

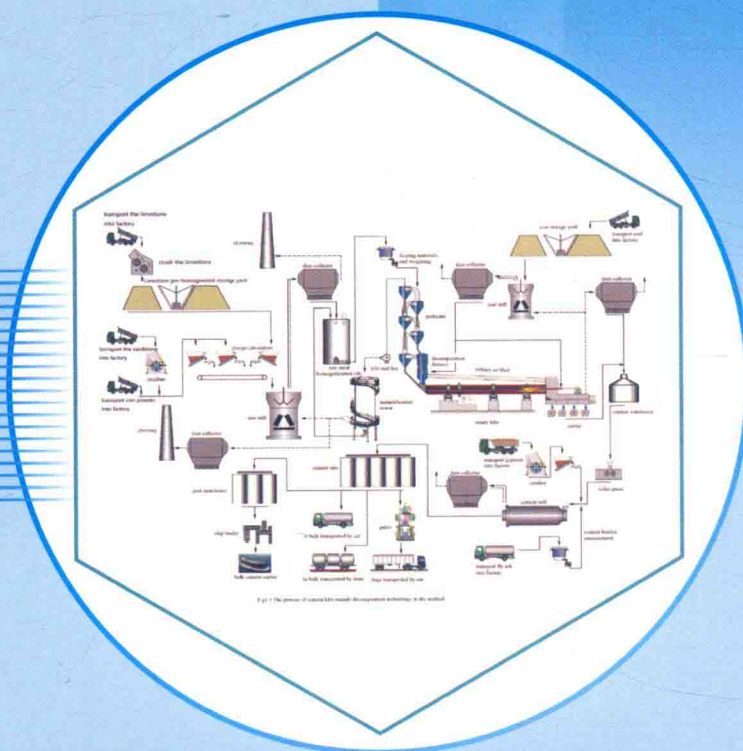
General Colleges and Universities
Materials Science and Engineering Discipline
Planning Textbook

Cementitious Material Science

Editor in chief: Lin Zongshou

Associate editor: Xing Weihong Chen Wei

Reviser in chief: Shui Zhonghe



Wuhan University of Technology Press

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Second Edition

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【Synopsis】

The book of *Cementitious Materials Science* is a disciplinary textbook for undergraduates in the division of materials science and engineering in colleges and universities. It can be used as an undergraduate teaching book for majors in inorganic nonmetallic materials, building materials and products.

The relationship between the composition, structure and properties of various cementitious materials, especially, ordinary Portland cement, is expounded in this book. Hydration and hardening mechanisms of cementitious materials and the way to improve structure and properties of hardened materials are introduced. The production and application technologies of gypsum, lime and magnesia cementitious materials, as well as the composition and characteristics of blending materials are also introduced in details.

Except as a textbook for high education, this book can also be used as a reference for scientific research, design and engineering technicians engaged in the construction and building materials industry.

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Preface

Cementitious Materials Science was firstly 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 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 for many times later. In 2014, the textbook of "Cementitious Materials Science" was updated by Professor Lin Zongshou in contents of each chapter according to the requirements of the teaching program for the major of cementitious materials, including the latest national standards and research results, and 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 Zongshou.

The chapters of this edition "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; and the relationships among the structure, properties and application conditions of hardened cementitious materials, etc. However, the production equipments 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 in 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 hoped that readers should not apply the data in the book mechanically in the actual work, but apply the basic principles and laws in the book according to the actual situation, and solve practical problems through further experiments. Please 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 Professor Lin compiles the *Preface*, *Introduction* and Chapters of 1 and 2;

Associate Professor Xing Weihong works as subeditor, and compiles Chapters of 3, 4 and 5;

Professor Chen Wei is subeditor, and compiles Chapter 6.

The English translation of this book is implemented as follows:

Dr. Yu Rui translates the *Preface*, *Introduction* and Sections of 1.1 to 1.5;

Dr. Liu Zhichao translates Sections of 1.6.1 to 1.6.3, 1.7.6 to 1.7.12 and *Problems* of Chapter 1;

Dr. Rao Meijuan translates Sections of 1.6.5.7 to 1.6.5.8 and Chapter 5;

Dr. Hu Chuanlin translates Sections of 1.6.4 to 1.6.5.6 and 1.7.1 to 1.7.5;

Dr. Liu Yunpeng translates Sections of 2.1 to 2.3;

Dr. Yang Lu translates Sections of 2.4 to 2.10 and *Problems* of Chapter 2;

Dr. Jian Shouwei translates Chapter 3;

Associate Professor Xing Weihong translates Chapter 4;

Professor Chen Wei translates Chapter 6 and *References*.

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

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Dr. Rao Meiju proofreads Sections of 1.4 to 1.5;

Dr. Yu Rui proofreads Sections of 1.6.1 to 1.6.3, 1.6.5.7 to 1.6.5.8 and 1.7.6 to 1.7.12, and *Problems* of Chapter 1;

Associate Professor Xing Weihong proofreads Sections of 1.6.4 to 1.6.5.6 and 1.7.1 to 1.7.5, Chapter 2, and Chapter 3;

Dr. Liu Yunpeng proofreads Chapter 4;

Dr. Jian Shouwei proofreads Chapter 5, Chapter 6 and *References*.

