Chapter 4: Cement – Chemical Composition, Hydration, and Physical Tests

Introduction

Cement is the most essential binding material used in the construction industry. It acts as a glue in concrete, binding aggregates together and giving strength to the structure. The performance of cement depends significantly on its chemical composition and the physical characteristics it acquires through hydration. Understanding these factors is crucial for engineers, as they directly influence workability, durability, setting time, and long-term strength of concrete structures.

4.1 Chemical Composition of Cement

Ordinary Portland Cement (OPC), the most commonly used type of cement, is primarily composed of the following major compounds, which are produced during the manufacturing process:

4.1.1 Major Compounds in Cement (Bogue's Compounds)

Compound	Name	Chemical Formula	Typical % by weight
C_3S	Tricalcium silicate	$3CaO \cdot SiO_2$	45–60%
C_2S	Dicalcium silicate	$2CaO \cdot SiO_2$	15–30%
C_3A	Tricalcium aluminate	$3CaO \cdot Al_2O_3$	6–12%
C_4AF	Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	6–10%

C_3S – Tricalcium Silicate

- Responsible for early strength (1 to 7 days).
- Reacts quickly with water, releasing a significant amount of heat (exothermic).

- Contributes to the initial setting and early hardening.

C_2S – Dicalcium Silicate

- Contributes to strength beyond 7 days.
- Reacts slowly with water, releasing less heat.
- Important for long-term strength and durability.

C_3A – Tricalcium Aluminate

- Reacts quickly with water and is responsible for the initial setting.
- Generates a lot of heat.
- Prone to sulfate attack; hence, regulated in sulfate-resistant cements.

C_4AF – Tetracalcium Aluminoferrite

- Influences the color of cement (gives greyish hue).
- Has a minor role in strength development.
- Low heat of hydration.

4.1.2 Minor Constituents in Cement

These include:

- **Magnesium oxide (MgO)** – Should be <5%; excess leads to expansion.
- **Sulfur trioxide (SO_3)** – Controls setting; excessive SO_3 can cause soundness issues.
- **Alkalis (Na_2O, K_2O)** – Affects durability and risk of alkali-aggregate reaction (AAR).

4.2 Hydration of Cement

Hydration is the chemical reaction between cement and water that results in the formation of a hardened mass. It is an exothermic process and is the key to strength development.

4.2.1 Stages of Hydration

1. **Initial Hydrolysis:**
    - Upon contact with water, cement compounds begin to dissolve.
    - C_3A reacts rapidly unless gypsum is added to control flash setting.
2. **Induction or Dormant Period:**
    - Reaction slows down.

   - Concrete remains plastic and workable for about 2–4 hours.
   - Ideal time for mixing, transporting, and placing.
3. **Acceleration Period:**
   - C_3S and C_2S react to form calcium silicate hydrate (C–S–H) and calcium hydroxide ($Ca(OH)_2$).
   - Initial set occurs; heat evolution increases.
4. **Deceleration and Steady-State Period:**
   - Hydration continues at a slower pace.
   - Strength development continues for months, primarily due to C_2S.

4.2.2 Hydration Products

Calcium Silicate Hydrate (C–S–H):

- Main product of hydration.
- Provides most of the strength.
- Amorphous in nature, forms a dense gel.

Calcium Hydroxide ($Ca(OH)_2$):

- Also known as lime.
- Does not contribute to strength.
- Makes the concrete alkaline (pH ~12.5), which helps prevent corrosion of steel.

Ettringite:

- Formed from the reaction between C_3A and gypsum.
- Controls the setting time.
- Excess ettringite later can lead to expansion (delayed ettringite formation).

4.2.3 Heat of Hydration

- The exothermic nature of hydration releases heat.
- Heat is more in cements with higher C_3A and C_3S.
- Important to monitor in mass concreting to avoid thermal cracks.

4.3 Physical Tests on Cement

To ensure the suitability of cement for construction, several physical tests are conducted as per **IS: 4031** standards. These tests evaluate properties like fineness, setting time, soundness, strength, and consistency.

4.3.1 Fineness Test

- Measures the particle size of cement.
- Finer cement has more surface area for hydration.
- Conducted by:
    - **Sieve Test** using 90 µm sieve.
    - **Air Permeability Test (Blaine's Apparatus)**.
- Fineness affects rate of hydration and strength development.

4.3.2 Standard Consistency Test

- Determines the amount of water required to form a paste of standard consistency.
- Conducted using the **Vicat apparatus**.
- Standard consistency: 26–33% water by weight.
- Important to determine water requirement for setting time and soundness tests.

4.3.3 Setting Time Test

- Determines the time cement takes to set after adding water.
- **Initial Setting Time:** Not less than 30 minutes.
- **Final Setting Time:** Not more than 600 minutes.
- Done using **Vicat apparatus**.
- Influenced by temperature, fineness, and composition.

4.3.4 Soundness Test

- Checks the volume stability (expansion) after setting.
- **Excessive expansion** causes cracking.
- Conducted using:
    - **Le-Chatelier apparatus**.
    - **Autoclave test** for high precision.
- Sound cement should not expand more than 10 mm.

