Effects of the Major Impurity Elements in Limestone Ore on the Production of Its Deep Processed Products

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Abstract: Limestone ($CaCO_3$) is one of the most common minerals on Earth, widely used in industries such as construction, chemical, metallurgical, and environmental protection. With the advancement of technology and the diversification of demand, the deep-processed products of limestone, such as nano calcium carbonate, light calcium carbonate, activated calcium oxide, ultra-fine calcium hydroxide, etc., have become indispensable and important materials in modern industry. However, limestone raw ore often contains different kinds of impurities (such as magnesium (Mg), silicon (Si), iron (Fe), aluminum (Al), sulfur (S), etc.), which have a significant effect on the performance and quality of limestone deep processed products. This paper will investigate the distribution and existence state of main impurities in limestone ore through SEM and EDS characterization methods, review and analyze the effects of five common impurities in limestone ore - Mg, Si, Fe, Al, and S - on the production of different deep-processed products such as nano calcium carbonate, light calcium carbonate, activated calcium oxide, ultra-fine calcium hydroxide, lime, and cement. By exploring the occurrence and reaction mechanism of these impurities, understanding their effects on the production process, as well as a summary of impurity removal techniques, to provide a reference for the efficient utilization and optimization of limestone.

Keywords: Limestone; Impurities; Deep Processed

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1 Introduction

Limestone (mainly composed of calcium carbonate, $CaCO_3$) is one of the most abundant minerals in the Earth's crust, widely used in various fields such as building materials, fertilizers, steel, and chemical industry [1]. With the advancement of industrialization, the demand for limestone continues to grow. The utilization of limestone is not limited to the traditional building materials industry, but also extends to the production of high-tech materials such as nano calcium carbonate, light calcium carbonate, active calcium oxide, ultrafine calcium hydroxide and other new chemical products [2-5].

However, raw ore of limestone is often accompanied by different types of impurities, such as magnesium (Mg), silicon (Si), iron (Fe), aluminum (Al), sulfur (S), and other elements. The presence of these impurities can have a significant effect on the processing of limestone and the performance of the final product [6]. Different impurities have significant effects on the high-temperature calcination process, chemical reactions, and final product properties of limestone, which may alter the quality, stability, and performance of the product [7]. Therefore, in-depth research on the types and contents of impurities in limestone raw ore and their effects on limestone products is of great practical significance for optimizing production processes and improving product performance.

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This article will review the main impurities (Mg, Si, Fe, Al, S, etc.) in limestone ore and explore their effects on products such as nano calcium carbonate, light calcium carbonate, activated calcium oxide, ultrafine calcium hydroxide, lime, etc.

2 Types and Sources of Impurities in Limestone Raw Ore

The main component of limestone is calcium carbonate ($CaCO_3$). However, in nature, limestone raw ore often contains a certain amount of impurities, which are mixed in during the geological formation of limestone. Common impurity elements include the following:

(1) Magnesium (Mg): Mg typically exists in the form of magnesium minerals, such as dolomite ($CaMg(CO_3)_2$). Limestone with high magnesium content is called magnesian limestone. The SEM image is shown in Figure 1, the dark areas are Mg element-rich regions.