The book is refereed by Professor Shui Zhonghe. The editor wants to express his sincere appreciation for the hard work made by English translators and the careful review made by chief referee. Thanks for the great effort of De Gruyter Press in improving the quality of the textbook. In addition, the editor also wants to express 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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0 Introduction

0.1 Definition and Classification of Cementitious Materials

Based on the physical and chemical effects, in the process of the gradual transformation of the plastic slurry into 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 non-hydraulic types, according to 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 non-hydraulic 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.

According to 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, and sulphoaluminate that mostly produce calcium sulphoaluminate hydrate, and so on. In addition, there are also some other classification methods.

0.2 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 great amount of attentions.

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 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, etc. Based on the points mentioned above, a large category of new composite materials could be developed;
- (6) Beneficial for reusing industrial wastes.

The application of cementitious materials has 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 new technology revolution and varietal development with the rapid growth of science and technology. Simultaneously, its application areas will also be boarded, which could further strengthen its key role in the national economy.

0.3 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, gypsum-lime, 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 3000 BC to 2000 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 building constructions. 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 dissolving it with water firstly, mixing it with sand, and then building the structures with mortar. Some of the ancient Roman architecture, which was built with lime mortar, was very strong and even remains 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 was. In the areas without volcanic ash, it was replaced by the ground brick, which had the same effect with 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 "Roman mortar".

The development of Chinese construction cementitious materials is unique and historical. As early as 5000 BC to 3000 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 16th century BC, Shang Dynasty, the cave buildings 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. But, the yellow mud and yellow mud mixed with grasses as cementitious materials were utilized until modern society.

In the 7th 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 cause that it has been widely used in Chinese history for a long period.

In the 5th 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" and the three component mortar (Roman mortar). After tamping, 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 by 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 18th 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 19th 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 firstly 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 called Portland cement originally. 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 20th Century, various cements of different application were gradually produced. In the recent half a century, sulphoaluminate cement, fluoroaluminate cement, aluminoferrite cement and other types of cement were successively developed, which promote the 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 field and development speed. Nowadays, cementitious materials have entered a stage of vigorous development.

0.4 The Development of Cementitious Materials Science

In the broad field of productive and scientific practice for cementitious materials, a lot of knowledge has been accumulated, especially with the formation and development of materials science, new and profound changes are being taken 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 internal structure. Thus, this provides a theoretical basis for developing new varieties of cementitious materials and expanding their application areas;

(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 the future, no natural resources should be used for the production of cementitious materials, while various industrial solid wastes should 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 and great improvement.

1 Common Portland Cement

Normally, the cement can be defined as a hydraulic cementitious powder material that if 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 kinds of cement, based on their application purpose and property. Three general types can be divided: 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 with special purposes, such as Oil Well Cement, Masonry Cement, etc. Characteristic cement is a kind of cement that exhibits one unique performance, such as High Early Strength Portland Cement, Sulfate-resistant Portland Cement, Moderate Heat Portland Cement, Sulphoaluminate Expansive Cement, Self-stressing Aluminate Cement and so on.

According to the main hydraulic minerals, cement can be classified as silicate cement, aluminate cement, sulfoaluminate cement, fluoaluminate cement, and the cement produced from industry solid waste and local materials. At present, there are more than 100 different kinds of cements.

1.1 The Invention and Production of Cement

1.1.1 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 can not 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 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 in 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. A 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 dry substance was calcined in the limekiln at a certain temperature for complete the volatilization of CO_2 in the material. Finally, the calcined product presents 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_2 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, so it was named "Portland cement".

The "Portland cement" manufacturing method described in the patent certificate of Aspdin is similar as 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.

In Britain, another cement research genius at the same time as Aspdin 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: Firstly, the temperature of the kiln must be high enough to ensure that the calcined bulk contains a certain amount of dark green glass. Secondly, 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, which was established by the Chinese in 1889, it 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", "foreign ash" and etc. The name "Cement" was firstly used by "Hubei cement factory" that located in Huangshi harbor, Daye county, Hubei province. which was the predecessor of Huaxin cement co., LTD. It was built in May 2nd, 1909, and was capable to produce cement with 180 ~ 200 t/d.

1.1.2 The Process of Cement

According to the raw materials' preparation methods, the process of cement production can be divided into two categories, the dry method and the wet method. When the raw materials are dried and crushed into raw material powder, and then added into the kiln clinker, this way is called dry method. 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 way is called semidry method, it also can be classified as dry method. When raw materials with water are ground into slurry, then add into the rotary kiln, this way is called wet method.

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, the continuous advance of drying and grinding equipment improved the clinker quality. Hot air of cooler was used for kiln outside 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 in the cooler was successfully used to regenerate power, which cause that the waste heat was fully utilized. About nearly a decade, with the further optimization of new dry process production technology, the further reduce 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