Alternative cements

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LC3 Doctoral School
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EPFL- Lausanne

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Introduction

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Concrete

=

Cement (clinker +gysum)

+ water

+ rock

+ sand

Worldwide most used cement is Portland cement

CO_2

7% of manmade CO_2 emissions

Decomposition of limestone (~ 60% of the total CO_2 generated in the process)

Combustion of fuel → to reach 1450°C (~ 40% of the total CO_2 generated in the process)

Production step is the most emissive step

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Solutions to reduce the CO_2 footprint of cement

Replacing a proportion of the fossil fuel by alternative fuels

Biomass
waste tires
Waste oil, Plastics

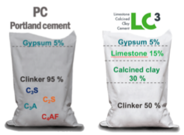
Partial substitution of raw materials

Partial replacement of cement raw materials: municipal waste incinerator ash

Mineralizers: fluorine and SO_3 → ◄ the burning temperature

Developing green binders "low CO_2 binders"

Partial substitution of cement by supplementary cementitious materials (SCMs)



Use of alternative cements

→ **Inorganic materials**

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Alternative cement: concept and requirements

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An alternative cement is an **inorganic cement** that can be used as a **complete replacement** of **Portland cement** or **blended hydraulic cements**

To be considered as a good opportunity, it needs to respect a set of requirements:

- Raw materials must be globally abundant, locally available → in order to have a small transportation distances + obtainable at low cost
- Stable quality of raw materials and composition → for a stable production
- Technical feasibility at industrial scale
- Lower CaO demand in the final products
- Possibility of recycling of its own waste and by-products

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Motivation to develop alternative cements

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- Lower environmental impact
- The need for specific properties (unattainable with Portland cement)
  - Rapid strength development
  - Specific durability requirements: improve ASR performance, better resistance to sulfate and chloride
- Reduced cost (both initial and life cycle cost)

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A wide range of alternative cements

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- Calcium Aluminate Cement (CAC)
- Calcium Sulfoaluminate Cement (CSA)
- Reactive Belite-rich Portland Cement (RBPC)
- Carbonatable Calcium Silicate Cement (CCSC)
- Magnesium Oxides derived from Magnesium silicates (MOMS)
- Binders based on reactive calcium silicates produced by hydrothermal processing
- Binders based primarily on precipitated calcium carbonates
- Geopolymer or Alkali-activated binders
- etc…

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Ref: N.Chitvoranund, From LC3 doctoral school , 2019

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A wide range of alternative cements

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Calcium aluminate cement (CAC)

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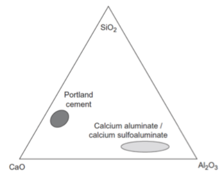
- Hydraulic cement also known as "high-alumina cement, HAC" and "ciment fondu"
- Was first developed as a replacement to the poor resistance of Portland cement to sulfate environments
- This cement is a fast setting cement → but it is not stable
- Was widely used to repair runways during World War II



Limestone + Bauxite —(T= 1450-1600°C, Sintered or fused)→ CAC: Calcium aluminate reactive phases; Amorphous: one amorphous phase

Bauxite ↓ the only suitable mineral on a scale for cement production

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Ref: Lea's Chemistry of Cement and Concrete , fifth edition, 2019

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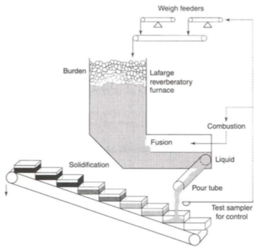
Manufacturing process of CACs

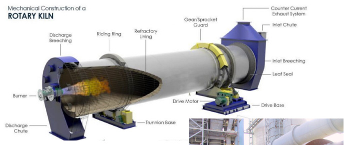
- The alumina content is the main factor that determines the manufacturing method

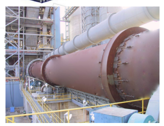
1. Reverberatory furnace (Fusion)



→ Most common method
→ Production of standard grades (40%Al_2O_3)

