Chapter 2: Cement Chemistry

Introduction

Cement is the binding material that holds concrete together. Understanding cement chemistry is crucial for civil engineers, as it governs the strength, durability, setting time, and performance of concrete. This chapter delves into the chemical composition of cement, its hydration process, the role of various compounds, and how modifications in chemistry can tailor the cement to specific engineering needs.

2.1 Chemical Composition of Cement

Ordinary Portland Cement (OPC), the most commonly used cement in concrete technology, is manufactured by calcining a mixture of calcareous and argillaceous materials at high temperatures (around 1450°C). The resulting product is called **clinker**, which is then ground with a small amount of gypsum.

Major Oxides Present:

Oxide	Symbol	Typical Content (%)
Lime	CaO	60–67
Silica	SiO_2	17–25
Alumina	Al_2O_3	3–8
Iron oxide	Fe_2O_3	0.5–6
Magnesia	MgO	0.1–4
Sulphur trioxide	SO_3	1–3
Alkalis (Na_2O, K_2O)	-	0.2–1.3

Functions of Oxides:

- **CaO (Lime):** Responsible for strength gain. Excess can cause unsoundness.
- **SiO_2 (Silica):** Combines with CaO to form strength-giving C-S-H.
- **Al_2O_3 (Alumina):** Aids in quick setting and reduces clinkering temperature.
- **Fe_2O_3 (Iron oxide):** Adds hardness and contributes to color.

- **MgO:** Small amounts add strength; excess causes expansion.
- **SO_3 (Sulphur trioxide):** Controls setting time.
- **Alkalis (Na_2O, K_2O):** Affect durability and may cause efflorescence.

2.2 Major Compounds (Bogue's Compounds)

Using the oxide composition, four main compounds in cement can be identified through **Bogue's equations**:

Compound Name	Chemical Formula	Abbreviation	Typical Content (%)
Tricalcium silicate	$3CaO \cdot SiO_2$	C_3S	40–60
Dicalcium silicate	$2CaO \cdot SiO_2$	C_2S	15–35
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	C_3A	5–12
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	6–10

Role of Major Compounds:

- **C_3S (Tricalcium silicate):**
  - Fast-reacting, contributes to early strength (1–7 days).
  - Generates significant heat (heat of hydration).
- **C_2S (Dicalcium silicate):**
  - Reacts slowly.
  - Contributes to strength after 7 days and improves durability.
- **C_3A (Tricalcium aluminate):**
  - Highly reactive, controls setting time.
  - Responsible for initial flash set (controlled using gypsum).
  - Most vulnerable to sulphate attack.
- **C_4AF (Tetracalcium aluminoferrite):**
  - Minor contribution to strength.
  - Reduces clinkering temperature.

  - Imparts grey color to cement.

2.3 Heat of Hydration

Hydration is the chemical reaction between cement compounds and water. This process is **exothermic**, releasing heat, known as the **heat of hydration**.

Typical Heat Released by Compounds:

Compound	Heat of Hydration (cal/g)
C_3S	120
C_2S	62
C_3A	207
C_4AF	100

Importance:

- Helps in the setting and hardening of concrete.
- High heat is beneficial in cold weather.
- In mass concrete structures (e.g., dams), excessive heat can cause cracking.

2.4 Hydration Reactions

C_3S and C_2S Hydration:

These compounds react with water to form:

- **Calcium silicate hydrate (C-S-H):** Responsible for strength.
- **Calcium hydroxide ($Ca(OH)_2$):** Improves pH but makes concrete vulnerable to chemical attack.

Reactions:

- $C_3S + H_2O \rightarrow$ C-S-H (gel) + $Ca(OH)_2$ + Heat
- $C_2S + H_2O \rightarrow$ C-S-H (gel) + $Ca(OH)_2$ (less) + Less Heat

C_3A Hydration:

- Very fast reaction; gypsum is added to slow it down and prevent flash set.
- Forms **ettringite** (a stable product):
  - C_3A + Gypsum + Water → Ettringite ($C_6A\hat{S}_3H_{32}$)

As gypsum is consumed, ettringite can convert to **monosulphate**:

- Ettringite + C_3A → Monosulphate ($C_4A\hat{S}H_{12}$)

2.5 Role of Gypsum

Gypsum ($CaSO_4 \cdot 2H_2O$), added during the final grinding of cement clinker, plays a critical role:

- Retards the hydration of C_3A.
- Prevents flash setting.
- Ensures manageable setting time (30 min to 10 hours).
- Typically added at 3–5% by weight of cement.

2.6 Setting and Hardening of Cement

- **Setting:** Transition from fluid to rigid state (plastic to solid).
    - **Initial setting time:** When paste begins to lose plasticity (~30 min).
    - **Final setting time:** When it fully loses plasticity (~600 min).
- **Hardening:** Gain of strength due to continued hydration.
    - Strength develops over weeks and months.
    - C-S-H gel formation is key.

2.7 Fineness of Cement and Chemical Activity

- Finer cement particles increase surface area → faster hydration.
- However, too fine cement increases shrinkage and reduces workability.
- Standard test: **Blaine's Air Permeability Method**.

2.8 Unsoundness in Cement

Unsoundness refers to undesirable expansion after setting, causing cracking.

Causes:

- Free lime (uncombined CaO)
- Excess MgO

- Excess sulphates

Test:

- **Le Chatelier test** is used to detect unsoundness.

2.9 Alkali-Aggregate Reaction (AAR)

Alkalis (Na_2O and K_2O) present in cement can react with reactive silica in aggregates to form an **alkali-silica gel**, which absorbs water and expands, leading to **cracking**.