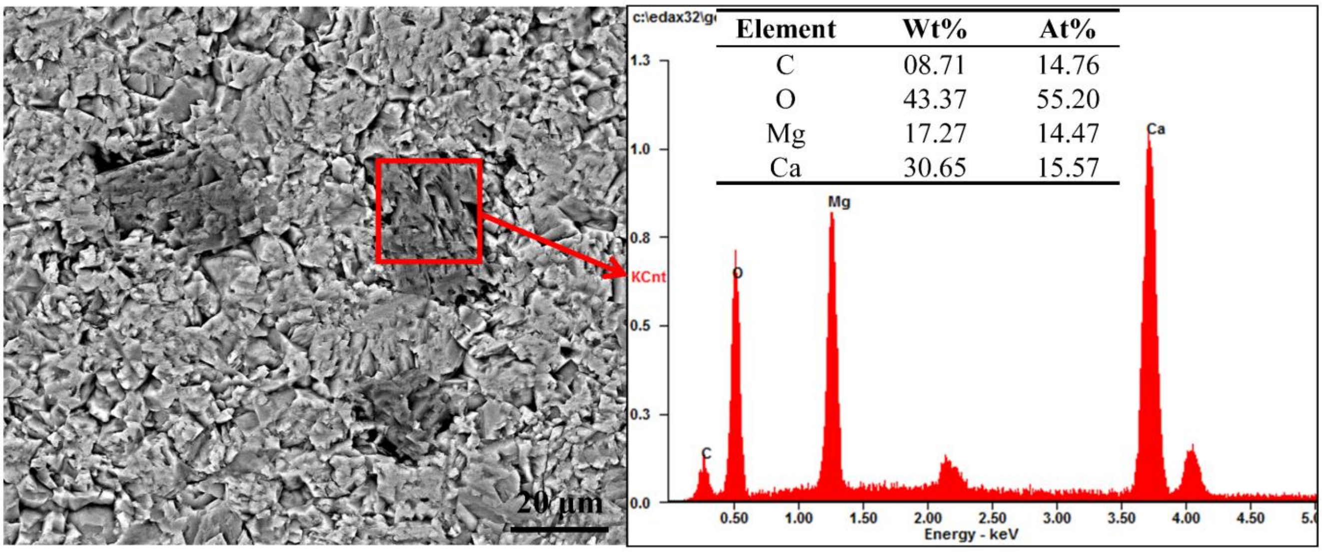

Figure 1 SEM image and EDS result of impurity element enrichment area-Mg

(2) Silicon (Si): Si mainly exists in the form of silicate minerals, such as quartz, clay minerals (kaolin, montmorillonite), etc. The SEM image is shown in Figure 2, the dark areas are Si element-rich regions.

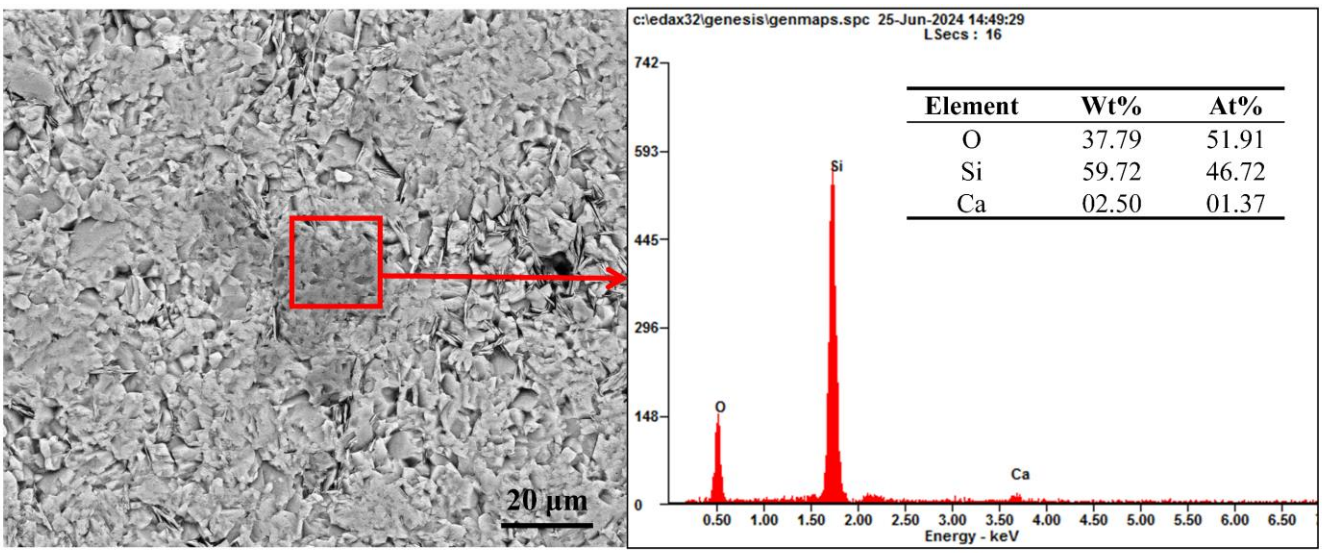

Figure 2 SEM image and EDS result of impurity element enrichment area-Si

(3) Iron (Fe): Fe often exists in the form of iron oxides or iron silicate minerals. The SEM image is shown in Figure 4, the bright area is Fe element-rich region.