2. Rotary kiln





→ High CAC alumina grades (>60-80%Al_2O_3)
→ Metallurgical alumina is used instead of bauxite

Ref: Lea's Chemistry of Cement and Concrete , fifth edition, 2019 Ref: http://www.rotarykilnfactory.com/rotary-kiln-for-calcium-aluminate/

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Composition range for CAC

- CACs are a large family with a range of compositions → wide variety of applications
- CACs contain much larger proportion of alumina relative to silica

Grade	Colour	Al_2O_3	CaO	SiO_2	Fe_2O_3+FeO
'Standard' low alumina	Grey or buff to black	36 - 42	36 - 42	3 - 8	12 - 20
Low alumina, low iron	Light buff or grey to white	48 - 60	36 - 42	3 - 8	1 - 3
Medium alumina	White	65 - 75	25 - 35	< 0.5	< 0.5
High alumina (Refractory grade)	White	≥ 80	< 20	< 0.2	< 0.2

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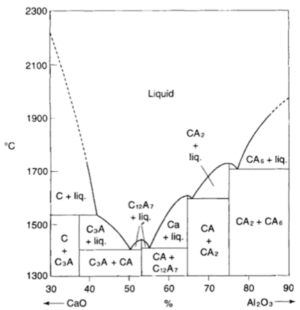
Mineralogy of CAC



Phase diagram CaO-Al_2O_3

5 intermediate calcium aluminate phases:

- Tricalcium aluminate ($Ca_3Al_2O_6$, *C_3A*) produces flash set if C$ is not added
- Dodecacalcium hepta-aluminate ($Ca_{12}Al_{14}O_{33}$ or **$C_{12}A_7$**): always present in CAC
- Monocalcium aluminate ($CaAl_2O_4$ or **CA**): Main component >40%
- Monocalcium dialuminate ($CaAl_4O_7$ or **CA_2**): found in higher-alumina grade
- Monocalcium hexa-aluminate ($CaAl_{12}O_{19}$ or **CA_6**): rarely present

Reactivity ↓ CaO ↓

Ref: Lea's Chemistry of Cement and Concrete , fifth edition, 2019

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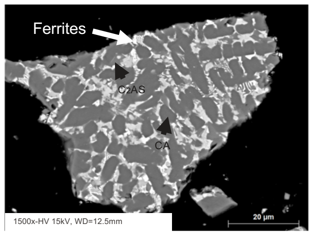
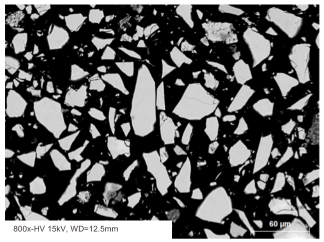
Microstructure of CAC

Crystalline CAC



Polyphase: several phases

Amorphous CAC



One phase chemically homogeneous that includes all the components of CAC

Ref: S.EL HOUSSEINI (2018)

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Hydration of CAC with water alone

- The hydration of CAC depends on temperature and age

Temperature

Temp < 15°C	Temp 15-27°C	Temp 27-50°C	Temp > 50°C
$CA + 10H \rightarrow CAH_{10}$	$CA + 10H \rightarrow$ **CAH_{10}** $2CA + 11H \rightarrow$ **C_2AH_8** $+ AH_3$	$2CA + 11H \rightarrow$ **C_2AH_8** $+ AH_3$	$3CA + 12H \rightarrow C_3AH_6 + 2AH_3$

Metastable hydrates (hexagonal aluminate hydrate)

Conversion

Stable hydrates (cubic hydrates)

$2CAH_{10} \rightarrow C_2AH_8 + AH_3 + 9H$

$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H$

Stable hydrate: denser structure → Porosity ◀

- Conversion process impacts properties (strength and durability): led to some damage in the past

How can this conversion process be avoided/reduced ? → **change the phase assemblage**

