

# Ettringite revisited

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# Ettringite (1)

- Since its discovery in nature and its subsequent identification as a minor phase in hydrated Portland cement, this substance has attracted much interest.
- It contains more water (~50%) and has a lower density ( $1.77\text{g/cm}^3$ ) than any other cement hydrate

# Ettringite (2)

- A wide variety of opinions –often negative -exist about ettringite in cement: that it is associated with dimensional instability and contributes little if anything to strength.
- Like many generalizations, these statements contain a grain of truth but are not absolute.

# Making ettringite

- Almost any source of reactive alumina (hydroxide gel, aluminium sulfate hydrate, tricalcium aluminate) will do. Add calcium sulfate, calcium hydroxide and water to get the desired composition (with some excess water) and stir or agitate for a few hours to weeks at 20°C.
- Product consists of laths or needles of ettringite.

# Ettringite: structure and composition

Nominal composition is :



where :

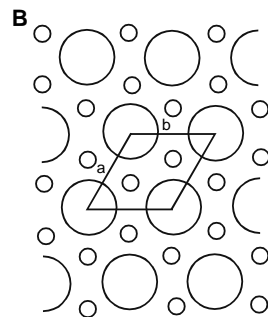
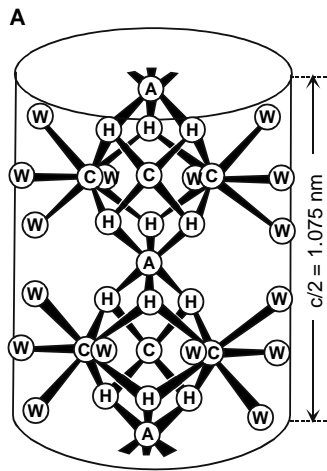
X = Al, Fe(III) Si(IV)

Y = sulfate, carbonate, borate, hydroxide

Z = 24 to 36 (normally 26- 32)

*The crystal structure shows how these diverse ions can be accommodated in one structure*

# Ettringite



# Water in ettringite

- Water is packed between the columns.
- The number of H<sub>2</sub>O ranges between 24 to 36
- When made in water at 5°C, it contains ~36 H<sub>2</sub>O. But if dried, or made wet at 25°C, this decreases to ~30-32 H<sub>2</sub>O.
- In the range 30-32 H<sub>2</sub>O, water is “zeolitic”
- Below 30 H<sub>2</sub>O, the structure begins to collapse.

# Ettringite family

- Replacement of one ion kind by another is not necessarily continuous: solid miscibility gaps may result.
- For example, replacement of  $\text{Al}(\text{OH})_6$  in ettringite by  $\text{Si}(\text{OH})_6$  is limited: the phase with silicate has, however, essentially the same structure as ettringite and is **thaumasite**.
- This is one reason for using a collective family name: **AFt** where (A= Alumina, F= ferric iron, t= trisulfate).

# Ettringite and thaumasite

- Water contents above 32 H<sub>2</sub>O have not been reported for thaumasite.
- While ettringite is a stable phase in Portland cement- even if calcite is added-, thaumasite is not stable under these conditions: it is characteristically a product of cement which has been altered in service

# Range of compositions

In practise, the range of compositions is limited by:

- Some potential substituents, eg., borate, are virtually absent from cement
- Some substituents are partitioned into other phases, for example sulfate, which is in part, sorbed by C-S-H.
- All components are slightly soluble, so some sulfate is dissolved in pore fluid

