

INDUSTRIAL EARTH RESOURCES

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FINAL

CHAPTER FIVE

FIRED PRODUCTS: THE NEED FOR HIGH TEMPERATURE PROCESSING

- **Industrial product is derived by** heating of raw materials alone or in appropriate proportions that transformed into a new material which has the physical & chemical properties required by the manufacturers
- **Two types of processes are involved:**
 1. **Heating to produce chemical change:** forms very reactive materials such as plaster or cement
 2. **Heating to produce chemical & physical change:** forms unreactive material under the conditions of use (e.g. refractory bricks, glass, & building bricks)
- **Firing process & energy intensive process** covering T from 150°C(plaster manufacture) to 1600°C(glass man.)
 - **The firing process** should be understood as fully as possible, so that the effect can be predicted
 - **High T processing** is carried out at atmospheric pressure, but a number of materials are produced at elevated pressures, under autoclave conditions
- The behavior of minerals at high T-P has been of interest to geologists, but a quantitative understanding of mineral phase relationships, under experimental or geological conditions (by Bowen's & Gibbs etc...)
- **Phase diagram:** is the standard way of presenting the relationship between different phases, & is a graphical illustration of stability ranges of minerals & melts as a function of P, T, & X (bulk composition)

- **Phase diagrams follows the phase rule**

$$F = C - \Phi + X$$

Number of degrees of freedom (F), Number of Phase (Φ), Number of Components (C), & Number of Variables (X)

F	Degrees of freedom: minimum number of intensive parameters or variables that specified in order to completely determine the state of a system at equ.	
	<ul style="list-style-type: none"> • Number of variable that must be specified or that we are free to change independently 	
Φ	Phase: is a mechanically separable constituents	
	<ul style="list-style-type: none"> • Some minerals consists > 1P: e.g. ice is 1P but ice water is 2P that are separable, & 2 pieces of ice are separable but equivalent so is 1P • Polymorphs: minerals with >1P but have same compositions (sanidine, microcline, orthoclase) 	
C	Components: is the minimum number of chemical constituents that must be specified in order to define the system & all of its phases	
	C	System
	1	Unary
	2	Binary
	3	Ternary
4	Quaternary	
	Example	
	Ice water with 2P but the components is just 1C (H ₂ O) but can be 2C if define it as H & O ions	
X	Number of intensive variables (include P & T)	
	C	Variables
	1	Changing Temperature <u>OR</u> Pressure
2	Changing Temperature <u>AND</u> Pressure	

EXAMPLE: If we heat ICE on hot plate

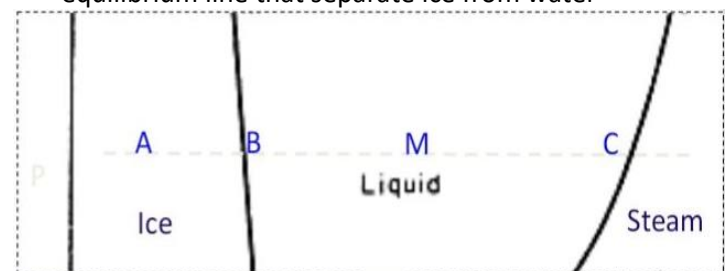
Before heating ($T < 0^\circ\text{C}$)

$$P = 1 \text{ (ice)}, C = 1 \text{ (H}_2\text{O)}, X = 2 \rightarrow F = 2$$

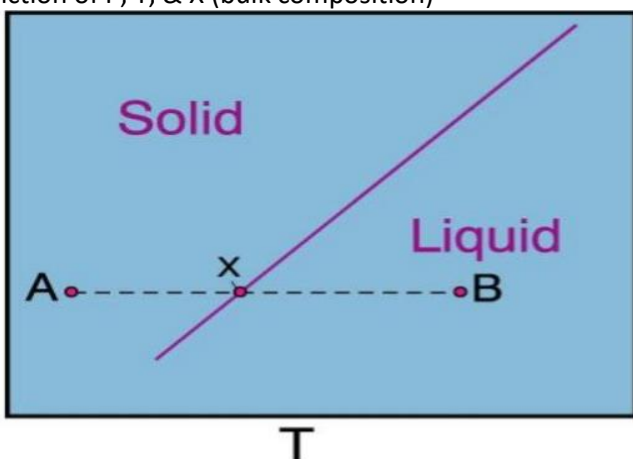
Heating ice on hot plate at constant pressure

$$P = 2 \text{ (ice, water)}, C = 1 \text{ (H}_2\text{O)}, X = 2 \rightarrow F = 1$$

