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Lecture 7 – Pozzolans

CE 344 Materials of Construction

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Ordinary portland cement (OPC)

- Typical mineralogical composition of OPC:

Abbreviation	Compound	Formula	Wt% in OPC
C_3S	Tricalcium Silicate (Alite)	$3(CaO).SiO_2$	50-55
C_2S	Dicalcium Silicate (Belite)	$2(CaO).SiO_2$	19-24
C_3A	Tricalcium Aluminate	$3(CaO).Al_2O_3$	6-10
C_4AF	Tetracalcium aluminoferrite	$4(CaO).Al_2O_3.Fe_2O_3$	7-11
$C\bar{S}H_2$	Gypsum	$CaSO_4.2H_2O$	3-7

(C_3S) Clinker mineral; imparts early strength and set.
(C_2S) Clinker mineral; imparts long-term strength.
(C_3A) Clinker mineral; contributes to early strength and set
(C_4AF) Clinker mineral; acts as a flux to lower clinkering temp; imparts gray color.
($C\bar{S}H_2$) Interground with clinker to make portland cement. Controls early set.

Hydrated Cement Paste

- Solids
  - C-S-H
  - CH
  - Ettringite
  - Monosulfate hydrate
  - Residual unhydrated cement
- Voids
  - Entrapped air (>1mm)
  - Entrained air (75-500um)
  - Capillary pores (macro → meso)
  - Interlayer space (micropores)
- Water
  - Capillary water
  - Adsorbed water
  - Interlayer water
  - Chemically combined water

Hydration of Calcium Silicates

$$2C_3S + 6H \rightarrow C\text{-}S\text{-}H + 3CH + 120\ cal/g$$

$$2C_2S + 4H \rightarrow C\text{-}S\text{-}H + CH + 62\ cal/g$$

- Both produce C-S-H and CH as reaction products
- C_2S produces less CH
  - Important for durability in sulfate rich environments
- More heat is evolved during C_3S hydration
- C_3S hydration is more rapid
  - Higher contribution to early age strength (2-3 hrs to 14 days)
- C_2S hydration occurs more slowly
  - Contributes to strength after 14 days

Hydration of Calcium Aluminates

- C_3A
  - Reaction of C_3A with water occurs very quickly and liberates high heat → Flash Set
  - Gypsum $C\bar{S}H_2$ is added to the clinker to control the hydration of C_3A:

    C_3A + 26 H + 3 $C\bar{S}H_2$ → $C_6A\bar{S}_3H_{32}$ (Ettringite) + 207 cal/g
  - When more C_3A remains:

    2 C_3A + 4 H + $C_6A\bar{S}_3H_{32}$ → 3 $C_4A\bar{S}H_{12}$ (Monosulfate)

Hydration of Calcium Alumino Ferrites

- C_4AF
  - Reaction of C_4AF (ferrite) phase is slower and evolves less heat than C_3A:

    C_4AF + 14 H + 2 CH → $C_4(A,F)H_{13}$ + $(A,F)H_3$ + Heat
  - Also heavily retarded by gypsum ($C\bar{S}H_2$):

    C_4AF + 21 H + 3 $C\bar{S}H_2$ → $C_6(A,F)\bar{S}_3H_{32}$ + $(F,A)H_3$ + Heat

    C_4AF + $C_6(A, F)\bar{S}_3H_{32}$ → 3 $C_4A(A,F)\bar{S}H_{12}$ + $(F,A)H_3$ + Heat
  - Products of C_4AF are more resistant to sulfate attack than those of C_3A hydration

CE 344 – Tentative Outline

Week	Dates		Topic
1	16-Feb	20-Feb	1 – INTRODUCTION to MATERIALS of CONSTRUCTION ✓ -- Q1
2	23-Feb	27-Feb	2 – GYPSUM ✓ -- Q2 3 – LIME ✓ -- Q3
3	2-Mar	6-Mar	4 – PORTLAND CEMENT – manufacture, hydration, tests, types
4	9-Mar	13-Mar	(1st Lab)
5	16-Mar	20-Mar	
6	23-Mar	27-Mar	5 – POZZOLANS
	Specific date TBA		1st MIDTERM
7	30-Mar	3-Apr	
8	6-Apr	10-Apr	6 – AGGREGATES
9	13-Apr	17-Apr	(2nd Lab)
10	20-Apr	24-Apr	7 – CONCRETE
11	27-Apr	1-May	(3rd Lab)
12	4-May	8-May	
	Specific date TBA		2nd MIDTERM
13	11-May	15-May	8 – POLYMERS
14	18-May	22-May	9 – FERROUS METALS, ALLOYS, AND CONCRETE REINFORCEMENT 10 – CLAY BRICKS

(*) The detailed course schedule is available at the course web page.

