Portland cement, cement clinker and heat of hydration of cement

Rak-82.3131 Concrete technology 2
Exercise 2
Cement chemistry uses a form of notation which may seem a little strange...

Oxides are referred to by their first letter

- C represents CaO
- M is MgO and so on, for all the oxides likely to be encountered in cementitious systems.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>S</td>
</tr>
<tr>
<td>S</td>
<td>A</td>
</tr>
<tr>
<td>A</td>
<td>F</td>
</tr>
<tr>
<td>F</td>
<td>K</td>
</tr>
<tr>
<td>K</td>
<td>N</td>
</tr>
<tr>
<td>N</td>
<td>M</td>
</tr>
<tr>
<td>M</td>
<td>T</td>
</tr>
<tr>
<td>T</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>=</td>
</tr>
</tbody>
</table>

C=CaO₂
S=SiO₂
A=Al₂O₃
F=Fe₂O₃
K=K₂O
N=Na₂O
M=MgO
T=TiO₂
H=H₂O
and
S=SO₃
C=CO₂
This is done because it shortens what are otherwise very long names.

- **Alite:** Ca$_3$SiO$_5$ in terms of its oxides is 3CaO.SiO$_2$. The CaO term is shortened to C and the SiO$_2$ to S. The compound thus becomes C$_3$S.

- **Belite:** Similarly, Ca$_2$SiO$_4$ is 2CaO.SiO$_2$, which is shortened to C$_2$S.

- **Tricalcium aluminate:** Ca$_3$Al$_2$O$_6$ is 3CaO.Al$_2$O$_3$. The Al$_2$O$_3$ term is shortened to A and the compound becomes C$_3$A.

- **Tetracalcium aluminoferrite:** 2(Ca$_2$AlFeO$_5$) is 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$. Fe$_2$O$_3$ is shortened to F and the compound becomes C$_4$AF.
Portland cement

Formation and hydration of Portland Cement

Figure from the book "Properties of Concrete", A. M. Neville. 1995. p. 12.
Chemical composition of Portland cement

<table>
<thead>
<tr>
<th>Component</th>
<th>Abbreviation</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>C</td>
<td>60-70 %</td>
</tr>
<tr>
<td>SiO₂</td>
<td>S</td>
<td>17-25 %</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>A</td>
<td>3-8 %</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>F</td>
<td>0.5-6.0 %</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td>0.1-4.0 %</td>
</tr>
<tr>
<td>Na₂O + K₂O</td>
<td></td>
<td>0.2-1.3 %</td>
</tr>
<tr>
<td>SO₃</td>
<td>☯</td>
<td>1-3 %</td>
</tr>
</tbody>
</table>

Mineral composition of Portland cement

<table>
<thead>
<tr>
<th>Name</th>
<th>Oxide composition</th>
<th>Abbreviation</th>
<th>Content, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate (Alite)</td>
<td>3CaO · SiO₂</td>
<td>C₃S</td>
<td>65 - 45 %</td>
</tr>
<tr>
<td>Dicalcium silicate (Belite)</td>
<td>2CaO · SiO₂</td>
<td>C₂S</td>
<td>30 - 10 %</td>
</tr>
<tr>
<td>Tricalcium aluminate (Celite)</td>
<td>3CaO · Al₂O₃</td>
<td>C₃A</td>
<td>15 - 5 %</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite</td>
<td>4CaO · Al₂O₃ · Fe₂</td>
<td>C₄AF</td>
<td>12 - 5 %</td>
</tr>
</tbody>
</table>

- Portland cement clinker
- Additives (GGBS, fly ash, etc.)
- Gypsum, admixtures

The mineral composition of cement can be calculated from the chemical composition.
Mineral composition of Portland cement clinker

• Clinker’s chemical analysis is normally given in oxide form (CaO, SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ & SO$_3$) in weight %
  \[
  \overline{O} = \{ \text{C, S, A, F, } \overline{S} \} \%
  \]

• From the chemical analysis, the quantity of each of the four main minerals can be calculated using the 'Bogue' calculation
  \[
  \overline{K} = \{ \text{C}_3\text{S, C}_2\text{S, C}_3\text{A, C}_4\text{AF, } \overline{C}\overline{S} \} \%
  \]
The Bogue calculation

- The Bogue calculation is used to calculate the approximate proportions of the four main minerals in Portland cement clinker.

