns and scalds on workers occur frequently. Worse, the chimney effect occurred in the vertical-retort process makes the ash and fire emit from the upper and lower ports of retort during the charging and discharging. The environment and labor conditions in the workshop becomes worse under high temperature and high dust. Still, the service life of vertical retort is the same as that of the horizontal one, which is also only 2~3 months. Therefore, problems such as the adhesion and glaze, chimney effect, short life of retort, and long production cycle due to scaling up the magnesium yield have to be solved to further develop the vertical-retort silicothermic process.

A new silicothermic process, namely compound-vertical-retort magnesium production technology, was successfully developed going through basic theoretical research of the engineering thermophysics and thermochemistry related to

the silicothermic process, innovating structure design of key equipment (compound vertical retort, compound crystallizer, compound reducing furnace, slag heat recovery boiler), process flow design of system, and the scale-up test validation. A demonstration plant with annual capacity of 1200 tons magnesium was established in China. This new technology was proved to have solved comprehensively series of problems such as adhesion and glaze, short life of retort, low efficiency in magnesium reduction rate, high impurity of crude magnesium, nonuniform furnace temperature, large heat losses, high carbon emissions and poor working environment, making a great technological breakthrough in this field. This paper comprehensively and systematically introduces the achievements of fundamental theoretical research and those of the compound-vertical-retort technology research on the main technical process, construction of key equipment, scale-up test, establishment and operation of demonstration plant. Finally, through comparison in the technical and economic indicators of the compound-vertical-retort silicothermic process with those of the Pidgeon process and normal vertical-retort silicothermic process, the advancement and superiority of the compound-vertical-retort magnesium production technology are discussed.

2. Fundamental research and key equipment development of the compound-vertical-retort magnesium production technology

2.1. Compound vertical retort

2.1.1. Research of adhesion and glaze problem and its control

For the compound-vertical-retort technology, a basic goal is to achieve automatic feeding and automatic slag-discharging by gravity so as to improve mechanization and automation level. However, the adhesion and glaze cause the

slag to be unable to be smoothly discharged out of the retort, and also the fly ash sticking on the inner wall of retort very hard to be removed by worker. Thus, the adhesion and glaze are the primary problem need to be firstly solved in the development of compound-vertical-retort technology.

Actually, the adhesion and glaze could occur in the Pidgeon process or vertical-retort silicothermic process, but the latter is more severely restricted. It was found that the “adhesion” is the phenomenon that the reducing slag agglomerates and adheres to the retort wall (see Fig. 1g), making the slag be unable to discharge automatically. While the “glaze” is the phenomenon of forming enamel layer in the inner wall of retort (see Fig. 1f), resulted from the loose floating ash that adheres to the retort wall when discharging and cooling. In essence, both the “adhesion” and “glaze” is the fusion and agglomeration phenomenon as the charge and reducing slag are melted and softened.

The component analysis shows that the main substances in the reducing residue includes CaO, SiO₂, MgO, Fe₂O₃, Al₂O₃, and their composite oxides, as well as CaF₂ [11]. Through analyzing in detail the phase diagrams of the binary or ternary systems among the above five oxides, it was found that the occurrence of fusion and agglomeration in the silicothermic reduction process is mainly related to the three substances of 2FeO·SiO₂ (melting point 1205 °C), CaO·2FeO (melting point 1150 °C) and CaO·Fe₂O₃ (melting point 1220 °C), which all contain FeO or Fe₂O₃. Thus, it was speculated that formation of the FeO or Fe₂O₃ and further reaction with the SiO₂ or CaO to form the low melting point composite oxides, are the key factor that causes fusion and agglomeration. Our team confirmed it through a large number of thermophysical and chemical experiments [12]. (*More details on experiments, phase diagram analysis can see in the supplementary material*). Furthermore, analysis on these experiment results shows that the low-melting-point oxides play as the intermediates to soften and bond the raw materials and finally lead to the fusion and agglomeration, rather than the final solid-phase products of reduction reaction. Among them, the intermediate of liquid iron orthosilicate (fayalite), 2FeO·SiO₂, plays more significant effects on the fusion and agglomeration. The mechanism of catalytic reaction causing the fusion and agglomeration is shown in Fig. 2(b).

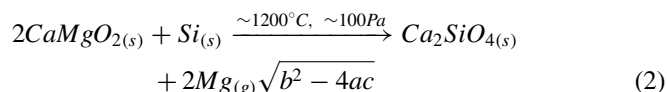
Accordingly, several measures have been taken by our team to control the fusion and agglomeration in the silicothermic process. Firstly, it can strictly control the raw materials' impurity and the raw materials' moisture absorption rate. According to the Ca₂SiO₄-Fe₂SiO₄ pseudo-binary phase diagram shown in Fig. 2(c), the liquid-phase substances can not produce as long as the content of 2FeO·SiO₂ do not exceed 6%, thus the condition of preventing the fusion and agglomeration was derived and given as equation (1). Where, M_r is the molar ratio of silicon, i.e., Si/2MgO, CM is the CaMgO₂ content in 100 g charge or briquette, Fe_2O_3 , SiO_2 , K_2O , Na_2O , $CaMgO_2$ represent the mass fraction in raw materials, F_1 , F_2 represent the amount of FeO introduced from the raw materials and generated by the reaction between air and the remaining ferrosilicon, respectively, S_1 , S_2 , S_3 represent the

mass of SiO₂, introduced from the raw materials, generated by the reaction between CO₂/H₂O and remaining ferrosilicon, and also the generated by the reaction between air and ferrosilicon, respectively. Secondly, the ceramic-lined steel retort has been designed and constructed to prevent the high-temperature reducing slag from directly contacting with the iron-based alloy thus from the fusion and agglomeration.

$$\begin{cases} \frac{0.9Fe_2O_3}{CaMgO_2} + 0.0625M_r \leq 0.0402, & \frac{F_1+F_2}{143.6} \leq \frac{S_1+S_2+S_3}{60.1} \\ \frac{SiO_2+0.132K_2O+0.485Na_2O}{CaMgO_2} + \frac{S_2}{CM} + \frac{S_3}{CM} \leq 0.0168, & \frac{F_1+F_2}{143.6} > \frac{S_1+S_2+S_3}{60.1} \end{cases} \quad (1)$$

2.1.2. Study of silicothermic reduction process and optimization of retort structure

In the silicothermic reduction process, the FeSi75 alloy is used as the reducing agent to extract Mg from the CaO·MgO under high temperature and vacuum. According to the thermodynamic calculations, the reaction in Eq. (2) mainly occurs in the silicothermic reduction, of which the onset temperature was calculated and given in Table 1.



In reality, the silicothermic process is conducted with the walnut-shaped briquettes in ~22 mm diameter. It is a typical solid-phase endothermic reaction, of which the rate is controlled by the heat conduction and reaction kinetics itself. Researches by Xu et al. [13], Wu [14], Li et al. [15], You et al. [16] studied the mechanism and kinetics of silicothermic reduction, but a consensus on the kinetics has still not been reached. Our team proposed a method “very-thin briquette” to determine the rate of reaction kinetics itself without the influence of heat conduction [17]. A series of kinetic experiments were conducted [17,18], the kinetic model [19] of describing the silicothermic reduction reaction on the briquette (typically, silicon molar ratio $M_r \approx 1.2$, calcium fluoride additive ratio $f \approx 2.85\%$, calcined dolomite's activity $A \geq 30$ g, briquette-forming pressure $P_b \approx 150 \pm 20$ MPa) was finally obtained as Eq. (3).

$$\begin{cases} \alpha = 11.84 \times e^{-\frac{30546}{RT}} \left(1 - e^{-\frac{T-T_0}{108460}} \right) \\ r_{Mg} = \frac{d\alpha}{d\tau} = 1.0916 \times 10^{-4} \times (T - T_0) \times e^{-\left(\frac{30546}{RT} + \frac{T-T_0}{108460}\right) \times \tau} \\ T_0 = \frac{12021.1}{11.6242 - \lg p} \\ p \approx 150 + p_{Mg} \end{cases} \quad (3)$$

Where, α is the magnesium reduction extent, r_{Mg} the kinetic rate, T the reaction temperature, K, T_0 the reaction onset temperature, K, τ the reaction time, s, R the molar gas constant, 8.314 J·mol⁻¹·K⁻¹, p the local magnesium vapor equilibrium pressure inside the briquette, Pa, p_{Mg} the ambient magnesium vapor partial pressure outside the briquette in the retort, Pa.