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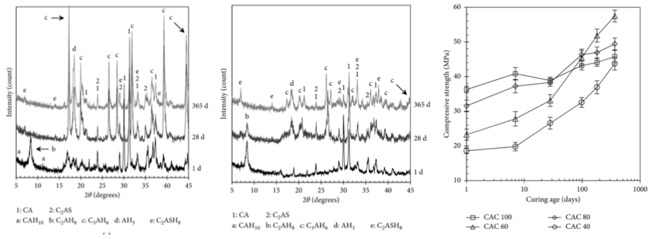
SCMs addition to reduce conversion of CAC

- Silica fume and GGBS favour the formation of strätlingite (C_2ASH_8) instead of C_3AH_6

CAC with GGBS:



→ strengths were improved

Ref: H.Yang et al., development of strength for calcium aluminate cement mortars blended with GGBS, 2019

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$CaSO_4$ (C$) to reduce conversion of CAC

- C$ addition: new hydrates appear and metastable hydrates formation is reduced

$3CA + 3C\$H_x + (38\text{-}3x)H \rightarrow C_3A.3C\$.H_{32} + 2AH_3$

Ettringite — Amorphous aluminum hydroxide

- After C$ depeletion monosulfoaluminate is formed

$6CA + C_3A.3C\$.H_{32} + 16H \rightarrow 3C_3A.C\$.H_{12} + 4AH_3$

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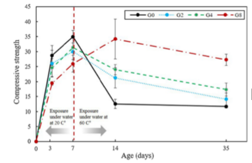
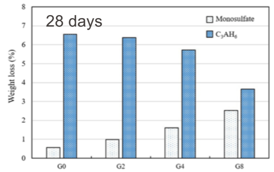
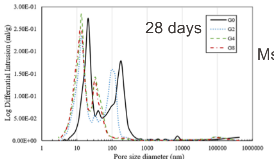
$CaSO_4$ to reduce conversion of CAC



$CaSO_4$ ◀
↓
Loss in strength ◀

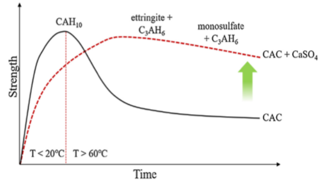


$CaSO_4$ ◀
↓
C_3AH_6 ◀
Ms ◀



Ms formation filled the voids
+
Total porosity ◀

Specimen code	G0	G2	G4	G8
Porosity (%)	30.90	28.64	27.60	26.52



Ref: H.Son et al. , Effect of CaSO4 on hydration and phase conversion of calcium aluminate cement, 2019

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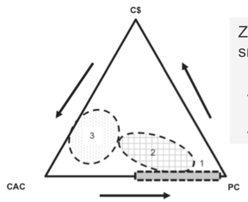
Blends of CAC with PC and C$

- Hydration is different from pure CAC systems
- CAC,C$ and PC proportions can be varied depending on the desired properties



Zone 1, 2 and 3 are the most important composition zones from an application standpoint

Zone 1: binary system of CAC and PC: quick or flash setting → small repair works

Zone 2: addition of C$ to avoid flash setting

Zone 2→ 3: reduction of PC: **Ettringite** is a major hydrate

⇩

Rapid strength development
Rapid drying
Shrinkage compensation

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Ref: Lea's Chemistry of Cement and Concrete , fifth edition, 2019

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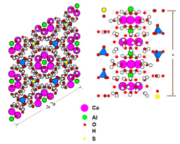
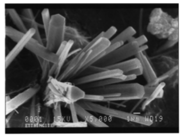
Blends of CAC with PC and C$



Crystallographic hexagonal cell



Morphology of ettringite

Main hydration product
Ettringite
$3CaO.Al_2O_3.3CaSO_4.32H_2O$

{ Low density 1.8g/cm^3
High water content
Good space filling

Other hydrates also forms….

