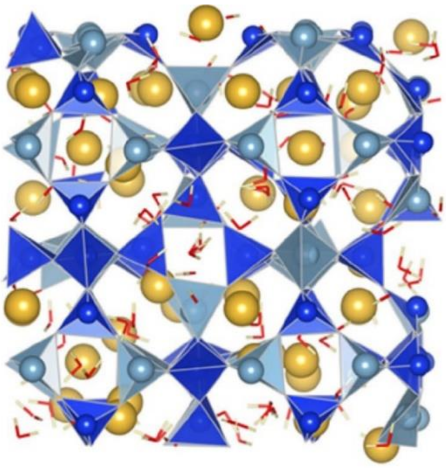
Introduction to AAM technology

Lecture notes of the
DuRSAAM training course
held January 2020



Edited by

Stijn Matthys and Alessandro Proia

Introduction to AAM technology

Lecture notes of the
DuRSAAM training course
held January 2020

The PhD Training Network on Durable, Reliable and Sustainable Structures with Alkali-Activated Materials

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Foreword

The design, durability and performance of structures play a crucial role in fostering societal and economic growth. Concrete structures are used extensively for buildings, transport, infrastructure and maritime applications. By using concrete extraordinary structures can be realised, and these are often designed for long service lives to gain optimal value from the material, environmental, intellectual and financial input into the making of the structure. Although concrete has a fairly limited environmental impact per cubic meter used, concrete is also one of the most frequently used building materials. In Europe, around 4 tonnes of concrete per capita are consumed annually. This makes that concrete is often associated with durability issues and huge environmental costs, for example as the cement industry accounts for about 8% of global anthropogenic carbon dioxide emissions.

There is a clear demand for a new, sustainable generation of construction materials, since Ordinary Portland Cement (OPC)-based concrete cannot meet all the challenges of modern society concerning durability and sustainability. A number of more eco-friendly concrete technologies have appeared over the years, among which a growing interest in concrete technology based on alkali-activated materials (AAM), sometimes also referred to as geopolymers. AAM materials can represent a valuable alternative to OPC for a more sustainable built environment.

This eBook has been made in the framework of the European Training Network on Durable, Reliable and Sustainable Structures with Alkali-Activated Materials (DuRSAAM), which organized a training course on AAM technology held at Karlsruhe Institute of Technology 27-29 January 2020. This open source book collects the lecture notes by the teachers of this training course and provides building professionals and stakeholders new insights on alkali-activated concrete as an emerging building technology.

Stijn Matthys
Alessandro Proia
Ghent, 2020

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1. Outline

Stijn Matthys

Concrete is a popular and efficient building material. However, being used that widely all over the world, its environmental impact sums up to large numbers. The upside of this observation is that when improving the environmental impact of concrete, significant improvements can be made in terms of for example reducing carbon dioxide emissions and using less primary raw materials. There are various options to reduce the environmental impact of concrete further, including more efficient cement production, use of recycled aggregates, use of blended cements via secondary cementitious materials and the use of alternative binders. One of these alternative binder technologies is alkali-activated materials (AAM).

The information bundled in this eBook is that of a 3-day course, formatted as a training school open to researchers, practicing engineers, etc., in fact, for all those who want to obtain profound starting knowledge on AAM technology. The original training course, specifically developed and delivered collaboratively by the DuRSAAM action, was held at the Karlsruhe Institute of Technology (KIT), spring 2020. A course introduction video is provided here (time to watch 4 minutes).

