

CE 244 - HW1

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Question 1

Problem Statement:

Oxide composition of a portland cement is given in the following table. Calculate the compound composition of this portland cement. (hint: CaO in Bogue's equations is equal to "total CaO – free CaO").

Table 1: Chemical Composition of Portland Cement

Component	Percentage (%)
CaO	63.6
SiO ₂	20.7
Al ₂ O ₃	6.0
Fe ₂ O ₃	2.4
MgO	2.6
SO ₃	2.1
K ₂ O	0.9
Na ₂ O	0.1
Free lime	1.4

Bogue proposed a method in 1929 and some models in 1955 to quantify the composition of cement compounds [1, 2]. To develop the models including the CaO, SiO₂, Al₂O₃, and Fe₂O₃ terms denoted with C, S, A, and F, respectively, the following assumptions are used. [5]

- Fe₂O₃ reacts with Al₂O₃ and CaO to form C₄AF.
- The remaining Al₂O₃ reacts with CaO to yield C₃A.
- The remaining CaO reacts with SiO₂, forming C₂S that successively reacts with any CaO left over to give C₃S. After these reactions, eventually, the unreacted CaO remains uncombined. MgO remains essentially uncombined.

Based on these assumptions, the produced cement compounds are C₃S, C₂S, C₃A, and C₄AF. When their chemical compositions are defined, the models to calculate their amounts according to the initial raw oxides of CaO, SiO₂, Al₂O₃, and Fe₂O₃ can be derived as follows [2]:

$$\begin{aligned}
 C_3S\% &= (4.0710 \times CaO\%) - (7.6024 \times SiO_2\%) - (6.7187 \times Al_2O_3\%) - (1.4297 \times Fe_2O_3\%) \\
 C_2S\% &= -(3.0710 \times CaO\%) + (8.6024 \times SiO_2\%) + (5.0683 \times Al_2O_3\%) + (1.0785 \times Fe_2O_3\%) \\
 &= (2.8675 \times SiO_2\%) - (0.7544 \times C_3S_2) \\
 C_3A\% &= (2.6504 \times Al_2O_3\%) - (1.6920 \times Fe_2O_3\%) \\
 C_4AF\% &= (3.0432 \times Fe_2O_3\%)
 \end{aligned}$$

Calculations

Let $\Omega = \{\text{CaO}, \text{SiO}_2, \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \dots\}$ represent the set of relevant oxides in cement chemistry. Let $\mathcal{C} = \{\text{C}_3\text{S}, \text{C}_2\text{S}, \text{C}_3\text{A}, \text{C}_4\text{AF}, \dots\}$ be the set of potential major clinker phases. A raw cement composition can be represented as a vector $\mathbf{w} \in \mathbb{R}^{|\Omega|}$, where w_i is the weight percentage of oxide $i \in \Omega$. Similarly, let the clinker compound composition be represented by vector $\mathbf{c} \in \mathbb{R}^{|\mathcal{C}|}$, with c_j denoting the weight percentage of compound $j \in \mathcal{C}$. Let w'_{CaO} denote the CaO percentage after adjusting for free lime content. The raw oxide vector is modified to \mathbf{w}' , reflecting the fact that unreacted CaO does not participate in the primary clinker phase formation. Similarly, let the clinker compound composition be represented by vector $\mathbf{c} \in \mathbb{R}^{|\mathcal{C}|}$, with c_j denoting the weight percentage of compound $j \in \mathcal{C}$.

$$\begin{aligned}\text{C}_3\text{S} &= 4.071w'_{\text{CaO}} - 7.6w_{\text{SiO}_2} - 6.718w_{\text{Al}_2\text{O}_3} - 1.43w_{\text{Fe}_2\text{O}_3} - 2.852w_{\text{SO}_3} \\ &= 4.071 \times 62.2 - 7.6 \times 20.7 \dots = 46.17\%\end{aligned}$$

$$\text{C}_2\text{S} = 2.867w_{\text{SiO}_2} - 0.7544\text{C}_3\text{S} = 2.867 \times 20.7 - 0.7544 \times 46.17 = 24.52\%$$

$$\text{C}_3\text{A} = 2.65w_{\text{Al}_2\text{O}_3} = 2.65 \times 6.0 = 15.90\%$$

$$\text{C}_4\text{AF} = 3.043w_{\text{Fe}_2\text{O}_3} = 3.043 \times 2.4 = 7.30\%$$

