Cements – Composition, Types

- Finish up cement manufacture
- Properties of component phases
- Types of cements

- Chapter 2 – Properties of Concrete – Neville
- Chapter 6 – Concrete….Mehta and Monteiro
Summary of Kiln Reactions

4 Main Zones

Gas Temp.  450  800  1200  1350  1550 °C
Feed Temp.  50  600  1000  1350  1450 °C

After Mindess and Young Figure 3.2
CLINKER

- Clinker is what comes out of the kiln
- 3 to 25 mm in diameter
- 20-25% Molten
Compound Composition of Clinker / Cement

- Four major compounds formed from the oxides under high temperature in the kiln
  - **Name (Oxide Notation) - Shorthand**
  - Tricalcium silicate (3 CaO. SiO$_2$) – $\text{C}_3\text{S}$
  - Dicalcium silicate (2 CaO. SiO$_2$) – $\text{C}_2\text{S}$
  - Tricalcium aluminate (3 CaO. Al$_2$O$_3$) – $\text{C}_3\text{A}$
  - Tetracalcium aluminoferrite (4 CaO. Al$_2$O$_3$. Fe$_2$O$_3$) – $\text{C}_4\text{AF}$
### Summary of Cement Compounds

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Shorthand</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate (Alite)</td>
<td>3 CaO. SiO$_2$</td>
<td>C$_3$S</td>
<td>~55-60</td>
</tr>
<tr>
<td>Dicalcium silicate (Belite)</td>
<td>2 CaO. SiO$_2$</td>
<td>C$_2$S</td>
<td>~15-20</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>3 CaO. Al$_2$O$_3$</td>
<td>C$_3$A</td>
<td>~5-10</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite</td>
<td>4 CaO. Al$_2$O$_3$. Fe$_2$O$_3$</td>
<td>C$_4$AF</td>
<td>~5-8</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO$_4$. 2H$_2$O</td>
<td>CSH$_2$</td>
<td>~2-6</td>
</tr>
</tbody>
</table>
Implications of compound composition

- Determines the physical and mechanical characteristics of the cement
- Determines its chemical activity
- Determines its scope of use
- Determines the cost
Contributions of Compounds to Strength

- $C_3S$ contributes to high early strength – to make high early strength concrete, higher $C_3S$ proportions needed
- $C_2S$ contributes to later age strength – defines the long term strength
- $C_3A$ reacts immediately with water – defines set
- In the absence of gypsum, $C_3A$ causes flash set
Compressive strength development of pure cement compounds

- $C_3A$ reacts instantaneously
- Final strength determined by $C_3S$ and $C_2S$
- Increase $C_3S$ for high early strength
Making Life Harder - I

- Remember the compound name, oxide notation, and the shorthand notation...
- Just to make sure that cement and concrete is complicated, tricalcium silicate in its impure form in clinker is historically called **Alite**
- Even more complication arises – various crystalline polymorphs of tricalcium silicates exist
- Similar troubles for other compounds also
Not all cement components can be expressed by the oxide formulae and shorthand notation

- Chlorides, Fluorides etc
- Expressed using normal chemical formulae

Mineral names are commonly used for raw materials (calcite, quartz) and for some cement hydration products (ettringite, portlandite etc)
Beware of “LIME”

- Be clear what you mean when you say “Lime”
  - “Lime” can be used for CaO, either by itself or in combination with other components
  - “Lime” can be used for Calcium hydroxide (also called portlandite, abbreviated as CH)
  - “Lime” is sometimes used for limestone rock or its major chemical component calcium carbonate
Manufacturing control criteria in the Kiln

- Silica Modulus (SM) : 2.3 to 3.5 (desired at least 3.0), slow reaction if SM is high
- Alumina Modulus (AM): ~2, controls melt temp
- Lime Saturation factor (LSF): 0.92-0.96
  - Designed to insure against equilibrium free lime

\[
SM = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}
\]
\[
AM = \frac{Al_2O_3}{Fe_2O_3}
\]
\[
LSF = \frac{CaO}{2.2SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3}
\]
Bogue’s Equations – Compound composition

- To calculate the amounts of $C_3S$, $C_2S$, $C_3A$, and $C_4AF$ in clinker (or the cement) from its chemical analysis (from the mill certificate)

- Assumptions in calculations
  - Chemical equilibrium established at the clinkering temperature
  - Components maintained unchanged through the rapid cooling period
  - Compounds are “pure”
Bogue’s Equations

- Case 1 : $A/F \geq 0.64$
  - $C_3S = 4.071C - 7.6S - 6.718A - 1.43F - 2.852S$
  - $C_2S = 2.867S - 0.7544C_3S$
  - $C_3A = 2.65A - 1.692F$
  - $C_4AF = 3.043F$
Bogue’s Equations

Case 2 : A/F < 0.64

- \( C_3S = 4.071C - 7.6S - 4.479A - 2.859F - 2.852S \)
- \( C_2S = 2.867S - 0.7544C_3S \)
- \( C_3A = 0 \)
- \( C_4AF = 2.10A + 1.702F \)
Clinker components and Temperature
Summary of Kiln Reactions