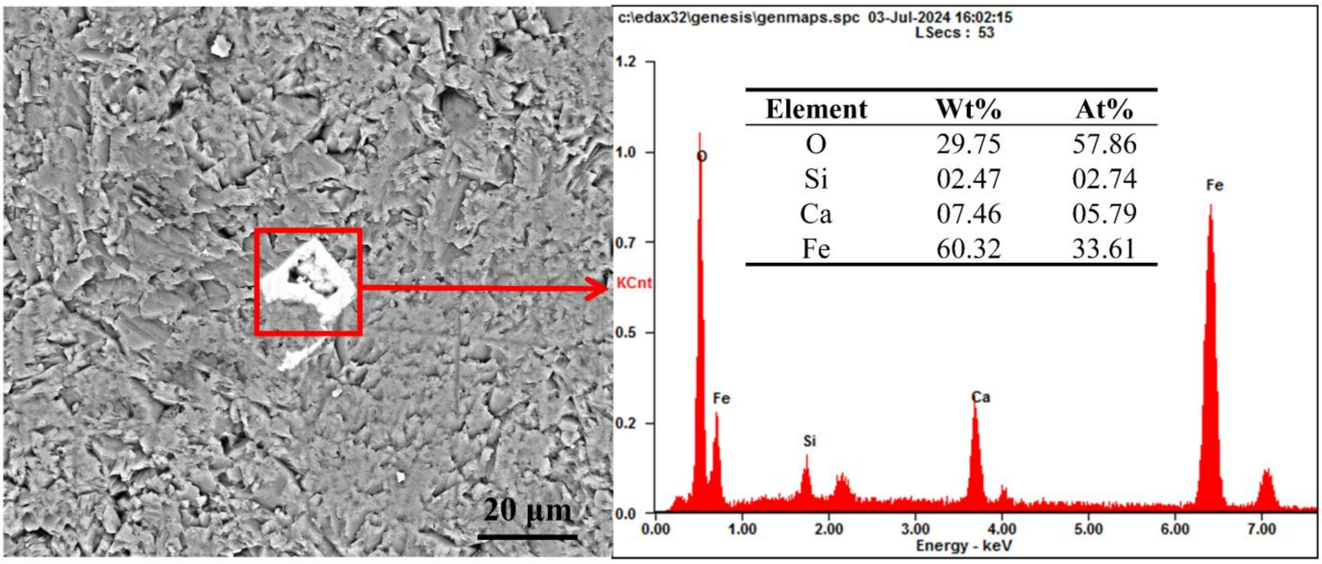

Figure 3 SEM image and EDS result of impurity elements enrichment area-Fe, Si

(4) Aluminum (Al): Al usually exists in the form of aluminosilicate minerals, especially clay minerals with high aluminum content. The SEM image is shown in Figure 4, Al and Si elements appear together.

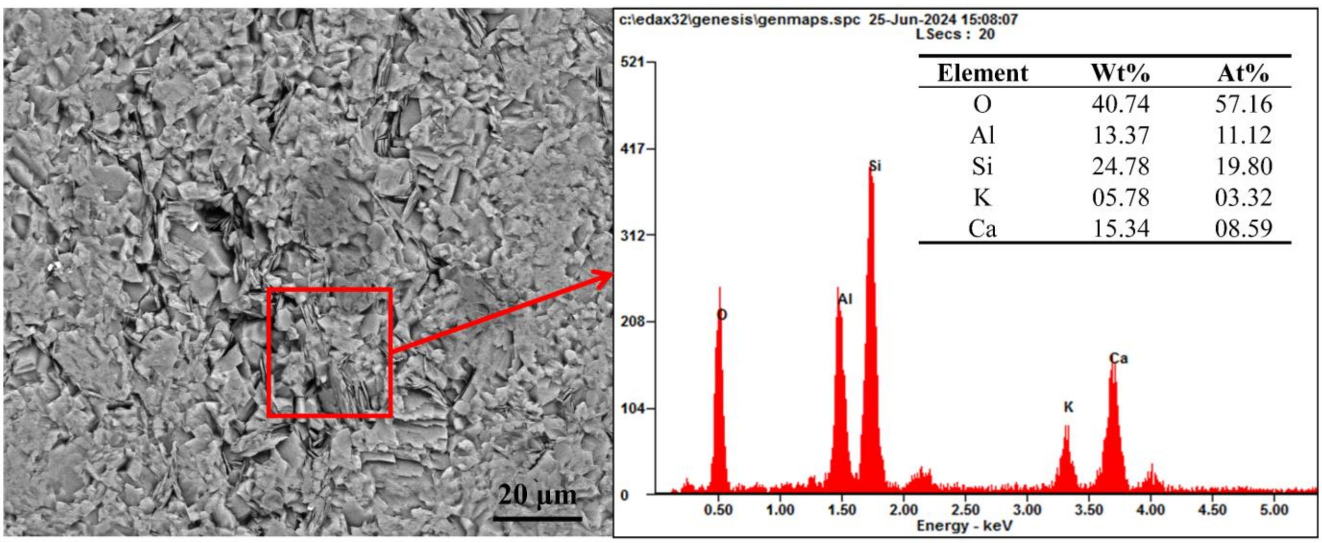

Figure 4 SEM image and EDS result of impurity elements enrichment area-Al, Si, K

(5) Sulfur (S): S often exists in the form of sulfates, such as gypsum, pyrite, etc. The SEM image is shown in Figure 5, S and Fe elements appear together, this area should be pyrite.

