The effect of calcium fluoride on extracting magnesium from magnesite and calcium carbonate by silicothermal reduction in flowing argon

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Abstract

At present, the production of magnesium is mainly carried out semi-continuously with ferrosilicon as reducing agent under high temperature and high vacuum. In order to continuously produce magnesium, a new method of extracting magnesium from low-grade magnesite and calcium carbonate by silicothermal method in flowing inert gas was proposed. The effects of calcium fluoride (CaF₂) on decomposition rate, decomposition kinetics, reduction rate of magnesia and crystal type of dicalcium silicate in reduction slag were investigated in the paper. The experimental results showed that calcium fluoride could accelerate the decomposition of carbonate, and had no side effect on the calcined products. In addition, the analysis results of DTA curves showed that calcium fluoride could reduce the decomposition reaction activation energy and the reaction temperature of carbonate in the prefabricated pellets. The results of reduction experiments showed that proper calcium fluoride could promote the reduction rate of magnesia, and in the temperature range of 1250℃ ~ 1350℃, with same timeframe, the corresponding calcium fluoride contents were 5%, 3% and 1% respectively when the reduction rate reached the maximum. Excessive calcium fluoride could reduce the reduction rate of magnesia, but it could promote the transformation of dicalcium silicate to γ phase in the reduction slag.

Keywords: Magnesium; Calcium fluoride; Magnesite; Dicalcium silicate; Silicothermal process

1. Introduction

Magnesite resources are rich in China, accounting for about one third of the world magnesite production [1]. It is mainly distributed in Liaoning Province with proven reserves of 3.4 billion tons [2]. Magnesite is an important raw material for magnesium industry and refractory industry, which is widely used in metallurgy, building materials, chemical industry and other industries [3-5]. Magnesite is
considered as one of the most important refractory materials because of its high fire resistance. However, there are impurities such as silica, calcium oxide and iron oxide in magnesite, which react with magnesia and produce low melting point phases at high temperature, such as merwinite, monticellite, which have adverse effects on the thermomechanical properties of magnesia refractories [6]. Therefore, high-grade magnesite in China is widely exploited, while low-grade magnesite is discarded or stockpiled, resulting in a waste of resources. Therefore, increasingly more attention has been paid to how to efficiently and comprehensively utilize low-grade magnesite resources. As magnesite is rich in magnesium, it can be used as raw material for magnesium production in the work.

Magnesium and its alloys are widely used in transportation, aerospace and other fields due to their unique properties, such as better reducibility, specific strength and light weight, and have become the third largest metal engineering materials after steel and aluminum [7, 8]. The main production method of magnesium is Pidgeon process. Since the Pidgeon process was put forward in 1941, it has developed rapidly in China due to its simple technology and flexible scale, but it has also increasingly highlighted the problems of high labor intensity, interrupted production and high energy consumption [9-11]. Therefore, some new processes such as aluminothermal process [12], carbothermal process [13, 14], MTMP process [15] have been studied, which also provide new ideas for industrial magnesium production.

Pidgeon process is a method of extracting magnesium by thermal reduction in vacuum. The process is that dolomite is first calcined at about 1150°C to obtain dolime. When the dolime is cooled at room temperature, the dolime, ferrosilicon (containing 75% Si) and calcium fluoride are mixed and pressed into pellets, and finally the pellets are reduced in vacuum. From the above process, it can be seen that there is a problem that the high-temperature dolime need to be cooled to room temperature, resulting in heat loss. In addition, due to the reduction of raw materials under high temperature and high vacuum conditions, the whole magnesium production process needs to be operated intermittently, which increases the magnesium production cycle. In order to solve the above problems and consider the comprehensive utilization of low-grade magnesite, Zhang et al. [16] proposed the process of magnesium production by silicothermal method with prefabricated pellets in flowing inert gas, and the process flow is shown in Fig. 1. In this process, the mixture of magnesite and calcium carbonate is used to replace dolomite. The specific process is that dolomite (magnesite and calcium carbonate), ferrosilicon and calcium fluoride are mixed and pressed into pellets (called prefabricated pellets), and then the pellets are calcined and reduced in flowing inert gas. Finally, the generated magnesium vapor is carried to the crystallizer for condensation by flowing inert gas. Therefore, calcination and reduction are carried out in a reduction tank. The advantage of this method is that it can make full use of the low-grade magnesite, realize the integration of calcination and reduction in the smelting process, and avoid the loss and water absorption of highly activity calcined white in the process of transportation and storage. In addition, because the whole process is not carried out in vacuum, continuous production of magnesium can be realized. Due to the existence of
flowing argon, the convection heat transfer can also be increased and the heat transfer efficiency can be improved, and the argon can be recycled.

