Introduction

Cement is the material of the 20th century, a century-old material. The Scottish inventor Joseph Aspdin obtained a patent in 1824 for the production of a binder made from a mixture of lime and clay, which he called "Portland cement" because its hardened appearance resembled the limestone of the Portland Peninsula. This was the first cement, the ancestor of a long lineage. Thus, the 20th century paved the way for artificial cements, which gradually replaced lime. This acceleration became more evident after World War II when the construction sector focused primarily on producing new housing made from prefabricated elements, no longer using lime.

1. Raw materials

1.1. Calcareous materials

1.1.1. Lime stone

The production of lime begins with the calcination of limestone ($CaCO_3$) in a rotary or vertical kiln. In this process, the limestone is heated to high temperatures, typically ranging from 900°C to 1000°C. A simple chemical reaction occurs, leading to the decomposition of limestone or calcium carbonate ($CaCO_3$) into calcium oxide (CaO) and carbon dioxide (CO_2). Carbon dioxide is released as a gas, while calcium oxide remains in the kiln in the form of quick lime (CaO).

$$CaCO_3 \xrightarrow{\text{Chaleur}} CaO + CO_2$$

1.1.2. Types of Lime : There are two main types of lime used in industry :

a. Quicklime (CaO)

Quicklime is the primary product of the calcination process, and it is characterized by its chemically active properties, making it suitable for various uses, such as in cement production, where it helps bind other materials like clay and limestone. Quicklime is also used in the removal of impurities from metals and in glass manufacturing.

b. Hydrated lime ($Ca(OH)_2$

Hydrated lime is produced by adding water to quicklime, where a chemical reaction occurs that absorbs the water and converts quicklime into calcium hydroxide ($Ca(OH)_2$). Hydrated lime is used in other fields such as water treatment and gas purification. It has less chemical activity than quicklime, making it suitable for these applications.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

1.2. Argillaceous material

Argillaceous materials are natural substances that primarily contain clay minerals such as kaolinite, illite, or montmorillonite. These materials are used in cement production as a major source of silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3). These oxides enhance the properties of cement, such as strength and durability. Common argillaceous materials used in cement production include natural clay, shale, and claystone.

1.3. Gypsum

Gypsum is a soft sulfate mineral composed of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$). It is widely used in construction materials, especially in the production of cement. Gypsum is added to Portland cement to control the setting and prevent excessively rapid hardening. Gypsum is obtained by transforming gypsum rocks under specific conditions.

1.3.1. Production of gypsum

a. Extraction and treatment of gypsum

- The production process of gypsum plaster begins with the extraction of raw gypsum from mines or quarries.
- The extracted gypsum is then crushed and ground into a fine powder to facilitate further processing.
- Impurities such as sand and clay can be removed through separation and purification processes to ensure high-quality gypsum.

b. Transformation process

- After processing the raw gypsum, it is heated at specific temperatures (around 120-180°C) in special kilns to remove part of the water contained in its chemical structure.
- This heating process produces gypsum plaster ($CaSO_4 \cdot ½H_2O$), known as "semi-hydrated gypsum" or "Plaster of Paris," which is the primary material used in construction.
- When mixed with water, gypsum plaster reacts quickly to reform hydrated calcium sulfate ($CaSO_4 \cdot 2H_2O$) and hardens within minutes, making it ideal for quick applications.

c. Quality control

- The gypsum plaster manufacturing process undergoes strict monitoring to ensure the final product meets construction standards.
- The fineness of particles, setting time, and strength of the final product are carefully controlled.

2. Cement

Cement is a hydraulic binding material made from three main raw materials: calcium carbonate found in limestone, silica found in clay and sand, and alumina (aluminum oxide). It is a finely ground inorganic substance that, when mixed with water, forms a dark-colored material with adhesive and cohesive properties. These properties enable it to effectively bind concrete components and ensure strong adhesion with reinforcement steel.