This analytical process culminates in the compound composition of Portland cement being determined as:

$$\mathbf{c}^T = [46.17, 24.52, 15.9, 7.3]$$



$$\text{ans. } \mathbf{c}^T = [46.17, 24.52, 15.9, 7.3].$$

Question 2

Problem Statement:

Write the reactions taking place in the rotary kiln during portland cement manufacturing.

During the manufacturing of Portland cement, the raw material mixture undergoes high-temperature firing. The aforementioned procedure encompasses many chemical processes that culminate in the formation of clinker, hence influencing the attributes of the finished product. During the clinker production process, the initial ingredients undergo a progressive transformation, leading to the creation of mineral phases that ultimately constitute the essential constituents of cement. The aforesaid transformations transpire via a series of reactions that transpire within distinct temperature intervals.

A comprehensive overview of these reactions is presented in a figure graciously provided by KHD Humboldt Wedag AG. [3]

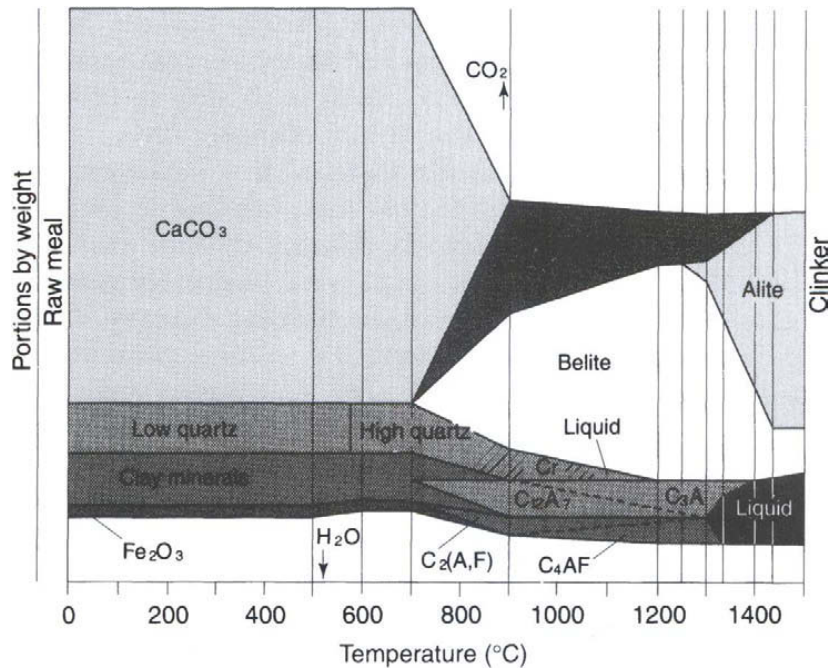


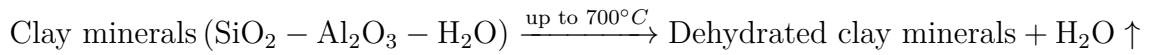
Figure 1: Reactions taking place during raw-meal burning to clinker (reproduced by courtesy of KHD Humboldt Wedag AG).

So, consider the system \mathcal{K} representing the kiln, within which a series of transformations \mathcal{T} occurs on the input raw materials $\mathcal{R} = \{\text{CaCO}_3, \text{SiO}_2, (\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}), \text{Fe}_2\text{O}_3\}$. Let $\Phi : \mathcal{R} \times \mathbb{R} \rightarrow \mathcal{C}$ denote the transformation function mapping the raw materials and temperature to the set of clinker components \mathcal{C} .