- T-P relationship is expressed as the slope of the equilibrium line that separate ice from water



In (A) 2 variable are independent (changes P or/ & T, we still have one phase), at (B) & (C) 2 phases coexist so P & T aren't independent (if you change P you should change T)



Example of Phase Diagram

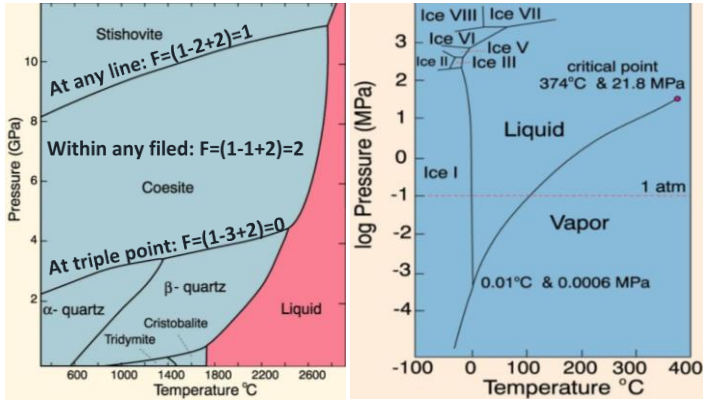
Pressure favors lower volume so liquid has larger volume & then the solid is more stable under high P

Temperature favors randomness (entropy) so liquid has higher entropy & more stable under higher T

The slope of solid-liquid equilibrium is +ve so increased pressure raises the melting point

ONE COMPONENT SYSTEM

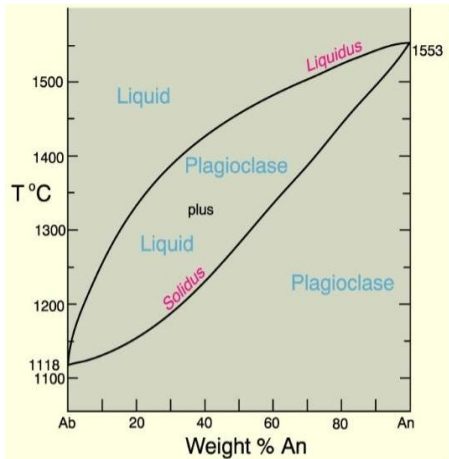
- Experiment on silicate system (need high P furnace capable of melting rocks at high P) lead to discover of number of solid silica polymorphs & liquid phase



Position	C	P	F	Called	F Interpretation
In any field	1	1	2	Divariant filed	We can change T or/P independently
Curves	1	2	1	Univariant line	We can change P or T independently
3-phases Points	1	3	0	Invariant point	Point determined by specific P & T

2C SYSTEM (BINARY)

- If the P is constant (0.1Mbar), the phase rule become $F = C - \Phi + 1$



Binary System of plagioclase with complete solid solution
 Albite-Anorthite (NaAlSi₃O₈-CaAl₂Si₂O₈)
 Solid solution: Na⁺+Si⁴⁺ → Ca²⁺+Al³⁺
 Adding Ab to An will lower the melting point

Position	C	P	F	F Interpretation
Plagioclase Field	2	1	2	Any point in these fields represents a true phase composition
Liquid Filed	2	1	2	Any point in these fields represents a true phase composition
Pl + Liquid Filed	2	2	1	Represents bulk composition with 2P & connected by horizontal line
At curves	2	2	1	We can changes P or T
3-filed	2	3	0	We cannot changes P or T

To determine proportions

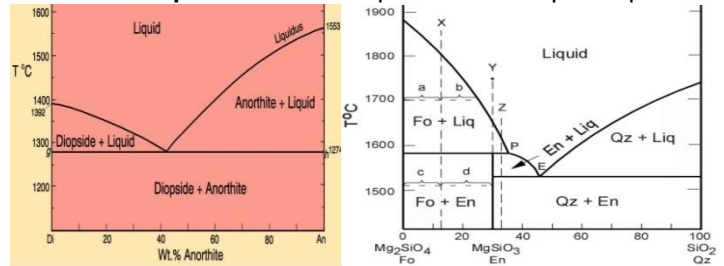
$$X(\text{An})_{\text{Liq}} = \frac{n_{\text{An}}}{n_{\text{An}} + n_{\text{Ab}}} \text{ (if n in grams)}$$