2.1. Types of Cement

There are many types of cement, each with specific properties suited to particular applications. However, their basic components remain the same, with variations in their proportions from one type to another. The most common types include :

- Ordinary Portland Cement (OPC)
- Rapid Hardening Cement

• Low Heat Portland Cement
• Sulfate-Resisting Cement
• White Cement
• Pozzolanic Cement

3.3. Chemical composition of cement

Cement is composed primarily of four key compounds, each playing a vital role in the setting and hardening process :

3.3.1. Calcium Oxide (CaO)

- Makes up about 60-67% of the cement weight.
- Extracted from limestone.
- Reacts with silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) to form the main compounds that provide the cement with its strength and hardness.

3.3.2. Silicon Dioxide (SiO_2)

- Makes up about 17-25% of the cement composition.
- Extracted from clay or sand.
- Contributes to the formation of silicate compounds, which give the cement its hardness and durability.

3.3.3. Aluminum Oxide (Al_2O_3)

- Makes up about 3-8% of the cement composition.
- Extracted from clay or bauxite.
- Increases the rate of setting and contributes to the cement's heat resistance.

3.3.4. Iron Oxide (Fe_2O_3)

- Makes up about 0.5-6% of the composition.
- Responsible for giving cement its characteristic gray color.
- Helps balance the chemical reactions during the manufacturing process.

3.3.5. Magnesium Oxide (MgO)

- Makes up less than 5% of the cement composition.
- Although it is a minor component, its increase beyond a certain limit may lead to expansion and cracking of concrete.

3.3.6. Calcium Sulfate ($CaSO_4$)

- Typically added as gypsum during the cement manufacturing process.
- Helps slow down the initial setting of cement and aids in controlling the working time.

3.3.7. Alkalis (K_2O and Na_2O)

- Present in very small amounts in cement.

- Excessive alkali content can lead to harmful reactions with certain concrete components, such as alkali-aggregate reactions, which can cause long-term deterioration of concrete quality.

4. Portland cement

Portland cement is the most widely used cement in construction. It takes its name from Portland stone, a highly valued limestone building material found on the Isle of Portland in England. Portland cement is manufactured by heating a mixture of limestone and clay in a rotary kiln at extremely high temperatures (around 1450°C) to produce **"clinker,"** an intermediate material that is then ground with gypsum to produce the final cement product.

4.1. Properties of Portland Cement

a. **Strength** : Portland cement has high compressive strength in a short period of time, making it suitable for projects that require quick strength development.
b. **Long-Term Durability** : Although it sets quickly, it retains its strength and durability over time, making it ideal for long-lasting construction.
c. **Reaction with Water** : When cement is mixed with water, a chemical reaction known as "hydration" occurs, producing calcium hydroxide and calcium silicate salts. These compounds are responsible for providing cement with its strength and toughness over time.

4.2. Production of Portland Cement

The process of producing portland cement involves several key stages, starting with the extraction of raw materials and ending with the production of ready-to-use cement. Here are the main stages :

4.2.1. Extraction of raw materials

Cement production relies on key raw materials : limestone provides calcium oxide (CaO) for the basic structure, clay supplies silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) to enhance strength and hardness, while gypsum (containing calcium sulfate, $CaSO_4{\cdot}2H_2O$) controls the setting time during manufacturing.

4.2.2. Preparation of raw materials

The raw materials are extracted from various quarries and then processed by grinding to produce a fine powder. Lime stone and clay are mixed in specific proportions according to a precise chemical composition.

4.2.3. Grinding and mixing

After extracting the raw materials, they are finely ground in mills to obtain a very fine powder. These materials are then mixed together to achieve a homogeneous blend.

4.2.4. Calcining in a rotary kiln

The raw materials are heated to high temperatures, reaching up to **1450°C** in the hottest section, facilitating the formation of essential clinker compound.