CE 344 – Tentative Outline

Week	Dates		Topic
1	22-Feb	26-Feb	**1. Introduction to materials of construction** **2. Gypsum**
2	29-Feb	4-Mar	**3. Lime**
3	7-Mar	11-Mar	**4. Portland cement: manufacture, hydration**, tests, types
4	14-Mar	18-Mar	(1st Lab around these dates)
5	21-Mar	25-Mar	
6	28-Mar	1-Apr	**5. Pozzolans**
	Specific date TBA		1st MIDTERM EXAMINATION
7	4-Apr	8-Apr	6. Aggregates
8	11-Apr	15-Apr	(2nd Lab around these dates)
9	18-Apr	22-Apr	7. Concrete
10	25-Apr	29-Apr	(3rd Lab around these dates)
11	2-May	6-May	
12	9-May	13-May	
	Specific date TBA		2nd MIDTERM EXAMINATION
13	16-May	20-May	8. Ferrous metals, alloys and concrete reinforcement
14	23-May	27-May	9. Polymers
			10. Clay bricks

(*) The detailed course schedule is available at the course web page.

POZZOLANS

(Supplementary Cementitious Materials)

Official definition of pozzolan

- **Siliceous or aluminous material**, which in itself possesses little or no cementitious value but will, in **finely divided** form and in **the presence of moisture**, chemically react with calcium hydroxide $Ca(OH)_2$ to form compounds possessing hydraulic cementitious properties.

Mineral Admixtures – Pozzolans

- Definition of pozzolan:
  - ***Pozzolan*** is a finely divided amorphous aluminous/siliceous material that reacts with $Ca(OH)_2$ = (CH) to form C-S-H or C-A-S-H.
- Pozzolanic reaction:

$$\left.\begin{matrix} C_3S \\ C_2S \end{matrix}\right\} + H_2O \rightarrow C\text{-}S\text{-}H + \mathbf{CH}$$

$$\mathbf{Silica\ (SiO_2) + CH \rightarrow C\text{-}S\text{-}H} \longrightarrow \text{Pozzolanic reaction: a slow reaction}$$

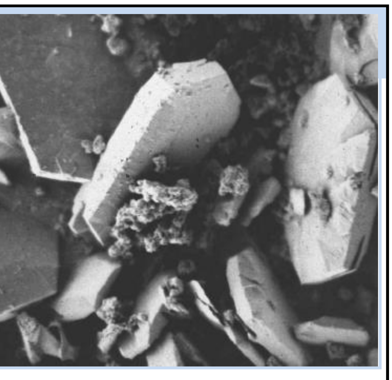
- It needs lime (calcium) to hydrate. Adding water to pure pozzolan will not yield hydration products.

Calcium Hydroxide

Cement

- Notation: CH
- Large, weak crystals with hexagonal – prism morphology
  - Lower Van der Walls forces

    ↓
  - Lower strength contribution
- 20-25% of solids in hydrated portland cement paste
- Contributes to increase PH



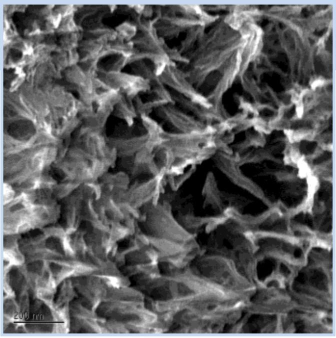
* Image courtesy of P.J.M. Monteiro

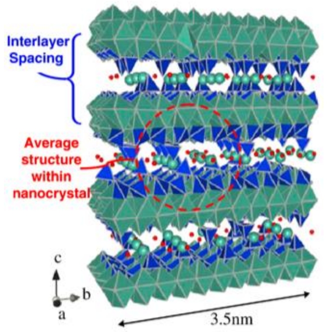
Calcium Silicate Hydrates

Cement

- Notation: C-S-H
- A DISORDERED TOBERMORITE!
- Layered structure with very high surface area
  - High Van der Walls forces

    ↓
  - Highest contribution to strength
- 50-60% of solids in hydrated portland cement paste





