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Lin Zongshou, Xing Weihong, Chen Wei

# **Cementitious Materials Science**

Theories and Applications



DE GRUYTER

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## Preface

*Cementitious Materials Science* was first printed and published by the China Construction Industry Press in 1980, as a university teaching material for undergraduates with majors of construction engineering materials and products, cementitious materials and products and inorganic nonmetallic materials. This textbook was then published by the Wuhan Polytechnic University Press (now it is the Wuhan University of Technology Press) with a comprehensive revision made by Professor Yuan Runzhang in 1989. In 1996, the book was revised and modified again by Professor Yuan Runzhang, and it was published by the Wuhan University of Technology Press and reprinted many times later. In 2014, the textbook, *Cementitious Materials Science*, was updated by Professor Lin Zongshou; the contents of each chapter was updated according to the requirements of the teaching program for the major of cementitious materials, including the latest national standards and research results. The new edition of the book was published by the Wuhan University of Technology Press. In 2017, the copyright of this book was bought by German De Gruyter Press. The book is, therefore, re-edited by Professor Lin Zonghou.

The chapters of this edition on "Cementitious materials" have reserved the conventional classification of the original version. Starting from the common basic principles and rules of cementitious materials, and based on the characteristics and applications of various cementitious materials, the relationship between the composition, structure and properties of cementitious materials is systematically expatiated more deeply, with the emphasis of general-purpose Portland cement. In addition, it is also expatiated in the book about the basic laws of hydration and hardening process of cementitious materials; the relationship between the structural and engineering properties of hardened cementitious materials; the relationship between the forming process of hardened cementitious materials and process parameters; the relationships among the structure, properties and application conditions of hardened cementitious materials and so on. However, the production equipment and process parameters for each type of cementitious materials are not elaborated in this book. Hopefully, readers can master the basic principles and properties of various cementitious materials, and innovate and develop them in applications.

It must be pointed out that readers should analytically read some of the theories introduced in this book and test/develop them in practice because the cementitious material science itself is still developing with imperfect theories. It should also be mentioned that some of the data quoted in this book are from different authors obtained under different conditions, and the data quoted in the book are used to illustrate some principles and laws. It is expected that readers should not apply the data in the book mechanically in the actual work, but should apply the basic principles and laws in the book according to the actual situation and should solve practical problems through further experiments. Note that the principles and rules of materials science are established through experiments. It is very important to understand that the application of these principles and laws to a specific production practice will also be carried out by experiments.

This book is a university teaching material for the major of cementitious materials and products; it can also be used as a reference for technicians in the fields of building material products factories and civil engineering, such as cement, concrete and other cementitious materials. Readers should have the basic knowledge of physical chemistry and phase analysis when reading this book.

The detailed work on writing and edition of this book is divided as follows: Professor Lin Zongshou is the chief editor of this book, and has compiled the *Preface, Introduction* and Chapters 1 and 2; Dr Xing Weihong works as a subeditor, and has compiled Chapters 3, 4, 5 and Professor Chen Wei is a subeditor, and has compiled Chapter 6.

The English translation of this book is implemented as follows: Dr Yu Rui has translated the *Preface, Introduction* and Sections 1.1–1.5; Dr Liu Zhichao has translated Sections 1.6.1–1.6.3, 1.7.6–1.7.12 and *Problems* of Chapter 1; Dr Rao Meijuan has translated Sections 1.6.5.7–1.6.5.8 and Chapter 5; Dr Hu Chuanlin has translated Sections 1.6.4–1.6.5.6 and 1.7.1–1.7.5; Dr Liu Yunpeng has translated Sections 2.1–2.3; Dr Yang Lu has translated Sections 2.4–2.10 and *Problems* of Chapter 2; Dr Jian Shouwei has translated Chapter 3; Dr Xing Weihong has translated Chapter 4 and Professor Chen Wei has translated Chapter 6 and *References*.

Proofreading of English version of this book is implemented as follows:

Professor Chen Wei has proofread *Introduction* and Sections 1.1–1.3; Dr Rao Meiju has proofread Sections 1.4–1.5;

Dr Yu Rui has proofread Sections 1.6.1–1.6.3, 1.6.5.7–1.6.5.8 and 1.7.6–1.7.12 and *Problems* of Chapter 1;

Dr Xing Weihong has proofread Sections 1.6.4–1.6.5.6 and 1.7.1–1.7.5 and Chapters 2 and 3;

Dr Liu Yunpeng has proofread Chapter 4; Dr Jian Shouwei has proofread Chapters 5 and 6 and *References*.

The book is refereed by Professor Shui Zhonghe. The editor expresses his sincere appreciation for the hard work done by English translators and the careful review done by chief referee. Thanks to De Gruyter Press in improving the quality of the textbook. In addition, the editor also expresses his appreciation to all readers for supporting this book.

Additionally, it will be appreciated if researchers, teachers, students or other readers can put forward valuable suggestions for further improvements of this book.

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## Brief introduction to the author

Lin Zongshou was born in Fuding, Fujian Province, in 1957. He graduated from Tongji University in December, 1981. In June 1985, he got his master's degree in Wuhan University of Technology. In 1990, he returned to China from Japan after studying in Tokyo Institute of Technology.

He was a representative in the Ninth and Tenth Chinese National People's Congress (NPC), a member of the Eleventh Chinese People's Political Consultative Conference (CPPCC) committee and a member of the CPPCC population resources and environment committee, and he was awarded the Chinese National "May 1" Labor Medal. He is an expert and has the special allowance of the Chinese State Council. He is currently a professor and doctoral supervisor at Wuhan University of Technology.

Professor Lin is mainly engaged in research of chemical and technological processes of cement. He has 33 patents and five computer software copyrights, and has published more than 120 papers. He has chiefly compiled "Inorganic Nonmetallic Materials Technology," "Cement Technology," "Cementitious Materials Science" and other teaching materials. He has written books of "Hundred Thousand Questions of Cement" with a set of 10 volumes, "Excess-Sulfate Phosphogypsum Slag Cement and Concrete," "Causes and Countermeasures of Sand-out in Cement" and "Slag-based Ecological Cement." He has established Wuhan Yisheng Science and Technology Co., Ltd., and presided the Chinese National "863" Program and several other projects. He is awarded for a new Chinese national key product, two first prizes in scientific and technological progress in Hubei Province and an outstanding achievement prize in comprehensive utilization of national natural resources.



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## **1** Introduction

#### 1.1 Definition and classification of cementitious materials

On the basis of the physical and chemical effects, in the process of the gradual transformation of plastic slurry into a solid stone, the substances that can bind other materials to form a whole structure with mechanical strengths are collectively referred as cementitious materials, also known as glued materials.

Cementitious materials can be generally divided into two categories: inorganic and organic types. All kinds of resin and asphalt are organic cementitious materials. The inorganic cementitious material can be divided into hydraulic and nonhydraulic types based on its hardening conditions. The hydraulic cementitious material, after mixing with water, can be hardened both in air and in water and generate strength, which is normally called cement, such as Portland cement, aluminate cement, sulphoaluminate cement and so on. Instead of hardening in water, the nonhydraulic cementitious materials could be hardened in air or other conditions. The one that can only be hardened in the air are called air-hardening cementitious materials, such as lime, gypsum and magnesium cementitious materials.

On the basis of the classification of hydration products, the inorganic cementitious materials can be divided into silicates that mostly produce calcium silicate hydrate, aluminate that mostly produce calcium aluminate hydrate, sulphoaluminate that mostly produce calcium sulphoaluminate hydrate and so on. In addition, there are also some other classification methods.

#### **1.2** The role of cementitious materials in national economy

Cementitious materials can not only be widely used in industrial constructions, civil engineering, transportation, water conservancy, agriculture and forestry, national defense, seaport, urban and rural constructions, aerospace industry, nuclear industry and other new industrial constructions, but also replace steel and timber to produce sleeper, electrical pole, pressure pipe, cement carrier and various structures used for marine development and so on. Besides, it is also an indispensable material for a series of large-scale modern technical facilities and national defense engineering. Therefore, as one of the most important raw materials, cementitious materials have attracted a significant attention.

In the foreseeable decades, cement, concrete and other cementitious materials are still the main building materials. With the development of science and technology, the ability of mankind to transform nature has been continuously improved, and the scale has gradually expanded, which simultaneously has put forward a series of new requirements for the cementing materials. Therefore, the cementitious material

#### 2 — 1 Introduction

has a broad development prospects. The reasons for the continuous development of cementitious materials should be attributed to the following characteristics:

- (1) abundant raw materials, raw materials locally available, low production costs;
- (2) good durability, high adaptability, can be used in water, sea, hot or cold environments;
- (3) advanced fire-resistance capacity;
- (4) less maintenance work, low depreciation costs;
- (5) as a substrate, it is capable to combine or composite with other materials, such as fiber-reinforced cementitious materials, polymer-reinforced cementitious materials, fiber-polymer-cementitious material multiple composites and so on. Based on the aforementioned points, a large category of new composite materials could be developed;
- (6) beneficial for reusing industrial wastes.