4.3.5 Compressive Strength Test

- Most important strength test.
- Done on **cement mortar cubes (1:3 ratio with standard sand)**.

- Cured and tested at 3, 7, and 28 days.
- Minimum 28-day strength for OPC (33 grade): 33 MPa.

4.3.6 Specific Gravity Test

- Indicates density and helps calculate mix proportions.
- Standard value for OPC: **3.15**.
- Measured using a **Le Chatelier flask**.

4.3.7 Heat of Hydration Test

- Important in mass concrete applications.
- Determines total heat evolved during hydration.
- Conducted using **calorimeters** under controlled conditions.

4.4 Storage and Handling of Cement

Cement is a hygroscopic material, meaning it easily absorbs moisture from the atmosphere. Improper storage can lead to lump formation, loss of strength, and setting issues. Hence, proper storage and handling are critical.

4.4.1 Storage Guidelines

- Store in **airtight silos or moisture-proof bags**.
- Keep bags **away from walls and off the floor** (minimum 150 mm).
- Stack no more than **10 bags high** to prevent lumping due to pressure.
- Use the **First-In-First-Out (FIFO)** principle.
- Avoid storing for more than **3 months**, as strength reduces over time.

4.4.2 Effects of Prolonged Storage

- Reduction in early strength.
- Delay in setting time.
- Increased risk of soundness failure.
- Hydration may start even in bags under humid conditions.

4.5 Deterioration Mechanisms in Cement-Based Materials

Understanding potential degradation mechanisms helps engineers prevent long-term damage and select appropriate cement types.

4.5.1 Sulfate Attack

- External sulfates from soil or groundwater react with C_3A, forming **ettringite**, which causes expansion and cracking.
- **Use low-C_3A or sulfate-resistant cement** in such conditions.

4.5.2 Alkali-Aggregate Reaction (AAR)

- Reaction between alkalis (Na_2O, K_2O) in cement and reactive silica in aggregates.
- Forms **gel** that expands and causes cracking.
- Prevent by using **low-alkali cement** or non-reactive aggregates.

4.5.3 Carbonation

- Atmospheric CO_2 reacts with $Ca(OH)_2$ to form $CaCO_3$.
- **Lowers pH**, potentially leading to **corrosion of steel** in reinforced concrete.
- Use of dense, well-cured concrete reduces carbonation.

4.6 Special and Advanced Tests on Cement

In addition to conventional tests, modern construction may require more specialized testing for quality control or research.

4.6.1 X-ray Diffraction (XRD)

- Identifies crystalline phases in cement.
- Helps in quality assurance and detecting adulteration.

4.6.2 Scanning Electron Microscopy (SEM)

- Examines microstructure of hydrated products like C–S–H.
- Useful in studying deterioration, porosity, and failure causes.

4.6.3 Differential Thermal Analysis (DTA)

- Monitors heat changes during chemical reactions in cement.
- Helps understand hydration kinetics.

4.6.4 Isothermal Calorimetry

- Measures heat evolution in real time during hydration.
- Useful for analyzing admixture compatibility and early-age performance.

4.7 Types of Cement (as per Composition and Application)

Different types of cement are available to suit specific environmental and structural requirements.

4.7.1 Ordinary Portland Cement (OPC)

- Available in grades 33, 43, and 53 based on compressive strength (in MPa at 28 days).
- Used in general construction work.

4.7.2 Portland Pozzolana Cement (PPC)

- Contains fly ash or calcined clay as pozzolanic material.
- Offers better workability, long-term strength, and sulfate resistance.
- Suitable for marine and sewage structures.

4.7.3 Portland Slag Cement (PSC)

- Contains granulated blast furnace slag.
- Has low heat of hydration and high sulfate resistance.
- Ideal for mass concreting and coastal structures.

4.7.4 Rapid Hardening Cement

- Higher C_3S content.
- Achieves early strength in 3 days equivalent to 7-day OPC strength.
- Used in road repairs and precast works.

4.7.5 Low Heat Cement

- Lower C_3A and C_3S, higher C_2S.
- Generates less heat during hydration.
- Suitable for large dams and mass concreting.

4.7.6 Sulfate Resisting Cement

- Low C_3A content (<5%).
- Minimizes ettringite formation.
- Used in structures exposed to high sulfate environments.

4.7.7 White Cement

- Made from raw materials low in iron and manganese.
- Used for architectural finishes, tile grouting, and decorative works.

4.7.8 Hydrophobic Cement

- Contains water-repellent additives (soap, acidol).
- Resists moisture absorption during storage.
- Suitable for remote or long-term storage.

4.8 International Standards and Codes for Cement

Cement production and testing are regulated by national and international standards to ensure quality and performance.

Standard Body	Code	Scope
Bureau of Indian Standards (BIS)	IS: 269, IS: 1489, IS: 455, etc.	Covers OPC, PPC, PSC, white cement, etc.
American Society for Testing and Materials (ASTM)	ASTM C150, C595	Specifies chemical and physical requirements for various cements.
British Standards (BS EN)	BS EN 197-1	Standardizes European cement types and compositions.
ISO	ISO 679	Provides methods for testing compressive strength.