The kinetic model was coupled with the heat transfer model to numerically study the silicothermic reduction pro-

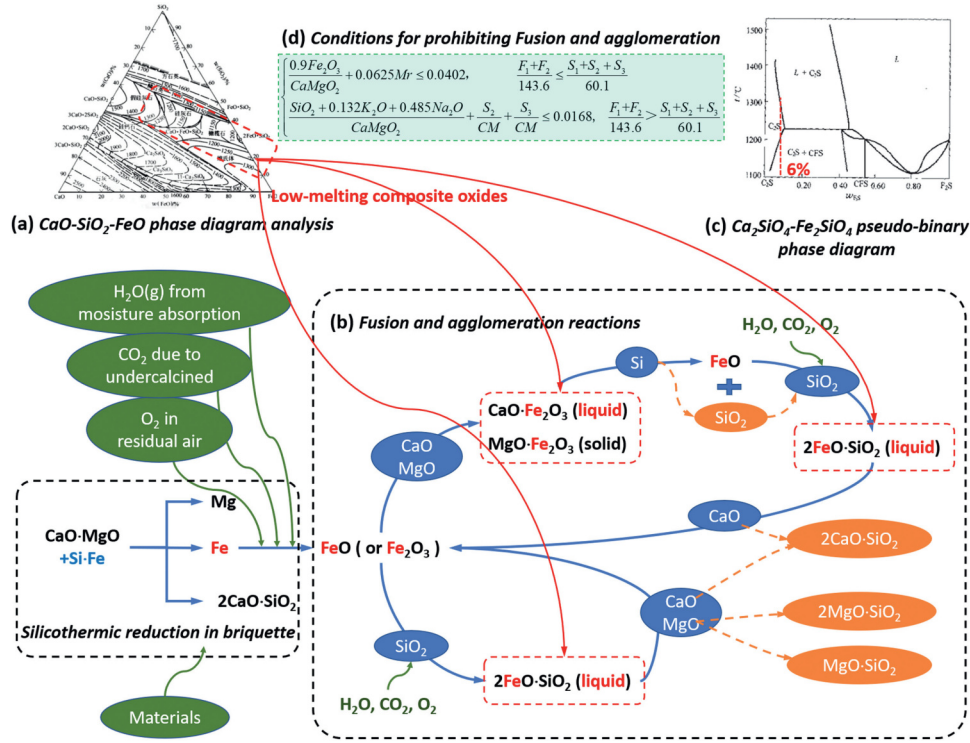


Fig. 2. Research of fusion and agglomeration in the silicothermic reduction process. (a) Phase diagram analysis of CaO-SiO₂-FeO system as representative, (b) Catalytic reaction mechanism of fusion and agglomeration, (c) Ca₂SiO₄-Fe₂SiO₄ pseudo-binary phase diagram, (d) Control measure of fusion and agglomeration according to the raw material impurities.

Table 1

Relationship between Mg vapor equilibrium pressure and reaction onset temperature.

Mg vapor equilibrium pressure, Pa	10	100	1000	10,000
Onset temperature of reaction by Si, °C	858	976	1121	1304

cess in single briquette and in the retort [20,21]. As shown in Fig. 3, for the briquette or briquette layer in the retort, the silicothermic reduction is mainly concentrated in a thin layer at a certain time. It can be considered that there is a wholly reacted region outer side of the thin layer while an unreacted region inner side of thin layer. And, the heat transfer including the heat conduction or radiation plays the main limiting factor on the rate of silicothermic reduction. Based on the coupled model, a detail numerical investigation of various retort inner radius and thickness of briquette layer was conducted and then the optimized retort structure was obtained [22]. The reduction time for same reduction extent in the optimized retort is comparable to that in the horizontal retort, but 1/3 shorter than that in the normal vertical retort.

2.1.3. Research of mechanical properties of high-temperature heat-resistant materials and prolonging service life of retort

The compound vertical retort serves for a long term in high temperature of about 1200 °C and vacuum of about 10~200 Pa, as well as in the environment containing the oxygen, sulfur dioxide and sulfur trioxide. It is prone to creep deformation, oxidation and sulfide corrosion. At present, the retort used in the Pidgeon process is generally 300 mm in diameter, of which the service life is less than three months.

However, limited by the high-temperature, low-load, long-term creep test accuracy and short life of instrument heating element, test of the mechanical properties of high-temperature heat-resistant materials of retort at ~1200 °C continuous working condition is extremely lacking. Thus, reasonable design of strength and creep for the vertical retort is critical to prolong the service life of retort.

The special heat-resistant steel ZG35Cr26Ni8NRE has excellent oxidation resistance up to 1200 °C, and room temperature tensile strength of 500~600 MPa [23]. It was adopted as the material of reduction section of compound vertical retort. Our team conducted creep experiments of the steel ZG35Cr26Ni8NRE at different tensile stress/time of 3.0 MPa/100 h, 0.5 MPa/500 h, and 0.9 MPa/3200 h (until specimen fracture) at 1200 °C. The creep curves with time and extrapolation analysis are shown in Fig. 4. The fitted equations at 0.9 MPa and 0.5 MPa tensile stress and those obtained by extrapolation at 0.9 MPa and 0.5 MPa compressive stress were given as Eqs. (4) & (5), respectively, in the following.

$$\begin{cases} \varepsilon_{t,0.9} = -7 \times 10^{-13} \tau^4 + 4 \times 10^{-9} \tau^3 - 3 \times 10^{-6} \tau^2 \\ \quad + 0.0036 \tau - 0.0275, \sigma = 0.9 \text{ MPa} \\ \varepsilon_{t,0.5} = 0.002 \tau - 0.2461, \sigma = 0.5 \text{ MPa} \end{cases} \quad (4)$$

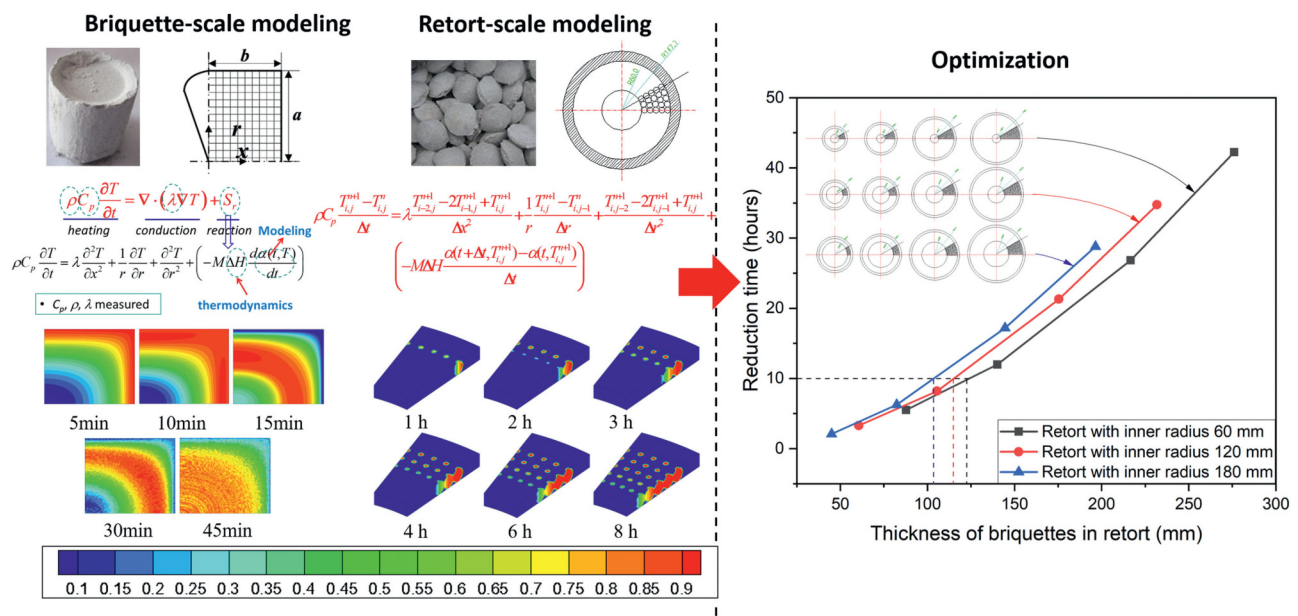


Fig. 3. Modeling and simulation of silicothermic reduction process in single briquette and in the retort, and optimization of retort structure.