To determine amount of materials using liver rule

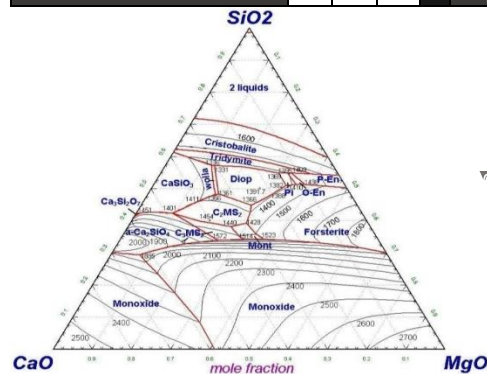
$$\text{Liquid}\% = \frac{\text{Distance from solidus to point}}{\text{Solidus to Liquidus Distqnce}}$$

$$\text{Solid}\% = \frac{\text{Distance from liquidus to point}}{\text{Solidus to Liquidus Distqnce}}$$

- There are 2 types of reactions:
 - Equilibrium melting & crystallization:** if the inital composition is same as the final composition
 - Fractional crystallization:** Remove crystals as forms so can't undergo a continuous reaction with melt
 - Partial Melting:** by remove first melt as forms
- Eutectic point:** represent the temperature limit below which no liquid can occur for intermediate composition
- Peritectic point:** a reaction point where 3 phase present



Eutectic System				Peritectic System			
Filed	C	P	F	Filed	C	P	F
Solid + Liquid	2	2	1	Solid field			
Liquid	2	1	2	Solid + Liquid			
Solid	2	1	2	Peritectic point	2	3	0
Eutectic point	2	3	0	Eutectic point	2	3	0



TERNARY SYSTEM

Phase Diagram Applications

- LOI:** water & organic matter that can be lost when ignited at 1000°C. Lost when clay field so neglected
- Col 2 recalculated remaining analytical data
- Predict how clay behave on firing
- Loss of volatile when material is ignited (e.g. loss of CO₂ from carbonate rocks & minerals)
- To mark the position of dolomite

TIME-TEMPERATURE-TRANSFORMATION DIAGRAM

- To understand the way in which reactions approach equilibrium, the effect of time has to be considered.
- TTT diagrams:** compiled by experimentally firing raw materials of interest at a variable T over time, quenching & identifying the mineral products.
- Minimum amount of time or the minimum temperature required to produce a given mineral product can be determined to fire the material.