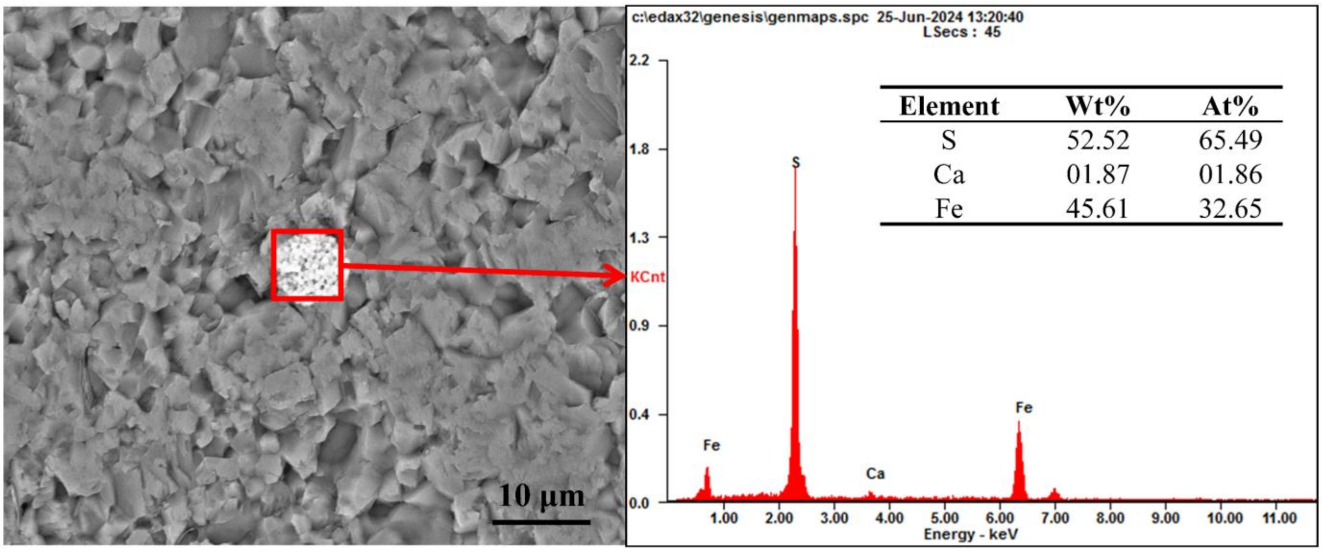

Figure 5 SEM image and EDS result of impurity elements enrichment area-S, Fe

From Figure 6, it can be seen that most impurity elements, Al and Si impurity elements are uniformly distributed, while Fe and Mg are prone to aggregation. These impurities will affect the quality of the final product in different ways during the processing of limestone.

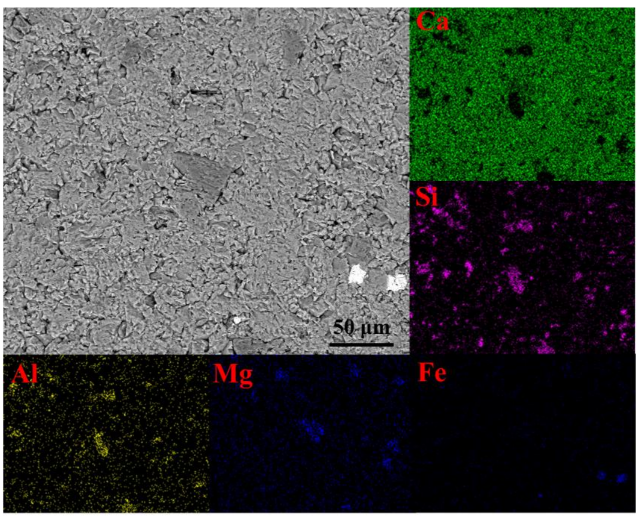

Figure 6 SEM image and EDS area scan results of impurity elements enrichment area

3 Effects of Impurities on Limestone Processing

The processing of limestone usually includes steps such as crushing, screening, calcination, and grinding. The presence of impurities can have varying degrees of effects on these processing steps, thereby affecting the quality of the product.