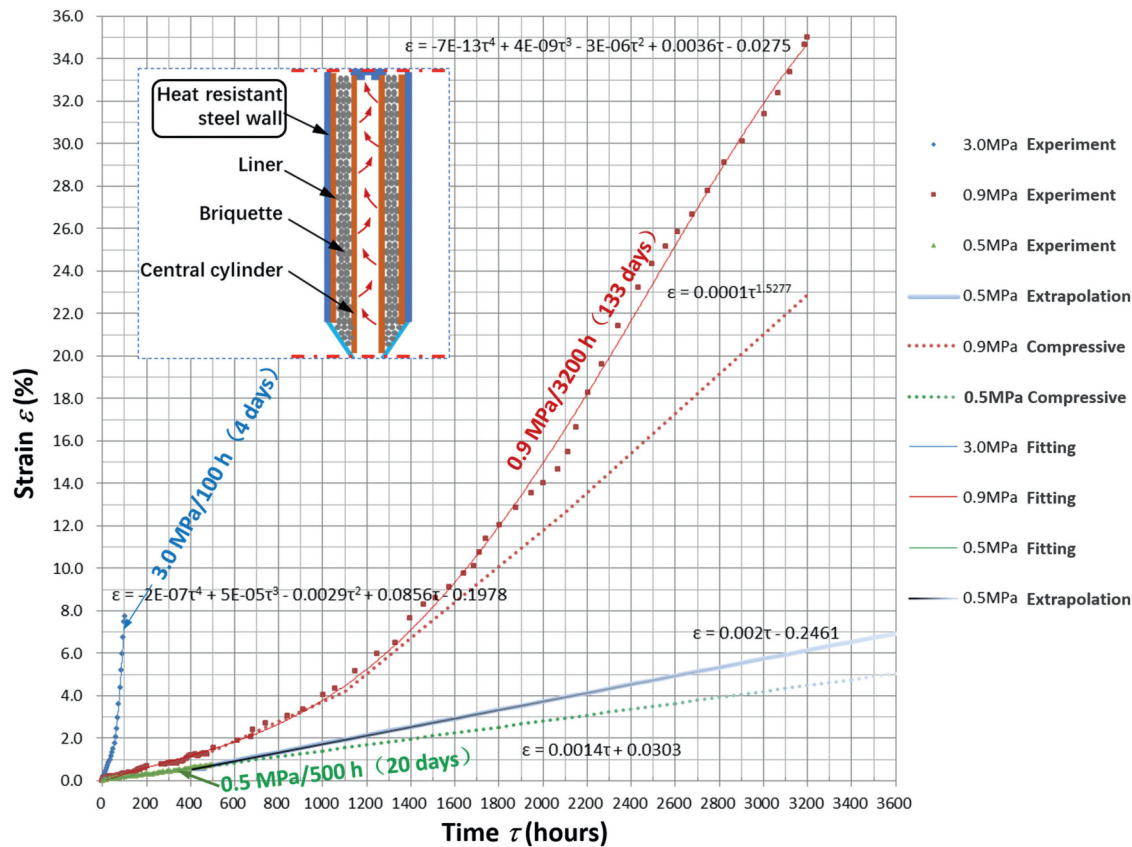


Fig. 4. Creep curves of the steel ZG35Cr26Ni8NRE at different tensile stress/time of 3.0 MPa/100 h, 0.5 MPa/500 h, and 0.9 MPa/3200 h at 1200 °C and extrapolation analysis.

$$\begin{cases} \varepsilon_{c0.9} = 0.0001\tau^{1.5277}, \sigma = 0.9\text{MPa} \\ \varepsilon_{c0.5} = 0.0014\tau + 0.0303, \sigma = 0.5\text{MPa} \end{cases} \quad (5)$$

When the retort is installed vertically with good suspension design, the retort can only bear the weight itself and the highest stress is at the bottom of the retort. It was calculated to be up to 0.5 MPa for the compound vertical retort. According to the actual application situation, the retort would be rapidly deformed and destructed as the creep strain exceeds the limiting strain of 4%. Thus, it was predicted from the creep curve of compressive pressure 0.5 MPa in Fig. 4 that the working time τ of well-designed retort can be prolonged to be 3000~3600 h, i.e., 4~5 months. It can be expected that the working time of retort would be further prolonged should reinforcing ribs be constructed along the vertical retort.

2.2. Compound crystallizer

2.2.1. Flow patterns and multiphase change of magnesium vapor in the retort and crystallizer

After the magnesium vapor is produced in the briquette, it will evolve from the surface of briquette, pass through the interspace between briquettes to flow into the magnesium vapor channel and then through the heat baffle, finally arrive at the magnesium crystallizer. There is pressure difference of about 150 Pa during magnesium vapor flow process [24]. According to the kinetic-molecular theory of gasses, the Knudsen number K_n for magnesium vapor in the range of pressure 0.01 Pa~1000 Pa and temperature 450 °C~1050 °C was calculated by Eqs. (6) & (7), and given in Fig. 5(a), for three characteristic structure sizes $D = 0.5$ m, 0.24 m, and 0.01 m, which corresponds to the inner diameter of the crystallizer, the inner diameter of the central cylinder and the size of the magnesium vapor aperture on the central cylinder wall, respectively.

$$\lambda = \frac{k_B T}{\sqrt{2\pi} d^2 p} \quad (6)$$

$$K_n = \frac{\lambda}{D} \quad (7)$$

Where, λ is Mg molecular free path, m, k_B the Boltzmann constant, 1.38×10^{-23} J·K⁻¹, T temperature, K, d the Mg molecular diameter, m, 3.2×10^{-10} m, p the pressure, Pa, D characteristic structure size, m.

As the pressure at outlet of crystallizer is maintained at about 10 Pa, the magnesium vapor flow in the crystallizer and in the central cylinder is viscous, while the magnesium vapor flow through the aperture of the central cylinder is viscous-molecular. Specifically, taking the pressure difference into account, the magnesium vapor pressure at the inlet of crystallizer is as high as 100 Pa, where it is viscous. While at the outlet of crystallizer, the magnesium vapor pressure may be only a few tenths of Pascal (Pa) or even a few percent of Pascal, where it should be molecular. In the middle of the crystallizer, the magnesium vapor is in the viscous-molecular transition state.

2.2.2. Condensation behavior of Mg and metallic impurities vapor and sectional crystallization

The crystallized magnesium produced by silicothermic process contains a small quantity of oxide impurities, and some metal impurities such as K, Na, Zn, Mn, Fe, Cu, Ni which resulted from the reduction of oxides.