The applications of cementitious materials have played an important role in all aspects of industry and civil engineering, and the cementitious material industry is an industry that cannot be ignored in the national economy. With the development of modern science and technology, new technologies in other fields will also inevitably penetrate into the cementitious material industry. The traditional cementitious material industry is bound to spring up the new technology revolution and varietal development with the rapid growth of science and technology. Simultaneously, its application areas will also be broadened, which could further strengthen its key role in the national economy.

#### 1.3 The brief history of cementitious materials

The development of cementitious materials can be traced back to the prehistoric period of mankind. It has gone through several stages such as natural clay, gypsumlime, lime-volcanic ash and hydraulic cementitious materials made from artificial ingredients. The ancient Egyptians used the Nile's slurry to make bricks without calcination. To increase strength and reduce shrinkage, sand and grass are also mixed into the mud. About 3,000–2,000 BC, the ancient Egyptians began to use calcined gypsum as a building cementitious material, and calcined gypsum has already been used in the construction of the ancient pyramids in Egypt.

Unlike the ancient Egyptians, the Greeks preferred to use the lime generated from calcined limestone in the construction of buildings. In 146 BC, the ancient Roman Empire conquered the ancient Greece, inheriting the tradition of producing and using lime in ancient Greece. The ancient Romans used lime by first dissolving it with water, mixing it with sand and then building the structures with the mortar. Some of the ancient Roman architecture, which was built with lime mortar, was very strong and remains even until today.

The ancient Romans improved the utilization technology of lime. Not only the sand was mixed in the lime, but also the ground volcanic ash. In the areas without volcanic ash, it was replaced by the ground brick, which had the same effect as that of volcanic ash. The mortar was much better in strength and water resistance than the lime–sand two-component mortar, and it was more durable in its regular buildings and underwater construction. Some people called the "lime–ash–sand" three-component mortar."

The development of Chinese construction cementitious materials is unique and historical. As early as 5,000–3,000 BC, the period of Yangshao culture in the Neolithic, Chinese have already used "white ash" to daub the cave, the ground and the four walls of the excavation, which can result in a smooth and hard structure. The "white ash" was named because of its white powder appearance, which was made from grinding natural ginger stone. The ginger stone is a kind of limestone with high silica content. It is often mixed in the loess, and it is the calcareous concretion in loess. The "white ash" is the earliest building cementitious material that has ever found in ancient China.

In the sixteenth century BC, Shang Dynasty, the cave buildings were rapidly replaced by wooden structure. At this time, in addition to using "white ash" to daub the ground, the yellow mud was used to build walls. From 403 BC to 221 BC, the Warring Stage period, the grass was mixed with yellow mud to build walls and glue wall tiles. In the history of Chinese architecture, the "white ash" was eliminated long time ago. However, the yellow mud and yellow mud mixed with grasses as cementitious materials were utilized until modern society.

In the seventh century BC, lime appeared in the Zhou Dynasty, which was mainly made from the calcined shell of the large clam. The main component of clam shell is calcium carbonate. When  $CO_2$  is exhaustively eliminated, the remaining substance is lime. It has been found in the Zhou Dynasty that the produced lime has good moisture absorption and resistance properties, which is the reason why it has been widely used in Chinese history for a long period.

In the fifth century, South and North Dynasties, a kind of building material named "three-mixture-soil" appeared, which was composed of lime, clay and fine sand. In the Ming Dynasty, the "three-mixture-soil" was composed of lime, pottery powders and gravels. In the Qing Dynasty, except for the lime, clay and fine sand-based "three-mixture-soil," the lime, slag and sand were utilized to produce a new "three-mixture-soil." Based on the modern point of view, "three-mixture-soil" can be treated as a kind of concrete, in which the lime, loess or other volcanic ash materials were utilized as cementitious materials and fine sand, gravel or slag played the role of fillers. There are many similarities between the "three-mixture-soil" has relatively high strength and good waterproofness capacity. It was used to build dams in the Qing Dynasty.

One of a striking feature for the development of cementitious materials in Chinese ancient architecture is the application of cementitious materials composed of organic materials and lime, such as "lime-glutinous rice," "lime-tung oil," "lime-blood," "lime-bletilla," "lime-glutinous rice-alum" and so on. In addition, in the application of "three-mixture-soil," the glutinous rice and blood were also added.

The development process of the cementitious materials in ancient Chinese architecture originated from "white ash" and yellow mud, which further transferred to the lime and "three-mixture-soil," and finally developed to the cementitious materials of lime doped with organic materials. The cementitious material in ancient Chinese architecture had its glorious histories. Compared to the development of that in ancient western architecture, due to the widespread adoption of the cementitious material of lime and organic materials, the Chinese ancient cementitious materials were even better.

In the second half of the eighteenth century, hydraulic lime and Roman cement were developed, which were made from calcined limestone containing clay. Based on this foundation, a natural cement was developed from calcined and finely ground natural cement rock (a limestone with clay content at 20–25%). Subsequently, it gradually developed to grind and mix the limestone with a certain amount of clay, and produced the hydraulic lime based on the calcination of artificial ingredients. This is actually the prototype for Portland cement production.

In the early nineteenth century (1810–1835), according to artificial ingredients, high-temperature calcination and grinding, the hydraulic cementitious materials can be produced. The calcination temperature has reached the melting points of several raw materials, which can also be treated as sintering. In 1824, the British Joseph Aspdin first obtained the patent for the product. Since the produced cementitious material has similar appearance and color in the hardened state as that limestone produced on Portland Island, it was originally called Portland cement. In our country, it was called silicate cement. Due to the fact that it has relatively high silicate content, the Portland cement can harden in water and show relatively high strength. An example of the first large-scale application of Portland cement was the Thames Tunnel Construction, which was built in 1825–1843.

The appearance of Portland cement has played an important role in engineering construction. With the demands of modern science and industrial development, in the early twentieth century, various cements for different applications were gradually produced. In the recent half of the century, sulphoaluminate cement, fluoroaluminate cement, aluminoferrite cement and other types of cement were successively developed, which promote further development of Portland cement to more categories. At the same time, new cognition has been acquired on ancient cementitious materials such as lime and gypsum, which enlarge their application fields and development.

#### 1.4 The development of cementitious materials science

In the broad field of productive and scientific practice for cementitious materials, considerable knowledge has been accumulated, especially with the formation and

development of materials science, new and profound changes are taking place in the understanding of cementitious materials. The characteristics and trends of this change can be summarized as follows:

- (1) The understanding of cementitious materials is gradually deepened, from macroscopic to microscopic, which gradually reveals the relationship between its performance and the internal structure. Thus, this provides a theoretical basis for developing new varieties of cementitious materials and expanding their areas of applications.
- (2) The understandings for cementitious materials productive process and their hydration and hardening process have gradually improved from experience and phenomenon to theory and essence, which provides a theoretical basis for effectively controlling the productive process of cementitious materials products and adopting new technologies and new methods. There is no doubt that cementitious materials are being formed progressively as an important part of material science.
- (3) The traditional cementitious materials were produced by natural raw materials. In future, no natural resources would be used for the production of cementitious materials, while various industrial solid wastes could be the main raw materials to produce near-zero emission environment-friendly cementitious materials with simple manufacturing process and little energy consumption.

The main research contents of cementitious materials can be summarized as follows:

- (1) the relationship between composition, structure and cementitious properties of cementitious materials;
- (2) the law of hydration and hardening process and structure formation of cementitious materials;
- (3) the relationship between composition and structure of harden cementitious materials and their engineering properties;
- (4) preparation of cementitious materials with specified properties and structure and technological approaches for the production of environment-friendly cementitious materials.

We are convinced that with the development of cementitious materials science, the cementitious materials and products industry will have a new neap in the future.

## 2 Common Portland cement

Generally, the cement can be defined as a hydraulic powder material. When cement is mixed with proper amount of water, a plastic paste can be formed, which can harden both in the air and in water; and the sand, stone and other materials can be firmly combined together.

There are many types of cement, based on their application purpose and property. Three general types are common Portland cement, special cement and characteristic cement. Common Portland cement is widely used in civil engineering, including Portland cement, ordinary Portland cement, Portland blast furnace slag cement, Portland pozzolana cement, Portland fly-ash cement and composite Portland cement. Special cement refers to cement serving special purposes such as oil well cement and masonry cement. Characteristic cement exhibits unique performances such as high early strength Portland cement, sulfate-resistant Portland cement, moderate heat Portland cement, sulfoaluminate expansive cement and self-stressing aluminate cement.