4.2.5. Cooling the resulting clinker

Air is blown over the hot clinker to reduce its temperature to around 100°C. to stabilize the chemical compounds formed during calcination, such as C_3S, C_2S, C_3A, and C_4AF.

4.2.6. Mixing clinker with gypsum

After cooling the clinker, it is mixed with a small amount of gypsum (calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$) before the final grinding process. Typically, 3-5% of gypsum is added to the clinker. Gypsum slows down the hydration reaction of tricalcium aluminate (C_3A), thus preventing the immediate setting of the cement.

4.2.7. Milling

This process involves grinding the materials into a fine powder using large steel balls or cylindrical rollers inside a rotating drum to produce a uniform and fine cement powder with a specific particle size. This ensures an ideal setting time, high strength, and durability when mixed with water.

4.2.8. Storage

The finely ground cement powder is transported to **storage silos**. These large, cylindrical containers protect the cement from moisture and contamination, ensuring its quality remains intact until it is ready for distribution

4.2.9 Bagging

The final stage of cement production involves **bagging** the cement into standardized packaging, typically in **25 kg** or **50 kg** bags, though bulk packaging for industrial uses is also common.

4.3. Clinker Constituents

C_4AF (Ferrite) : $4CaO + Al_2O_3 + Fe_2O_3 = 4CaO.Al_2O_3.Fe_2O_3$

C_3A (Aluminate) : $3CaO + Al_2O_3 = 3CaO.Al_2O_3$

C_2S (Belite) : $2CaO + SiO_2 = 2CaO.SiO_2$

C_3S (Alite) : $2CaO.SiO_2 + CaO = 3CaO.SiO_2$

The table bellow presents the chemical compounds in Portland Cement, their percentage ranges, and their effects on cement properties.

Compound	Range (%)	Effect on Cement Properties
C_3S (Tricalcium Silicate)	45% - 65%	Responsible for rapid setting and early strength development. Higher content increases setting speed and early concrete strength.
C_2S (Dicalcium Silicate)	15% - 35%	Improves long-term strength as it reacts slowly compared to C_3S, enhancing durability and resistance over time.
C_3A (Tricalcium Aluminate)	5% - 15%	Increases setting speed but reduces resistance to sulfates, making it unsuitable for sulfate-rich environments.
C_4AF (Tetracalcium Aluminoferrite)	5% - 15%	Has minimal impact on strength but affects cement color and improves some physical properties.

Be attention

Clinker = (Calcareous + Argillaceous) Materials

Cement = (Clinker + Gypsum) 2/3

Gypsum is used for retardation of setting of Cement

4.4. Bogue Equations in Cement

Bogue Equations are used to calculate the mineral composition of Portland cement based on the percentage of key oxides (CaO, SiO_2, Al_2O_3, Fe_2O_3). These are approximate estimates to determine the percentage of the main mineral components in clinker, which affect cement properties such as initial and final strength, and setting. The percentage of each compound is calculated using the following equations (weight percentages).

Alite (C_3S) = 4.071 (CaO) – 7.600 (SiO_2) – 6.718 (Al_2O_3) – 1.430 (Fe_2O_3) – 2.852 (SO_3)
Belite (C_2S) = 2.867 (SiO_2) – 0.754 (C_3S)
Aluminate (C_3A) = 2.650 (Al_2O_3) – 1.692 (Fe_2O_3)
Ferrite(C_4AF) = 3.043 (Fe_2O_3)

Example

If we have the following chemical composition for Ordinary Portland Cement, using the Bogue equations, calculate the main mineral compound. What do you conclude ?