* Meral et al., Cement and Concrete Research 41 (2011)

Natural pozzolans

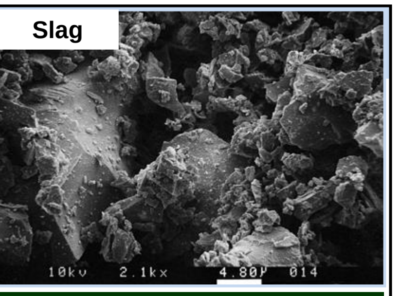
- Volcanic glass
- Volcanic tuffs
- Calcined clays or shales
- Pumicite

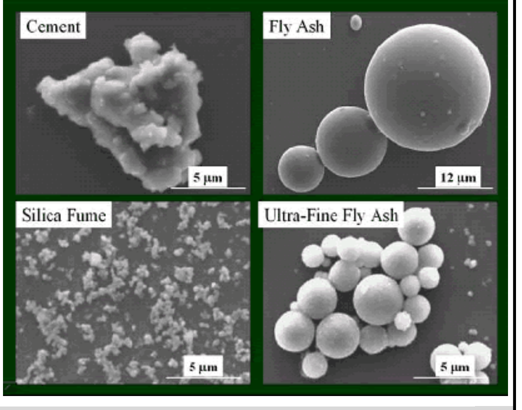
Volcanic Tuff

Pumice

Artificial Pozzolans

- Class C and Class F Fly Ash
- Iron blast furnace slag
- Silica fume
- Rice husk ash





Artifical pozzolans

- Class C and Class F Fly Ash
  - Widely available
  - Most commonly used mineral admixture
  - High-calcium Fly Ash (Type C) has both cementitious and pozzolanic effects
  - High-volume fly ash concretes (“Green Concrete”)
- Iron blast furnace slag
- Silica fume
  - Silica fume has very small particles
  - Consists essentially of pure amorphous silica
  - Very reactive
  - Commonly used for high-strength concretes
- Rice husk ash

Pozzolanic reaction

POZZOLANS

- Silica & alumina (higher amounts)
- Iron oxide, calcium oxide, magnesium oxide, alkalies (lesser amounts)

$$\underset{\text{Calcium Hydroxide}}{Ca(OH)_2} + \underset{\text{Silica}}{SiO_2} + \text{Water} \longrightarrow \underset{\text{Calcium–Silicate -Hydrate}}{\text{C-S-H}}$$

- C-S-H provides the hydraulic binding property of the material.
- Pozzolanic Activity: Capacity of pozzolan to form alumino-silicates with lime to form cementitious products. (How good, how effective the pozzolan is!)

Advantages of using Pozzolans

- Strength enhancement:
  - CH crystals are converted to C-S-H
    - CH crystals: crystalline (hexagonal plates) → low surface area to weight ratio → weak van-der-waals attraction →weak contribution to strength
    - C-S-H: high surface area to weight ratio → strong van-der-waals attraction → good contribution to strength
- Low heat of hydration (for some climates)
- Workability enhancement for some pozzolans (example: fly ash)
- Prevents bleeding
- Reduces porosity/permeability → enhances durability and resistance to chemical attacks

Disadvantages of using Pozzolans

- Slow strength development in most cases
- Low heat of hydration (for some climates)
- Workability decreased for some pozzolans (example: silica fume may prevent bleeding, but increases water requirement)

Pozzolan Basics

- The name Pozzolan comes from the town Pozzuoli, Italy.
- Ancient Romans (~100 B.C.) produced a hydraulic binder by mixing hydrated lime with soil (predominantly volcanic ash)
- Horasan mortar, mixing lime with finely divided burned clay (calcined clay), is extensively used by Ottomans
- Nowadays, the word pozzolan covers a broad range of natural and artificial materials.

Concrete Core from Baianus Sinus

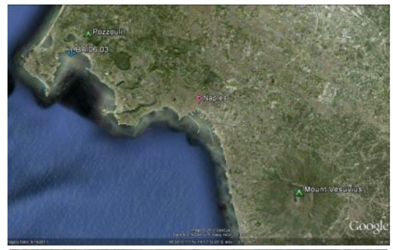
~ early 1st century BC: the harbor of Baiae, or *Portus Baianus*, built in Pozzuoli Bay within the central crater of Campi Flegrei.

2006: ROMACONS project, five cores were extracted from the sunken remains of the harbor.