In order to quantitatively study the magnesium crystallization and control the impurity content, three-phase diagram of Mg, K, Na, Zn, Mn, Fe, Cu, Ni, is shown in Fig. 5(b), based on the thermodynamic properties and the Gibbs free energy of phase transition. It can be seen that when the pressure inside the crystallizer is kept at 10 Pa~30 Pa (the partial pressure of magnesium vapor is close to the total pressure inside the crystallizer), the Mg crystallization temperature calculated is 766 K~806 K (493 °C~533 °C). The Mg vapor would be condensed directly from the gas to solid phase. However, the partial pressure of impurities is much lower than that of Mg vapor, leading to different condensations. Specifically, at temperature of 493 °C~533 °C the K, Na, and Zn cannot be condensed and would flow in gas phase through the Mg crystallization area; the Mn is possible to condense together with the Mg vapor in the crystallization area when its partial pressure is lower than 10^{-6} Pa. And, the Fe, Ni, Cu has condensed to solid before entering the Mg crystallization area. Thus, theoretically, the content of various metal impurities in crystallized magnesium can be controlled below the level of $1/10^{-6}$, even $1/10^{-8}$, that is, the magnesium with high purity can be produced by the silicothermic process.

However, the impurity content of crystallized magnesium by the Pidgeon process is generally above 10^{-5} , and even as high as 10^{-3} or more, mainly due to the unreasonable structural design of the crystallizer. If the crystallizer has sufficient length to enable to construct an 806 K~1000 K condensation area where Fe, Ni, Cu, Mn is effectively condensed, these metallic impurities will be prevented from entering the Mg crystallization area. In addition, the triple point of Zn is 420 °C, Na 98 °C, and K 63 °C, so as long as the temperature in the magnesium crystallizer is higher than 420 °C, and the temperature of rear potassium-sodium-zinc trapper can be kept low enough, all the K, Na, and Zn will flow through the crystallizer instead of crystallizing with magnesium. Accordingly, our team designed and developed the sectional crystallizer as shown in Fig. 6(c).

2.3. Compound reducing furnace

The regenerative combustion furnace is generally used in the industrial production of silicothermic process for magnesium production. The retort filled with briquettes is placed in the furnace for heating, as shown in Fig. 6(a). The external heat flow field around the retort includes the convection of high-temperature flue gas flowing through the retort wall and the radiation heat transfer from high temperature flue gas to the retort wall. By establishing a coupling model of flow equations, heat transfer equations and the magnesium reduction kinetics equation as (3), our team simulated the

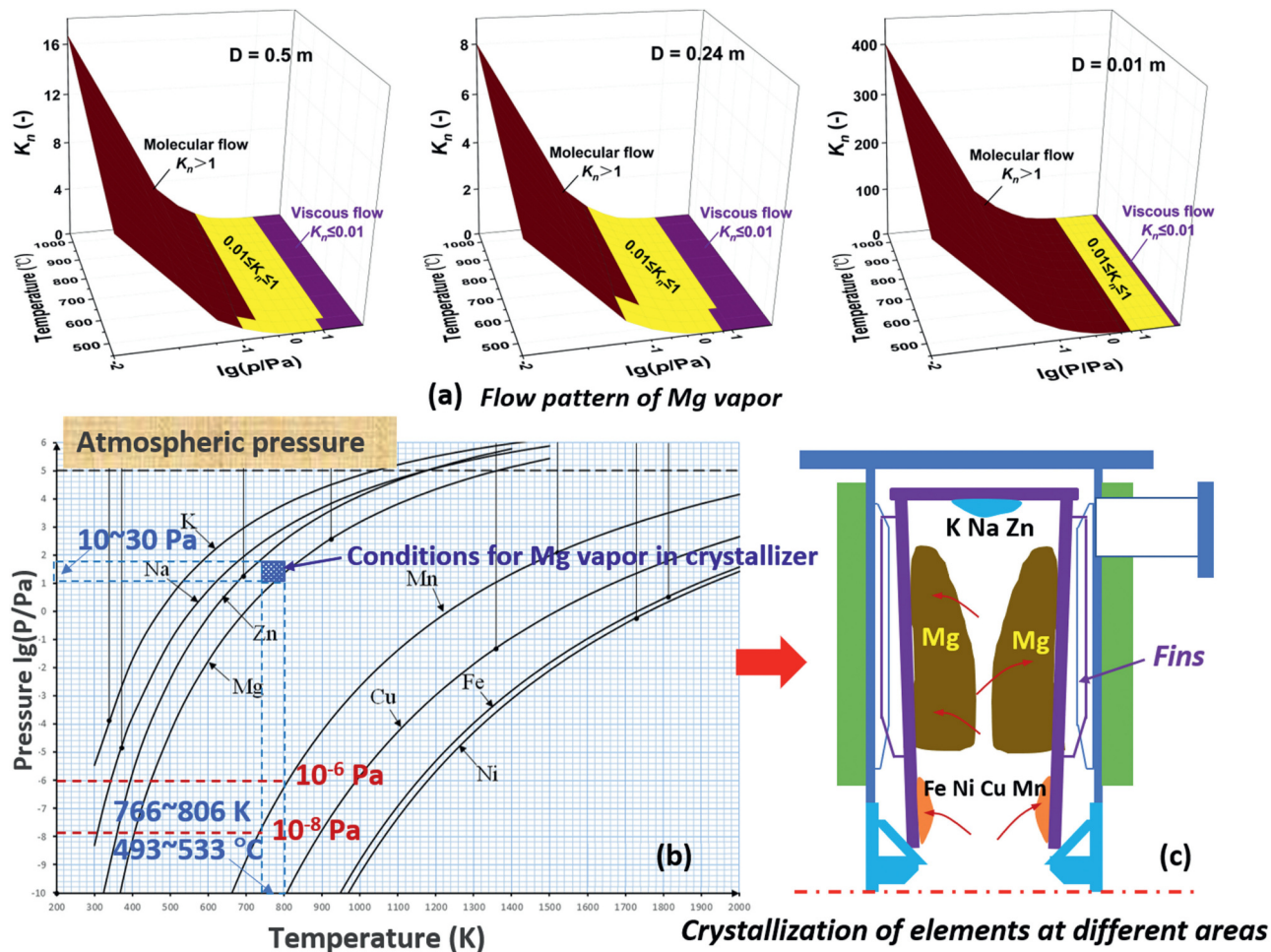


Fig. 5. Study on magnesium crystallization process. (a) flow pattern based on the calculated Knudsen number K_n for magnesium vapor in the range of pressure 0.01 Pa~1000 Pa and temperature 450 °C~1050 °C, (b) three-phase change diagram of Mg and impurities; (c) sectional crystallizer designed by our team.

temperature field and heat flow field distribution in the compound reducing furnace (see Fig. 6a).

Further, by optimizing the nozzle structure, fuel and air operating parameters, the temperature difference inside the furnace chamber of single-module reducing furnace is ≤ 50 °C [17] (see Fig. 7c), which can be confirmed by the actual temperature distribution monitored by S-type thermocouples in the supplementary material. In addition, the numerical simulation was carried out to predict the change of magnesium reduction extent in single retort and the averaged reduction extent in multiple retorts in the reducing furnace (see Fig. 7b). Based on simulation, double-layer/bidirectional/interleaved/hedged/jetting X flame, as shown in Fig. 7(d), was designed and adopted to fully realize the uniform temperature in the vertical and horizontal directions in the reducing furnace, as well as to improve the combustion efficiency and thermal efficiency of the reducing furnace. Significantly, the negative-pressure reducing-atmosphere combustion technology was realized and adopted to reduce the oxidation corrosion of the surface of the retort, improving the life of the retort and the furnace. A single-

module compound reducing furnace designed is shown in Fig. 7(e).