- The standard Bogue calculation refers to cement clinker, rather than cement, but it can be adjusted for use with cement. Although the result is only approximate, the calculation is an extremely useful and widely-used calculation in the cement industry.
The Bogue calculation

\[ \bar{O} = \bar{B} \times \bar{K} \quad (1) \]

\[ \bar{K} = \bar{B}^{-1} \times \bar{O} \quad (2) \]

Clinker is made by combining lime (Ca) and silica and also lime with alumina and iron. Some of the lime will almost certainly remain uncombined, thus in order to get the best estimate of the proportions of the four main clinker minerals present the calculation is done with a so called standard/modified Bogue.
Standard/modified Bogue:

\[ C_3S \approx 4,07 \cdot \text{CaO} - 7,60 \cdot \text{SiO}_2 - 6,72 \cdot \text{Al}_2\text{O}_3 - 1,43 \cdot \text{Fe}_2\text{O}_3 - 2,85 \cdot \text{SO}_3 - 4,07 \cdot \text{CaO}_{\text{free}} \]

\[ C_2S \approx 2,87 \cdot \text{SiO}_2 - 0,754 \cdot C_3S \]

\[ C_3A \approx 2,65 \cdot \text{Al}_2\text{O}_3 - 1,69 \cdot \text{Fe}_2\text{O}_3 \]

\[ C_4AF \approx 3,04 \cdot \text{Fe}_2\text{O}_3 \]

\[ \text{CaSO}_4 \approx 1,70 \cdot \text{SO}_3 \]
Problem 1

The chemical analysis of a clinker was:
\[ \overline{O} = \{C, S, A, F, \bar{S}\} = \{64.80, 21.08, 5.25, 2.71, 2.88\} \%

Using the above analysis, calculate the amounts of the four main clinker minerals (C$_3$S, C$_2$S, C$_3$A & C$_4$AF) and CaSO$_4$.

The amount of free lime was 0.96 %.
Solution, exercise 1

- $C_3S \approx 4,07 \cdot CaO - 7,60 \cdot SiO_2 - 6,72 \cdot Al_2O_3 - 1,43 \cdot Fe_2O_3 - 2,85 \cdot SO_3 - 4,07 \cdot CaO_{free}$

- $C_2S \approx 2,87 \cdot SiO_2 - 0,754 \cdot C_3S$

- $C_3A \approx 2,65 \cdot Al_2O_3 - 1,69 \cdot Fe_2O_3$

- $C_4AF \approx 3,04 \cdot Fe_2O_3$

- $CaSO_4 \approx 1,70 \cdot SO_3$
Solution, exercise 1

\[ C_3S \approx 4,07 \times 64,8 - 7,60 \times 21,08 - 6,72 \times 5,25 - 1,43 \times 2,71 - 2,85 \times 2,88 - 4,07 \times 0,96 = 52,3\% \]

\[ C_2S \approx 2,87 \times 21,08 - 0,754 \times 52,3 = 21,1\% \]

\[ C_3A \approx 2,65 \times 5,25 - 1,69 \times 2,71 = 9,3\% \]

\[ C_4AF \approx 3,04 \times 2,71 = 8,2\% \]

\[ CaSO_4 \approx 1,70 \times 2,88 = 4,9\% \]
Problem 2

Bogue matrix is a 5x5 square matrix. What significance does the element $B(i,j)$ have? Formulate the Bogue matrix and use it to calculate the compound composition of the clinker presented above.
Bogue matrix

\[
\bar{B} = \begin{bmatrix}
\frac{3^*C}{C_3S} & \frac{2^*C}{C_2S} & \frac{3^*C}{C_3A} & \frac{4^*C}{C_4AF} & \frac{C}{CS} \\
\frac{S}{C_3S} & \frac{S}{C_2S} & 0 & 0 & 0 \\
0 & 0 & \frac{A}{C_3A} & \frac{A}{C_4AF} & 0 \\
0 & 0 & 0 & \frac{F}{C_4AF} & 0 \\
0 & 0 & 0 & 0 & \frac{\bar{S}}{CS}
\end{bmatrix}
\]