CHAPTER SIX

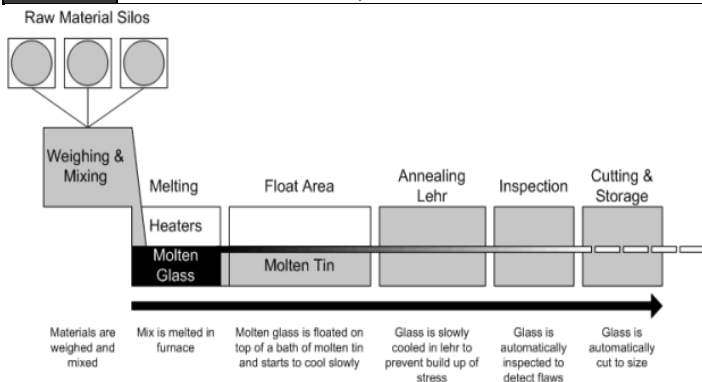
THE INDUSTRY OF GLASS

Shaas N Hamdan

RAW MATERIAL FOR GLASS

- **Top producers of glass:** USA & Japan

Types of glass	
Soda-Lime-silica-Glass	most quantity is of this type, used mainly for containers (bottles, jars...) & windows <ul style="list-style-type: none"> • Glass of particular specifications: as Heat-resistant as pyrex (add boric oxide)
Non-silicate Glass	Important for special ptical purposes <ul style="list-style-type: none"> • Example: infrared optics (from CaF_2, AlF_3, & P_2O_5), using of flouride glass in optical fibres
Composition of soda lime silica glass	
Major	<p>Contine Soda Ash, limestone, silica sand</p> <p>Al: help improve resistance to weathering</p> <p>Mg: can substitute Ca partially as in dolomite</p> <p>K: substitute for Na as in feldspar</p> <p>Opaque glass: forms by adding fluorides</p> <p>No CO_2: it is lost during decomposition</p>
Minor	<p>As small impurities may have a major +ve or -ve effect on the quality of the glass</p> <p>Fe: give green color (used in container glass)</p> <p>Li: reduce T required to melt (energy saving)</p> <p>Colouring agents (Fe, Ni, & Co): produce colored glass (Ni:brown, Co:blue) depends on bulk composition & amount of traces</p> <p>Solid inclusios: may introduced the color</p>

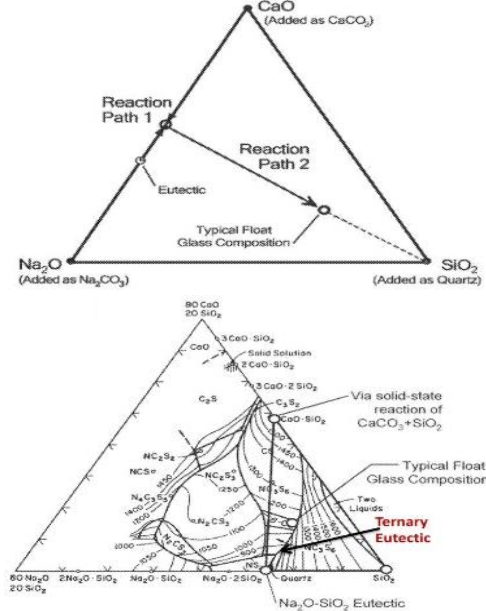


GLASS MANUFACTURING

- **Soda-Lime-silica-glass manufacture involves** melting the required raw material mixture at 1600°C , that leds to escaping of gases from the fluid melt
- **Float glass (Pilkington Process):** is a sheet of glass made by floating molten glass on a molten metal (tin) under reducing condition, & this method gives the sheet uniform thickness & very flat surfaces
- **Flat glass products:**
 1. Soda-lime glass, borosilicate, flat panel display glass
 2. Containers & other shaped products are made by blowing or pressing into moulds at working stage

CHEMISTRY & SOURCES

- **The chemistry:** referred to quenched silicate liquid. & represented by phase diagram of $\text{SiO}_2\text{-CaO-Na}_2\text{O}$



- Sources of soda & lime are Na-carbonate & limestone
- In formulation of batches consisting of silica sand, limestone & soda ash, proportions must be corrected to take into account loss of CO_2
- To carry out correction, atomic mass used to determine proportions of CaO within CaCO_3 & Na_2O in Na_2CO_3
 - 100 tons of limestone = 56Ton CaO + 44Ton CO_2
 - 100 tons of soda Ash = 58Ton soda + 42Ton CO_2
- As Na_2O & CaO don't occur naturally, the correspondent carbonates used (CO_2 removed & silica sand SiO_2 used)
- Glass compositions are variable & could be achieved by blending raw material in different possible combination, impurities can be tolerated
- Silica sand suitable for glass is relatively rare, because of the need for high degree of chemical purity.
- The "holy grail" for silica sand producers is sand that achieve 99.99% SiO_2 after beneficiation
- **Essential requirement:**
 1. **Grain size:** >90% should be between 125- 500 μm
 2. **Chemical composition:** must meet requirement
- Discolouring Fe & Cr occur within other phases in sand
 - **Fe:** occur as red-hematite-sand, or yellow or brown oxyhydroxide, as well as in silicate minerals
 - **Cr:** as chromite (heavy mineral) derived from mafic or ultramafic rocks, stable in glass manufacturing, persists as solid inclusions within finished product, which can cause it to be brittle
 - **Al:** from feldspars, mica or clay minerals (Beneficial)