A major accomplishment of Roman engineers was to construct enduring coastal underwater structures in seawater, which were important to long-distance trade and military endeavors.

Two millennia later, the reasons for the extraordinary durability of the maritime structures remain enigmatic.

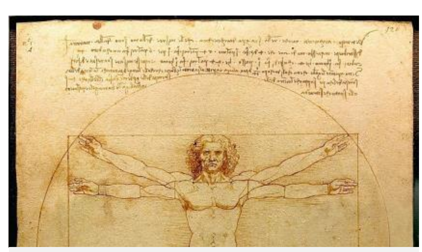
The concretes are highly complex composites composed of relict lime, tuff and pumice clasts and pozzolanic reaction products.



The International Journal of Nautical Archaeology (2008) **37** .2: 374–392

Vitruvius (~80BC-15BC)

- served as an artilleryman, the third class of arms in the military offices under Caesar
- a Roman author, architect, and civil engineer during the 1st century BC, known for his multi-volume work entitled De Architectura (The Ten Books of Architecture)
- Vitruvian virtues: a structure must exhibit the three qualities of firmitas, utilitas, venustas – that is, it must be solid, useful, beautiful

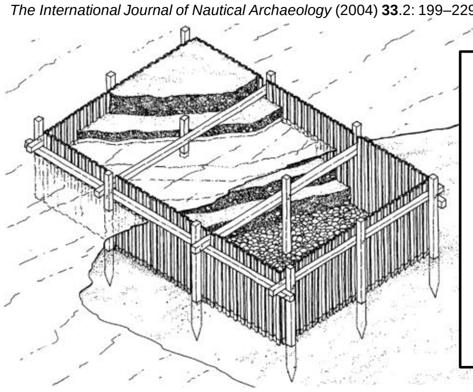


Vitruvian Man by Leonardo da Vinci

an illustration of the human body inscribed in the circle and the square derived from a passage about geometry and human proportions in Vitruvius' writings

Building hydraulic Roman concrete

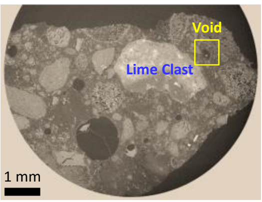
The International Journal of Nautical Archaeology (2004) **33**.2: 199–229



Hydraulic concrete hingredients

- *Calx, lime*
- Seawater
- *Pulvis*, pumiceous volcanic ash from Campi Flegrei
- *Caementa*, decimeter sized fragments of pumiceous tuff from Campi Flegrei

Vitruvius (2.6.1): " There is a kind of powdery sand [pulvis, i.e. pozzolana] which by its nature produces wonderful results. It is found in the neighbourhood of Baiae and in the lands of the municipalities around Mount Vesuvius. This material, when mixed with lime [calx] and rubble [caementum], not only furnishes strength to other buildings, but also, when piers are built in the sea, they set under water ... and neither the waves nor the force of water can dissolve them."



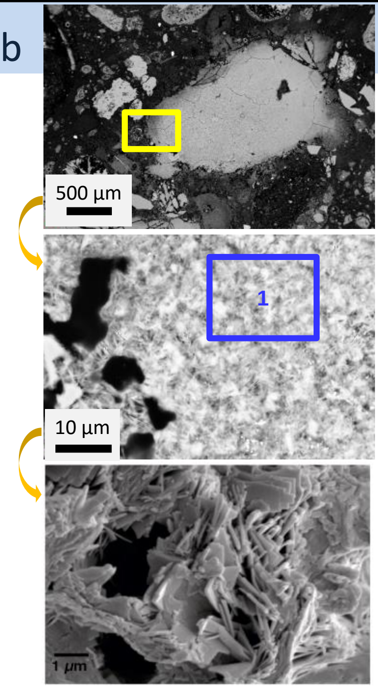
BSE/EDS SEM on a Polished Slab

Relict lime clast

Tobermorite, a hydrothermal alteration product of calcium carbonate rocks, due to contact metamorphism and metasomatism, fills the vesicles and cavities in basaltic rocks.