Define the function Φ as follows, within the domain of temperature T measured in degrees Celsius:

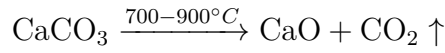
For $T \leq 700$, Φ primarily governs the dehydration of clay minerals, an endothermic reaction releasing H_2O from the clay.

$$\Phi(\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}, T) = \begin{cases} \text{Dehydrated Clay} + \text{H}_2\text{O}, & \text{if } T \leq 700 \\ \emptyset, & \text{otherwise} \end{cases}$$



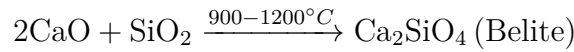
Within the interval $700 < T \leq 900$, decarbonation of CaCO_3 occurs, yielding CaO and CO_2 :

$$\Phi(\text{CaCO}_3, T) = \begin{cases} \text{CaO} + \text{CO}_2, & \text{if } 700 < T \leq 900 \\ \emptyset, & \text{otherwise} \end{cases}$$



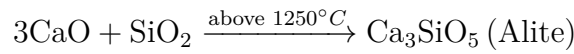
For $900 < T \leq 1200$, belite (Ca_2SiO_4) forms from CaO and SiO_2 :

$$\Phi(\text{CaO} + \text{SiO}_2, T) = \begin{cases} \text{Ca}_2\text{SiO}_4, & \text{if } 900 < T \leq 1200 \\ \emptyset, & \text{otherwise} \end{cases}$$

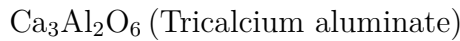


Above 1200°C , particularly evident above 1250°C , the system promotes the formation of alite (Ca_3SiO_5) through a liquid phase mechanism enabling the reaction between CaO and SiO_2 at an accelerated rate:

$$\Phi(\text{CaO} + \text{SiO}_2, T) = \begin{cases} \text{Ca}_3\text{SiO}_5, & \text{if } T > 1200 \\ \emptyset, & \text{otherwise} \end{cases}$$



For cooling and finalization, as the clinker cools, various minerals begin to crystallize out of the liquid phase, including:



Question 3

Problem Statement:

3) Write the names of the main test apparatus for the following tests on cements:

1. Fineness:
2. Soundness:
3. Setting time:
4. Normal consistency:
5. Flow:

Test	Apparatus	Standard
Fineness	Blaine Air Permeability Apparatus or Sieve Method	ASTM C204, ASTM C786 / C786M
Soundness	Le Chatelier Apparatus	ASTM C151 / C151M, EN 196-3
Setting Time	Vicat Apparatus	ASTM C191, EN 196-3
Normal Consistency	Vicat Apparatus	ASTM C187
Flow	Flow Table	ASTM C230 / C230M, EN 1015-3

Table 2: Apparatus and Standards for Cement Testing

Question 4

Problem Statement:

Prepare a table showing the chemical analysis of at least 4 pozzolans. Indicate the main differences between them.

The table below presents a comparison of different pozzolans, focusing on important features like surface area, amorphousness, and chemical composition. The analysis is backed by foundational research, particularly the study conducted by Walker and Pavía (2011) [7] regarding the physical properties and reactivity of pozzolans. Additionally, practical insights from the Concrete Countertop Institute [6] have been considered in relation to their application in concrete.

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Table 3: Comprehensive Chemical Analysis of Selected Pozzolans

Pozzolan Type	Surface Area (m ² /g)	Rate of Amorphousness	Mineralogical Composition	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	Main Differences
GGBS	2.65	Totally amorphous	No crystalline fraction	35-45	10-15	0.5-2	Extremely reactive due to its mostly amorphous form; relatively low SiO ₂ concentration as compared to alternatives.
Metastar	18.33	Mostly amorphous	Quartz, tohdite, aluminum oxide, wollastonite, paragonite	40-50	20-30	5-10	Reactivity enhanced by a large surface area; distinctive pozzolanic characteristics brought forth by complicated mineralogy.
Fly Ash	–	Variable	Primarily quartz and mullite	40-60	15-30	4-10	The composition may vary greatly depending on the coal source; the levels of alumina and silica can vary greatly as well. Improved ease of use. Increases in replacement dosages have little effect on early strength.
Silica Fume	–	Totally amorphous	Predominantly amorphous silica	85-95	0.5-4	0.1-1	The combination of a small particle size and a high SiO ₂ concentration causes concrete to be more durable and strong.