Fig. 1 Comparison of improved process and Pidgeon process

In the traditional industrial production of magnesium by Pidgeon process, it was often necessary to add a certain amount of calcium fluoride to the material to improve the reduction rate of magnesium oxide in the reduction process. Previous studies [17-19] had shown that CaF$_2$ could increase the reaction energy on the surface of oxide, accelerate the interaction between materials, and reduce the reaction temperature. However, due to the excessive CaF$_2$ content, the reduced slag would bond to the reduction tank in a semi molten state, which made it difficult to slag out.

For the novel magnesium production technology, the preparation process, properties and calcination decomposition kinetics of pellets had been investigated [20, 21], and the reduction kinetics and element diffusion mechanism had been studied by thermogravimetric experiments and isothermal reduction experiments [22, 23]. However, the effect mechanism of CaF$_2$ on the calcination and reduction process of magnesium production process with prefabricated pellets was still unclear. In addition, previous studies on the role of CaF$_2$ in magnesium smelting were carried out in vacuum, and there were no relevant reports in flowing argon. Therefore, in this paper, the influence of CaF$_2$ on the calcination and reduction process in the process of magnesium production in flowing argon was studied by using prefabricated pellets, and the influence of CaF$_2$ on the reduction slag in the reduction process was also explored, which had a certain guiding significance for continuous production of magnesium by using prefabricated pellets.

2. Experiments

2.1 Raw materials

The raw materials used in this experiment were magnesite from Haicheng, Liaoning Province, China, and analytical grade calcium carbonate. Magnesite and calcium carbonate were mixed according to the molar ratio of calcium to magnesium 1: 1 instead of dolomite. The chemical composition of magnesite is shown in Table 1. In the experiment, the reducing agent and additive were ferrosilicon and calcium fluoride respectively. The content of silicon in ferrosilicon was 74.13%, which was from Anyang, Henan Province, China. Calcium fluoride was a chemical reagent purchased from Sinopharm Chemical Reagent Co., Ltd.

| Ore        | Ignition loss | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO  |
|------------|---------------|---------|-------------|-------------|-----|------|
| Magnesite/%| 51.92         | 0.75    | 0.19        | 0.74        | 0.90| 45.50|
2.2 Experimental apparatus

The experiment was carried out in a vacuum resistance furnace, and the schematic diagram of the equipment is shown in Fig. 2. The temperature of the furnace can reach 1600℃, and the temperature control system was programmed in different stages so that the calcination and reduction process can be carried out successively. The resistance furnace is equipped with a vacuum pump, the air in the furnace is exhausted before the experiment so as to realize the exchange of vacuum and argon, which can prevent the oxidation of ferrosilicon and reduce the experimental error.

Fig. 2 Schematic diagram of the equipment

1—Water jacket; 2—Silicon-Molybdenum bar; 3—Porous crucible; 4—Vacuum display instrument; 5—Control dial; 6—Thermocouple; 7—Vacuum pump

2.3 Experimental procedures

The magnesite and ferrosilicon were crushed and finely ground to about 200 mesh, and then mixed according to the molar ratio of magnesite, calcium carbonate and ferrosilicon of 2:2:1. The amount of calcium fluoride was added according to different experiments, and the addition range was 0~10% of the total mass of the above three raw materials. The mixed powder was pressed into cylindrical pellets with diameter of 15 mm by hydraulic equipment, and the briquetting pressure was 209.07 MPa. Due to the difference between the temperature displayed in the furnace and the temperature at the pellet reaction position, in order to ensure the accuracy of the experimental data, the temperature of the pellet reaction position and the temperature of different positions in the furnace were remeasured by thermocouple before the experiment. The temperature mentioned in this paper was the temperature remeasured by thermocouple. Then the prefabricated pellets were placed in the corundum crucible with holes, and calcined in the furnace at 1000℃ for 1 h. After that, the crucible was lifted 25 cm away from the reaction zone, and the furnace continued to heat up. It should be emphasized that the pellets would not carry out reduction reaction during the heating up process of the furnace. After reaching the reduction temperature, the crucible was put back to the original position for reduction experiment. The specific isothermal reduction operation method had been described
in detail in the previous literature [23]. After the experiment, the phase analysis and magnesium content in the cooling slag were determined by X-ray diffraction (XRD, Bruker D8, Germany) and inductively coupled plasma emission spectrometer (ICP-OES, Optima 8300DV, Perkin-Elmer, USA), respectively. The reduction rate of magnesium was calculated by formula (1).