Based on the main hydraulic minerals, cement can be classified as silicate cement, aluminate cement, sulfoaluminate cement, fluoroaluminate cement and the cement produced from industrial solid waste and local materials. At present, there are more than 100 different types of cements.t

#### 2.1 The invention and production of cement

#### 2.1.1 The invention of cement

In the mid-eighteenth century, the lighthouses in England were mainly made of wood and "Roman mortar." Due to the fact that the used materials cannot withstand the corrosion and erosion from the sea, the lighthouse was often damaged. Hence, J. Smeaton, who was honored as the Father of British civil engineering, undertook the task of building new lighthouses. In 1756, in the process of lighthouse construction, it was observed that after adding some water to the calcinated and ground limestone containing clay, the formed mortar can harden slowly and has much higher strength than "Roman mortar" in the sea, which could simultaneously resist the erosions from seawater. The lime that is made of clay and limestone was called hydraulic lime. The discovery of Smeaton was a great leap in the knowledge accumulation and played an important role in the invention of Portland cement. In 1796, the British researcher J. Parker milled clayey limestone (called Sepa Tria) into pellets, and calcined them at a higher temperature than that of lime, and finally ground them again to produce cement. Parker called this cement "Roman Cement" and patented it. "Roman Cement" set quickly and can be used for engineering in water, which was widely used by British until the invention of "Portland Cement."

Almost at the same time when the "Roman cement" was produced, the French produced cement in the area of Boulogne by using the marl that has similar chemical compositions as that of modern cement. The natural marl, whose chemical composition is close to the modern cement, is called cement-used limestone, and the cement made from the limestone is called natural cement. Natural cement was also produced in America by using the cementitious rock in the areas of Rosendale and Louisville. For a long time in the 1880s, and later, natural cement was widely used in the United States and had played an important role in the construction industry.

The British researcher J. Foster mixed chalk and clay with a mass ratio of 2:1, and grounded the mixture with water to form slurry. Then, the slurry was subjected into the hopper to precipitate, and the precipitated fraction is dried in the atmosphere. After that, the dried substance was calcined in the limekiln at a certain temperature for complete volatilization of  $CO_2$  in the material. Finally, the calcined product is yellowish and was ground to cement after cooling. The obtained cement was named "British cement" by Forster, which was also the British No. 4679 patent in October 22, 1882. Due to the lower calcination temperature, the quality of "British cement" was much lower than the "Roman cement." Although it has not been widely used, its manufacturing method was the prototype of the modern cement, which was another major leap in cement knowledge accumulation.

In October 21, 1824, J. Aspdin, a plasterer in Leeds, obtained the 5022nd "Portland cement" (silicate cement) patent, and became an inventor of cement. The "Portland cement" method that described in his patent certificate is: "The limestone was crushed into fine powder, blended with a certain amount of clay, mixed with waste to form slurry by artificial or mechanical stirring. Then the mud was placed on the plate, heated and dried. The dried material was hit into pieces, and fed into the limekiln to calcine until all the CO<sub>2</sub> is escaped. After that, the calcined product was cooled, crushed and ground to generate the cement. When mixing the cement with a small amount of water, the produced mortar with proper consistency could be applied to various work situations." The color of the cement after hydration and hardening was similar to the building stone in Portland, England, hence it was named "Portland cement."

The "Portland cement" manufacturing method described in the patent certificate of Aspdin is similar to Foster's "British cement," since the calcination temperatures were both up to the complete volatilization of  $CO_2$  within the material. Based on the general knowledge of cement production, the quality of the produced "Portland cement" under this temperature should be lower than "British cement." However, "Portland cement" was more competitive than "British cement" in the market. In 1838, when the Thames tunnel construction was rebuilt, the "Portland cement" was finally chosen even its price is much higher than that of "British cement." It is a personal assumption that Aspdin did not show the "Portland cement" production technology completely on the patent certificate for the sake of confidentiality. He actually had more knowledge of cement production than that described in the patent.

Aspdin must have used higher calcination temperature in the manufacturing; otherwise, the cement after hardening would not have the same color as the stone in Portland, and it would not have won the competition in the market.

However, according to the contents described in the patent certificate and the relevant information, Aspdin failed to grasp the exact calcination temperature of "Portland cement" and the correct ratio of the raw materials, which cause that the quality of the product was very unstable, and even some buildings were collapsed due to the low quality of the produced cement.

Another cement research genius at the time of Aspdin in Britain was I. C. Johnson. He was the manager of the British Swan Valley White Company, specialized in the manufacture of "Roman cement" and "British cement." In 1845, in an experiment, Johnson accidentally found that the calcined cement bulk with a certain amount of glass results in good hydraulicity after grinding. In addition, it was also noticed that the cement would crack if the calcined bulk contained lime. According to these unexpected findings, Johnson identified two basic conditions for cement production: First, the temperature of the kiln must be high enough to ensure that the calcined bulk contains a certain amount of dark green glass. Second, the ratio of raw materials must be correct and fixed, the calcined bulk cannot contain excessive lime and the cement should not crack after hardening. These conditions ensured the quality of "Portland cement" and solved the problem of quality instability that Aspdin faced. Since then, the basic parameters of modern cement production were determined.

The earliest Chinese cement factory was the Green Island Cement Factory, a foreign-funded enterprise in Macao, which was founded in 1886. Tangshan cement factory was the earliest Chinese national cement enterprises, established by Chinese in 1889, which was three years later than Macao Green Island Cement Factory. Later, cement factories were built in Dalian, Shanghai and Guangzhou successively. According to the pronunciation of English word "cement," the productions of these factories were named "Ximiantu," "Shimintu," "Shuimenting" and "foreign ash". The name "Cement" was first used by "Hubei cement factory" located in Huangshi harbor, Daye county, Hubei province, which was the predecessor of Huaxin cement co., Ltd. It was built in May 2, 1909, and was capable to produce cement with 180–200 t/day.

#### 2.1.2 The process of cement

According to the preparation methods of raw materials, the process of cement production can be divided into two categories: the dry method and the wet method. In the dry method, the raw materials are dried and crushed into powder, and then added into the kiln clinker. When an appropriate amount of water is added to the raw materials to generate pellets, then add into the kiln or Lepol kiln clinker to calcine. This is also called semidry method. In the wet method, raw materials with water are ground into slurry, and then added into the rotary kiln.

The suspension preheater, which was invented in the 1950s, experienced great development in the 1960s and greatly reduced the heat consumption of the clinker. In the 1970s, the kiln outside decomposition technology appeared, which significantly improved the output of clinker, and the heat consumption had decreased obviously. At the same time, the development of homogenization and pre-homogenization of the raw materials, and the continuous advancement of drying and grinding equipment improved the clinker quality. Hot air of the cooler was used for kiln outside the decomposition furnace, exhaust gas of kiln was used for drying raw materials and coal powder, the waste gas of kiln tail and the waste heat of the cooler were successfully used to regenerate power, so that the waste heat was fully utilized. About nearly a decade, with further optimization of new dry process production technology, further reduction of environmental load, various alternative materials and fuels, and the degradation and utilization of wastes, cement industry is treating the new dry production technology as the foundation and transforms to the ecological environment materials industry. The process of cement kiln outside the decomposition technology in dry method is shown in Figure 2.1.

In Figure 2.1, the limestone was broken into gravels, and then poured into the raw material warehouse after the homogenization executing in limestone pre-homogenization yard. The sandstone is transported into the factory, broken by the crusher, and then transported into the raw material warehouse. Iron powder is transported into the factory by car and directly stored in the raw material warehouse. According to the specified proportion calculation, the limestone, sandstone and iron powder are added into the raw mill for grinding to produce the raw material powders. Then the raw material powders were fed into the raw material warehouse. The homogenized raw materials are added into the preheater, decomposition furnace and rotary kiln to produce clinkers. The calcined clinkers are transported into the cooler for cooling, and the cooled clinkers are stored in the clinker warehouse. Gypsum is transported into the factory by car and stored into a gypsum warehouse after breaking. The fly ash is directly transported into the fly ash warehouse after being transported into the factory. After pressed by the roller press, the clinker is mixed with gypsum and fly ash at a certain proportion, and the mixture is added into the cement mill for grinding to produce the final cement. The produced cement is stored in the cement warehouse, and then packed up, or shipped in bulk by car, or transported by bulk cement vessels. The coal is transported into coal yard to be homogenized, and then the coal powder is prepared from coal mill, which can be used for calcination of rotary kiln and decomposing furnace. The hot gas required for the drying of coal mill is originated from the cooler. The high-temperature exhaust gas from the kiln tail preheater is cooled by the humidification tower, some of which is used for raw mill to dry raw materials and then discharged after dust collection, and the remaining part is discharged directly through dust collection. The hot gas generated after cooling the clinker can be partly used as secondary wind directly entering into the kiln to help coal powder combustion, while the other part is transported by tertiary air duct to the kiln tail decomposition furnace





to help coal powder combustion. The excessive gas is used for drying the coal mill or been discharged by the dust system of the kiln. In the cogeneration pre-decomposition kiln system, some of the heat gas generated from the cooler and the exhaust gas of the kiln tail preheater are discharged after providing steam for boiler generator.

#### 2.2 Composition of Portland cement clinker

When the raw materials containing CaO (abbreviation: C),  $SiO_2$  (abbreviation: S),  $Al_2O_3$  (abbreviation: A),  $Fe_2O_3$  (abbreviation: F) are ground into powders with a certain proportion, and then calcined to partially melt, the obtained hydraulic cementitious material composed of calcium silicate can be called as Portland cement clinker, abbreviated as clinker.