Table 3 – continued from previous page

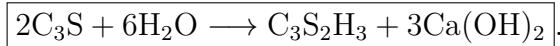
Pozzolan Type	Surface Area (m ² /g)	Rate of Amorphous-ness	Mineralogical Composition	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	Main Differences
Natural Pozzolan	–	Intermediate to slightly amorphous	Variety depending on source	50-70	15-25	3-8	Distinct variations in pozzolanic activity result from inherent heterogeneity in composition, which in turn is heavily influenced by the geological source.
Slag	3-11	Mostly amorphous	Glassy phase with minor crystalline phases	30-40	10-20	1-5	Extremely sensitive because of its glassy nature; its reactivity changes as it cools and as it changes chemically.
Metakaolin	20.00	Totally amorphous	Dehydroxylated kaolinite	50-55	40-45	0.5-2	High pozzolanic reactivity due to amorphous silica and alumina.
Leca	1.28	Variable	Predominantly amorphous with some crystalline phases	55-65	10-20	5-15	Lightweight, increased insulation properties, and moderate pozzolanic activity.
Tile	4.16	Low to intermediate	Varied crystalline phases with minor amorphous content	60-70	5-15	3-7	Because of its increased crystallinity, recycled content has low reactivity and a broad range of possible compositions.

Question 5

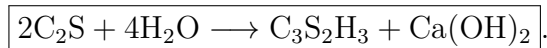
Problem Statement:

Write the hydration reactions of C_3S and C_2S .

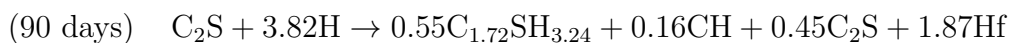
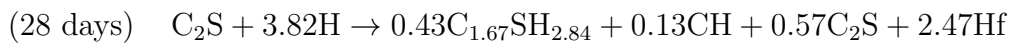
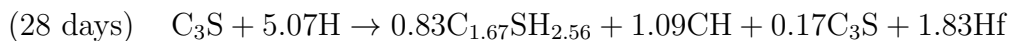
The interaction between tricalcium silicate (C_3S) and water (H_2O) triggers the hydration process,



And the hydration reaction for dicalcium silicate (C_2S) is,



Observing the stoichiometric coefficients is essential to appreciate the reaction's balance, in the study [4]



References

- [1] R.H. Bogue. "Calculation of the Compounds in Portland cement". In: *Ind. Eng. Chem.* 1 (1929), pp. 1207–1214. DOI: 10.1021/ie50340a001.
- [2] R.H. Bogue. *The Chemistry of Portland Cement*. 2nd. Washington, DC, USA: Reinhold Publishing Corporation, 1955.
- [3] P. Del Strother. "Manufacture of Portland cement". In: *Lea's Chemistry of Cement and Concrete* 1 (2019), pp. 31–56.
- [4] Sara Goñi et al. "Quantitative study of hydration of C_3S and C_2S by thermal analysis". In: *Journal of Thermal Analysis and Calorimetry* 102.3 (2010), pp. 965–973. ISSN: 1572-8943. DOI: 10.1007/s10973-010-0816-7. URL: <https://doi.org/10.1007/s10973-010-0816-7>.
- [5] S. H. Shim et al. "Calculation of Cement Composition Using a New Model Compared to the Bogue Model". In: *Materials (Basel, Switzerland)* 14.16 (2021), p. 4663. DOI: 10.3390/ma14164663. URL: <https://doi.org/10.3390/ma14164663>.

- [6] *The Use of Pozzolans in Concrete*. <https://concretecountertopinstitute.com/free-training/the-use-of-pozzolans-in-concrete/>. Accessed: insert the date here.
- [7] R. Walker and S. Pavía. “Physical properties and reactivity of pozzolans, and their influence on the properties of lime–pozzolan pastes”. In: *Materials and Structures* 44.6 (2011), pp. 1139–1150. ISSN: 1871-6873. DOI: 10.1617/s11527-010-9689-2. URL: <https://doi.org/10.1617/s11527-010-9689-2>.