The **outline** of the teaching material bundled in this book, is as follows:

- ➔ “The cement perspective” (Chapters 2 till 4):
  - Cements and the need for improvements
  - Alternative solutions, including alkali-activated materials
  - Cement characterisation
- ➔ “The concrete perspective” (Chapters 5 till 7):
  - Standardisation of cements and concretes
  - Mechanical properties of AAM concretes
  - Durability testing of concrete and their applicability to AAM
- ➔ “Further into the details” (Chapters 8 till 10):
  - Modelling of AAM concretes
  - Shrinkage of AAM concretes
  - Fibre-reinforced AAM concretes
- ➔ “Hands-on” (Chapter 11):
  - AAM lab work

The **aim** of the teaching material is to impart basic understanding as well as up-to-date knowledge about AAM binders and concretes. The specific **learning objectives** are as follows:

- ✓ Understanding about traditional cement versus this new binder technology.
- ✓ Obtaining insight into the workability, mechanical and durability behaviour of AAM concretes.
- ✓ Build knowledge on AAM technology and about how these binders and concretes behave compared to traditional hydraulic cements and concretes, respectively.

✓ Being able to position the emerging AAM technology and its application amongst other construction technologies, and to recognize its value for circular concrete.

In short, for the reader of this eBook to grasp the AAM binder technology for concrete construction.

A **brief description of AAM concrete**, sometimes also referred to as geopolymer concrete, is given as follows. The composition of traditional concrete and AAM concrete is analogous, as indicated in Figure 1.1. The cement is replaced in AAM concrete by mineral powders (fineness comparable to cement) that will harden by activating these mineral powders with an aqueous solution of alkalis, in contrast to cement that only needs water to harden. Therefore, both concrete types use an alternative chemical route to hydrate into an overall similar artificial rock, based on C(A)SH-like compounds (calcium (alumino)silicate hydrates).