Prevention:

- Use low-alkali cement (<0.6% equivalent Na_2O).
- Use non-reactive aggregates.
- Add pozzolanic materials (e.g., fly ash).

2.10 Types of Cement Based on Chemical Composition

1. Rapid Hardening Cement:

- Higher C_3S content.
- Used where early strength is needed.

2. Low Heat Cement:

- Lower C_3A and C_3S content.
- Used in mass concreting to reduce heat.

3. Sulphate Resisting Cement:

- Very low C_3A.
- High resistance to sulphate attack.

4. Portland Pozzolana Cement (PPC):

- Contains fly ash or pozzolana.
- Reduces $Ca(OH)_2$ content, improves durability.

5. White Cement:

- Iron oxide content minimized.
- Used for architectural works.

2.6 Setting Time and Its Chemical Control

The setting time of cement is largely determined by the hydration of **C_3A and C_3S**, both of which react very quickly when mixed with water. Without chemical control (gypsum addition), these reactions can lead to **flash setting**, making the concrete unusable. The balance between these reactions is vital.

Factors Affecting Setting Time:

1. **C_3A Content:**
    - High C_3A = Faster setting.
    - Controlled using gypsum.
2. **Temperature:**
    - Higher temperatures accelerate hydration and reduce setting time.
3. **Fineness of Cement:**
    - Finer cement sets faster due to increased surface area.
4. **Water-to-Cement Ratio (w/c):**
    - Lower w/c = stiffer paste and shorter setting time.

Controlling Setting Time with Admixtures:

- **Retarders (e.g., sugar, citric acid):** Delay setting.
- **Accelerators (e.g., calcium chloride):** Speed up setting.

Note: Calcium chloride is not recommended in reinforced concrete due to the risk of corrosion.

2.7 Microstructure of Hydrated Cement Paste

The internal structure of hydrated cement paste largely determines the strength and durability of concrete.

Main Microstructural Components:

- **C-S-H gel (Calcium Silicate Hydrate):**
    - Amorphous, poorly crystalline structure.
    - High surface area, binds aggregates together.

  - Major contributor to mechanical strength.
- **$Ca(OH)_2$ (Calcium Hydroxide):**
  - Crystalline, hexagonal platelets.
  - Contributes to alkalinity (pH ~ 12.5), which protects rebar from corrosion.
  - However, it is soluble and leachable, making concrete vulnerable to chemical attack.
- **Ettringite and Monosulphate:**
  - Needle-like crystals.
  - Formation depends on sulphate content and available alumina.
- **Capillary Pores:**
  - Result from excess water in mix.
  - Large pores reduce strength and increase permeability.

2.8 Pozzolanic Reaction and Secondary Cementitious Reactions

Pozzolanic materials like fly ash, silica fume, or ground granulated blast-furnace slag (GGBFS) are commonly added to improve cement performance.

Pozzolanic Reaction:

- $Ca(OH)_2 + SiO_2$ (from pozzolana) + $H_2O \rightarrow$ C-S-H (gel)

Benefits:

- Improves long-term strength.
- Reduces permeability.
- Enhances resistance to sulphate and chloride attack.
- Consumes free lime, reducing leaching and efflorescence.

2.9 Cement Durability and Chemical Attacks

Concrete is often exposed to harsh environments, where certain compounds in cement can make it more or less resistant.

Common Chemical Attacks:

1. **Sulphate Attack:**
    - Sulphates (from soil/water) react with C_3A.
    - Leads to **expansive ettringite**, causing cracking and disintegration.
    - Use **sulphate-resisting cement** (low C_3A).
2. **Chloride Attack:**
    - Chlorides penetrate and reach reinforcement, leading to corrosion.
    - Use **low-permeability concrete** and **pozzolanic cement**.
3. **Acid Attack:**
    - Cement is not acid-resistant.
    - Acids dissolve $Ca(OH)_2$ and C-S-H.
    - Use protective coatings in industrial settings.
4. **Carbonation:**
    - CO_2 reacts with $Ca(OH)_2 \rightarrow CaCO_3$
    - Lowers pH, initiating rebar corrosion.
    - Slower in dense concrete; cover depth matters.

2.10 Advances in Cement Chemistry

1. Blended Cements:

- **Portland Slag Cement (PSC):** GGBFS blended for better durability.
- **Portland Pozzolana Cement (PPC):** Fly ash improves long-term performance.
- **Ternary Blends:** Cement + Fly ash + Silica fume/GGBFS.

2. Nano-Cement and Nano-Additives:

- Addition of nano-silica enhances:
    - Early strength.
    - Pore refinement.
    - Resistance to microcracking.

3. Eco-Friendly Cements:

- **Geopolymer Cement:**

  - No limestone used.
  - Based on alkali-activated materials like fly ash or slag.
  - Nearly zero CO_2 emissions.
- **LC3 Cement (Limestone Calcined Clay Cement):**
  - Reduced clinker content.
  - Reduces carbon footprint by ~40%.

2.11 Quality Control Tests for Cement Chemistry

1. Chemical Tests:

- **Loss on ignition:** Detects unburnt materials or moisture.
- **Insoluble residue:** Measures non-reactive particles.
- **Sulphur content (SO_3):** Assessed for regulating C_3A hydration.
- **Free lime test:** Ensures soundness.

2. Physical Tests Related to Chemistry:

- **Fineness (Blaine's method):** Related to hydration rate.
- **Setting Time (Vicat apparatus):** Affected by gypsum and C_3A.
- **Heat of Hydration:** Measured using calorimetry.
- **Soundness Test (Le Chatelier method):** Detects free lime or MgO expansion.