Binder phase	Ions	Hydrates
CA	$Al(OH)_4^-$ Ca^{2+}	CAH_{10} C_2AH_6, C_3AH_6, AH_3
CA+C$	$Al(OH)_4^-$ Ca^{2+} SO_4^{2-}	$C_3A.3C\$.32H$ (AFt) $C_3A.C\$.H_{19}$ (AFm)
Combined system ($CA,C\$, C_3S$)	$Al(OH)_4^-$ Ca^{2+} SO_4^{2-} $SiO(OH)_3^-$	$C_3A.3C\$.32H$ (AFt) $C_3A.C\$.H_{12}$ (AFm) C-S-H CH

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Ref: Lea's cement chemistry book, 2019

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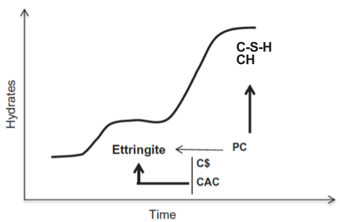
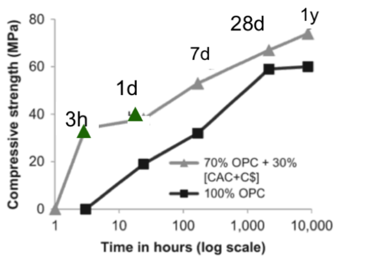
Blends of CAC with PC and C$

Schematic evolution of hydrates



Compressive strength



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Ref: Lea's cement chemistry book, 2019

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Effect of SCMs in CAC-C$ binders

- **Limestone**
  - Early age : Limestone acts as fillers → has a physical effect and strongly affect the kinetics
  - Late age : Limestone reaction depends on the amount of calcium sulfate in the system
    IF C$ reacts completely → the remaining CA will react with calcite → Hc and Mc formation
    IF C$ remaining → Limestone acts as fillers
- **Slag**
  - Early age : Slag acts as fillers during the first 4 days
  - Late age :
    Sulfate depletion → pH increases → the slag release silica → C_2ASH_8 (Strätlingite) formation
    With an excess of C$ → pH stays below 11.5 and thus the slag dissolution is slowed down

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J. Bizzozero, EPFL thesis (2014)

Examples of applications of CAC

Repair of precast element

Tile adhesives

Fixing mortar on road surface

Self-leveling underlay

Repairs of airport runways and ramps

Ref: Lea's Chemistry of Cement and Concrete , fifth edition, 2019

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Calcium sulfoaluminate cement (CSA)

- Main anhydrous phase of CSA is Ye'elimite ($C_4A_3\$$, $Ca_4(Al_6O_{12})(SO_4)$) → **30-70%**
- Is a Ye'elimite rich-cement
- Was patented in 1960 by Klein →the aim was to achieve shrinkage compensation
- Same raw materials as PC: Limestone, clay, bauxite and calcium sulfate
- CSA has lower CaO and SiO_2 but far higher Al_2O_3 and SO_3 compared to PC

Ye'elimite rich-cements type

- Ye'elimite rich-cements can be classified in two groups:
  - High belite cement, known as BYF: with/ without Boron

    →Main mineralogical phases are: belite C_2S, $C_4A_3\$$ and ferrite C_4AF
  - Low belite cement, known as CSA

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Manufactoring process of CSA

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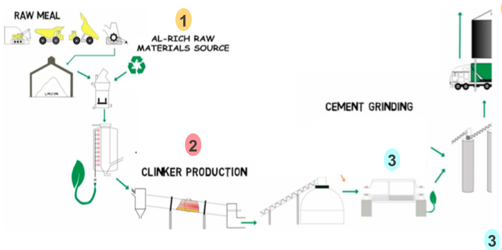

1 **Raw materials**
- **Al-Rich (Kaolin, Bauxite)**
- **less limestone requirement**

2 **lower clinkering temperature ~1250C± 50C**

3 **Clinker + gypsum or anhydrite**
This cement can be also easier ground

Great advantage in terms of capital investment costs

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Ref: M.B. Haha, et al., Advances in understanding ye'elimite-rich cements, (2019)

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Portland cement Vs ye'elimite rich-cements