#### 2.2.1 Chemical and mineral compositions of clinker

#### 2.2.1.1 Chemical composition

Portland cement clinker is mainly composed of four oxides: CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> (normally more than 95 wt%). When the content of the main oxides [w(CaO)+w(SiO<sub>2</sub>)+w(Al<sub>2</sub>O<sub>3</sub>)] is converted to 100% (Fe<sub>2</sub>O<sub>3</sub> content is calculated in Al<sub>2</sub>O<sub>3</sub>), the composition of Portland cement clinker can be described by the graphic area of C<sub>3</sub>S-C<sub>2</sub>S-C<sub>3</sub>A triangle shown in Figure 2.2.



Figure 2.2: Cement areas of CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system.

In the modern Portland cement clinker, the fluctuation ranges of the main oxides are as follows: w(CaO) is 62–67%;  $w(SiO_2)$  is 20–24%;  $w(Al_2O_3)$  is 4–7%;  $w(Fe_2O_3)$  is 2.5–6.0%.

In some cases, due to the differences in cement variety, the composition of raw materials and the manufacturing process, the oxide contents may not be within the above-mentioned range. For instance, in white Portland cement, the content of Fe<sub>2</sub>O<sub>3</sub> must be less than 0.5%, while the content of SiO<sub>2</sub> can be higher than 24%, or even up to 27%. Except for the four main oxides, there are also MgO (abbreviation: M), SO<sub>3</sub> (abbreviation:  $\overline{S}$ ), K<sub>2</sub>O (abbreviation: K), Na<sub>2</sub>O (abbreviation: M), TiO<sub>2</sub> (abbreviation: T) and P<sub>2</sub>O<sub>5</sub> (abbreviation: P).

#### 2.2.1.2 Mineral composition

In Portland cement clinker, CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> do not exist as separate oxides, but as multimineral aggregates produced by two or more oxides after high-temperature chemical reaction. Its crystal is small and the size of the clinker is usually  $30-60 \,\mu\text{m}$ . There are four main minerals:

- (1) Tricalcium silicate: 3CaO·SiO<sub>2</sub>, represented as C<sub>3</sub>S
- (2) Dicalcium silicate:  $2CaO \cdot SiO_2$ , represented as  $C_2S$
- (3) Tricalcium aluminate:  $3CaO \cdot Al_2O_3$ , represented as  $C_3A$
- (4) Ferrite solid solution:  $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$  are represented typically as  $C_4AF$ .

In addition, there are also small amount of free calcium oxide (f-CaO), periclase (crystalline magnesium oxide), alkali-containing minerals and glass within the clinkers. Figure 2.3 presents a petrographic photograph of Portland cement clinker under a reflecting microscope. The black polygonal particles are  $C_3S$ ; the round particles with black and white twin striation are  $C_2S$ , and between these two kinds of crystals are white mesophase  $C_4AF$  (light color) with strong reflection and black mesophase  $C_3A$  (dark) with weak reflection.



**Figure 2.3:** Petrographic photograph of clinker under reflecting microscope.

Generally, the content of  $C_3S$  and  $C_2S$  in clinker is about 75 wt%, which is called the silicate mineral. The theoretical content of  $C_3A$  and  $C_4AF$  accounts for about 22 wt%. During the calcination of cement clinker,  $C_3A$  and  $C_4AF$ , MgO and alkali will be

gradually melted at 1,250–1,280 °C to form liquid phases, promoting the formation of  $C_3S$ . Hence, it is called the fluxing mineral.

#### (1) Tricalcium silicate

 $C_3S$  is the main mineral of Portland cement clinker. The content is usually about 50%, and sometimes even up to above 60%. The pure  $C_3S$  is stable only under the temperature of 1,250–2,065 °C; when the temperature is above 2,065 °C, it incongruently melted to CaO and liquid phase; when the temperature is below 1,250 °C, it decomposes into  $C_2S$  and CaO, but the reaction is slow, so pure  $C_3S$  can be a metastable state at room temperature.  $C_3S$  has three types of crystals and seven variants:

 $R \xleftarrow{1070^{\circ}C} M_{III} \xleftarrow{1060^{\circ}C} M_{II} \xleftarrow{990^{\circ}C} M_{I} \xleftarrow{960^{\circ}C} T_{III} \xleftarrow{920^{\circ}C} T_{III} \xleftarrow{520^{\circ}C} T_{III}$ 

The R type belongs to the trigonal system, M type belongs to the monoclinic system and T type belongs to the triclinic system. The crystal structures of these variants are similar. In the Portland cement clinker, it usually does not exist as pure  $C_3S$ , while it always contains a small amount of MgO,  $Al_2O_3$ ,  $Fe_2O_3$  and so on. The mentioned composites can form solid solution, which is known as Alite or A mineral. Alite usually belongs to M type or R type.

Pure  $C_3S$  is white, with a density of  $3.14 \text{ g/cm}^3$ , and its crystal cross section is hexagonal or prismatic. The Alite single crystal of monoclinic system is hexagonal schistose or tabular. It often exists as an inclusion of  $C_2S$  and CaO in Alite.

 $C_3S$  presents the normal setting time, relatively fast hydration rate and high heat release amount. It has relatively high early strength, while its strength improvement at later age is also significant. Its strength at 28 days can reach 70–80% of that obtained after hydrating for one year, which is the highest among the four minerals. However, the hydration heat release for  $C_3S$  is high, and its water resistance is relatively poor.

#### (2) Dicalcium silicate

The content of  $C_2S$  in clinker is generally around 20%, which is one of the main minerals of Portland cement clinker. Moreover, it usually does not exist as pure  $C_2S$ , while it always contains a small amount of MgO,  $Al_2O_3$ ,  $Fe_2O_3$  and so on. The mentioned composites can form solid solution, which is known as Blite or B mineral. Below 1,450 °C, the pure  $C_2S$  has the following polycrystalline transformation:



(H: high temperature; L: low temperature)

At room temperature,  $\alpha$ ,  $\alpha'_{\rm H}$ ,  $\alpha'_{\rm L}$  and  $\beta$  are not stable, which have a tendency to transform into  $\gamma$ . In the clinker, there are less  $\alpha$  and  $\alpha'$ . When the calcination temperature is relatively high and the cooling rate is relatively fast,  $\beta$  can exist in the clinker, since the solid solution contains a small amount of MgO, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and so on. The normally named C<sub>2</sub>S or B mineral refers to  $\beta$ -C<sub>2</sub>S.

The strength of  $\alpha$ -C<sub>2</sub>S and  $\alpha'$ -C<sub>2</sub>S is excellent, while  $\gamma$ -C<sub>2</sub>S shows little hydraulicity. In the process of clinker calcination, when there is poor ventilation, strong reducing atmosphere, low sintering temperature, insufficient liquid phase and slow cooling rate, under 500 °C,  $\beta$ -C<sub>2</sub>S with a density of 3.28 g/cm<sup>3</sup> can be easily transformed into  $\gamma$ -C<sub>2</sub>S with a density of 2.97 g/cm<sup>3</sup>, while the volume expansion is 10% resulting in clinker pulverization. If the liquid phase is too much, the fluxing mineral can be formed into glass, the  $\beta$ -C<sub>2</sub>S can be included by glass, it can jump the transition temperature that  $\beta$ -C<sub>2</sub>S transfer to  $\gamma$ -C<sub>2</sub>S by rapid cooling.

Pure  $C_2S$  is white in color.  $C_2S$  is brown when it contains  $Fe_2O_3$ . The hydration speed of Blite is slow, and only about 20% can be hydrated after 28 days. Its setting and hardening are also slow, early strength is low, but the later strength growth rate is high, while the later strength can reach the level similar as Alite after a year. The hydration release heat of  $C_2S$  is small and its water resistance is advanced.

#### (1) Mesophase

The material filled between Alite and Bailey is collectively referred to as the mesophase. In the process of calcination, the mesophase is melted into liquid phase. During cooling, some liquid phases crystallize and the remaining solidify into glass.

#### (i) Tricalcium aluminate

The crystal structure of  $C_3A$  can be cube, octahedral or dodecahedron. Its shape varies with the cooling rate in the cement clinker. Clinker with high content of  $Al_2O_3$  and slow cooling rate may crystallize into the complete large crystals. Generally, it could come into the glass phase or in irregular microcrystalline precipitation. The potential content of  $C_3A$  in clinker is 7–15%. Pure  $C_3A$  is a colorless crystal with a density of  $3.04 \text{ g/cm}^3$  and a melting temperature of 1,533 °C. Under the reflecting microscope, it is drip-like with fast cooling rate, and rectangular or cylindrical with slowing cooling rate. Due to its poor reflective ability and dark gray color,  $C_3A$  is also called black mesophase.