3.1 Effects of Magnesium

Magnesium is one of the common impurity elements in limestone, mainly present in dolomite and magnesian limestone. The higher the Mg content, the higher the melting point and calcination temperature of limestone. Therefore, the calcination process of high Mg limestone is relatively difficult and its reactivity is low. During the calcination process of limestone, excessive Mg can lead to a decrease in the quality and reactivity of the generated quicklime (CaO).

The presence of Mg in the production of calcium based compounds such as nano calcium carbonate and light calcium carbonate may lead to a decrease in product purity and affect their application performance. For example, the dispersibility and flowability of nano calcium carbonate may be affected, and the particle morphology and specific surface area of lightweight calcium carbonate may also be compromised [8].

3.2 Effects of Silicon

Silicon typically exists in limestone in the form of quartz and clay minerals. The presence of Si has a significant effect on the high-temperature calcination process of limestone. Limestone with high Si content can lead to a decrease in the efficiency of the reaction between the generated quicklime and carbon dioxide, reducing the reactivity of quicklime. Si may also react with Ca to form insoluble calcium silicates (such as C_2S, C_3S, etc.), reducing the reactivity of limestone.

In cement production, the silicon content determines the mineral composition of cement clinker. Excessive Si can lead to a decrease in the early strength of cement and affect its hardening performance. For the production of ultrafine calcium hydroxide, limestone with high Si content may lead to a decrease in the purity of calcium hydroxide, thereby affecting its water absorption and reactivity [9].

3.3 Effects of Iron

Iron often exists in limestone in the form of iron minerals and iron oxides. The presence of Fe can have an effect on the calcination process of limestone, especially under high temperature conditions, Fe can react with Ca to form new substances such as calcium iron ore ($CaFe_2O_4$), which not only affect the reactivity of limestone but may also darken the color of the product.

In cement production, an increase in Fe content can affect the mineral composition of cement, especially during the burning process of cement clinker. The chemical reaction between Fe and Al can affect the quality and strength of cement. For the production of nano calcium carbonate and light calcium carbonate, the presence of Fe may affect the appearance of the products, causing color differences on the surface of the particles [8, 9].

3.4 Effects of Aluminum

Aluminum usually exists in limestone in the form of aluminosilicate minerals. The presence of Al has a significant impact on the calcination of limestone and the firing process of cement clinker. In cement production, aluminum is one of the main constituent elements of cement minerals such as calcium aluminate. Excessive Al can affect the early strength of cement and increase its hydration heat.

For the production of lightweight calcium carbonate and ultrafine calcium hydroxide, high Al content may affect their crystal structure, resulting in changes in product particle size and morphology, and affecting their application performance [10].

3.5 Effects of Sulfur

Sulfur usually exists in limestone in the form of sulfate minerals, such as gypsum, pyrite, etc. During the high-temperature calcination process, S reacts with Ca to form calcium sulfate ($CaSO_4$). The excessive presence of S not only reduces the reactivity of limestone, but may also lead to excessive S content in the generated products, thereby affecting the quality of the products.

In cement production, the presence of sulfur is one of the important mineral components in cement clinker, but excessive S can cause the setting time of cement to be too long or too short, affecting the hardening process of cement. For the production of active calcium oxide, excessive S may lead to the formation of calcium sulfate, reducing the activity of calcium oxide [11].

Considering the influence of different impurity elements on lime products, the content of these elements can be graded. The content of impurity elements in different grades of limestone is shown in Table 1, which is divided into three grades: high grade, medium grade, and low grade limestone.

Table 1 Contents of impurity elements in the three grades of limestone

	Mg /wt.%	**Si /wt.%**	**Fe /wt.%**	**Al /wt.%**	**S /wt.%**
High grade	<0.4	<1.0	<0.1	<0.4	<0.1
Medium grade	0.4-0.7	1.0-1.5	0.1-0.5	0.4-2.0	0.1-0.5
Low grade	>0.7	>1.5	>0.5	>2.0	>0.5

4 Effects of Impurities on Different Calcium Products

4.1 Nano Calcium Carbonate

Nano calcium carbonate is an important functional material widely used in coatings, plastics, rubber, and other fields. Impurities in limestone, especially Mg, Si, and Fe, may affect the purity and dispersibility of nano calcium carbonate. The presence of Mg and Si will lead to a decrease in the solubility of calcium, affecting the formation process of nano calcium carbonate; Fe may cause a color change in nano calcium carbonate, affecting its application effectiveness in coatings and plastics [8].