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	OPC	CSA	BYF
Main Components	C_3S 50-70% C_2S 10-20% $C_4A_3\$$ - C_3A 5-10% C_4AF 5-15%	C_3S 0-5% C_2S 0-55% $C_4A_3\$$ 45-75% Aluminates 0-20% C_4AF 0-40%	C_3S 0-5% C_2S 45-75% $C_4A_3\$$ 20-45% Aluminates 0-5% C_4AF 2-40%
Raw Materials	Limestone High Alumina Clay	Limestone Al-rich (Kaolin and Bauxite) Gypsum/Anhydrite	Limestone Al-rich (Kaolin and Bauxite) Gypsum/Anhydrite
Burning Temperature (°C)	1450	~1250	~1250
CO_2 from Calcination (kg_{CO2}/ton clinker)	~522	~335	~345

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Ref: N.Chitvoranund, From LC3 doctoral school , 2019

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Main anhydrous phases in CSA

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Ye'elimite
- pure aluminate sodalite that contains calcium instead of sodium
- Two stable modifications: cubic symmetry at temperature above 800°C and undergoes phase transition to an orthorhombic symmetry at room temperature

Calcium aluminates (several intermediate phases)
- Tricalcium aluminate (C_3A)
- Krotite (CA)
- Grossite (CA_2)
- Mayenite ($C_{12}A_7$)

Calcium sulfate or Anhydrite : present as a minor phase in CSA

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Hydration of Ye'elimite ($C_4A_3\$$)

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Ye'elimite with water

$$C_4A_3\$ + 18H \rightarrow C_4A\$H_{12} + 2AH_3$$

Ms; Aluminum hydroxide

$$3C_4A_3\$ + 98H \rightarrow C_6A\$_3H_{32} + 2CAH_{10} + 2AH_3$$

Ettringite; Metastable CAH_{10}

Ye'elimite with $C\$H_2$

Molar ratio < 1:2 $$2C_4A_3\$ + 2C\$H_2 + 52H \rightarrow C_6A\$_3H_{32} + C_4A\$H_{12} + 4AH_3$$

Ettringite; Ms

Molar ratio ≥ 1:2 $$C_4A_3\$ + 2C\$H_2 + 34H \rightarrow C_6A\$_3H_{32} + 2AH_3$$

Ettringite

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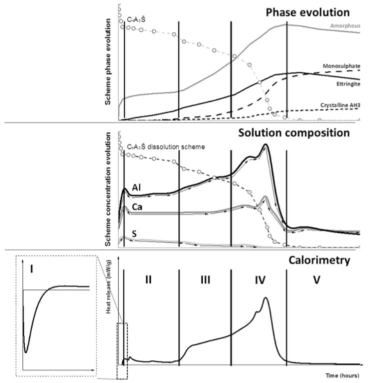
Hydration of Ye'elimite ($C_4A_3\$$)



Stage I : Initial dissolution and formation of amorphous AH_3 and Ettringite

Stage II : ± nucleation + growth of mainly ettringite

Stage III : Onset Ms + AH_3 formation

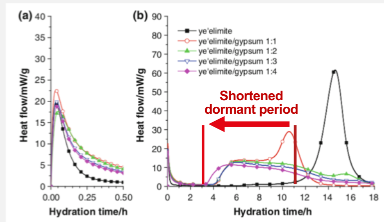
Stage IV : Anhydrous depletion continuous growth of hydrates

Stage V : Transformation Recrystallization and continuous growth

Ref: F. Bullerjahn, EPFL thesis (2018)

Effect of calcium sulfate addition

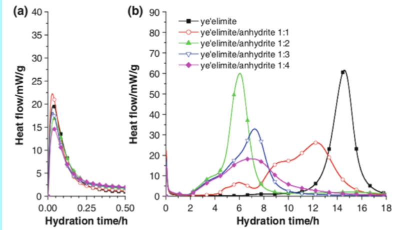
Gypsum



Shorter dormant period (with gypsum)
→ it accelerates the hydration of Ye'elimite

Ye elimite: Gypsum >1:2 : ett / AH_3 form
Ye elimite: Gypsum < 1:2 : Ms after Gypsum depletion