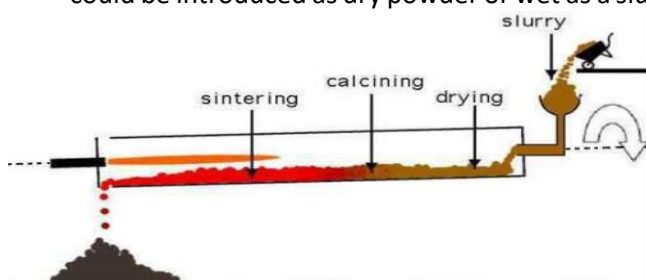
CHAPTER SEVEN

CEMENT & PLASTER

- The essential characteristic of cement & plaster is that they are calcined materials which harden on reaction with water when mixed as paste

Types of cement	
Portland	<p>Most widely used cement, limestones (cement stones)</p> <ul style="list-style-type: none"> Patented in England by Joseph Aspdin Calcining impure (argillaceous) Composed of: <ol style="list-style-type: none"> 3 dominant components: lime (CaO), silica (SiO₂), alumina (Al₂O₃), dominant raw materials are limestone or chalk & shale (Silica & Alumina dominant in shale), & these components are reacted together by calcining at about 1500°C. Additional component (such as iron) are important for clinker compounds
	<p>Pozzolanic Portland is stronger than Pozzolanic cement</p>

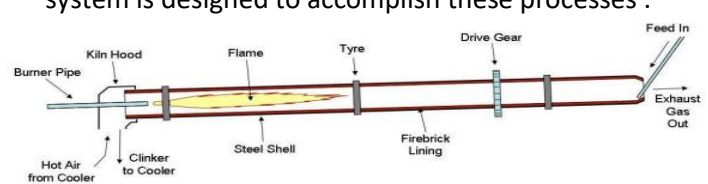
- Manufacturing of cement as Clinker** (ground to give a powder as finished products) & process involved in its hydration are of major importance
- Plaster:** a building material used for coating walls & ceilings, manufactured as a dry powder & mixed with water to form a paste when used
 - Lime-based (during Roman time)
 - Modern Gypsum-based Plaster of Paris
- Clinker:** refers to lumps or nodules, usually 3-25mm in diameter, produced by sintering (fused together without melting to the point of liquification) limestone & alumino-silicate materials such as clay in kiln cement
 - Calcining is carried out in long, inclined, rotating kilns, through which the raw material gradually move, with T rising steadily & then cooling rapidly
 - A number of reaction took place in a sequence
 - Rate of flow needs to be controlled. & Raw material could be introduced as dry powder or wet as a slurry



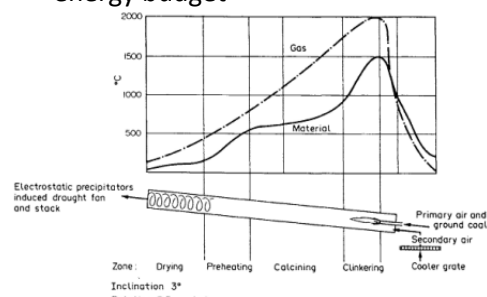
- Stages of a process of manufacture of cement clinker:**
 - Grinding** a mixture of limestone & clay or shale to make a fine "rawmix"
 - Heating** the rawmix to sintering temperature (up to 1450°C) in a cement kiln
 - Grinding** the resulting clinker to make cement
- In 2nd stage, the rawmix is fed into the kiln & gradually heated by contact with the hot gases from combustion of the kiln fuel. Successive chemical reactions take place as the temperature of the rawmix rises

70-110°C	Free water is evaporated
400-600°C	Clay-like minerals are decomposed into their constituent oxides; principally SiO ₂ & Al ₂ O ₃ Dolomite (CaMg(CO ₃) ₂) decomposes to calcium carbonate, MgO & CO ₂
650-900°C	CaCO ₃ react with SiO ₂ to form belite Ca ₂ SiO ₄
900-1050 °C	The remaining calcium carbonate decomposes to calcium oxide & CO ₂
1300 - 1450°C	Partial (20-30%) melting takes place, & belite reacts with calcium oxide to form alite (Ca ₃ O-SiO ₄)

- Alite:** characteristic constituent of Portland cement, a peak T of 1400-1450°C is required to complete reaction
- Partial melting causes the material to aggregate into lumps or nodules of diameter 1-10mm. This is **clinker**
- The hot clinker next falls into a cooler which recovers most of its heat, & cools the clinker to around 100 °C, at which T it can be conveyed to storage. The cement kiln system is designed to accomplish these processes.