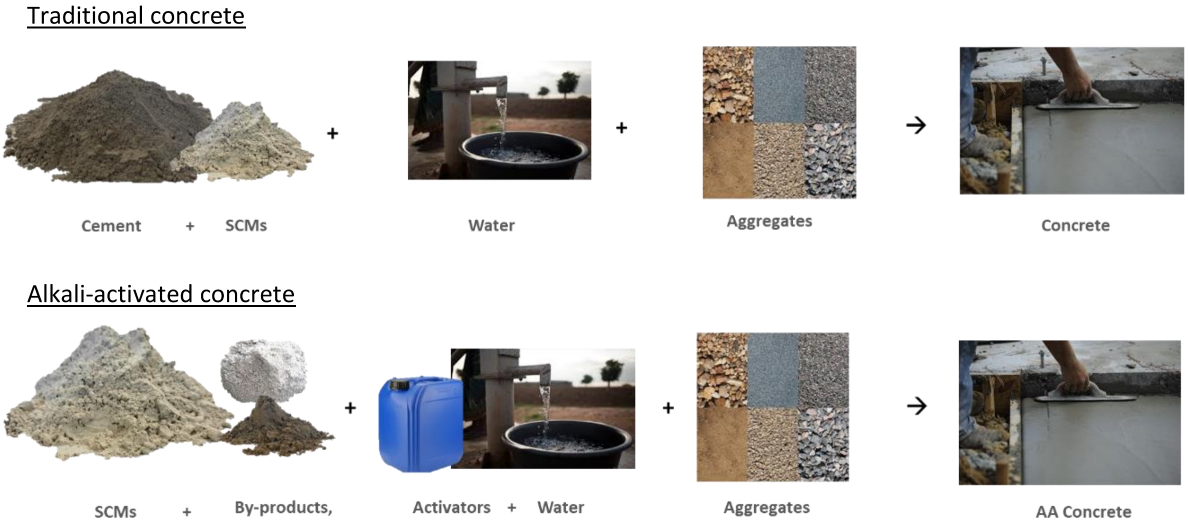


Figure 1.1 – Composition of traditional versus AAM concrete

The binder component of AAM concrete are mineral powders (called ‘precursors’), which are activated by means of alkalis (called ‘activators). The mineral powders are industrial by-products such as metallurgical slags, combustion ashes and calcined clays, of which some of them have already a tradition to be used as secondary cementitious materials (SCMs) in blended cements. The dosage of these mineral powders, which act as binders instead of cement, is slightly higher than for traditional concrete. As an order of magnitude, the dosage is around 400 kg per m^3 of concrete, but depends on the specific mix. Various chemical components can be used for the alkalis, but often a combination of sodium silicate (water glass) and sodium hydroxide is used. The dosage in terms of dry mass of alkalis is, for example, an order of magnitude of 5 mass% with respect to the binder content, for an AAM concrete based on blast furnace slag. The further mix proportioning in terms of fine (sand) and coarse aggregates is the same as with traditional concrete and is performed on the basis of optimal packing distribution. In this respect, is also possible to use recycled or artificial aggregates in AAM concrete. The application of a hybrid solution of concrete with a low dosage of cement and a high dosage of by-products additionally activated, belongs further to the options.

AAM concrete is compatible with current solutions for reinforcing concrete (reinforcing steel, fibre reinforced concrete,…) and pilot projects with AAM concrete have already been realized in various countries. The characterization and application of AAM concrete is however less advanced than traditional concrete, and the regulatory framework is still limited. Like for traditional reinforced or prestressed concrete, AAM concrete mixes are designed to have good workability, mechanical performance and durability:

- The workability of AAM concrete is generally somewhat more viscous and hardens faster, whereby attention is given in the mix design to obtain a sufficient workable time for the fresh concrete.
- High compressive strengths are generally easy to achieve, but requires attention in the mix design and curing to keep shrinkage deformations under control.
- Due to its generally denser microstructure, AAM concretes have the ability to achieve strong durability properties. On the other hand, the chemical structure of AAM concrete and traditional concrete is not identical, so that further durability tests are recommended to characterize the durability of AAM concrete mixes. In general terms, the durability of AAM concrete is comparable to that of a cement-based concrete, although there might be differences (e.g. carbonation resistance of AAM concrete may be slightly less, resistance to chloride penetration slightly better).
- A common concern of engineers considering AAM concretes for the first time is damage by ASR (alkali-silica reaction). This durability aspect has been examined by various researchers and has not been reported as a problem so far. This is attributed to the fact that alkalis are not freely available in the hardened concrete, but participate in the chemical processes that allow AAM concrete to harden.

In addition to workability, strength and durability, AAM concretes have a lower environmental impact. This is at one hand due to the fact that Portland clinker based cement, with its relatively high environmental impact, is avoided and on the other hand because less primary raw materials are used. The exact gain in environmental impact is not always straightforward to establish, because this depends on (1) the details of the AAM concrete composition, (2) the type of cement based concrete used as a reference for comparison (e.g. concrete based on CEM I or CEM III), and (3) to which extent the environmental impact of the by-products are allocated to its originating production or to the AAM concrete. Under the assumption that mainly the environmental impact of the grinding of the mineral powders is assigned to the AAM concrete and if reference to concrete types with high Portland clinker amounts, values are mentioned of an environmental gain of 50% and more, in terms of carbon footprint. Furthermore, in terms of end-of-service-life, AAM concrete is recyclable and reusable according to common practices. This has been reported, though studies in this respect are still limited.