Anhydrite

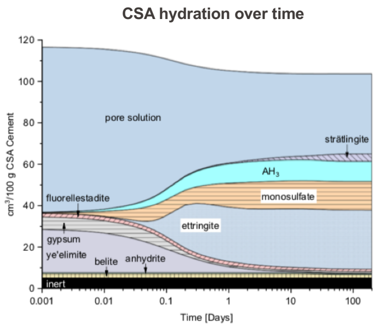


Shorter dormant period (with anhydrite)

Different peak shape to gypsum
→ slow dissolution of anhydrite compared to gypsum : Ms is favoured to ettringite

Ref: F.Winnefeld , S.Barlag, Calorimetric and thermogravimetric study on the influence of calcium sulfate on the hydration of ye'elimite, (2010)

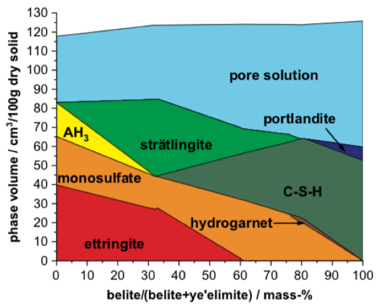
Phase assemblage from thermodynamic modelling



- Ye'elimite (the main reacting phase) and gypsum dissolve rapidly
- Ettringite, Ms and AH_3 are stable hydrate phases
- Silicate containing phase belite and fluorellestadite dissolve much slower, leading to the formation of strätlingite (at later age)

Ref: M.B. Haha, et al., Advances in understanding ye'elimite-rich cements, (2019)

Hydration reaction of BYF: $C_4A_3\$$-C_2S-$C\$$-H_2O



Belite ⇧

- Strätlingite formation
- Consumed AH_3
- Stabilized C-S-H and monosulfate

Belite > 60%

- Ettringite is no longer stable

Belite > 75%

- Portlandite formation occurs

Belite > 80%

- Strätlingite is no longer stable

Ref: M.B. Haha, et al., Advances in understanding ye'elimite-rich cements, (2019)

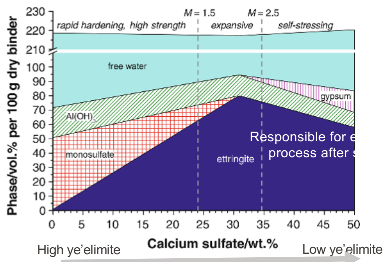
Properties of CSA cements

- Control the properties by adjusting the composition

n.d. = not determined

		Rapid hardening		Normal hardening	Slow hardening	
Mineralogical composition (%)						
Belite	C_2S	25	30	45	50	65
Ye'elimite	$C_4A_3\bar{S}$	20	20	20	10	10
Ferrite	$C_2(AF)$	40	30	15	30	15
Anhydrite	$C\bar{S}$	15	20	20	10	10
Compressive strength development (MPa)						
	1 d	34.8	28.3	9.5	5.6	5.2
	3 d	36.9	33.8	19.3	7.6	8.9
	7 d	37.4	37.7	27.4	11.7	12.4
	28 d	n.d.	n.d.	49.8	14.1	14.5
	90 d	n.d.	n.d.	n.d.	21.4	22.4
	120 d	51.8	53.8	86.2	n.d.	n.d.

Ref: F. Bullerjahn, EPFL thesis (2018)



Ref: F. Winnefeld and S. Barlag, (2010)

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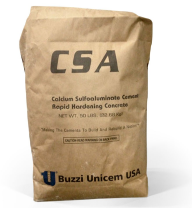
Applications

CSA

- Shrinkage compensation
- Road reparation
- Special work: sulfate resistance



BYF

- Rapid setting
- Concrete construction

LC3 Doctoral School, alternative cements

LABORATORY OF CONSTRUCTION MATERIALS

A wide range of alternative cements

- Calcium Aluminate Cement (CAC)
- Calcium Sulfoaluminate Cement (CSA)
- **Reactive Belite-rich Portland Cement (RBPC)**
- Carbonatable Calcium Silicate Cement (CCSC)
- Magnesium Oxides derived from Magnesium silicates (MOMS)
- Binders based on reactive calcium silicates produced by hydrothermal processing
- Binders based primarily on precipitated calcium carbonates
- Geopolymer or Alkali-activated binders
- etc…