Al-Tobermorite

	Ca	Al	Si
Area 1	0.8	0.2	1.0



Factors that affect the reactivity of pozzolans

1. $SiO_2 + Al_2O_3 + Fe_2O_3$ content
2. The degree of amourpheness of its structure
3. Fineness of its particles

1. $SiO_2 + Al_2O_3 + Fe_2O_3$ content

$SiO_2 + Al_2O_3 + Fe_2O_3$ content increases → pozzolanic activity increases

- Natural pozzolans
  - ASTM C 618 & TS 25
  - min "SiO_2+Al_2O_3+Fe_2O_3" for natural pozzolans > 70%
- Blast Furnace Slag
  - SiO_2 ~ 30-40%
  - Al_2O_3 ~ 7-19%
  - CaO ~ 30-50%
- Silica fume
  - $SiO_2 \approx$ 85-98%
- Fly Ash – ASTM
  - Class C :
    - from lignitide or subbituminous coals
    - $SiO_2+Al_2O_3+Fe_2O_3>50\%$
  - Class F:
    - from bituminous coals
    - $SiO_2+Al_2O_3+Fe_2O_3>70\%$

2. Amorphousness

- For chemical reaction → pozzolans must be amorphous
- Volcanic ash, volcanic tuff, fly ash, silica fume are all amorphous by nature.
- Clays → contain high amounts of silica & alumina but have a crystallic structure!
  - Clay → does not possess pozzolanic property
  - However, by heat treatment, such as calcining ~700-900°C crystalline structure is destroyed & a quasi-amorphous structure is obtained.
  - Burned clay → possess pozzolanic property

2. Amorphousness

- Blast furnace slag → contain high amounts of silica, alumina & lime.
  - If molten slag is allowed to cool in air, it gains a crystal structure → does not possess pozzolanic property.
  - If it is cooled very rapidly by pouring it into water, it becomes a granular material & gains amorpousness → possess pozzolanic property.

3. Fineness

- Pozzolanic activity increases as fineness increases.
- Volcanic ash, rice husk ash, fly ash, condensed silica fume are obtained in finely divided form.
- Volcanic tuff, granulated blast furnace slag & burned clay must be ground.

Determination of pozzolanic activity

- Pozzolanic activity is determined by “strength activity indexes”
- Six mortar cubes are prepared (ASTM):
  - Control Mixture
    - 500 g portland cement + 1375 g sand+242 ml water
  - Test Mixture
    - 400 g of portland cement +100 g of pozzolan+1375 g of sand + some water for the same consistency

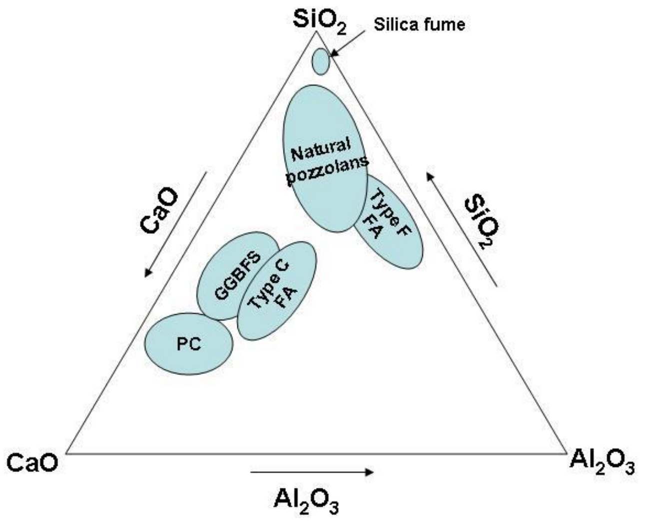
Determination of pozzolanic activity

- Conduct compressive testing at 7 or 28 days
- Calculate strength activity Index (SAI)
  - SAI = A/B*100
  - A = f'_c of test mixture
  - B = f'_c of control mixture
- ASTM C 618 → SAI ≥ 75%

Chemical composition of common pozzolans

	Artificial Pozzolans				Natural Pozzolans		
	Class F fly ash	Class C fly ash	Ground blast furnace slag	Silica fume	Calcined clay	Calcined shale	Metakaolin
SiO_2, %	52	35	35	90	58	50	53
Al_2O_3, %	23	18	12	0.4	29	20	43
Fe_2O_3, %	11	6	1	0.4	4	8	0.5
CaO, %	5	21	40	1.6	1	8	0.1
SO_3, %	0.8	4.1	9	0.4	0.5	0.4	0.1
Na_2O, %	1.0	5.8	0.3	0.5	0.2	—	0.05
K_2O, %	2.0	0.7	0.4	2.2	2	—	0.4
Total Na eq. alk, %	2.2	6.3	0.6	1.9	1.5	—	0.3

Chemical composition of common pozzolans



Chemical composition of pozzolans

- Silica Fume
  - mostly SiO_2
- G. Granulated Blast Furnace Slag
  - high amounts of CaO (self-cementitious)
- Class C Fly Ash
  - has CaO (self-cementitious)

Pozzolans

Q

1. If you use pure quartz sand in concrete, would you expect it to participate in a pozzolanic reaction? What would be its influence on the strength of concrete?