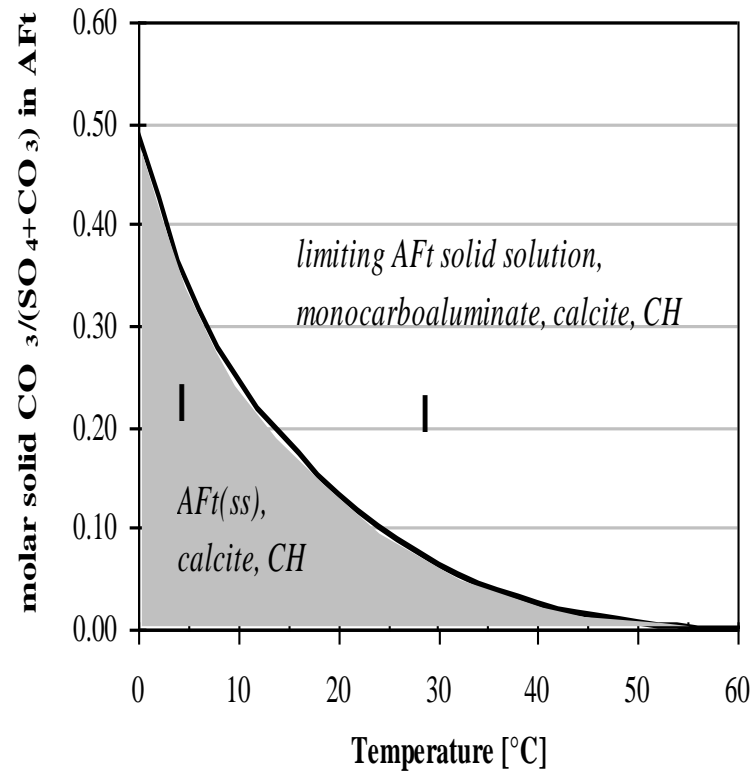
# Other limitations on composition

- Hydrated Portland cement has a series of buffers which limit species activities (~composition).
- For example, pH is buffered by the solubility of  $\text{Ca}(\text{OH})_2$  while the carbonate activity is buffered by the coexistence of two solids, calcite and calcium monocarboaluminate with water.

# Temperature/ composition

- Additionally, temperature plays an important role, with the degree of substitution often being temperature dependent.
- As an example, consider carbonate substitution in ettringite. To focus calculations, we assume that (i) pH is controlled by  $\text{Ca}(\text{OH})_2$  and (ii) carbonate activity is controlled by calcite

# Limits of carbonate substitution in AFt



# Buffers in Cement systems

- Their operation greatly simplifies a comprehensive description of the internal chemistry and mineralogy
- In turn, it simplifies the linking of chemistry and mineralogy with physical and engineering parameters: shrinkage, porosity and permeability, strength, etc.

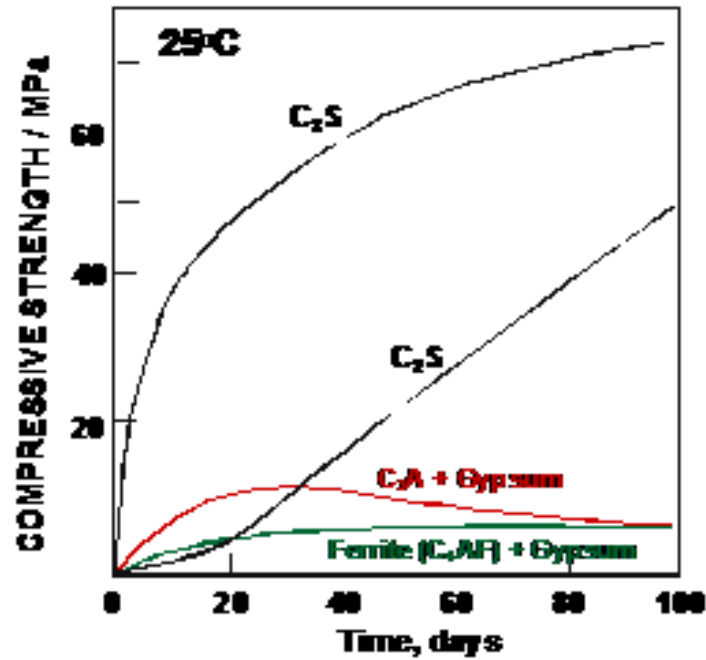
# Applications and examples

- Note that all commercial cements shrink: the volume of solids formed in hydration is less than the original volume of (cement+water).
- In the course of hydration, water goes from liquid form to solids: Portland cements do **NOT** set by drying
- Some phases, like ettringite, are very good at filling space

# Consequences of carbonate substitution

- Maximum amount of ettringite need not be limited by sulfate content.
- Bound water tends to increase as more ettringite forms
- Better space filling of solids but with potential for expansion
- Scope for seasonal temperature-dependant changes in mineralogy and microstructure as carbonate is exchanged.