- Fuel combustion (coal) is used to provide heat required, & ash incorporated chemically in the clinker. Organic matter in clays contributes to combustion, assisting the energy budget



The T of the clinker (material) lags behind, & doesn't rise at the same rate as gas T, reflecting the overall endothermic nature of the dehydration & clinker-forming reaction

- CaO is highly reactive material, & once formed it reacts with dehydrated clay to give one or more of the calcium aluminum silicates.
- These form the content of clinker material, which are occasionally found in nature in contact metamorphism of impure limestone.
- A number of minerals are characteristic of freshly made cement clinkers, including alite & belite
- **compound composition of p.c. (or clinker):** Oxides interact with each other in the kiln to form more complex products (compounds)

Name	Formula	Symbol
Tri Ca-Silicate	3CaO.SiO ₂	C3S
Di Ca-Silicate	2CaO.SiO ₂	C2S
Tri Ca-Aluminate	3CaO.Al ₂ O ₃	C3A
Tetra Ca-Alumino, Ferrite	3CaO.Al ₂ O ₃ .Fe ₂ O ₃	C4AF

- Portlandite Ca(OH)₂ or CH, occurs in hydrated cement
- is catalyzed by the presence of C4AF, & produces tricalcium silicate, which is responsible for the strength of concrete & is therefore an essential component

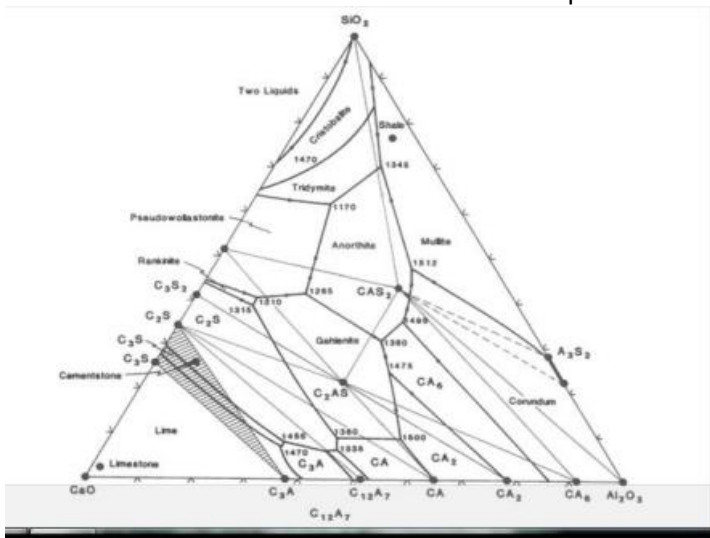


Figure 7.2 Phase relationships at one atmosphere pressure in the carbon dioxide and water-free system C-A-S, showing plotting positions of limestone, cementstone and shale, and highlighting the C₂S-C₃S-C₃A triangle. Compositions in this diagram are expressed as weight %.

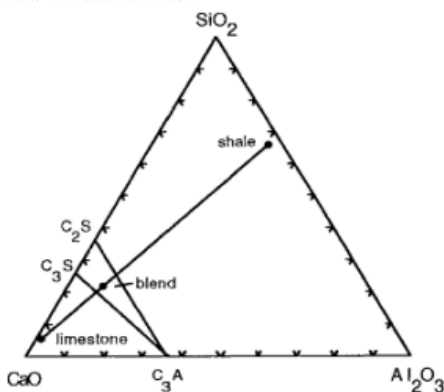


Figure 7.3 Estimation of proportions of limestone and shale required to make cement. In this example, a blend of 66% lime and 34% shale will give the required composition. If we assume that the shale volatile content is 10% and that the limestone is pure calcium carbonate (i.e. 56% CaO; 44% CO₂), the proportions of limestone and shale are corrected to 76% and 24% respectively. However, this does not compensate for the shale's lime content (see text).

- Once it leaves the kiln, the cement clinker is ground & mixed with 4-7% gypsum, which helps inhibit setting while the cement is being worked. This mixture does not set for a number of hours.

- National quality standards may allow the grinding of proportions of other materials with the cement & gypsum if they show hydraulic or pozzolanic properties, or otherwise usefully contribute to concrete properties.