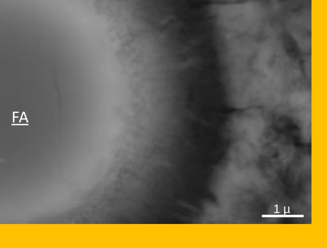
2. Why are clays and shales usually calcined (heat treated) to make more suitable for use as a pozzolan?

How do they look?

SILICA FUME

GRANULATED BLAST FURNACE SLAG

FLY ASH



Selected properties of common pozzolans

	Class F fly ash	Class C fly ash	GBFS	Silica fume	Calcined clay	Calcined shale	Metakaolin
Loss on ignition, %	2.8	0.5	1.0	3.0	1.5	3.0	0.7
Blaine fineness, m^2/kg	420	420	400	20,000	990	730	19,000
Specific gravity	2.38	2.65	2.94	2.40	2.50	2.63	2.50

Typical amounts of pozzolans in concrete by mass of cementing materials

- Fly ash
  - Class C 15 - 40%
  - Class F 15 - 20%
- Slag 30 - 45%
- Silica fume 5 - 10%
- Calcined clay 15 - 35%
  - Metakaolin 10%
- Calcined shale 15 - 35%

Requirements for an acceptable quality of pozzolan

- TS 25 → Natural Pozzolans
- TS 639 → Fly Ash
- ASTM C 618 → For Natural Pozzolan & Fly Ash

	Natural	**Class F**	**Class C**
Fineness (max. % retained when wet sieved on 45 µm sieve)	34%	34%	34%
Strength Activity Index	75	75	75
min "SiO_2+Al_2O_3+Fe_2O_3"	70	70	50

Uses of pozzolans

1. Direct use of pozzolan by mixing it with calcium hydroxide
   - Extensively used in ancient times but not very common now.
2. Use of pozzolan in producing blended cements
   - Grinding "Clinker+Pozzolan+Gypsum"
   - Portland-pozzolan cements → extensively used
3. Use of pozzolan as an admixture in concrete
   - Mix "Cement+Pozzolan+Aggregate+Water"
   - Portland-pozzolan concrete

Pozzolan content

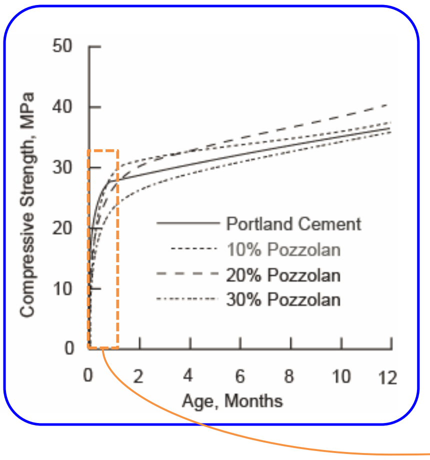
Q

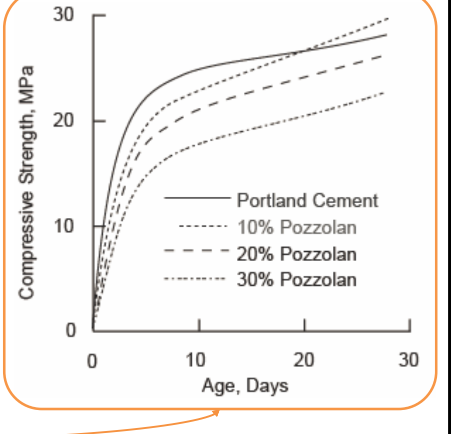
- Estimate early and late compressive strength evolution for portland cement with 0%, 10%, 20% and 30% fly ash.

Answer

A

- Estimate early and late compressive strength evolution for portland cement with 0%, 10%, 20% and 30% fly ash.