LC3 Doctoral School, alternative cements

LABORATORY OF CONSTRUCTION MATERIALS

Reactive Belite rich Portland Cement (RBPC)

- Also known as high belite cement (HBC), is an hydraulic cement that belongs to the same family as PC
- Main anhydrous phases : C_2S, C_3S, C_4AF, C_3A (C_2S is the most abundant one)
- The difference to PC is the belite / alite ratio (C_2S > 40% and C_3S < 35%)
- Can be manufactured in conventional cement plants with lower burning temperature (~ 1350 °C)
- To make belite sufficiently reactive: SO_3 or rapid clinker cooling might be needed

LC3 Doctoral School, alternative cements

LABORATORY OF CONSTRUCTION MATERIALS

Reactive Belite rich Portland Cement (RBPC)

RBPC Vs PC

- Lower water demand
- Similar setting time to PC
- Lower early age strength but higher later age strength
- Lower drying shrinkage
- Better resistance to sulfates and chloride (less CH)

Applications

The maximum concrete temperatures reached with RBPC can be much lower than with PC → avoid thermal cracking especially in large concrete pours (in mass concrete applications, such as dams)

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Carbonatable calcium silicate cements (CCSC)

- Low lime calcium silicates, such as Wallastonite ($CaSiO_3$, Cs) can harden by carbonation

$$CaSiO_3(s) + CO_2(g) \xrightarrow{H_2O} CaCO_3(s) + SiO_2(s)$$

Major **advantages** of CCSC technology:

- Low CO_2 due to low calcium content → 30% less CO_2 emission than in PC production
- Absorption of additional CO_2 during curing (consuming 300kg of CO_2 per ton during curing)
- Ability to reach final high strength in 24h (28days strength of PC)

Limitations:

- Mainly suited to the fabrication of precast articles but not too large cross section to allow thorough curing
- Because of its low pH <9, the steel is not protected by concrete against corrosion

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Magnesium Oxides derived from Magnesium silicates (MOMS)

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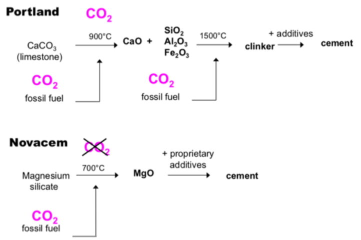
- New type of MgO-based hydraulic cement, called magnesium hydroxy-carbonate cement
- Mixture of MgO + hydrated magnesium (hydroxy-)carbonates



Ref: http://www3.imperial.ac.uk/pls/portallive/docs/1/50161701.PDF

Magnesium Oxides derived from Magnesium silicates (MOMS)

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Raw materials:

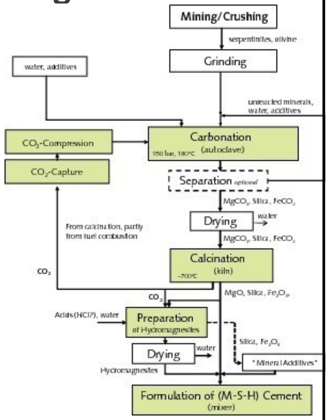
Magnesium silicate rocks

- Olivines
- Peridotite
- Serpentine

Global peridotite and serpentine ore location

Manufacturing process: different from PC

- MgO can be hardened by direct carbonation at modest CO_2 pressures
- Demonstrated on a small scale



Ref: N.Chitvoranund, From LC3 doctoral school , 2019

Magnesium Oxides derived from Magnesium silicates (MOMS)

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Properties:

- good water resistance
- relatively high level of CO_2 capture in the hydration product

Applications:

- Not yet been seriously explored

Ref: N.Chitvoranund, From LC3 doctoral school , 2019

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Thank you for your attention
Questions?