\[ \eta_{Mg} = \frac{M_1 \times \alpha - M_2 \times \beta}{M_1 \times \alpha} \]  

where \( \eta_{Mg} \) is the reduction rate of magnesium, \( M_1 \) is the initial mass of prefabricated pellets, \( \alpha \) is the magnesium contents of the prefabricated pellets, \( M_2 \) is the mass of magnesium slag, \( \beta \) is the magnesium content of magnesium slag.

**Results and discussion**

3.1 Effect of CaF\(_2\) on the decomposition rate of prefabricated pellets

In the experiment, prefabricated pellets were used as raw materials for magnesium production, and they must be calcined before the reduction process. Therefore, the effect of CaF\(_2\) on the calcination of prefabricated pellets was studied. In order to eliminate the effect of ferrosilicon on the calcination of pellets, the mixture of magnesite and calcium carbonate was only added with different content of calcium fluoride (0\%, 3\%, 5\%, 10\%). **Fig. 3** is the effect of CaF\(_2\) on the decomposition rate of the mixture of magnesite and calcium carbonate after calcination at 1000\(^\circ\)C for different time. The results showed that the decomposition rate of raw materials with CaF\(_2\) was faster than that of 0\% CaF\(_2\), but the decomposition rate of pellets remained unchanged after 30 min, and fluctuated around 48.86\% (theoretical calcination decomposition rate). XRD analysis of the calcined product is shown in **Fig. 4**. It could be found that the product phases were MgO, CaO and CaF\(_2\), and no other phases were produced, which indicated that CaF\(_2\) did not participate in the reaction during the calcination process, but only accelerated the calcination decomposition rate.

![Fig. 3 Effect of CaF\(_2\) on decomposition rate of the mixture of magnesite and calcium carbonate (1000\(^\circ\)C)]
3.2 Effect of CaF$_2$ on decomposition kinetics

The effect of CaF$_2$ on the calcination of prefabricated pellets was investigated by using a synchronous thermal analyzer (NETZSCH STA 449F3, Germany). The heating rate was 8°C·min$^{-1}$, the temperature range was 25°C ~ 1100°C, the protective gas was argon, and the flow rate was 30 ml·min$^{-1}$. The DTA curves of carbonates and carbonates containing 3% CaF$_2$ were investigated, as shown in Fig. 5. The endothermic peaks of DTA curve were analyzed comprehensively, and the results are shown in Table 2. From the analysis results, the peak values of calcium carbonate and magnesite with CaF$_2$ are 855.3°C and 676.6°C respectively, which are lower than those of calcium carbonate and magnesite without calcium fluoride. In addition, the peak areas are smaller.

![XRD analysis of calcined products (3% CaF$_2$)](image)

**Fig. 4 XRD analysis of calcined products (3% CaF$_2$)**

**Table 2 Comprehensive analysis of endothermic peak**

| Sample         | Peak values/°C | Temperature range/°C | Peak area /μVs·mg$^{-1}$ |
|----------------|----------------|----------------------|--------------------------|
| CaCO$_3$       | 856.5          | 756.8~872.0          | 299.3                    |
| CaCO$_3$+CaF$_2$ | 855.3          | 758.4~875.1          | 268.0                    |
In view of the above phenomena, the dynamic analysis and calculation were carried out. Dynamic thermal analysis method is generally used to calculate the kinetic parameters of thermal decomposition of solid materials. So far, there are many methods to calculate the kinetic parameters, such as ASTM E693, ASTM E2890, ASTM E2070, Ozawa-Flynn-wall method, Freeman-Carroll method, Kinserger method, etc. [24-26], among which Kinserger method and Freeman Carroll method are more commonly used, but each has its own advantages and disadvantages. In this paper, the Freeman-Carroll method was used to calculate the kinetic parameters of decomposition of magnesite and calcium carbonate with calcium fluoride. According to the basic kinetic equation:

$$\frac{d\alpha}{dT} = \frac{A}{\Phi} e^{-\frac{E}{RT}} (1 - \alpha)^n$$

(2)