Pozzolan content vs Heat of hydration

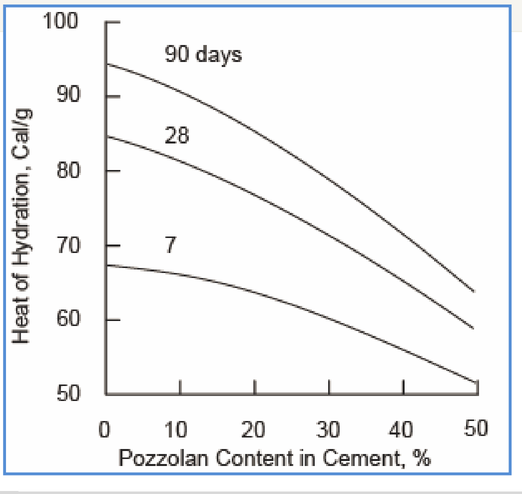
Q

- Plot a (heat of hydration) vs (pozzolan content in cement, %) plot.

Pozzolan content vs Heat of Hydration

A

- Plot a (heat of hydration) vs (pozzolan content in cement, %) plot.



Pozzolans

Q

- The table below lists the properties of four different pozzolans: Ground blast furnace slag, Silica Fume, Class F fly ash, Class C fly ash
  - Determine which one is which pozzolan?
  - Identify the natural and artificial pozzolans.
  - Determine which ones are self cementing? Explain why?

Chemical Composition	A	B	C	D
SiO_2, %	50	35	90	35
Al_2O_3, %	25	20	0.4	12
Fe_2O_3, %	10	5	0.4	1
CaO, %	5	25	1.6	40
Physical Property				
Blaine fineness, m^2/kg	390	430	19,000	400

Next lecture…

- Cement types

Ana Tipler	27 ürüne ait işaret (Genel Çimento Tipleri)		Bileşim (kütlece[a] % olarak) – Ana Bileşenler: Klinker K	Yüksek Fırın Cürufu S	Silis Dumanı D [b]	Puzolan Doğal P	Puzolan Doğal Kalsine Edilmiş Q	Uçucu Kül Silisli V	Uçucu Kül Kalkersi W	Pişmiş Şist T	Kalker L	Kalker LL	Minör İlave Bileşen
CEM I	Portland Çimento	CEM I	95-100	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-Cüruflu Çimento	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	0-5
	Portland-Silis Dumanlı Çimento	CEM II/A-D	90-94	-	6 - 10	-	-	-	-	-	-	-	0-5
	Portland-Puzolanlı Çimento	CEM II/A-P	80-94	-	-	6 - 20	-	-	-	-	-	-	0-5
		CEM II/B-P	65-79	-	-	21- 35	-	-	-	-	-	-	0-5
		CEM II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	-	0-5
	Portland-Uçucu Küllü Çimento	CEM II/A-V	80-94	-	-	-	-	6 - 20	-	-	-	-	0-5
		CEM II/B-V	65-79	-	-	-	-	21-35	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	0-5
	Portland-Pişmiş Şistli Çimento	CEM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B-T	65-79	-	-	-	-	-	-	21-35	-	-	0-5
	Portland-Kalkerli Çimento	CEM II/A-L	80-94	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	6-20	0-5
		CEM II/B-LL	65-79	-	-	-	-	-	-	-	-	21-35	0-5
	Portland-Kompoze Çimento [c]	CEM II/A-M	80-94	←—— 6 – 20 ——→									0-5
		CEM II/B-M	65-79	←—— 21 - 35 ——→									0-5
CEM III	Yüksek fırın Cüruflu Çimento	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	0-5
CEM IV	Puzolanik Çimento [c]	CEM IV/A	65-89	-	←—— 11 - 35 ——→					-	-	-	0-5
		CEM IV/B	45-64	-	←—— 36 - 55 ——→					-	-	-	0-5
CEM V	Kompoze Çimento [c]	CEM V/A	40-64	18-30	-	←—— 18 - 30 ——→			-	-	-	-	0-5
		CEM V/B	20-38	31-50	-	←—— 31 - 50 ——→			-	-	-	-	0-5

a Çizelgedeki değerler ana ve minör ilâve bileşenlerin toplamı ile ilgilidir.
b Silis dumanının oranı % 10'la sınırlanmıştır.
c Portland Kompoze çimento CEM II/A-M ve CEM II/B-M'de, Puzolanik Çimento CEM IV/A ve CEM IV/B'de, Kompoze Çimento CEM V/A ve CEM V/B'de klinkerin yanındaki diğer ana bileşenler çimentoya ait işaretle beyan edilmelidir (Madde 8).