2.4. Reducing slag heat recovery boiler

The average temperature of the reduction slag discharged from the retorts is about 1150 °C, which contains a large quantity of sensible heat. According to the calculation, the energy released by cooling 1 ton of the slag from 1150 °C to 250 °C is equivalent to 27 kg of standard coal. Usually, it produces about 5~6 tons of slag for producing 1 ton of magnesium. Accordingly, the total heat per ton of magnesium produced is equivalent to 135~162 kg of standard coal, accounting for about 5% of the total energy consumption for the compound-vertical-retort technology. The pellet-shaped slag produced under high temperature in the silicothermic process will expand and pulverize into powder when the temperature drops below 675 °C. The α -Ca₂SiO₄ in the high-temperature slag will transfer into β -Ca₂SiO₄ in the cooling process.

Accordingly, our team simulated the cooling process of the reduction slag, by establishing the mathematical and physical

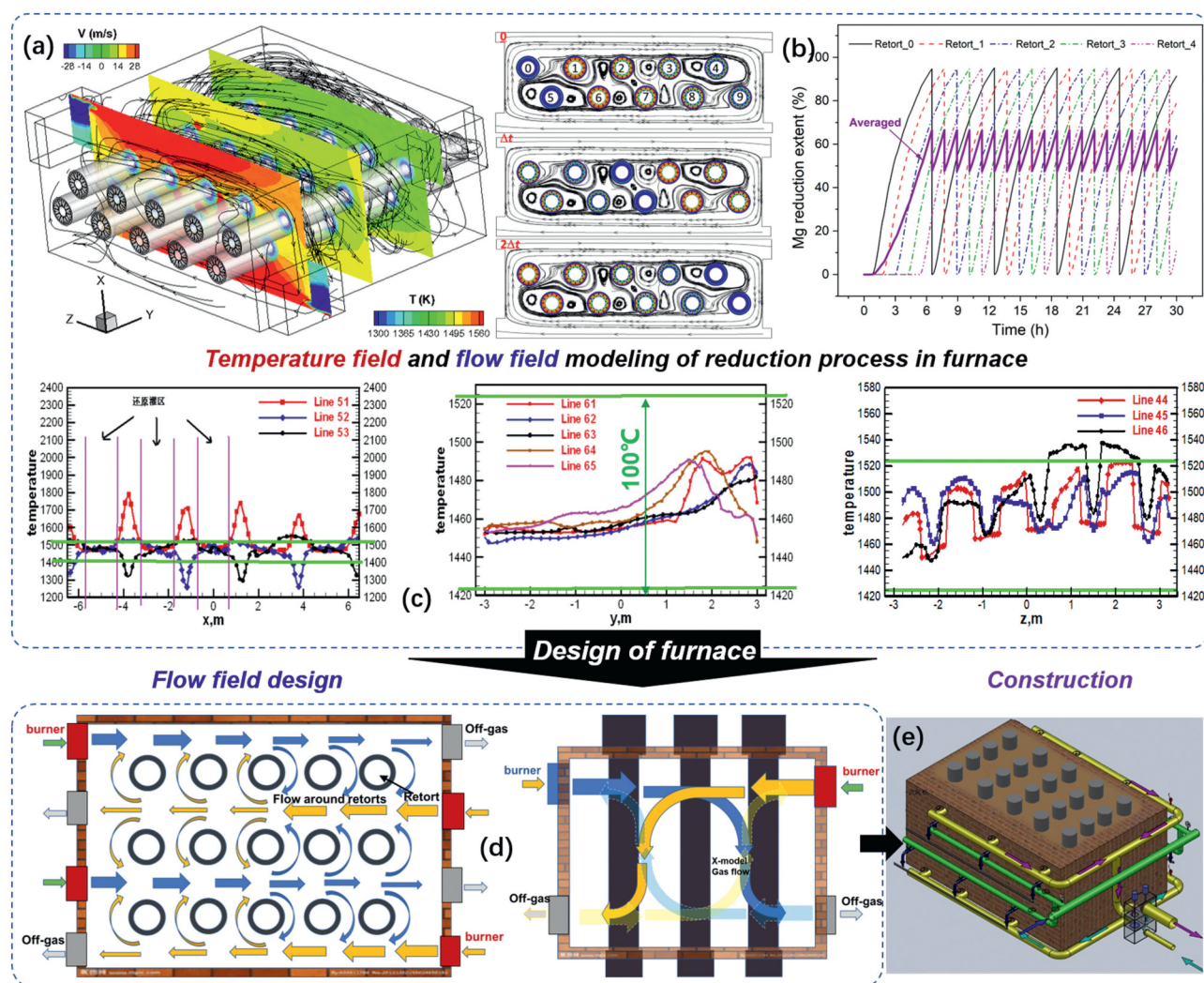


Fig. 6. Modeling and design of compound reducing furnace. (a) temperature and heat flow field in the compound reducing furnace, (b) Mg reduction extent in single retort and averaged extent in multiple retorts, (c) temperature difference inside the furnace chamber, (d) design of double-layer/bidirectional/interleaved/hedged/jetting X flame, (e) design of single-module compound reducing furnace.

models of pipe route and shell route of a designed heat recovery boiler (see Fig. 7a). It was found that the cooling and heat transfer of high-temperature slag is a very slow process. It takes more than 6 h to cool the slag below 250 °C. In addition, the water temperature in pipe and shell routes fluctuates greatly in the slag-filling process (see Fig. 7b). Based on the simulation and optimization, a shell-and-pipe water-cooled heat recovery boiler for supporting the compound-vertical-retort magnesium technology, was designed as shown in Fig. 7(c).

3. Scale-up test of compound-vertical-retort magnesium production

In order to confirm the rationality and reliability of the material and structure of the compound vertical retort as well as process design, our team has built a platform for scaling up test of the compound vertical retort system, as shown in

Fig. 8(a). The platform includes the compound vertical retort, the compound crystallizer, and the high-power resistance furnace for heating. A power supply system, vacuum system, and raw material preparation equipment are equipped as supporting unit.

Several batches of tests were carried out on this platform, focusing on investigation on the fusion and agglomeration of briquette and slag during the reduction process, smoothness of slag discharge, reliability of the center cylinder, and rationality of structure of retort and crystallizer. Situation of test and crystallized magnesium obtained are shown in Fig. 8(b) & (c).

The results of scale-up test are summarized in Table 2. The ratio of charge-to-Mg was calculated to be 6.38~7.28, close to that in the actual production in industry. It was confirmed that the slag can be discharged smoothly, and there is almost no smoke and no fire when lifting the crystallizer during the compound-vertical-retort magnesium production process. The

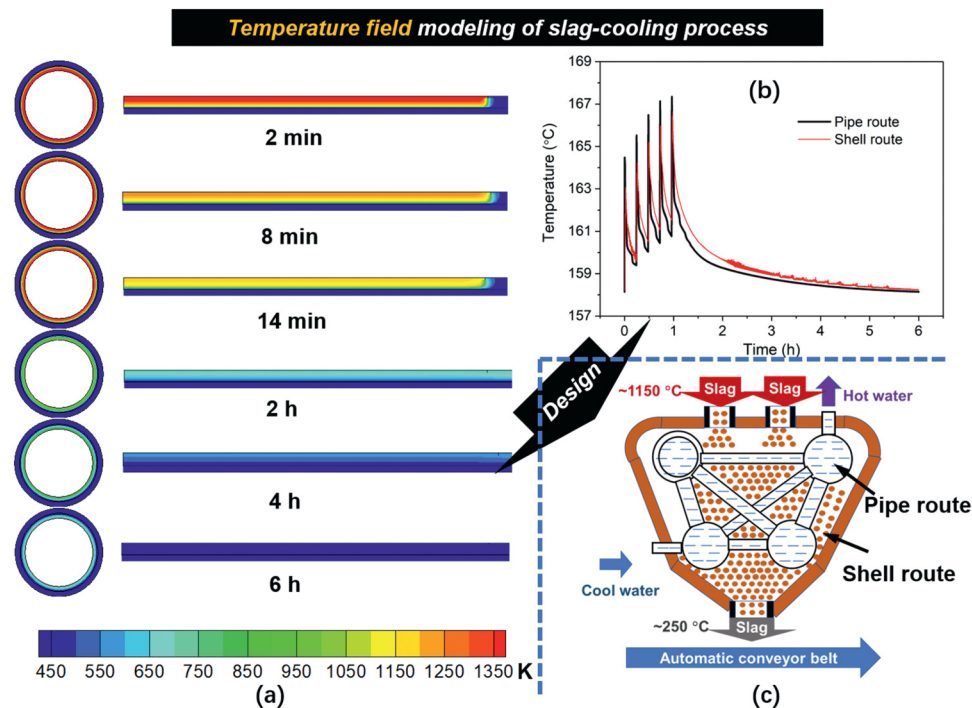


Fig. 7. Simulation of reduction slag cooling process and design of heat recovery boiler. (a) mathematical and physical models of pipe route and shell route, (b) vary in water temperature of pipe route and shell route, (c) structure design of the boiler.