Where $\alpha$ is the conversion, $E$ is the activation energy and $A$ is the pre-exponential factor, $T$ is the temperature, $K$, $R$ is the gas constant (J·mol$^{-1}$·K$^{-1}$), $n$ is reaction order, $\Phi$ is the heating rate, K·min$^{-1}$.

Formula (2) was derived and expressed by logarithm and subtraction:

$$\frac{\Delta \lg I}{\Delta \lg S''} = -\frac{E}{2.303R} \frac{\Delta \left( \frac{1}{T} \right)}{\Delta \lg S''} + n$$

(3)

Where $I$ is the value of DTA curve, V·g$^{-1}$, that is, the temperature difference between the sample and the reference material. $T$ is the temperature, K, $S''$ is the area of DTA curve from $T$ to $T_\infty$, (V·s·g$^{-1}$), $T$ is the temperature of the reaction at a certain time, and $T_\infty$ is the temperature at which the reaction ends.

According to the formula (3), the curves of $\Delta \lg I/\Delta \lg S''$ and $\Delta (1/T)/\Delta \lg S''$ were drawn. The slope was $-E/2.303R$, the intercept was the reaction order $n$, and $R$ was 8.314 J·mol$^{-1}$·K$^{-1}$.
According to the DTA results in Fig. 5, the fitting curves of $\Delta \lg I/\Delta \lg S''$ and $\Delta (1/T)/\Delta \lg S''$ of carbonate were obtained, as shown in Fig. 6. The results showed that the decomposition activation energy of magnesite was 162.33 kJ\cdot mol^{-1} and the reaction order was 0.68; while the decomposition activation energy of magnesite with CaF$_2$ was 157.96 kJ\cdot mol^{-1} and the reaction order was 0.54. For calcium carbonate, the calculation results showed that the decomposition activation energy of calcium carbonate was 135.65 kJ\cdot mol^{-1}, and the reaction order was 0.12; while the decomposition activation energy of calcium carbonate with CaF$_2$ was 121.86 kJ\cdot mol^{-1}, and the reaction order was 0.31. Through comparative analysis, the activation energy
of carbonates (CaCO$_3$, MgCO$_3$) added with CaF$_2$ was lower than that of carbonates without CaF$_2$. Therefore, although CaF$_2$ did not participate in the reaction in the calcination stage, it could reduce the decomposition activation energy of carbonate and accelerate the decomposition rate.

3.3 Effect of CaF$_2$ on reduction rate of MgO in prefabricated pellets

In the process of magnesium production by silicothermal method, the reduction temperature and time are the important factors affecting the reduction rate of MgO. The higher the reduction temperature is, the faster the reduction rate is, and the shorter the reduction time to reach equilibrium is. Previous studies [17, 27] had found that the addition of CaF$_2$ could increase the reduction rate and shorten the equilibrium time, that was, the addition of CaF$_2$ could increase the reduction rate of MgO in the same reduction time. Most of the previous studies focused on the traditional Pidgeon process and aluminothermal process, which was characterized by the reduction process in vacuum, reduction temperature not more than 1250℃, and calcium fluoride addition not more than 6% [18, 19]. In this paper, magnesium was extracted by prefabricated pellets in flowing argon, so the effect of CaF$_2$ on the reduction rate of magnesium oxide was studied. The experimental conditions were as follows: reduction temperature was above 1250℃ (1250℃, 1300℃, 1350℃), CaF$_2$ content was 0 ~ 10% of the total mass of carbonate and ferrosilicon, argon flow rate was 0.2 m$^3$·h$^{-1}$, reduction time was 2 h.