The hydration rate of  $C_3A$  is relatively rapid. It can release relatively large amount of heat and coagulate quickly. If the gypsum and other retarders are not added, then the cement would condense and harden fast, and the strength within 3 days can be put out, but the absolute value is not high, and it hardly increase later, or even shrink. The cement with high content of  $C_3A$  has large shrinkage deformation and poor sulfate resistance.

#### (ii) Ferrite solid solution

The potential content of Ferrite solid solution in clinker is 10-18%. Its component is complex in clinker. It was considered as a component of  $C_2F-C_3A_3F$  continuous solid

solution; and also considered as a part of  $C_6A_2F-C_6AF_2$  continuous solid solution. In the general Portland cement clinker, its composition is close to  $C_4AF$ , so the  $C_4AF$  is usually used to represent Ferrite phase in clinker. If the  $w(Al_2O_3)/w(Fe_2O_3)$  is lower than 0.64 in clinker, the  $C_2F$  can be produced with certain hydraulic.

The early hydration rate of  $C_4AF$  is between  $C_3A$  and  $C_3S$ , but the subsequent development is not as good as  $C_3S$ . The early strength is similar to  $C_3A$ , and the later strength can increase continuously, which is similar to  $C_2S$ . Its impact resistance and sulfate resistance are great, and the heat of hydration is lower than that of  $C_3A$ , but the clinker with high content of  $C_4AF$  is difficult to be grinded. In road cement and sulfate-resistant cement, the high content of  $C_4AF$  is referable.

#### (iii) Glass

In the actual production, due to the faster cooling rate, some liquid phases are too late to crystallize and become a supercooled liquid, namely the glass. In glass, the particles are arranged disorderly, and the composition is also uncertain. Its main components are  $Al_2O_3$ ,  $Fe_2O_3$ , CaO and a small amount of MgO and alkali.

In the calcination process,  $C_3A$  and  $C_4AF$  are melted into liquid phase, which can promote the formation of  $C_3S$ , it is their important function. If there are few fulxing minerals in the material, it is easy to be burned, the CaO cannot be easily absorbed and the f-CaO in the clinker increases, which affect the quality of the clinker, reducing the production of the kiln and increasing the consumption of the fuel; if the melting mineral is too much, the material lump is easily formed in the kiln, the ring is formed inside the rotary kiln, the furnace accretion is formed in the vertical kiln and so on, which seriously affecting the normal production of rotary kiln and vertical kiln.

#### (2) f-CaO and periclase

f-CaO refers to calcium oxide, which has not been combined with high-temperature calcination, also known as free lime. The high-temperature calcined f-CaO structure is relatively dense, and the hydration is very slow. It usually takes 3 days to react obviously. During hydration, f-CaO creates calcium hydroxide and the volume is increased by 97.9%, which causes local swelling stress in the hardened cement paste. With the increase in f-CaO content, the flexural strength decreases first, then the strength is reduced after 3 days, it could result in poor soundness. Therefore, in the clinker calcination, the f-CaO content should be strictly controlled. It is generally controlled below 1.5% in rotary kiln, while below 3.0% in vertical kiln in China. Because part of the free oxide of clinker in vertical kiln is the raw material, which has not been calcined by high temperature. The hydration of the f-CaO is fast and is less destructive to hardened cement paste.

Magnesite refers to the free state of MgO crystals. MgO has a low chemical affinity with  $SiO_2$  and  $Fe_2O_3$ , so it generally does not participate in the chemical reactions during calcination. It is found in the following three forms in the clinker:

- (i) Dissolved in C<sub>3</sub>A and C<sub>3</sub>S to form solid solution
- (ii) Dissolved in glass
- (iii) In free form of magnesite

It is believed that MgO content of the first two forms is about 2% in clinker, which is not destructive to the hardened cement paste. In the form of magnesite, due to its low hydration rate, it starts hydration obviously after half a year to a year. The resulting hydrate is Mg(OH)<sub>2</sub> and the volume was expanded to 148%. Therefore, it also leads to poor stability. The extent of magnesia expansion is related to its crystal size and content. The bigger the size, the higher the content and the greater the expansion. In the production, fast cooling measurement should be carried out to reduce the size of the magnesite crystal.

#### 2.2.2 Modulus value of clinker

Portland cement clinker is composed of two or more oxides, so it can better reflect the effect of clinker mineral compositions and properties to control the ratio (i.e., modulus value) between the oxides in cement production than the content of the oxides separately. As a result, the modulus value indicating the relative content between oxides is often used as an index in production control.

#### 2.2.2.1 Limestone saturation coefficient

Among the four main oxides in clinker, CaO is the alkaline oxide and the other three are acidic oxides. They are combined with each other to form four main clinker minerals, such as C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF. It is not difficult to understand that once the content of CaO exceeds the demand of all acidic oxides, it would inevitably exist in the form of f-CaO, which will lead to poor cement stability and damage if with high content. So theoretically, there is a limit lime content. A. Guttmann and Gille believed that the highest alkaline minerals formed by acidic oxide are C<sub>3</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF, and the theoretical limit content of lime can be calculated. For the convenience of calculation, C<sub>4</sub>AF is rewritten as "C<sub>3</sub>A" and "CF," the resulting "C<sub>3</sub>A" is added to C<sub>3</sub>A and the demanded lime content of each 1% acidic oxide, respectively:

the demanded lime content for 1%  $Al_2O_3$  to form  $C_3A$ :  $\frac{3M_T\,(CaO)}{M_T\,(Al_2O_3)}=\frac{3\times56.08}{101.96}=1.65$  ;

the demanded lime content of 1% Fe<sub>2</sub>O<sub>3</sub> to form CF:  $\frac{M_r (CaO)}{M_r (Fe_2O_3)} = \frac{56.08}{159.70} = 0.35$ ;

the demanded lime content of 1% SiO<sub>2</sub> to form C<sub>3</sub>S:  $\frac{3M_{\rm r}({\rm CaO})}{M_{\rm r}({\rm SiO}_2)} = \frac{3 \times 56.08}{60.09} = 2.8$ .

The theoretical limit content of lime can be obtained by multiplying the demanded lime content of per 1% acidic oxides by the corresponding content of acidic oxide:

$$w(CaO) = 2.8w(SiO_2) + 1.65w(Al_2O_3) + 0.35w(Fe_2O_3)$$
(2.1)

Kindle and Junker announced that in the actual production,  $A1_2O_3$  and  $Fe_2O_3$  can always react with CaO (saturated with CaO), but only  $SiO_2$  may not be completely saturated to generate  $C_3S$ , and there is a portion of  $C_2S$ . Otherwise, f-CaO will appear in the clinker. Hence, a coefficient less than 1 should be multiplied before *w* (SiO<sub>2</sub>), that is, the lime saturation coefficient (KH). Therefore, the free lime content is calculated as

$$w(CaO) = KH \times 2.8w(SiO_2) + 1.65w(Al_2O_3) + 0.35w(Fe_2O_3)$$
(2.2)

The upper formula is rewritten as follows:

$$KH = \frac{w(CaO) - 1.65w(Al_2O_3) - 0.35w(Fe_2O_3)}{2.8w(SiO_2)}$$
(2.3)

In formula (2.3), the numerator shows the content of CaO to form calcium silicate  $(C_3S+C_2S)$ , and denominator shows the content of CaO demanded by all SiO<sub>2</sub> to form C<sub>3</sub>S in theory. Therefore, the KH in clinker is the ratio of the content of CaO to form calcium silicate  $[w(C_3S)+w(C_2S)]$  to the content of CaO that demanded by all of the SiO<sub>2</sub> to form C<sub>3</sub>S in theory. It means the degree of formation of C<sub>3</sub>S, when SiO<sub>2</sub> is saturated with CaO in the clinker. Theoretically, when KH = 1, the remaining CaO in the clinker reacts with all C<sub>2</sub>S to form C<sub>3</sub>S, and there is no C<sub>2</sub>S and only C<sub>3</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF are in the clinker. When  $[w(CaO)-1.65w(Al_2O_3)-0.35w(Fe_2O_3)]$  (the content of CaO combined with SiO<sub>2</sub>) is just enough for SiO<sub>2</sub> to entirely form C<sub>2</sub>S without C<sub>3</sub>S,  $[w(CaO)-1.65w(Al_2O_3)-0.35w(Fe_2O_3)]$  should be

$$\frac{2M_{\rm r}({\rm CaO}) \times w({\rm SiO}_2)}{M_{\rm r}({\rm SiO}_2)} = \frac{2 \times 56.08 \times w({\rm SiO}_2)}{60.09} = 1.8665w({\rm SiO}_2)$$

Then,

$$\mathrm{KH} = \frac{1.8665w(\mathrm{SiO}_2)}{2.8w(\mathrm{SiO}_2)} = 0.6666$$

That is to say, when KH = 0.6666 in the clinker, there are only C<sub>2</sub>S, C<sub>3</sub>A, C<sub>4</sub>AF without C<sub>3</sub>S. Therefore, KH is between 0.6666 and 1.0 in the actual clinker.