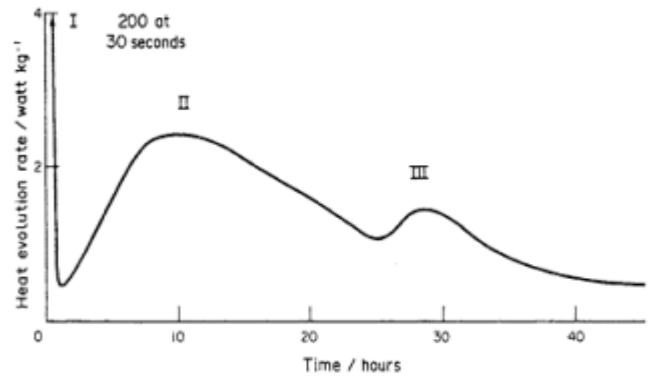
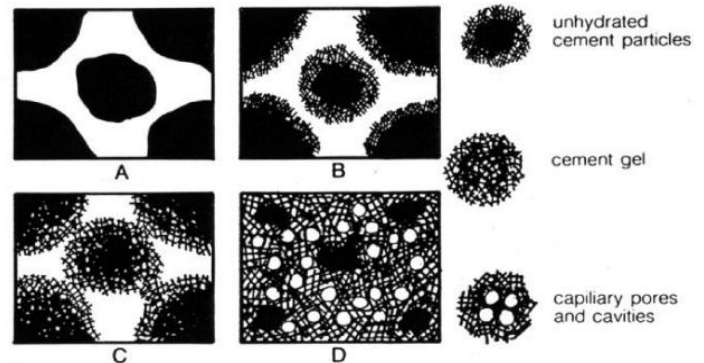


Figure 7.4 Variation in rate of heat evolution as Portland cement sets (from Bye, 1983).

- Setting of Portland Cement (SO₃→comes largely from gypsum). P.C. alone sets quickly so some gypsum is ground with clinker to retard the setting time
- **Hydration:** Chemical reactions with water.
- As water comes into contact with cement particles, hydration reactions immediately starts at the surface of the particles. Although simple hydrates such as C-H are formed, process of hydration is a complex one & results in reorganization of the constituents of original compounds to form new hydrated compounds



- A) Immediately after mixing
- B) Reaction around particles – early stiffening
- C) Formation of skeletal structure – first hardening
- D) Gel infilling – later hardening

- At any stage of hydration the hardened cement paste (hcp) consists of:

1. Hydrates of various compounds referred to collectively as GEL
2. Crystals of calcium hydroxide (CH).
3. Some minor compound hydrates.
4. Unhydrated cement
5. The residual of water filled spaces – pores.

- **Factors affecting setting time:** temperature & humidity, water amount, chemical composition of cement, fineness of cement (finer cement, faster setting)

- **Abnormal Settings:** Flash-set, False-set

- **Special cements** are produced for particular requirements: Quick setting cement, High alumina cement, Sulphate resistant cement, Low alkali cement

SPECIAL CEMENTS

Quick setting	set within 30-60 minutes, achieves its full strength only after 28 days. Achieved by addition of Bauxite & flourite to raw material mixture
Portland Pozzolan	By grinding & blending P.C.: Clinker+Pozzolan+Gypsum P.P.C. Produces less heat of hydration & offers higher sulfate resistance so it can be used in marine structures & mass concrete.
High Alumina Cement (HAC)	Raw materials: limestone & bauxite (Al_2O_3 & Fe_2O_3) that interground & introduced in kiln clinkered at $1700^\circ C$ <ul style="list-style-type: none"> Develop full strength much more rapidly No longer used in load bearing applications as loss of volume on recrystallization increasing porosity The oxide composition is quite different: $Al_2O_3 \rightarrow 40-45\%$, $CaO \rightarrow 35-42\%$, $Fe_2O_3 \rightarrow 5-15\%$, $SiO_2 \rightarrow 4-10$
Type V: Sulfate Resistant PC	Used in construction where concrete will be subjected to external sulfate attack (chemical plants, marine & harbor structures) <ul style="list-style-type: none"> During hydration C3A reacts with gypsum & water to form ettringite. In hardened cement paste Ca-alumino-hydrate can react with Ca & alumino sulfates, from external sources, to form ettringite which causes expansion & cracking. C-H & sulfates can react & form gypsum which again causes expansion & cracking. In Type C ₃ A, limited to below 3.5%. lowering Al-content
low alkali cement	In manufacture of concrete in which the use of a particular aggregate introduces alkalis, giving the grounds for alkali- silica reactivity might occur <ul style="list-style-type: none"> Max content of Na_2O of 0.6% = total alkali
White Portland Cement (WPC)	made from materials containing a little Fe-oxide & Mn-oxide ($Fe_2O_3 + MnO \leq 0.8\%$) to avoid contamination by coal ash, oil is used as fuel. To avoid contamination by iron during grinding, instead of steel balls nickelmolybdenum alloys are used. <ul style="list-style-type: none"> Major compounds are CA & C₂S, it's basically different from OPC. & the concrete made from this cement has very different properties. It has high sulfate resistance. Very high early strength (emergency repairs) About 80% of ultimate strength is obtained within 24hrs. But the strength is adversely affected by T. The setting time is not as rapid as gain of strength. Initial setting time 4hrs & final setting time is 5hrs