![Fig. 7 Effect of CaF$_2$ content on reduction rate at different temperatures](image)

**Fig. 7** Effect of CaF$_2$ content on reduction rate at different temperatures

**Fig. 7** is the effect of CaF$_2$ content on the reduction rate of MgO at different temperatures. It could be seen from **Fig. 7** that when the content of CaF$_2$ was 2%, the reduction rate of MgO could reach 83.18% after reduction at 1300℃ for 2 h, which was 15.24% higher than that of 0% CaF$_2$ under the same conditions. Therefore, adding appropriate amount of CaF$_2$ could improve the reduction rate. This phenomenon could be explained as follows: due to the high activity of F$^-$ ion, it could increase the lattice defects of magnesium oxide; and the radius of F$^-$ ion and O$^-$ ion was close, it could destroy the surface lattice of magnesium oxide, distort the magnesium oxide crystal, increase the crystal activity, and promote the fracture of
Compared with the bond energy, the bond energy of MgO is 347 kJ·mol⁻¹, and that of SiO₂ is 460 kJ·mol⁻¹. The bond energy of Mg-O bond is less than that of Si-O bond, which indicates that Si-O bond is more stable. Once Mg-O bond breaks, O will combine with Si atoms to form more stable Si-O bond, and Mg will leave the reaction system as Mg atoms. Therefore, after the addition of CaF₂, the melting point of the whole reaction material decreased, forming a melting system with certain fluidity, which was conducive to the contact between MgO, Si and F⁻ ion, and improved the reduction rate of MgO [17]. An interesting phenomenon could also be found in Fig. 7 that the reduction rate of MgO decreased due to the excessive content of CaF₂, which was consistent with the results reported by other researchers [28]. With the increase of temperature, this phenomenon was more obvious. That was, with the increase of temperature, the content of CaF₂ decreased when the reduction rate of MgO reached the maximum. For example, at 1250°C, when the reduction rate of MgO was the highest (77.67%), the content of CaF₂ was 5%. At 1300°C and 1350°C, the reduction rate of MgO was the highest (84.30% and 89.73%), and the content of CaF₂ was 3% and 1%, respectively. This may be due to the higher temperature, the more active molecules and the faster reaction rate, so adding a small amount of CaF₂ in the raw material could obtain better reduction effect.

3.4 Effect of CaF₂ content on phases in reduction slag

In the process of metal smelting, CaF₂ is usually used as a flux agent to reduce the melting point of reactants. In the magnesium production process, CaF₂ interacts with the reduction products to reduce the melting point of the reduction slag. Therefore, under the experimental conditions, with the increase of CaF₂ content, the slag obtained after the reduction process was more compact and sintered, and the slag adhered to the bottom of the crucible at high temperature. SEM analysis was carried out on the slag reduced by prefabricated pellets containing 4% CaF₂ at 1350°C, as shown in Fig. 8. The surface scan results showed that some unreacted MgO was wrapped by dicalcium silicate phase and could not participate in the reduction reaction. Therefore, the excessive formation and sintering of dicalcium silicate phase prevented the direct contact between MgO and Si, hindered the diffusion of reactants in the reduction process, and reduced the reduction rate of MgO in the same time.
Fig. 8 SEM of reduction products of prefabricated pellets containing 4% CaF$_2$ at 1350°C

XRD analysis was carried out on the reduced slag, and the results were shown in Fig. 9. It could be seen from Fig. 9 (a) that after reduction at 1250°C, Ca$_2$SiO$_4$ phase and unreacted MgO phase were the main phases in the reduced slag. However, with the increase of CaF$_2$ content, the crystal type of a large amount of dicalcium silicate in the cooled slag changed from monoclinic $\beta$-Ca$_2$SiO$_4$ to orthorhombic $\gamma$-Ca$_2$SiO$_4$. This transformation could also be found in the slag reduced at 1300°C in Fig. 9 (b) and 1350°C in Fig. 9 (c). The difference was that with the increase of reduction temperature, the content of CaF$_2$ required for this transformation gradually decreased, corresponding to 3% and 1% respectively. These data were consistent with the CaF$_2$ content corresponding to the maximum reduction rate of magnesium oxide in Fig. 7.
3.5 Effect of CaF$_2$ and MgO on crystal type of dicalcium silicate