Oxides = \{\text{C, S, A, F, } \bar{S}\} \rightarrow \text{Clinker minerals} = \{\text{C}_3\text{S, C}_2\text{S, C}_3\text{A, C}_4\text{AF, C}\bar{S}\}

\[
\bar{B} = \begin{bmatrix}
\frac{3^*C}{C_3S} & \frac{2^*C}{C_2S} & \frac{3^*C}{C_3A} & \frac{4^*C}{C_4AF} & \frac{C}{CS} \\
\frac{S}{C_3S} & \frac{S}{C_2S} & 0 & 0 & 0 \\
0 & 0 & \frac{A}{C_3A} & \frac{A}{C_4AF} & 0 \\
0 & 0 & 0 & \frac{F}{C_4AF} & 0 \\
0 & 0 & 0 & 0 & \frac{\bar{S}}{CS}
\end{bmatrix}
\]
When formulating the Bogue matrix, atomic and molecular weights are needed

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>ATOMIC WEIGHTS OF THE ELEMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>40,08</td>
</tr>
<tr>
<td>Si</td>
<td>28,06</td>
</tr>
<tr>
<td>Al</td>
<td>26,97</td>
</tr>
<tr>
<td>K</td>
<td>39,10</td>
</tr>
<tr>
<td>Fe</td>
<td>55,85</td>
</tr>
<tr>
<td>O</td>
<td>16,00</td>
</tr>
<tr>
<td>S</td>
<td>32,06</td>
</tr>
<tr>
<td>Na</td>
<td>23,00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MOLECULAR WEIGHTS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>For the oxides:</td>
<td></td>
</tr>
<tr>
<td>C (CaO)</td>
<td>56,08</td>
</tr>
<tr>
<td>A (Al₂O₃)</td>
<td>101,94</td>
</tr>
<tr>
<td>S (SiO₂)</td>
<td>60,06</td>
</tr>
<tr>
<td>F (Fe₂O₃)</td>
<td>159,90</td>
</tr>
<tr>
<td>H (H₂O)</td>
<td>18,00</td>
</tr>
<tr>
<td>K (K₂O)</td>
<td>94,20</td>
</tr>
<tr>
<td>N (Na₂O)</td>
<td>62,00</td>
</tr>
</tbody>
</table>

| For the minerals  |                   |
| C₃S               | 228,30             |
| C₃A               | 270,18             |
| C₃S               | 172,22             |
| C₄AF              | 485,96             |
| C₃S               | 136,14             |
| CH                | 74,08              |
In the Bogue matrix, the element $B(i,j)$ value is:

oxides $i = \bar{O}(i)$ content in 
clinker mineral $j = \bar{K}(j)$

For example: $B(1, 1) = \begin{bmatrix}
\text{C}_3\text{S} & \text{C}_2\text{S} & 0 & 0 & \text{C}_3\text{S} \\
\text{C}_3\text{S} & \text{C}_2\text{S} & 0 & 0 & \text{C}_3\text{S} \\
0 & 0 & \text{C}_3\text{A} & 0 & \text{C}_3\text{S} \\
0 & 0 & 0 & \text{C}_3\text{A} & \text{C}_3\text{S} \\
0 & 0 & 0 & 0 & \text{C}_3\text{S} \\
\end{bmatrix}$

In which the oxide is CaO (in cement chemistry C) and the clinker mineral is $\text{C}_3\text{S}$
# ATOMIC WEIGHTS OF THE ELEMENTS

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>40.08</td>
</tr>
<tr>
<td>Si</td>
<td>28.06</td>
</tr>
<tr>
<td>Al</td>
<td>26.97</td>
</tr>
<tr>
<td>K</td>
<td>39.10</td>
</tr>
<tr>
<td>Fe</td>
<td>55.85</td>
</tr>
<tr>
<td>O</td>
<td>16.00</td>
</tr>
<tr>
<td>S</td>
<td>32.06</td>
</tr>
<tr>
<td>Na</td>
<td>23.00</td>
</tr>
</tbody>
</table>

# MOLECULAR WEIGHTS

For the oxides:

- C (CaO): 56.08
- A (Al₂O₃): 101.94
- S (SO₃): 80.06
- H (H₂O): 18.00
- F (Fe₂O₃): 159.90
- K₂O: 94.20
- Na₂O: 62.00

For the minerals:

- C₃S: 228.30
- C₃A: 270.18
- C₄AF: 485.96
- CH: 74.08
- C₃S: 172.22
- K₂S: 136.14
In the Bogue matrix, the element $B(i,j)$ value is:

oxides $i = \overline{O}(i)$ content in clinker mineral $j = \overline{K}(j)$

For example: $B(1, 1) =$

\[
\begin{bmatrix}
\frac{2+\text{C}}{\text{C}_3\text{S}} & \frac{2+\text{C}}{\text{C}_2\text{S}} & \frac{3+\text{C}}{\text{C}_3\text{A}} & \frac{4+\text{C}}{\text{C}_4\text{AF}} & \frac{\text{C}}{\text{CS}} \\
\text{C}_3\text{S} & \text{C}_2\text{S} & 0 & 0 & 0 \\
0 & \text{C}_2\text{S} & \text{C}_3\text{A} & 0 & 0 \\
0 & 0 & \text{C}_3\text{A} & \text{C}_4\text{AF} & 0 \\
0 & 0 & 0 & \text{C}_4\text{AF} & \text{CS} \\
\end{bmatrix}
\]

In which the oxide is CaO (in cement chemistry C) and the clinker mineral is $\text{C}_3\text{S}$

\[B(1,1) = \frac{3\times\text{C}}{\text{C}_3\text{S}} \approx \frac{3\times56.08}{228.3} = 0.7369\]
In a similar way the other elements can be calculated

\[
B(1,2)
\]

\[
\begin{array}{cccccc}
\text{3C} & \text{2C} & \text{3C} & \text{4C} & \text{C} \\
\text{C}_3\text{S} & \text{C}_2\text{S} & \text{C}_3\text{A} & \text{C}_4\text{AF} & \text{CS} \\
\text{C}_3\text{S} & \text{C}_2\text{S} & \text{C}_3\text{A} & \text{C}_4\text{AF} & \text{CS} \\
\text{C}_3\text{S} & \text{C}_2\text{S} & \text{C}_3\text{A} & \text{C}_4\text{AF} & \text{CS} \\
\text{C}_3\text{S} & \text{C}_2\text{S} & \text{C}_3\text{A} & \text{C}_4\text{AF} & \text{CS} \\
\end{array}
\]

In which the oxide is CaO and the clinker mineral is \( \text{C}_2\text{S} \)

\[
= \frac{2\times \text{C}}{\text{C}_2\text{S}} \approx \frac{2 \times 56.08}{172.22} = 0.6513
\]
In a similar way the other elements can be calculated

\[ B(1,2) = \frac{2 \times C}{C_2S} = \frac{2 \times 56.08}{172.22} = 0.6513 \]

\[ B(1,3) = \frac{3 \times C}{C_3A} = \frac{3 \times 56.08}{270.18} = 0.6227 \]

\[ B(1,4) = \frac{4 \times C}{C_4AF} = \frac{4 \times 56.08}{485.96} = 0.9616 \]

\[ B(1,5) = \frac{C}{C_5} = \frac{56.08}{136.14} = 0.4119 \]

\[ B(2,1) = \frac{S}{C_3S} = 0.2631 \]

\[ B(2,2) = \frac{S}{C_2S} = 0.3487 \]

**B(2,3) = B(2,4) = B(2,5) = 0**, because \( C_3A \), \( C_4AF \) and \( C_5 \) do not contain \( SiO_2 \)

- etc.

The Bogue matrix can now be written as:
When calculating the compound composition with equation (2)
\[ K = \overline{B}^{-1} \times \overline{O}, \]
the inverse of the Bogue matrix \( \overline{B} \) is needed \( (\overline{B}^{-1}) \):

\[
\overline{B}^{-1} =
\begin{bmatrix}
4,0736 & -7,6086 & -6,7231 & -1,4299 & -2,8531 \\
-3,0736 & 8,6086 & 5,0727 & 1,0789 & 2,1527 \\
0 & 0 & 2,6504 & -1,6982 & 0 \\
0 & 0 & 0 & 3,0432 & 0 \\
0 & 0 & 0 & 0 & 1,7004
\end{bmatrix}
\]
Solving problem 1 with the Bogue matrix:

Since we know the amount of free lime (CaO\textsubscript{free}) (lime that is not bound to the clinker minerals) to be 0.96%, it must be subtracted from the amount of CaO before we can use the Bogue matrix

\[ C = 64.80 - 0.96 = 63.84 \]
\[ \bar{K} = \bar{B}^{-1} \times \bar{O} = \bar{B}^{-1} \times \{63.84, 21.08, 5.25, 2.71, 2.88\} \]
\[ \rightarrow \bar{K} = \{52.3, 21.0, 9.3, 8.2, 4.9\} \]
Exercise 3.
What is the total heat of hydration of the cement presented in exercise 1? How much is the heat production at 3 and 7 days?

| C₃S  | Tricalcium silicate (alite) | Hydrates & hardens rapidly  
|      |                              | Responsible for initial set and early strength |
| C₂S  | Dicalcium silicate (belite) | Hydrates & hardens slowly  
|      |                              | Contributes to later age strength (beyond 7 days) |
| C₃A  | Tricalcium aluminate         | Liberates a large amount of heat during first few days  
|      |                              | Contributes slightly to early strength development  
|      |                              | Cements with low %-ages are more resistant to sulfates |
| C₄AF | Tetracalcium aluminoferrite (ferrite) | Reduces clinkering temperature  
|      |                              | Hydrates rapidly but contributes little to strength  
|      |                              | Colour of hydrated cement (gray) due to ferrite hydrates |
From problems 1 and 2 we know that the cement compound composition is:

- $\text{C}_3\text{S} \ 52,3 \ %$
- $\text{C}_2\text{S} \ 21,1 \ %$
- $\text{C}_3\text{A} \ 9,3 \ %$
- $\text{C}_4\text{AF} \ 8,2 \ %$

$\rightarrow$ total heat of hydration of the cement is

$$502 \ \frac{kJ}{kg} \times 0,523 + 260 \ \frac{kJ}{kg} \times 0,211 + 867 \ \frac{kJ}{kg} \times 0,093$$
$$+ 419 \ \frac{kJ}{kg} \times 0,082 = 432,4 \ \frac{kJ}{kg}$$

The amount of heat produced by the klinker minerals at the ages of 3 and 7 days:

Heat of hydration at the age of 3 days:
\[ = 335 \text{J/g} \times 0.523 + 42 \text{J/g} \times 0.211 + 711 \text{J/g} \times 0.093 + 84 \text{J/g} \times 0.082 \]
\[ = 257 \text{J/g} \]

Heat of hydration at the age of 7 days:
\[ = 377 \text{J/g} \times 0.523 + 84 \text{J/g} \times 0.211 + 753 \text{J/g} \times 0.093 + 126 \text{J/g} \times 0.082 \]
\[ = 295 \text{J/g} \]
Problem 4: Three different cement compound compositions and specific surfaces are presented below:

A \{C_3S, C_2S, C_3A, C_4AF\} = \{57.1, 20.0, 7.0, 8.6\} \%, \quad 4840 \text{ cm}^2/\text{g}

B \{C_3S, C_2S, C_3A, C_4AF\} = \{69.9, 12.7, 1.7, 10.6\} \% \quad 3050 \text{ cm}^2/\text{g}

C \{C_3S, C_2S, C_3A, C_4AF\} = \{56.2, 19.0, 8.1, 9.4\} \% \quad 3490 \text{ cm}^2/\text{g}

Connect the appropriate heat of hydration curve with the equivalent cement and justify (perustele) your answer.
With cements whose content of C₃A is typically around 5-10 %, present at these temperatures (at 50 °C) a so called C₃A peak. When the amount of gypsum is right, this peak can be seen at the beginning of the IV phase.

The amounts of C₃A in the cements A, B and C are

A: \{C₃A\} = 7,0 %  
B: \{C₃A\} = 1,7 % 
C: \{C₃A\} = 8,1 %

I: peak 
II: peak 
III: no peak

→ cement III is cement B
Outlines of cements A and B are similar. However cement A is ground finer and thus reacts more quickly.

→ cement I is cement A

A(I)   B(III)   C(II)