4.2 Light Calcium Carbonate

Light calcium carbonate is usually obtained from limestone through carbonization, sedimentation, and other processes. Impurity elements such as Mg and Si may influence the sedimentation rate and particle morphology of calcium carbonate. Limestone with high Si content may lead to incomplete carbonation reaction during the carbonization process, thereby affecting the quality and yield of the final product [10].

4.3 Activated Calcium Oxide

Activated calcium oxide is a product obtained by high-temperature calcination of limestone, and is widely used in water treatment, environmental management, and other fields. Impurities such as S and Fe can affect the activity and purity of calcium oxide. The presence of S may reduce the reactivity of calcium oxide, because the formation of calcium sulfate (gypsum) will consume part of calcium and reduce the effective activity of calcium oxide. The presence of Fe may react with calcium oxide to form compounds such as calcium iron oxide, which not only affects the activity of calcium oxide, but also may have a negative effect on its stability and effectiveness in environmental remediation [12].

4.4 Superfine Calcium Hydroxide

Superfine calcium hydroxide is mainly obtained by reacting lime (CaO) with water, and is widely used in food, medicine, cosmetics, environmental protection and other fields. Impurities such as Si, Mg, Fe and Al will affect the purity, crystal structure and particle size distribution of superfine calcium hydroxide in the production process. Limestone with high Si content will complicate the sedimentation of calcium hydroxide, resulting in uneven particle size distribution and affecting the quality of the final product. Mg, Al and Fe impurities may react with calcium hydroxide to form different compounds, which will affect its water absorption, reactivity and final application performance [13].

4.5 Lime

Lime (CaO) is the product of limestone calcination, which is widely used in cement production, steel smelting, chemical industry and other fields. The quality of lime is greatly affected by impurities in limestone raw ore, especially Mg, Si, Fe and S. Limestone with high Mg content will reduce the reactivity of quicklime, and then affect the effect of lime in the industrial process. Si, Fe and S may affect the sintering process of lime and the stability of the final product, thus affecting the application effect of lime in various production [7, 9].

4.6 Cement

Limestone is one of the main raw materials in cement production. The quality of cement is significantly affected by the impurities of limestone raw ore. Si, Al, Fe and other impurities have a direct effect on the mineral composition and the hardening process of cement. Too high Si content will lead to the increase in the proportion of calcium silicate minerals (such as C_3S and C_2S) in cement, affecting the strength development of cement. Excessive Al and Fe may affect the sintering process of cement, resulting in high hydration heat or low early strength of cement clinker [9].

5 Impurity Removal Techniques

In order to improve the utilization value of limestone, different technical methods are often used to remove impurities from the raw ore. Common impurity removal methods include [14]:

5.1 Physical Methods

Physical methods are mainly used to remove most impurities in limestone through screening, ore washing, flotation, and other techniques. For example, through flotation technology, silicon minerals and some iron minerals in limestone can be effectively removed, and the purity of limestone can be further improved. Ore washing can effectively remove impurities such as clay and gravel in limestone [15].

5.2 Chemical Methods

Chemical methods are mainly used to remove certain impurities in limestone through techniques such as acid washing, acid leaching, alkali leaching, and other techniques. For example, acid washing can remove iron and aluminum minerals from limestone, and alkali leaching can remove magnesium minerals from limestone. Chemical methods can selectively remove certain specific impurities, thereby improving the quality of limestone.

5.3 Physical and Chemical Combination Methods

In practical production, physical and chemical methods are often combined to achieve the optimal impurity removal effect. For example, the combination of flotation and acid leaching can more effectively remove impurities such as Si, Fe and Mg from limestone and improve the purity of the product.

6 Conclusions and Prospect

The impurities in limestone ore, such as Mg, Si, Fe, Al, S, etc, directly affect the processing of limestone and the quality of its products. Different impurities have a significant effect on the calcination, carbonization, hydrogen oxidation, and other processes of limestone, which in turn affect the purity, particle size, reactivity, and other characteristics of the final product. Through effective impurity removal technology, the utilization efficiency of limestone and the quality of products can be improved, thereby meeting the demand for high-performance chemical products.

Future research can further explore novel impurity removal techniques to improve the quality of limestone and optimize production processes. In addition, with the continuous development of new materials, how to rationally select limestone ore and control its impurities to produce calcium-based compounds with higher properties and wider application fields will also become an important direction of research.

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