# Why use ettringite cements?



# Classical view

- “Ettringite does not contribute to strength”
- **But** the data taken in isolation are not necessarily relevant: as part of a balanced system, ettringite can contribute to:
  - Lowered permeability
  - Dimensional stability
  - And it is self-evident that commercial ettringite based cements (>70% ettringite) have adequate strengths

# This leads to two distinct types of sulfoaluminate cements;

- Cement additives used in conjunction with Portland cement to reduce shrinkage

(Generally also contain free lime, CaO)

- Cements used to form mortars and concretes (without OPC)

(Free lime normally absent or present in small amounts)

# Modern sulfoaluminate cements

- Developed in China in the 1970's
- Based on Kline's compound,  $C_4A_3\$$  ( $\$ = \text{Sulfur trioxide}$ )
- Clinker produced in conventional kilns at 1300-1330°C
- "Clinker" is soft and easily ground. Also contains belite,  $\sim Ca_2SiO_4$ , and ferrite, traces of  $MgO$ ,  $C_{12}A_7$ , anhydrite, etc.

# Sulfoaluminate cements

- CO<sub>2</sub> output per tonne is ~400-600Kg (compares with ~900 Kg for OPC)
- AND the clinker is blended with 10-16% calcium sulfate, which further dilutes the associated CO<sub>2</sub> content.
- Like OPC, it can be mixed with aggregate forming concrete.

# Sulfoaluminate concretes

- Require a set retarder to give a period of workability
- Set time usually adjusted to 2-4 hr
- Thereafter gain strength rapidly: 40-50 MPa at 24 hr readily attainable
- Water: cement ratio for complete hydration is  $\sim 0.5$  (OPC is about 0.35) ; heat output is higher and more intense than in equivalent OPC.

# History of use

- Extensively used in highway bridges, building foundations, cast pipes, etc
- Examination up to 25 years service reveals no loss of strength. Give good corrosion protection to embedded steel. Even in high chloride environments
- May carbonate slightly faster than OPC: surface often “chalky”.

# Advantages

- Amenable in fresh state to “property modifiers”

Therefore used in formulations such as

- Self-levelling screeds
- Self compacting formulations
- Sprayable mixes (where rapid hardening is also advantageous)
- Fireproofing (high latent heat of water).

# Selection of “property modifiers”

- Basically, any substance beneficial for functional modification of CAC (Calcium Aluminate Cements) is likely to work for sulfoaluminate cements.

# Disadvantages

- Cheap supply of aluminous raw materials (compete with aluminum manufacture for bauxite)
- Lack of standards (but Chinese standards exist and are satisfactory)
- Limited data on performance in severe environments

# Present potential

## Non- structural applications

- Repair materials (adhere to Portland cement)
- Self- levelling screeds
- Tile adhesives
- Tunnelling and stabilization applications
- Shrinkage- reducing admixes to OPC

# In mixtures with Portland cement C\$A may-

- Cause flash set, or false set, or both
- Reasons why this occurs are not clear but may relate to the amount and reactivity of the calcium sulfate added, rather than to the cement clinker.
- Provided it did not interfere with longer term strength gain, flash set may assist emplacement by spray processes.

# Durability at elevated T and low RH

- Water loss with structural degradation occurs at an increasing rate  $>45^{\circ}\text{C}$  at relative humidity 30-50%.
- The loss gives “metaettringite” - a poorly structured phase retaining some features of the ettringite structure.
- For practical purposes, this reaction is irreversible

# Chinese experience

- 25-40 years experience of sulfoaluminate concretes has not revealed any problems.
- They probably carbonate more rapidly than Portland cement (it is difficult to benchmark tests)
- They afford good protection for embedded steel even in chloride- rich environments and have outstanding resistance to sulfate attack.
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# Summary(1)

- Calcium sulfoaluminate cements have 30-40 years of use in civil engineering
- They are made with the same equipment as used for Portland cement
- Have gained acceptance in the west in specialty cements
- We do not yet know the limits of their performance envelope: no one “best” composition

# Summary (2)

**Sulfoaluminate compositions are attractive because:**

- Low CO<sub>2</sub> emissions associated with production
- Can incorporate slag, fly ash and by-product gypsum
- Do not require totally new technologies for production and use
- **Need cheap sources of reactive alumina**