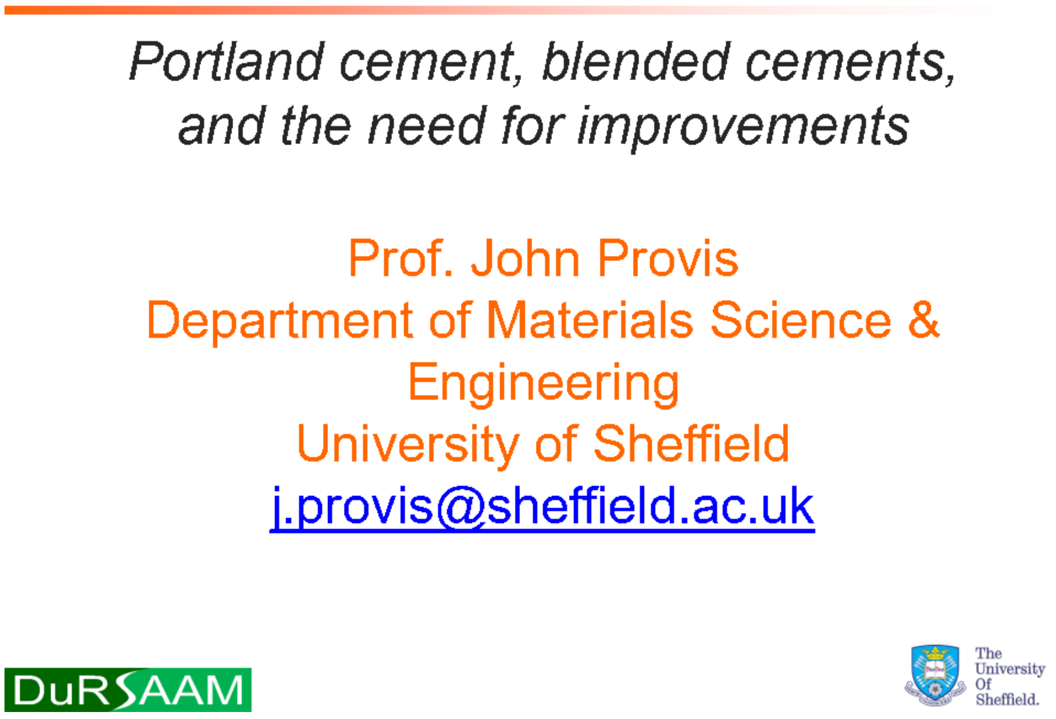
By-products for AAM concrete are selected or blended with care, to come to proper mix proportions and to exploit the reactivity of the by-products. It might also be of interest to apply beneficiation treatments on the by-products, to purify them from e.g. valuable metals and to make sure that there is no potential leaching of harmful elements. Environmental permits to use some types of by-products as constituent for concrete might be applicable, depending on national legislation.

Much more information on AAM binders and concretes, in a wider context of concrete technology, is provided in the following chapters. For further reading on AAMs, also reference is made to the RILEM Handbook “Alkali Activated Materials: State of the Art Report, RILEM TC 224 AAM”, ISBN 978-94-007-7671-5. A link to this handbook is provided here.

2. Cements and the need for improvements

John Provis

In this chapter an introduction is given to Portland cement and secondary cementitious materials to create blended cements. The cement hydration is discussed as well as some sustainability considerations with respect to cement usage. The shift from a single universal cement to an array of cement types is highlighted and taken.



Portland cement, blended cements, and the need for improvements

Prof. John Provis
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Cements (of various types)

What I will cover today:

- Portland cement production & mineralogy
- Portland cement hydration reactions & products
- Supplementary cementitious materials
- Introduction to AAMs and a few other non-Portland cements
- Characterisation of complex materials (e.g. cements) – materials science techniques

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Portland cement

- Definition:

  "*A hydraulic cement capable of setting, hardening and remaining stable under water. It consists essentially of hydraulic calcium silicates, usually containing calcium sulfate*".

- The basis of almost every (>95%) concrete used worldwide
- The closest thing to magic the human race has ever invented..?

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What is in Portland cement?

- Cement clinker
  - Tricalcium silicate (“alite”), $3CaO \cdot SiO_2$
  - Dicalcium silicate (“belite”), $2CaO \cdot SiO_2$
  - Tricalcium aluminate (“aluminate”), $3CaO \cdot Al_2O_3$
  - Tetracalcium aluminoferrite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
  (“ferrite solid solution” – composition can vary)

→ made from limestone and clays in a kiln, then ground to a fine powder

- Gypsum, $CaSO_4 \cdot 2H_2O$

→ added during grinding

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Developed 200 years ago…

- 1824, Joseph Aspdin, Leeds, UK
  - British Patent #5022, “Artificial Stone”
  - Developed & improved later, including by his son William Aspdin
  - Louis Vicat (France) worked at a similar time, as did others
  - First standard specification 1859, London Metropolitan Board of Works (London sewers)
- Similar materials used by the Romans
  - Used natural resources (volcanic soil & lime), no kilns, but basic chemistry is similar