KH actually represents the ratio of  $C_3S$  to  $C_2S$  in percentage (mass fraction, wt%) in the clinker. The higher the value of KH, the higher the proportion of  $C_3S$  in the silicate minerals, and the better the strength of clinker. Therefore, increasing the KH is beneficial to improve the quality of cement clinker. But if KH is too high, the calcination of clinker is difficult, so it is necessary to increase the calcination temperature and prolong the calcination time. Otherwise, the f-CaO will appear; at the same time, it will lead to low output of the kiln and high heat consumption, and the working conditions of kiln liner will be deteriorated.

Formula (2.3) is applicable to the clinker when  $w(Al_2O_3)/w(Fe_2O_3) \ge 0.64$ ; if  $w(Al_2O_3)/w(Fe_2O_3)<0.64$ , the clinker minerals are composed of C<sub>3</sub>S, C<sub>2</sub>S, C<sub>4</sub>AF and C<sub>2</sub>F. Similarly, C<sub>4</sub>AF is rewritten as "C<sub>2</sub>A" and "C<sub>2</sub>F," and the rewritten "C<sub>2</sub>F" is added to C<sub>2</sub>F, thus

$$KH = \frac{w(CaO) - 1.1w(Al_2O_3) - 0.7w(Fe_2O_3)}{2.8w(SiO_2)}$$
(2.4)

Considering that there are f-CaO, free silica and gypsum in the clinker, the formula can be rewritten as follows:

When  $w(Al_2O_3)/w(Fe_2O_3) \ge 0.64$ ,

$$KH = \frac{w(CaO) - w(f - CaO) - 1.65w(Al_2O_3) - 0.35w(Fe_2O_3) - 0.7w(SO_3)}{2.8[w(SiO_2) - w(f - SiO_2)]}$$
(2.5)

When  $w(Al_2O_3)/w(Fe_2O_3) < 0.64$ ,

$$KH = \frac{w(CaO) - w(f - CaO) - 1.1w(Al_2O_3) - 0.7w(Fe_2O_3) - 0.7w(SO_3)}{2.8[w(SiO_2) - w(f - SiO_2)]}$$
(2.6)

It is noteworthy that KH is normally adopted to control the lime content in clinker in Chinese cement factory (except some imported from abroad). But the modulus value formula used for controlling the lime content in clinker is not the same around the world. Some commonly used parameters are as follows:

#### (1) Hydraulic modulus

In 1868, the German W. Michaëlis proposed the hydraulic modulus as a coefficient to control optimum lime content in the clinker. It is the ratio of alkaline oxide to acidic oxide mass fraction (%) in clinker, expressed as HM (or m). The formula is as follows:

$$HM = \frac{w(CaO)}{w(SiO_2) + w(Al_2O_3) + w(Fe_2O_3)}$$
(2.7)

where w(CaO),  $w(SiO_2)$ ,  $w(A1_2O_3)$ ,  $w(Fe_2O_3)$  refer to the content (mass fraction, %) of CaO, SiO<sub>2</sub>, A1<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> in the clinker.

At present, the hydraulic modulus is used in Japan, and the HM *value* is usually between 1.8 and 2.4.

#### (2) Lea and Parker lime saturation factor

According to the study of the quaternary phase diagram of CaO-A1<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>, F.M. Lea and T.W. Parker suggested that although C<sub>3</sub>S, C<sub>3</sub>A and C<sub>4</sub>AF can be formed in Portland cement clinker, the maximum allowable lime content should not be determined directly according to these mineral compositions. Because the clinker cannot achieve equilibrium cooling during the actual cooling process, it is possible to precipitate f-CaO in the uncombined lime in clinker. So, it is necessary to limit the lime content to a lower value. Accordingly, they proposed the lime saturation factor (LSF).

In order to facilitate the derivation of the formula, first, the influence of the cooling process on the clinker composition of the  $CaO-C_2S-C_{12}A_7$  system is discussed. The phase transition of clinker in the  $CaO-C_3S-C_3A$  ternary system during cooling process is shown in Figure 2.4.



Figure 2.4: The Portland cement area of CaO-C<sub>2</sub>S-C<sub>12</sub>A<sub>7</sub> system.

Point *D* is the reaction point of the CaO–C<sub>3</sub>S–C<sub>3</sub>A ternary system. When the liquid phase is cooled to this point, the CaO in the solid phase is sunk back to precipitate C<sub>3</sub>S and C<sub>3</sub>A. Original components *K* and L are on each side of the C<sub>3</sub>S–*D* line. They are heated to firing temperature 1,500 °C to be balanced and then cooled.

When the composition *K* is heated to 1,500 °C, the liquid phase composition is the crossover point *P* of 1,500 °C isotherm in  $C_3S$  initial phase area and  $CaO-C_3S$ boundary *HD*. The solid phase composition is the crossover *Q* of the *PK* extension line and the CaO-C<sub>3</sub>S line. Solid phase *Q* consists of  $C_3S$  and CaO. When cooled, the liquid phase *P* was moved to *D*. At point *D*, CaO was sunk back to precipitate  $C_3S$  and  $C_3A$ . As the reaction proceeds, the product layer that the CaO pass through becomes thicker continuously, and the resistance becomes stronger. Only when the cooling process is very slow, it is then possible to sink back the CaO entirely. Otherwise, CaO residue must be there.

When the composition *L* is heated to 1,500 °C, the solid phase composition is  $C_3S$ , liquid phase composition is crossover point *V* of  $C_3S-L$  extension line and 1,500 °C isotherm. At this point, no matter how the cooling process is, there will be no CaO residue.

Therefore, the maximum lime content cannot exceed the  $C_3S-D$  line to ensure that there is no f-CaO in clinker in CaO- $C_2S-C_{12}A_7$  system.

The clinker phases variation in the CaO-C<sub>2</sub>S-C<sub>12</sub>A<sub>7</sub>-C<sub>4</sub>AF quaternary system during the cooling process is shown in Figure 2.5.



Figure 2.5: The maximum lime content in clinker of CaO-C<sub>2</sub>S-C<sub>12</sub>A<sub>7</sub>-C<sub>4</sub>AF system.

Based on the same mechanism, in order to ensure there is no f-CaO, the maximum lime content should not exceed the  $C_3S-D-C_4AF$  plane. The equation of the plane can be written by the composition of  $C_3S$ , *D* and  $C_4AF$ . The components of  $C_3S$ , *D* and  $C_4AF$  are given in Table 2.1.

Composition	Components (mass fraction, %)					
point	<i>w</i> (CaO)	w(A1 <sub>2</sub> 0 <sub>3</sub> )	<i>w</i> (SiO <sub>2</sub> )	<i>w</i> (Fe <sub>2</sub> O <sub>3</sub> )		
C₃S	73.6	0	26.4	0		
D	59.7	32.8	7.5	0		
C <sub>4</sub> AF	46.1	21.0	0	32.9		

Table 2.1:	The	components	of	points	C <sub>3</sub> S	. D	and	C <sub>4</sub> AF.
		00111001100	•••	0011100		, -	~	Q4

The determinant of the plane equation is written from the contents of  $Al_2O_3$ ,  $SiO_2$  and  $Fe_2O_3$  (mass fraction, %) from the three points:

$$\begin{vmatrix} w(Al_2O_3) & w(SiO_2) - 26.4 & w(Fe_2O_3) \\ 32.8 & 7.5 - 26.4 & 0 \\ 21.0 & 0 - 26.4 & 32.9 \end{vmatrix} = 0$$
(2.8)

Formula (2.8) can be rewritten as

$$3.78w(SiO_2) + 2.18w(Al_2O_3) + 1.65w(Fe_2O_3) = 100$$
 (2.9)

According to the quaternary system, this can be further written as

$$w(CaO) + w(SiO_2) + w(Al_2O_3) + w(Fe_2O_3) = 100$$
 (2.10)

From formulas (2.9) and (2.10), the maximum lime content in  $CaO-C_2S-C_{12}A_7-C_4AF$  system yields

$$w(CaO) = 2.78w(SiO_2) + 1.18w(Al_2O_3) + 0.65w(Fe_2O_3)$$
 (2.11)

The ratio of actual lime content to the maximum lime content in clinker is the Lea and Parker LSF:

$$LSF = \frac{100w(CaO)}{2.78w(SiO_2) + 1.18w(Al_2O_3) + 0.65w(Fe_2O_3)}$$
(2.12)

The LSF of Portland cement clinker usually fluctuates between 85 and 95, which is mostly used by the European and American countries at present.