LIME SATURATION INDEX

- Calculated from chemical analysis of raw materials & Measure ability of blend to react leaving no free lime. (i.e. solid phases are saturated with respect to CaO)
- The Lime Saturation Factor** is a ratio of CaO to the other 3 main oxides. Applied to clinker, in modern clinkers are 0.92-0.98, or 92%-98%. TYPICALLY 96%

$$LSF = \frac{CaO}{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3}$$

LSF	Mean
1	All lime should combined with belite to form alite
>1	Free lime is likely to be present in the clinker. surplus free lime has nothing with which to combine & will remain as free lime

- Impurities:** Mg, F, Alkalis, & Sulphur compounds
- Plaster Mineralogy & Production**
 - Calcining gypsum at $150-165^\circ C$
 - $CaSO_4 \cdot 2H_2O = CaSO_4 \cdot 0.5H_2O$
 - Calcined gypsum is used to produce a number of different plaster products
- Plaster Mineralogy & Production:** Calcining gypsum at $150-165^\circ C$, $CaSO_4 \cdot 2H_2O = CaSO_4 \cdot 0.5H_2O$, Calcined gypsum is used to produce a number of different plaster products

EXAMPLE

Blends of limestone & shale with LSF of 0.96, composition of limestone is 3.0 SiO_2 ; 0.7 Al_2O_3 ; & 0.3 Fe_2O_3 & continue 53.7% lime, the shale composition is 50.1 SiO_2 ; 22.9 Al_2O_3 ; & 7.9 Fe_2O_3 & continue 2.8% lime (Mw of CaO in $CaCO_3$). Calculate equivalent parts of lime CaO, content of limestone that available to react with shale, & Proportion of blend (amount of limestone required to satisfy one unit of shale)

The equivalent parts of lime CaO

$$LSF = \frac{CaO}{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3}$$

$$0.96 = \frac{CaO}{2.8 \times 3.0 + 1.2 \times 0.7 + 0.65 \times 0.3}$$

$$CaO = 0.96 \times (2.8 \times 3.0 + 1.2 \times 0.7 + 0.65 \times 0.3) = 9.06$$

Available limestone to react with shale

$$53.7 - 9.06 = 44.65 \text{ equivalent parts}$$

(one unit limestone can provide 44.65 ep of lime)

Proportion of blend (Limestone/Shale)

$$CaO_{shale} = 0.96 \times (2.8 \times 50.1 + 1.18 \times 22.9 + 0.65 \times 7.9)$$

$$CaO_{shale} = 165.54 \text{ equivalent parts}$$

$$\text{Available shale} = 165.54 - 2.8 = 162.74 \text{ ep}$$

(one unit of shale requires 162.74 ep of lime)

$$P_{blend} = \frac{\text{Limestone}}{\text{Shale}} = 1:3.645$$

$$\frac{\text{Available Shale}}{\text{Available Limestone}} = \frac{162.74}{44.65} = 3.645$$

$$\text{Shale} = \frac{1}{3.645} \times 100\% = 27.47\%$$

$$\text{Limestone} = 100\% - 27.47\% = 72.53\%$$