Generally, dicalcium silicate is $\gamma$-Ca$_2$SiO$_4$ at room temperature, which has a typical olivine structure. The $[\text{SiO}_4]$ tetrahedron in the structure is connected by $[\text{CaO}_6]$ octahedron to form a three-dimensional structure, and the coordination number of Ca$^{2+}$ is 6. The $[\text{SiO}_4]$ tetrahedron of high temperature dicalcium silicate is also connected by the calcium oxygen polyhedron, but the Ca$^{2+}$ coordination number is not fixed. With the change of temperature, phase transformation can occur between different crystal types of dicalcium silicate, even accompanied by obvious volume change, in which the volume increase of about 13% is produced when $\beta$-Ca$_2$SiO$_4$ transforms into $\gamma$-Ca$_2$SiO$_4$, which is also the reason for the pulverization of high temperature magnesium slag when cooling down [29, 30]. Previous studies have shown that [31, 33], in addition to the different crystal types of dicalcium silicate caused by temperature, foreign ions can also cause dicalcium silicate to present different crystal types. The solid solution of foreign ions into dicalcium silicate crystal can prevent the transformation of high temperature crystal type to low temperature crystal type in the process of temperature drop, thus stabilizing $\beta$-Ca$_2$SiO$_4$ or even $\alpha$-Ca$_2$SiO$_4$ to room temperature. The phenomenon that dicalcium silicate changed from $\beta$ to $\gamma$ with the change of CaF$_2$ content in Fig. 9 may be due to the joint action of MgO and CaF$_2$. Therefore, the effect of MgO on dicalcium silicate was studied experimentally. Firstly, MgO, CaO and SiO$_2$ were mixed according to the molar ratio of (0.5-2.5): 2: 1, and then kept at 1300°C for 2 h. The products were cooled to room temperature and analyzed by XRD, as shown in Fig. 10. It could be seen from the Fig. 10 that with the increase of MgO content, $\beta$-Ca$_2$SiO$_4$ was stably stored to room temperature, indicating that MgO can be used as a stabilizer of $\beta$-Ca$_2$SiO$_4$. Only when the molar ratio of MgO to CaO was greater than or equal to 2: 2, MgO could stabilize $\beta$-Ca$_2$SiO$_4$ to room temperature.
Fig. 10 (a) XRD patterns of MgO-CaO-SiO$_2$ reaction system; (b) Partial enlarged XRD pattern

Based on the above research and analysis in Fig. 9 and Fig. 10, under the experimental conditions, the molar ratio of MgO, CaO and Si in the prefabricated pellets was 2: 2: 1, so MgO could stabilize the β-Ca$_2$SiO$_4$ in the reduced slag, which could keep β-Ca$_2$SiO$_4$ at room temperature. This phenomenon could also be seen in Fig. 9. When there was no CaF$_2$ in the raw material, the main phase in the reduction slag was β-Ca$_2$SiO$_4$. However, when a certain amount of CaF$_2$ was added to the raw material, the stabilizing effect of MgO on β-Ca$_2$SiO$_4$ could be broken and dicalcium silicate could be changed from β-Ca$_2$SiO$_4$ to γ-Ca$_2$SiO$_4$. Therefore, CaF$_2$ can promote the transformation of dicalcium silicate to γ-Ca$_2$SiO$_4$ in the reduction slag of magnesium production by silicothermal process with prefabricated pellets.

Conclusion

In this work, the effect of CaF$_2$ on the process of magnesium production by silicothermal process with prefabricated pellets in flowing argon was investigated. The experimental results are as follows:

1. In the process of calcination, CaF$_2$ could accelerate the decomposition rate of the prefabricated pellets, and had no side effect on the calcined products; through the analysis and calculation of differential thermal experiment, CaF$_2$ could reduce the decomposition activation energy of calcium carbonate and magnesite in the prefabricated pellets, and reduce the reaction temperature.

2. In the process of reduction, appropriate CaF$_2$ could promote the reduction rate of MgO. At 1250°C ~ 1350°C for the same time, when the reduction rate was the highest, the CaF$_2$ content in the prefabricated pellets was 5%, 3% and 1%, respectively.

3. MgO had a stabilizing effect on β-Ca$_2$SiO$_4$ in the reduced slag. When a certain amount of CaF$_2$ was added, the stabilizing effect of MgO on β-Ca$_2$SiO$_4$ could be broken and dicalcium silicate could be changed from β-Ca$_2$SiO$_4$ to γ-Ca$_2$SiO$_4$. 

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