Exhaust Gases → Raw Feed → Free Water Decomposes → Clay Decomposes → Limestone Decomposes → Initial Formation of C₂S → Formation of Melt → Formation of C₃S → Clinker Out

4 Main Zones

Dehydration Zone → Calcination Zone → Clinkering Zone → Cooling Zone

Gas Temp. 450 800 1200 1350 1550 °C
Feed Temp. 50 600 1000 1350 1450 °C

After Mindess and Young Figure 3.2
Clinker Microstructure

Dark, Rounded – $\text{C}_2\text{S}$

$\text{C}_3\text{S}$ crystals magnified 3000 times

Light, Angular – $\text{C}_3\text{S}$
Schematic of a Grinding Mill
Grinding Mill

Loud Process

Fineness Influences Performance
Fineness of cement

- Grinding is the last step in processing
- Measures of fineness
  - Specific surface
  - Particle size distribution
- Blaine’s fineness
  - Measure of air permeability
- Typical surface areas
  - ~ 350 m² / kg (Normal cements)
  - ~ 500 m² / kg (High early strength cements)
PSD of cement

ciks.cbt.nist.gov/~garbocz/nistir6931/node29.htm
Significance of fineness

- Finer cement = Faster reaction
- Finer cement = Higher heat of hydration
- Large particles do not react with water completely
- Higher fineness
  - Higher shrinkage
  - Reduced bleeding
  - Reduced durability
  - More gypsum needed
Summary of the Cement Making Process
Some practical issues about cement making

- Scale of the business (local / national)
- LOCATION
- Plant operations
- Wet versus Dry process
- Energy savings – Preheaters, Dust
- Energy and fuels
- Environment
The economics of cement making

- Transportation costs – when shipped further than ~ 200 miles
- About 175 plants nationwide
- Cost of maintenance – plant and the environment
- Rising fuel costs – raw material quality and fuel dependence
- Continuous operability
Portland Cement Types (ASTM C 150)

- ASTM C 150 (AASHTO M 85)
- 5 types in general – types I to V
  - **Type I** – Normal (OPC)
  - **Type II** – Moderate Sulfate Resistance
  - **Type III** – High early Strength
  - **Type IV** – Low heat of hydration
  - **Type V** – High Sulfate Resistance
- **Chemical compositions different**
Other special Types

- Not very commonly used or manufactured
- Type IA – Normal (OPC) – air entraining
- Type IIA – Moderate sulfate resistance – air entraining
- Type IIIA – High early strength – air entraining
## Typical Compositions

<table>
<thead>
<tr>
<th>ASTM Type</th>
<th>C₃S %</th>
<th>C₂S %</th>
<th>C₃A %</th>
<th>C₄AF %</th>
<th>B. Fineness Kg/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>I General Purpose</td>
<td>55</td>
<td>19</td>
<td>10</td>
<td>7</td>
<td>370</td>
</tr>
<tr>
<td>II Mod Sulfate Mod Heat</td>
<td>51</td>
<td>24</td>
<td>6</td>
<td>11</td>
<td>370</td>
</tr>
<tr>
<td>III Early Strength</td>
<td>56</td>
<td>19</td>
<td>10</td>
<td>7</td>
<td>540</td>
</tr>
<tr>
<td>IV Low Heat</td>
<td>28</td>
<td>49</td>
<td>4</td>
<td>12</td>
<td>380</td>
</tr>
<tr>
<td>V Sulfate Resistant</td>
<td>38</td>
<td>43</td>
<td>4</td>
<td>9</td>
<td>380</td>
</tr>
</tbody>
</table>
Applications of Type-I cement
Applications of Type II and IV
BE AWARE OF THIS

- Type of cement is no guarantee against other bad concreting practices
- To be durable, you have to get the basics right: the cement type is just an aid
- Water-cement ratio is key
- **Top picture** – w/c 0.69, Type V
- **Bottom picture** – w/c 0.35, Type V
Applications of Type III (High early strength)
Applications of Type IV (Low Heat)
Blended Hydraulic Cements

- ASTM C 595 (AASHTO M 240)
- Blending supplementary materials into OPC
- Improves properties *(we will see in detail how this is effected)*
- Reduces cost – materials like fly ash are waste products from other industries
- Environmental effects – concrete acts as a sink to hazardous products
Blended Cements

- Type IS – Portland blast furnace slag cement
- Type IP, Type P – Portland Pozzolan cement
- Type I(PM) – Pozzolan modified Portland cement
- Type S – slag cement
- Type I (SM) – Slag modified pozzolan cement
Other Hydraulic Cements

- ASTM C 1157 – 6 types
- Type GU – General Use
- Type HE – High early strength
- Type MS – Moderate sulfate resistance
- Type HS – High sulfate resistance
- Type LH – Low heat of hydration
- Type MH – Moderate heat of hydration