#### 2.2.2.2 Silica modulus

The silica modulus is the abbreviation of the silica/oxygen ratio (also called silica modulus), which indicates the ratio of the percentage of  $SiO_2$  to the percentage of  $Al_2O_3$  and  $Fe_2O_3$  in clinker, abbreviated as SM (in Russian: *n*):

$$SM = \frac{w(SiO_2)}{w(Al_2O_3) + w(Fe_2O_3)}$$
(2.13)

The SM in Portland cement clinker is usually between 1.7 and 2.7. But the SM of white Portland cement can be up to 4.0 or even higher. In addition to reflecting the ratio of  $SiO_2$  content to that of  $Al_2O_3$  and  $Fe_2O_3$ , SM also indicates the ratio of silicate minerals to fluxing minerals in the clinker, which reflects the quality and burnability of the clinker. SM varies with the ratio of silicate minerals to fluxing minerals. If SM in the clinker is too high, the calcination of clinker is difficult and it would be difficult to form  $C_3S$  because at high temperatures, liquid phase decreases significantly. If the content of CaO is low, the content of  $C_2S$  would be too much, and the clinker would be easily pulverized. If the SM is too low, strength of clinker would decrease because of less silicate minerals, and due to the excessive liquid phase, the material lump, ring and furnace accretion would be easy to appear which will affect the operation of the kiln.

#### 2.2.2.3 Alumina modulus

Alumina modulus is short for alumina ratio (also called iron modulus, IM), which represents the mass ratio of  $Al_2O_3$  and  $Fe_2O_3$  in the clinker. It can be abbreviated as IM (in Russian: *p*). The calculation formula is

$$IM = \frac{w(Al_2O_3)}{w(Fe_2O_3)}$$
(2.14)

The IM of Portland cement clinker is usually between 0.9 and 1.7. The IM of sulfateresistant Portland cement or low heat cement can be as low as 0.7. IM indicates the ratio of the content of  $Al_2O_3$  to  $Fe_2O_3$  in clinker, which also suggests the proportional relationship between  $C_3S$  and  $C_4AF$ . IM is also related to the condensation speed of clinker and liquid phase viscosity, thus affecting the degree of difficulty in clinker calcination.

When the IM in clinker is high, the content of  $C_3A$  and the liquid phase viscosity are high. The material is difficult to calcine, so the setting time of cement is short. But when the IM is low, the liquid phase viscosity is low and the particles in the liquid phase are easy to diffuse, which is beneficial to form  $C_3S$ . When the sintering range is narrow, the material lump is easy to be formed in kiln, which affects the operation of kiln.

At present, KH, SM and aluminum modulus (IM) are used in China. In order to calcine smoothly, ensure the quality of clinker and stability of mineral composition. The three modulus values should be chosen by the raw materials, fuel and equipment and other details in the factory. The three values should be coordinated with each other properly. A certain modulus value cannot be individually emphasized. In general, three rate values cannot be both high and low at the same time.

#### 2.2.3 Calculation and conversion of mineral composition of clinker

The mineral composition of clinker can be determined by petrographic analysis and X-ray quantitative analysis. It can also be calculated according to the chemical composition. However, the calculated values based on chemical composition are theoretically possible minerals, which are called "potential minerals." In the case of stable production conditions, the true mineral composition of clinker has a certain correlation with the calculated mineral composition, which is able to indicate the effect of mineral composition on clinker and cement performance. Hence, it is still widely used in China.

The petrographic analysis is based on the percentage of each mineral in the unit area measured under a microscope, and then their percentage multiplies by the density of the corresponding minerals to obtain each mineral content. The calculation of mineral density is shown in Table 2.2.

Mineral	C₃S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Glass	MgO
Density (g/cm³)	3.13	3.28	3.00	3.77	3.00	3.58

Table 2.2: The density of mineral used for calculation.

The results of this mineral determination method are more consistent with the actual situation, but when the mineral crystals are smaller, the errors may result from overlapping.

X-ray analysis is based on the ratio of the characteristic peak intensity of each mineral in the clinker and the characteristic peak intensity of the single mineral to obtain its content. This method has less error, but when the content is too low, the measurement is not accurate. The error of infrared spectral analysis is relatively small. Quantitative analysis of clinker minerals can also be performed by electron probe analyses, X-ray spectrum analyses and so on.

#### 2.2.3.1 The method of KH

To calculate conveniently, first, the ratio of relative molecular mass is listed:

C<sub>3</sub>S: 
$$\frac{M_{\rm r}({\rm C}_3{\rm S})}{M_{\rm r}({\rm CaO})} = 4.07;$$
 C<sub>2</sub>S =  $\frac{M_{\rm r}({\rm CaO})}{M_{\rm r}({\rm SiO}_2)} = 1.87;$  C<sub>4</sub>AF:  $\frac{M_{\rm r}({\rm C}_4{\rm AF})}{M_{\rm r}({\rm Fe}_2{\rm O}_3)} = 3.04;$   
C<sub>3</sub>S:  $\frac{M_{\rm r}({\rm C}_3{\rm A})}{M_{\rm r}({\rm Al}_2{\rm O}_3)} = 2.65;$  CaSO<sub>4</sub>;  $\frac{M_{\rm r}({\rm CaSO}_4)}{M_{\rm r}({\rm SO}_3)} = 1.7;$   $\frac{M_{\rm r}({\rm Al}_2{\rm O}_3)}{M_{\rm r}({\rm Fe}_2{\rm O}_3)} = 0.64$ 

The content of CaO for the reaction with  $SiO_2$  is set as  $C_s$ , and the content of  $SiO_2$  for the reaction with CaO is set as  $S_c$ , then:

$$C_{\rm s} = w ({\rm CaO}) - [1.65w ({\rm Al}_2{\rm O}_3) + 0.35w ({\rm Fe}_2{\rm O}_3) + 0.75w ({\rm SO}_3)]$$
  
= 2.8KH • S<sub>c</sub> (2.15)

$$S_{\rm c} = w({\rm SiO}_2) \tag{2.16}$$

In the case of general calcination, first, CaO and SiO<sub>2</sub> react to form C<sub>2</sub>S, and the remaining CaO reacts with the partial C<sub>2</sub>S to produce C<sub>3</sub>S. The content of C<sub>3</sub>S can be calculated from the remaining CaO content ( $C_s$  – 1.87 $S_c$ ):

$$w(C_3S) = 4.07 (C_s - 1.87S_c)$$
  
= 4.07C<sub>s</sub> - 7.06S<sub>c</sub>  
= 4.07 (2.8KH • S<sub>c</sub> - 7.60S<sub>c</sub>)  
= 3.8 (3KH - 2) w(SiO\_2) (2.17)

Because

$$C_{\rm s} + S_{\rm c} = w (C_3 S) + w (C_2 S)$$
 (2.18)

Therefore,

$$w(C_2S) = C_s + S_c - w (C_3S) = C_s + S_c - (4.07C_s - 7.60S_c)$$
  
= 8.60S<sub>c</sub> - 3.07C<sub>s</sub> = 8.60S<sub>c</sub> - 3.07 (2.8KH - S<sub>c</sub>) (2.19)  
= 8.60 (1 - H) w (SiO<sub>2</sub>)

When the C<sub>3</sub>A content is calculated, the content of  $Al_2O_3$  [0.64w(Fe<sub>2</sub>O<sub>3</sub>)] consumed by the formation of C<sub>4</sub>AF should be deducted from the total content of  $Al_2O_3$ , and C<sub>3</sub>A content can be calculated from the remaining  $Al_2O_3$  [w(Al<sub>2</sub>O<sub>3</sub>) – 0.64w(Fe<sub>2</sub>O<sub>3</sub>)]:

$$w(C_3A) = 2.65 [w(Al_2O_3) - 0.64w(Fe_2O_3)]$$
(2.20)

where  $0.64w(Fe_2O_3)$  refers to the content of  $Al_2O_3$  consumed by the formation of  $C_4AF$ :

 $0.64 - \text{the ratio} \frac{M_r(\text{Al}_2\text{O}_3)}{M_r(\text{Fe}_2\text{O}_3)} = 0.64.$ 

According to  $\frac{M_r(C_4AF)}{M_r(Fe_2O_3)}$  = 3.04, the content of C<sub>4</sub>AF can be calculated:

$$w(C_4AF) = 3.04M_r(Fe_2O_3)$$
 (2.21)

The content of CaSO<sub>4</sub> can be calculated from the SO<sub>3</sub> content:

$$w(CaSO_4) = 1.71 w (SO_3)$$
 (2.22)

Similarly, the clinker mineral composition can be calculated when IM < 0.64:

$$w(C_3S) = 3.8 (3KH - 2) w(SiO_2)$$
 (2.23)

$$w(C_2S) = 8.60 (1 - KH) w(SiO_2)$$
 (2.24)

$$w(C_4AF) = 4.766 w(Al_2O_3)$$
 (2.25)

$$w(C_2F) = 1.70w(Fe_2O_3) - 2.666 w(Al_2O_3)$$
 (2.26)

$$w(CaSO_4) = 1.70 \ w(SO_3)$$
 (2.27)

#### 2.2.3.2 The Bogue method

The R.H. Bogue method is also called the algebraic method. It is based on the material balance. First, the formula between clinker chemical composition, mineral composition and clinker modulus value is listed from the simultaneous equations, and then solve the equations. The calculation formula of clinker mineral composition can be done. In fact, as long as a set of data among the clinker chemical composition, modulus values and mineral composition are known, the other two sets of the data can be calculated. That is to say, the three can be converted into each other.