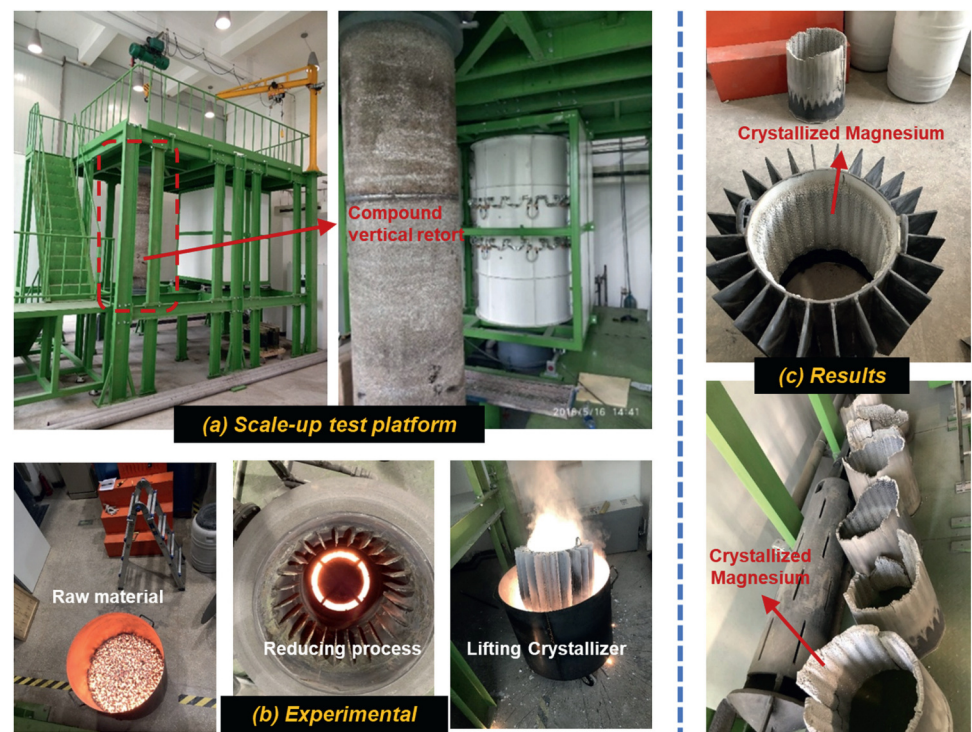


Fig. 8. Scale-up test of the compound vertical retort magnesium production.

Table 2
Results of scale-up test of the compound vertical retort magnesium production.

Retort wall temperature, °C	Amount of charge, kg	Mg yield, kg	Ratio of charge to Mg	Discharging	Environment
1200	118~133	17.5~20	6.38~7.28	smoothly, no fusion and agglomeration	almost no smoke, no fire

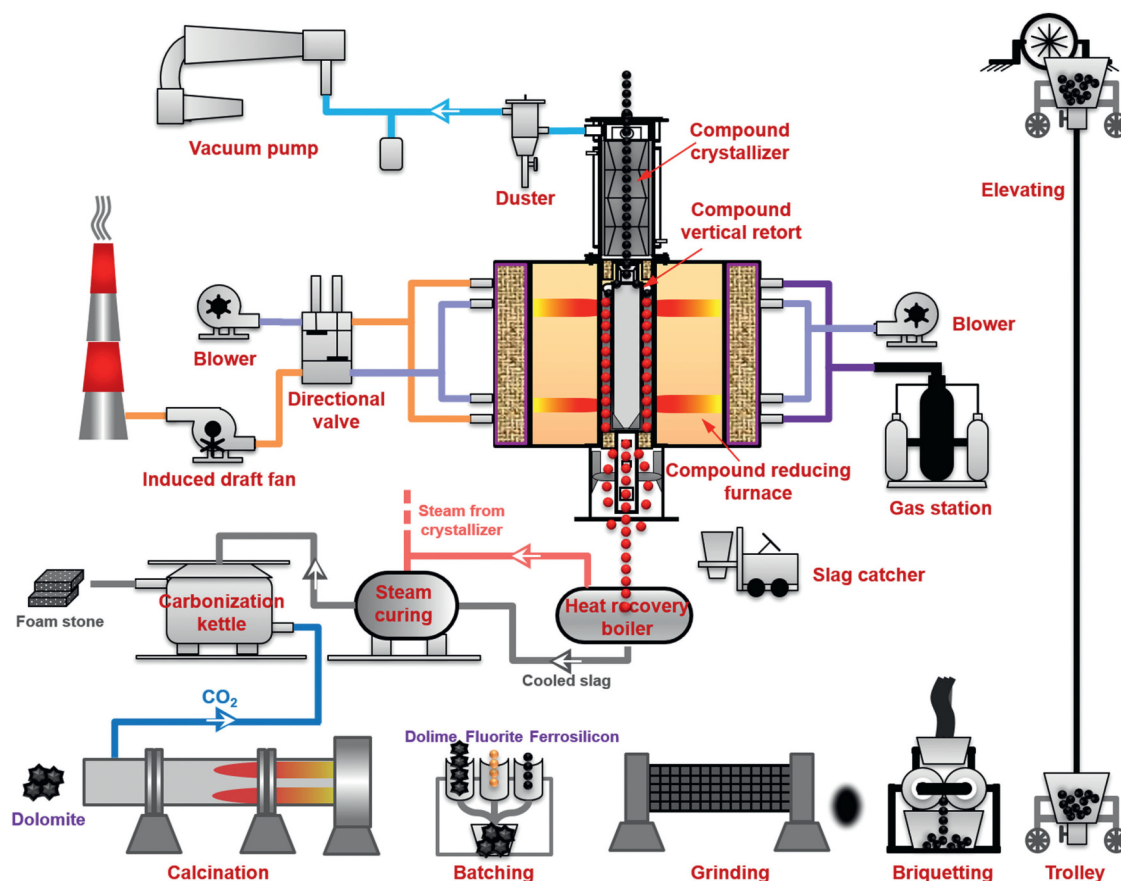


Fig. 9. Working flow of the compound-vertical-retort magnesium production technology.

structure of compound vertical retort with ceramic-lined steel material and equipped the ceramic central cylinder is reasonable and reliable.

4. Demonstration application of compound-vertical-retort magnesium production technology

4.1. Working flow

The working flow of compound-vertical-retort magnesium production technology is shown in Fig. 9, which is mainly composed of raw material production/transportation unit, magnesium reduction unit, magnesium/slag transportation unit, slag-to-foam stone production unit, and supporting auxiliary unit. The magnesium reduction unit is the core part of this magnesium production process, which consists of the upper compound crystallizer and mechanized feeding device, the middle regenerative compound reducing furnace equipped the compound vertical retorts, the lower mechanized slag discharging device and the slag heat recovery boilers.