CaO (64.5%) ; SiO_2 (21.0%) ; Al_2O_3 (5.5%) ; Fe_2O_3 (3.0%) ; SO_3 (2.5%)

Correction

4.5.Hardening and Strength of Portland Cement

4.5.1. Hardening

Hardening refers to the process that Portland cement undergoes after water is added, where it transforms from a soft paste into a solid material over time. This process occurs due to chemical reactions between the cement compounds and water, and it is known as the **hydration process**.

a. Stages of Hardening

- **Initial Reaction Phase** : This begins when cement is mixed with water, during which heat is released due to hydration reactions.
- **Initial Hardening Phase** : During this phase, the cement becomes more cohesive but has not yet reached its final strength.
- **Final Hardening Phase** : Hydration reactions continue for a long period, and the cement gradually hardens over the days and weeks.

b. Factors Affecting Hardening

- **Water-to-Cement Ratio (W/C Ratio)** : The higher the water content, the lower the strength of the hardened cement.
- **Temperature** : Higher temperatures accelerate the hydration process.
- **Type of Cement** : Some types of cement harden faster than others (e.g., rapid-hardening cement).
- **Interaction with Other Materials** : The presence of additives or oxides can influence the hardening process.

4.5.2. Tensile Strength

Tensile strength refers to the ability of cement to withstand tensile forces (i.e., forces that attempt to pull the material apart). Although Portland cement has high compressive strength, its tensile strength is relatively weak compared to reinforced concrete. Tensile strength is measured through indirect tensile testing, specifically the splitting test, on cylindrical or cubic samples. Tensile strength can be improved by adding fibers to the concrete mix (such as fiberglass or metal fibers) to enhance tensile resistance, or by using reinforced concrete where steel bars bear the tensile stresses.

Factors Affecting Tensile Strength

- **Type of Cement** : Some mineral additives improve tensile strength.
- **Setting Time** : The longer the setting time, the higher the tensile strength.
- **Water-to-Cement Ratio** : It affects the density and voids within the material, influencing its tensile strength.

5. Heat of Hydration of Cement

The heat of hydration refers to the heat generated by the chemical reaction between cement and water. When water is mixed with cement, a series of chemical reactions occur between the water and the clinker's main compounds, including alite (**C_3S**), belite (**C_2S**), tricalcium aluminate (**C_3A**), and tetracalcium aluminoferrite (**C_4AF**). These reactions lead to the formation of compounds such as calcium silicate hydrate (**C-S-H**), which plays a key role in enhancing the hardness and mechanical resistance of concrete. While this reaction is essential for the hardening of concrete, it can also cause issues such as thermal stresses and cracking, particularly in large concrete structures.

5.1. Factors affecting heat of hydration

1. **Type of Cement** : Ordinary Portland Cement (CEM I) generates higher heat of hydration compared to low-heat cements (CEM III/B or CEM IV).
2. **Chemical Composition** : An increase in the content of C_3S and C_3A leads to higher heat of hydration.
3. **Water-to-Cement Ratio (W/C Ratio)** : The lower the ratio, the faster the hydration process, leading to higher heat generation.
4. **Ambient Temperature** : As the ambient temperature increases, the rate of reaction accelerates, resulting in higher heat of hydration.
5. **Size and Shape of the Concrete Element** : In large structures such as dams and deep foundations, heat can accumulate, leading to cracks.

5.2. Stages of heat generation during hydration

1. **Initial Stage (0 - 15 minutes)** : Water is absorbed, with low heat release.
2. **Dormant Stage (15 minutes - 4 hours)** : There is minimal heat release, allowing the concrete to be transported and poured.
3. **Acceleration Stage (4 - 12 hours)** : Heat rises rapidly due to the reaction of C_3S and the formation of C-S-H gel.
4. **Deceleration Stage (12 - 24 hours)** : The rate of reaction gradually decreases, but heat continues to be released.
5. **Final Hardening Stage (Days to Weeks)** : Hydration continues at a slower rate.

6. Special cement

Special cement is a type of cement developed with specific formulations to meet particular requirements under certain environmental or structural conditions. These types of cement may include sulfate-resistant cement, low-heat cement, rapid-hardening cement, white cement, pozzolanic cement, heat-resistant cement, and waterproof cement.