# (1) When the clinker mineral composition is known, calculate the chemical component of clinker

The content of each mineral and oxide in the clinker is represented as  $w(C_3S)$ ,  $w(C_2S)$ ,  $w(C_3A)$ ,  $w(C_4AF)$ ,  $w(C_2F)$ ,  $w(CaSO_4)$  and w(CaO),  $w(SiO_2)$ ,  $w(Al_2O_3)$ ,  $w(Fe_2O_3)$ ,  $w(SO_3)$ , respectively. The chemical composition (mass fraction, %) of the five minerals and CaSO<sub>4</sub> is shown in Table 2.3.

Oxides	C₃S	C <sub>2</sub> S	C₃A	C <sub>4</sub> AF	C <sub>2</sub> F	CaSO <sub>4</sub>
CaO	73.69	65.12	62.27	46.16	41.26	41.19
SiO <sub>2</sub>	26.31	34.88				
Al <sub>2</sub> O <sub>3</sub>			37.73	20.98		
Fe <sub>2</sub> O <sub>3</sub>				32.86	58.74	
S0 <sub>3</sub>						58.81

Table 2.3: The chemical composition of the five minerals and CaSO<sub>4</sub> (mass fraction, %).

According to the data shown in Table 2.3, the following formula of each oxide in clinker can be calculated:

When IM  $\ge$  0.64:

$$w(CaO) = 0.7369w(C_3S) + 0.6512w(C_2S) + 0.6227w(C_3A) + 0.4616w(C_4AF) + 0.4119w(CaSO_4)$$
(2.28)

$$w(SiO_2) = 0.2361w(C_3S) + 0.3488w(C_2S)$$
(2.29)

$$w(Al_2O_3) = 0.3773w(C_3A) + 0.2098w(C_4AF)$$
(2.30)

$$w(Fe_2O_3) = 0.3286w(C_4AF)$$
 (2.31)

$$w(SO_3) = 0.5881w(CaSO_4)$$
 (2.32)

When IM < 0.64:

$$w(CaO) = 0.7369w(C_3S) + 0.6512w(C_2S) + 0.4616w(C_4AF) + 0.4126w(C_2F) + 0.4119w(CaSO_4)$$
(2.33)

$$w(SiO_2) = 0.2631w(C_3S) + 0.3488w(C_2S)$$
 (2.34)

$$w(Al_2O_3) = 0.2098w(C_4AF)$$
 (2.35)

$$w(Fe_2O_3) = 0.3286w(C_4AF) + 0.5874w(C_2F)$$
(2.36)

$$w(SO_3) = 0.5881w(CaSO_4)$$
 (2.37)

# (2) When the chemical component is known, calculate the mineral composition of clinker

Solve the equation set of formulas (2.28)-(2.32) and equation set of formulas (2.33)-(2.37), the percentage of each mineral is calculated as follows:

When IM  $\ge$  0.64:

$$w(C_3S) = 4.07w(CaO) - 7.5986 w(SiO_2) - 6.7171w(Al_2O_3) - 1.4286 w(Fe_2O_3) - 2.8506w(SO_3)$$
(2.38)

$$w(C_2S) = 8.5986 w(SiO_2) + 5.0667 w(Al_2O_3) + 1.0776 w(Fe_2O_3)$$

$$(2.39)$$

$$-3.07W(CaO) + 2.1502W(SO_3)$$

$$w(C_3A) = 2.6504w(Al_2O_3) - 1.6922w(Fe_2O_3)$$
(2.40)

$$w(C_4AF) = 3.0432w(Fe_2O_3)$$
 (2.41)

$$w(CaSO_4) = 1.7004w(SO_3)$$
 (2.42)

When IM < 0.64:

$$w(C_3S) = 4.07w(CaO) - 7.5986 w(SiO_2) - 4.4769 w(Al_2O_3) - 2.8588 w(Fe_2O_3) - 2.8506 w(SO_3)$$
(2.43)

$$w(C_2S) = 8.5986 w(SiO_2) + 3.3769 w(Al_2O_3) + 2.1564 w(Fe_2O_3) - 3.07 w(CaO) + 2.1502 w(SO_3)$$
(2.44)

$$w(C_4AF) = 4.7662 w(Al_2O_3)$$
 (2.45)

$$w(C_2F) = 1.7024w(Fe_2O_3) - 2.6663w(Al_2O_3)$$
 (2.46)

$$w(CaSO_4) = 1.7004w(SO_3)$$
 (2.47)

# (3) When the clinker mineral composition is known, calculate the modulus values of clinker

(i) When the clinker minerals consist of C<sub>3</sub>S, C<sub>2</sub>S, C<sub>3</sub>A, C<sub>4</sub>AF and CaSO<sub>4</sub>:

$$KH = \frac{w(C_3S) + 0.8837w(C_2S)}{w(C_3S) + 1.3256w(C_2S)}$$
(2.48)  
837w(C\_2S) = 1.3572w(f = C\_2O) = 0.9507w(SO\_2)

$$\mathrm{KH}^{-} = \frac{w(\mathrm{C}_{3}\mathrm{S}) + 0.8837w(\mathrm{C}_{2}\mathrm{S}) - 1.3572w(\mathrm{f} - \mathrm{CaO}) - 0.9507w(\mathrm{SO}_{3})}{w(\mathrm{C}_{3}\mathrm{S}) + 1.3256w(\mathrm{C}_{2}\mathrm{S}) - 3.8w(\mathrm{f} - \mathrm{SiO}_{2})}$$
(2.49)

$$SM = \frac{w(C_3S) + 1.325w(C_2S)}{1.434w(C_3A) + 2.046w(C_4AF)}$$
(2.50)

$$IM = \frac{1.15w(C_3A)}{w(C_4AF)} + 0.64$$
(2.51)

$$LST = \frac{73.69w(C_3S) + 65.12w(C_2S) + 62.27w(C_3A) + 46.16w(C_4AF) + 41.19w(CaSO_4)}{0.7367w(C_3S) + 0.9766w(C_2S) + 0.4452w(C_3A) + 0.4612w(C_4AF)}$$
(2.52)

$$HM = \frac{0.7369w(C_3S) + 0.6512w(C_2S) + 0.6227w(C_3A) + 0.4616w(C_4AF) + 0.4119w(CaSO_4)}{0.2631w(C_3S) + 0.3488w(C_2S) + 0.3773w(C_3A) + 0.5384w(C_4AF)}$$
(2.53)

(ii) When the clinker minerals consist of C<sub>3</sub>S, C<sub>2</sub>S, C<sub>2</sub>F, C<sub>4</sub>AF and CaSO<sub>4</sub>:

$$KH = \frac{w(C_3S) + 0.8837w(C_2S)}{w(C_3S) + 1.3256w(C_2S)}$$
(2.54)

$$KH^{-} = \frac{w(C_3S) + 0.8837w(C_2S) - 1.3572w(f - CaO) - 0.9507w(SO_3)}{w(C_3S) + 1.3256w(C_2S) - 3.8w(f - SiO_2)}$$
(2.55)

$$SM = \frac{0.2631w(C_3S) + 0.3488w(C_2S)}{0.5384w(C_4AF) + 0.5874w(C_2F)}$$
(2.56)

$$IM = \frac{0.2098w(C_4AF)}{0.3286w(C_4AF) + 0.5874w(C_2F)}$$
(2.57)

$$LST = \frac{73.69w(C_3S) + 65.12w(C_2S) + 46.12w(C_4AF) + 41.26w(C_4F) + 41.19w(CaSO_4)}{0.7367w(C_3S) + 0.9766w(C_2S) + 0.4612w(C_4AF) + 0.3818w(C_4F)}$$
(2.58)

$$HM = \frac{0.7369w(C_3S) + 0.6512w(C_2S) + 0.4616w(C_4AF) + 0.4126w(C_2F) + 0.4119w(CaSO_4)}{0.2631w(C_3S) + 0.3488w(C_2S) + 0.5834w(C_4AF) + 0.5874w(C_2F)}$$
(2.59)

- (4) When the modulus values of clinker are known, calculate the chemical component of clinker
- (i) When KH, SM, IM of clinker are known, calculate the mineral composition and chemical component:

$$w(Fe_2O_3) = \frac{\sum}{(2.8KH+1) (IM+1) SM + 2.65IM + 1.35}$$
(2.60)

$$w(Al_2O_3) = IM \cdot w(Fe_2O_3)$$
(2.61)

$$w(SiO_2) = SM \cdot [w(Al_2O_3) + w(Fe_2O_3)]$$
 (2.62)

$$w(CaO) = \Sigma - [w(SiO_2) + w(Al_2O_3) + w(Fe_2O_3)]$$
(2.63)

In the formulas,  $\Sigma$  represents the estimated value of total content of the four main oxides of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaO (97–99%).

(ii) When LSF, SM and IM of clinker are known, calculate the mineral composition and chemical component:

$$w(Fe_2O_3) = \frac{100\Sigma}{2.8LST \cdot SM(IM+1) + 1.18LST \cdot IM + 0.65LST + 100 (SM+1)(IM+1)}$$
(2.64)