During the production operation, the raw material dolomite is first calcined in a rotary kiln to produce dolime, which is mixed with ferrosilicon and fluorite at a fixed ratio. The mixture is finely ground in a ball mill, then sieved and pressed into briquettes. The trolley filled up briquettes is lifted to the top of the compound reducing furnace, and a closed mecha-

nized feeder loads the briquettes into one compound vertical retort at a time. Then, the vacuum system and regenerative combustion system are operated to make the temperature and pressure in the retort meet the conditions required for silico-thermic reduction process. The magnesium vapor produced flows upward through the central cylinder of the compound vertical retort and enters the crystallizer to complete the condensation. It takes about 10 h to complete the whole reduction process. The crystallizer full with crystallized magnesium is taken out of the retort to collect. Last, the reducing slag is discharged from the bottom of the retort into the heat recovery boiler, through the closed slag catcher. After the slag is cooled, it is conveyed, through an automatically closed conveyor, to the foam stone production unit, where the slag is made into foam stone by steam curing and carbonization. For the mechanical compound-vertical-retort technology, the man-hours for completing the feeding and discharging of one retort has been largely shortened to around 15 min compared to the Pidgeon process.

4.2. Establishment and operation of demonstration plant

Based on comprehensive completion of the design, validation, and development of the core equipment and supporting equipment, our team have built a demonstration plant of annual 1200 tons of magnesium production with the compound-

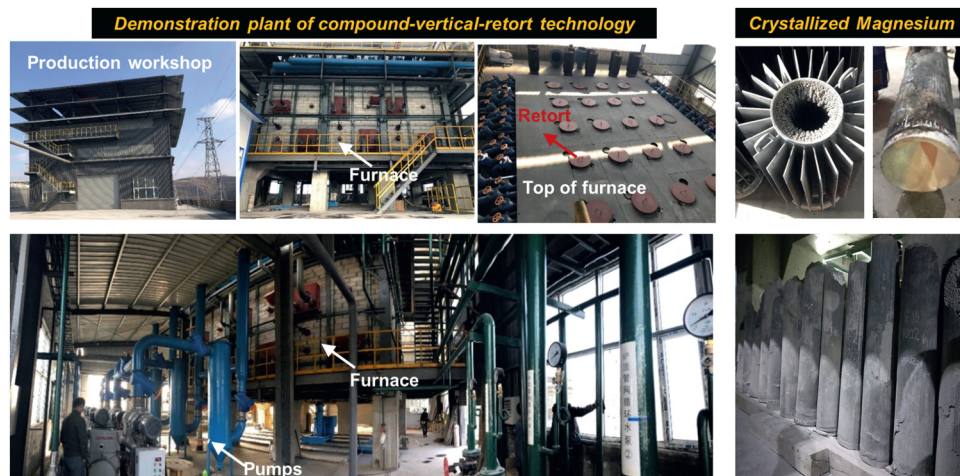


Fig. 10. Establishment and operation of the demonstration plant of the 1200 t/a compound-vertical-retort magnesium production.

Table 3

Representative of the 1200 t/a compound-vertical-retort magnesium production.

No.	Amount of charge*, kg	Vacuum, Pa	Production cycle, h	Mass of crystallized Mg*, kg	Ratio of charge-to-Mg	Reduction extent, %
1	622	3	11.5	98.8	6.30	90.2
2	710	3	11.4	108.1	6.57	86.5
3	638	3	12.0	108.4	5.89	96.5
4	660	5	11.5	100.2	6.59	86.2
5	683	5	12.0	113.6	6.01	94.5
6	631	5	12.0	107.6	5.86	96.8
Averaged	657	5	11.7	106.1	6.20	91.8
Designed	650	10	12	95	6.2	85

* Those for single compound vertical retort.

vertical-retort technology in Fugu, Shaanxi Province of China (see Fig. 10). It is composed of twenty compound vertical retorts, twenty compound crystallizers, the compound furnace, two slag boilers and supporting auxiliary equipment.

As the plant was put into operation, the problems such as excessive water and tar in the externally supplied gas, insufficient power, the feed backflow and jamming of external spiral slag dispenser were found and solved successively. The influence of external factors and supporting devices on the overall system operation was eliminated. The demonstration plant run continuously and stably for a long time. According to the actual operation and analysis, all the economic and technical indicators have reached/exceeded the design criteria. There is no need for manual raking, poking and shoveling to clean the retort. There is no "chimney effect", and there is basically no smoke, dust, open fire, high temperature, toxic and harmful gasses in the workshop. The operating environment is significantly improved compared with the Pidgeon process and normal vertical-retort process.

Representative of the 1200 t/a compound-vertical-retort magnesium production demonstration plant is shown in Table 3. It is shown that charging capacity of single retort is 622 kg~710 kg, the single retort's magnesium yield is 98 kg~113 kg, the reduction operation cycle is 11 h~ 12 h,

and the vacuum degree is maintained below 5 Pa. Accordingly, the ratio of charge-to-Mg is 5.8~6.6, and the reduction extent is 86.5%~96.8%.

Through chemical component analysis of the crystallized magnesium sampling at multiple points, all except the surface layer are of high purity, which proves that the compound-vertical-retort technology can produce high-purity magnesium. The chemical component analysis of 2 random sampling of crystallized magnesium is listed in Table 4, according to the national standard testing method by the National Light Metal Quality Supervision and Inspection Center. Compared with the commercial magnesium ingot, it can be found that all impurity elements except Al meet the requirements of magnesium ingot grade Mg9980 and basically meet the requirements of Mg9995B.

4.3. Technical and economic indicators

With the charge-to-Mg ratio of 6.2 as the measurement benchmark, the main technical and economic indicators of the compound-vertical-retort magnesium production technology are determined and listed in Table 5, as well as compared with indicators of the Pidgeon process and normal vertical-retort process. It is shown that all the technical and economic

Table 4
Chemical component analysis of sampling at the crystallized magnesium.

Chemical component (Mass fraction%)	Test result 1	Test result 2	Magnesium ingot grades*	
			Mg9980	Mg9995B
Mg	99.93	99.96	≥99.80	≥99.95
Al	0.064	0.013	≤0.05	≤0.015
Cu	<0.0001	0.0002	≤0.02	≤0.002
Fe	0.0010	0.0077	≤0.05	≤0.005
Mn	0.0025	0.0032	≤0.05	≤0.015
Ni	<0.0005	<0.0005	≤0.002	≤0.001
Si	0.0015	0.0014	≤0.05	≤0.015
Ti	<0.0001	<0.0001	–	–
Zn	0.0007	0.0046	–	≤0.01
Pb	<0.0010	<0.0010	–	≤0.005
Sn	<0.0010	<0.0010	–	–

* According to the GB/T 3499–2011 issued on September 29th, 2011 by Chinese government.

Table 5
Main technical and economic indicators of compound-vertical-retort technology.

No.	Items	Compound vertical retort	Normal vertical retort	Pidgeon Process (Horizontal retort)
1	Production cycle, h	12	18	12
2	Production efficiency per retort, kg-Mg/h	7.5	4~5	1.8~2.5
3	Reducing furnace's energy consumption, tce/t-Mg*	~1.0	~1.3	~1.6
4	Service life of retort, days	~180	60~90	60~90
5	Purity and quality of crystallized magnesium	>99.8%, dense	<99.5%, not dense	<99.5%, not dense
6	Production environment	Friendly	Worse	Worse

*tce/t-Mg represents only the energy consumption for producing 1 ton magnesium in reduction stage, those for raw materials of dolime and ferrosilicon not included.

indicators of the compound-vertical-retort technology are significantly better than that of the Pidgeon process and normal vertical-retort process. Specifically, the energy consumption for producing 1 ton Mg has been reduced to 1.0 ton of standard coal, i.e., 1.0 tce/t-Mg (not included the energy consumption for preparing raw materials of dolime and ferrosilicon). The service life of retort has been significantly prolonged to around 180 days, which is 2~3 times of that of Pidgeon process and normal vertical-retort process.

5. Summary

This paper comprehensively introduces a new magnesium production technology — the compound-vertical-retort magnesium production technology, including the fundamental theoretical research and core equipment development, main process flow design as well as the technical characteristics. Comparison in technical and economic indicators with the Pidgeon process and normal vertical-retort process was carried out to elucidate the superiority and advancement of the compound-vertical-retort magnesium production technology. A summary is as follows.

(1) Through studying the catalytic reaction mechanism of fusion and agglomeration, silicothermic reduction kinetics, and high-temperature mechanical properties of heat-resistant steel, a new ceramic-lined steel retort equipped with ceramic central cylinder was developed. The adhesion and glaze problem were solved, automatic slag-discharging and mechanized production was fully realized, significantly improving the pro-

duction efficiency and labor productivity. The service life of compound vertical retort was significantly prolonged to be more than 5 months.

(2) Through studying the multiphase change and heat flow mechanism of magnesium vapor and metal impurities, a compound crystallizer with function of sectional condensation and large magnesium capacity was developed. The yield, purity and quality of crystallized magnesium was significantly improved. The compound crystallizer can produce dense crude magnesium of ~100 kg per retort at one time, with purity of more than 99.8%.

(3) Through research and application of double-layer/bidirectional/interleaved/hedged/jetting X flame combustion technology and the negative pressure/reducing atmosphere combustion technology, a highly efficient and energy-saving compound reducing furnace with uniform temperature distribution was developed. The thermal efficiency of the furnace is significantly improved. Combined with the heat recovered by the crystallizer and slag boiler, the energy consumption in reduction stage had been reduced to 1.0 tce/t-Mg, which is 0.6 tce/t-Mg lower than the Pidgeon process and 0.3 tce/t-Mg lower than the normal vertical-retort process.

(4) Through integrating twenty compound vertical retorts, twenty compound crystallizers, the compound furnace, two slag boilers and supporting auxiliary equipment, a demonstration plant with annual capacity of 1200 tons magnesium was established. The daily output of the plant reaches 3~4 tons magnesium. The mechanical production was fully realized.

The operating environment is significantly improved. All the technical and economic indicators (on a basis of charge-to-Mg ratio 6.2) of the compound-vertical-retort technology are proved to be significantly better than Pidgeon process and normal vertical-retort process.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the financial support from the Zhengzhou Collaborative Innovation Major Funding (18XTZX12010), National Key Research and Development Project (2016YFB0301101), and Baosteel Metals Co., Ltd.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jma.2023.05.013.

References

- [1] P.H. Fu, L.M. Peng, W.J. Ding, *Strat. Stud. CAE* 20 (01) (2018) 84–90 (In Chinese), doi:10.15302/J-SSCAE-2018.01.012.
- [2] J.F. Song, J. Chen, X.M. Xiong, X.D. Peng, D.L. Chen, F.S. Pan, *J. Mag. Alloy.* 10 (4) (2022) 863–898, doi:10.1016/j.jma.2022.04.001.
- [3] S.V.S. Prasad, S.B. Prasad, K. Verma, R.K. Mishra, V. Kumar, S. Singh, *J. Mag. Alloy.* 10 (1) (2022) 1–61, doi:10.1016/j.jma.2021.05.012.
- [4] M.L. Shen, *Energy Sav. Nonferrous Metall.* 25 (5) (2009) 6–9+15. (In Chinese).
- [5] U.S.G.S. Mineral Commodity Summaries, 2022 <https://pubs.usgs.gov/periodicals/mcs2022/mcs2022-magnesium-metal.pdf> (accessed 28 October 2022).
- [6] L. Liu, S.S. Ruan, C.C. Qi, B. Zhang, B.B. Tu, Q.X. Yang, K.I.-I.L. Song, *J. Cleaner Prod.* 279 (2021) 123684, doi:10.1016/j.jclepro.2020.123684.
- [7] Y.S. Che, C.D. Wang, Y.F. Sun, W.D. Zhang, S.J. Zhang, *Hot Work. Technol.* 47 (12) (2018) 67–70 (In Chinese), doi:10.14158/j.cnki.1001-3814.2018.12.017.
- [8] A. Yu, H. Hu, N.Y. Li, *Model. Simul. Mater. Sc.* 10 (4) (2002) 413–423, doi:10.1088/0965-0393/10/4/304.
- [9] L. Ren, D.H. Xia, H.B. Bi, *Nonferrous Metal. (Extr. Metall.)* (02) (2012) 30–33 (In Chinese), doi:10.3969/j.issn.1007-7545.2012.02.008.
- [10] Q. Xu, J.X. Feng, J.Z. Zhou, *Chem. Ind. Eng. Prog.* 37 (02) (2018) 459–467 (In Chinese), doi:10.16085/j.issn.1000-6613.2017-0999.
- [11] X.B. Xu, H.J. Cao, *China Nonferrous Metall.* 45 (05) (2016) 73–76 (In Chinese).
- [12] R.B. Li, M. Chen, S.J. Zhang, J.L. Xu, H.T. Yuan, P.X. Yang, F.Q. Liu, *Nonferrous Metal. (Extr. Metall.)* (06) (2022) 30–36 (In Chinese), doi:10.3969/j.issn.1007-7545.2022.06.006.
- [13] R.Y. Xu, H.B. Yuan, *Light Met.* (02) (1991) 39–44+37. (In Chinese).
- [14] Y. Wu, *Light Met.* (7) (2016) 39–47. doi:10.13662/j.cnki.qjs.2016.07.010. (In Chinese)
- [15] R.B. Li, C. Zhang, S.J. Zhang, L.J. Guo, *Metall. Mater. Trans. B* 45 (1) (2014) 236–250, doi:10.1007/s11663-013-9934-5.
- [16] J. You, Y.W. Wang, *Chin. J. Process Eng.* 19 (3) (2019) 560–566 (In Chinese), doi:10.12034/j.issn.1009-606X.218236.
- [17] R.B. Li, A Research on the Experimental and Theoretical Modeling of the New-type Silicothermic Reduction to Magnesium and its Engineering Demonstration Ph.D. thesis, Xi'an Jiaotong University, 2013.
- [18] C. Wang, Investigation on the Effective Thermal Conductivity of Silicothermic Process Briquette and the Coupling Numerical Simulation of Heat Transfer and Reduction Reaction Ph.D. thesis, Xi'an Jiaotong University, 2017.
- [19] S.J. Zhang, Theoretical and Experimental Research on New Type of Silicothermic Reduction of Magnesium and Development of Key Technologies and Equipment Ph.D. thesis, Xi'an Jiaotong University, 2015.
- [20] R.B. Li, S.J. Zhang, L.J. Guo, J.J. Wei, *Int. J. Heat Mass Transfer* 59 (2013) 328–337, doi:10.1016/j.ijheatmasstransfer.2012.09.027.
- [21] R.B. Li, C. Wang, Z. Wang, P.X. Yang, F. Xue, F.Q. Liu, S.J. Zhang, *J. Min. Metall., Sect. B* 58 (3) (2022) 451–459, doi:10.2298/JMMB220111026L.
- [22] R.B. Li, X. Chen, J.J. Zhong, F.Q. Liu, P.X. Yang, S.J. Zhang, *Light Met.* (12) (2020) 34–39. doi:10.13662/j.cnki.qjs.2020.12.008. (In Chinese)
- [23] Y.F. Sun, *Hot Work. Technol.* (03) (2002) 41–42+44 (In Chinese), doi:10.14158/j.cnki.1001-3814.2002.03.017.
- [24] M. Chen, S.J. Zhang, R.B. Li, J.J. Nan, J.H. Liu, P.X. Yang, *J. Zhengzhou Univ.*, 1–6 [2022-10-24]. doi:10.13705/j.issn.1671-6833.2023.01.014. (In Chinese)