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Cement chemistry notation

- Abbreviations for all those ugly formulas

$CaO \rightarrow C$

$SiO_2 \rightarrow S$

$Al_2O_3 \rightarrow A$

$Fe_2O_3 \rightarrow F$

$H_2O \rightarrow H$

$SO_3 \rightarrow \overline{S}$ (or sometimes $\underline{S}$ or \$)

(plus some others not really used here:
$CO_2 \rightarrow$ c or $\overline{C}$, $Na_2O \rightarrow N$, $K_2O \rightarrow K$)

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Using this to abbreviate the compounds…

- Tricalcium silicate (alite), $3CaO{\cdot}SiO_2$
  $\rightarrow C_3S$
- Dicalcium silicate (belite), $2CaO{\cdot}SiO_2$
  $\rightarrow C_2S$
- Tricalcium aluminate, $3CaO{\cdot}Al_2O_3$
  $\rightarrow C_3A$
- Tetracalcium aluminoferrite, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$
  $\rightarrow C_4AF$
- Gypsum, $CaSO_4{\cdot}2H_2O$
  $\rightarrow C\overline{S}H_2$

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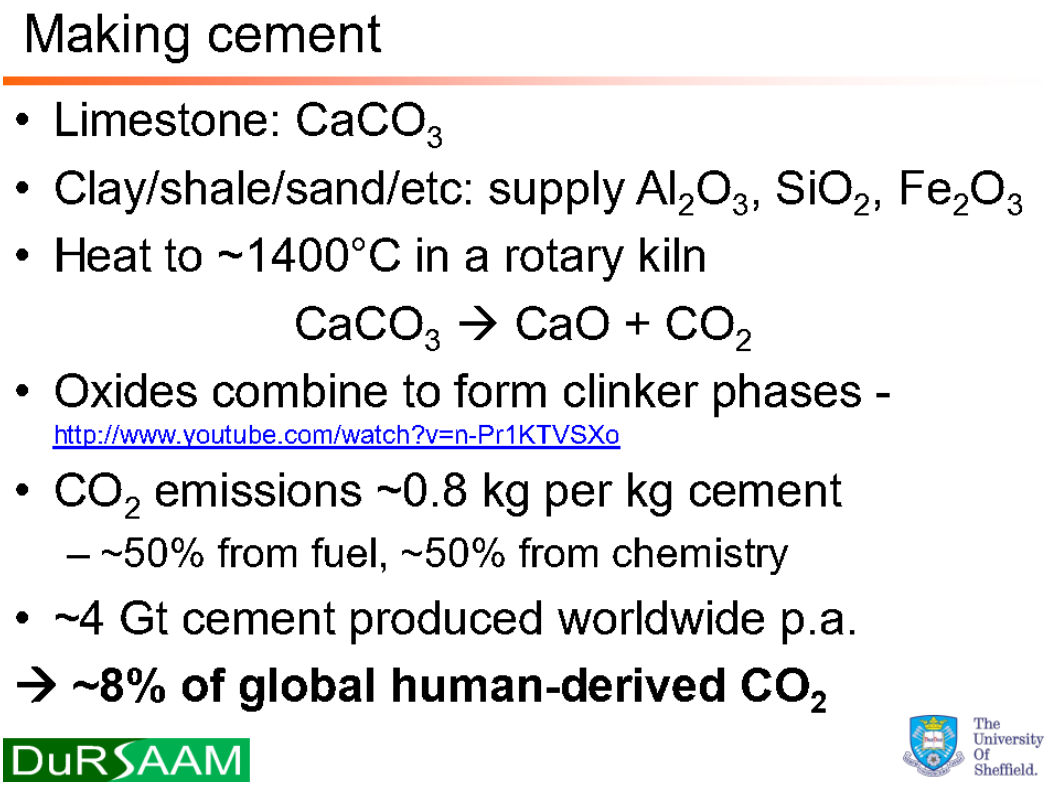


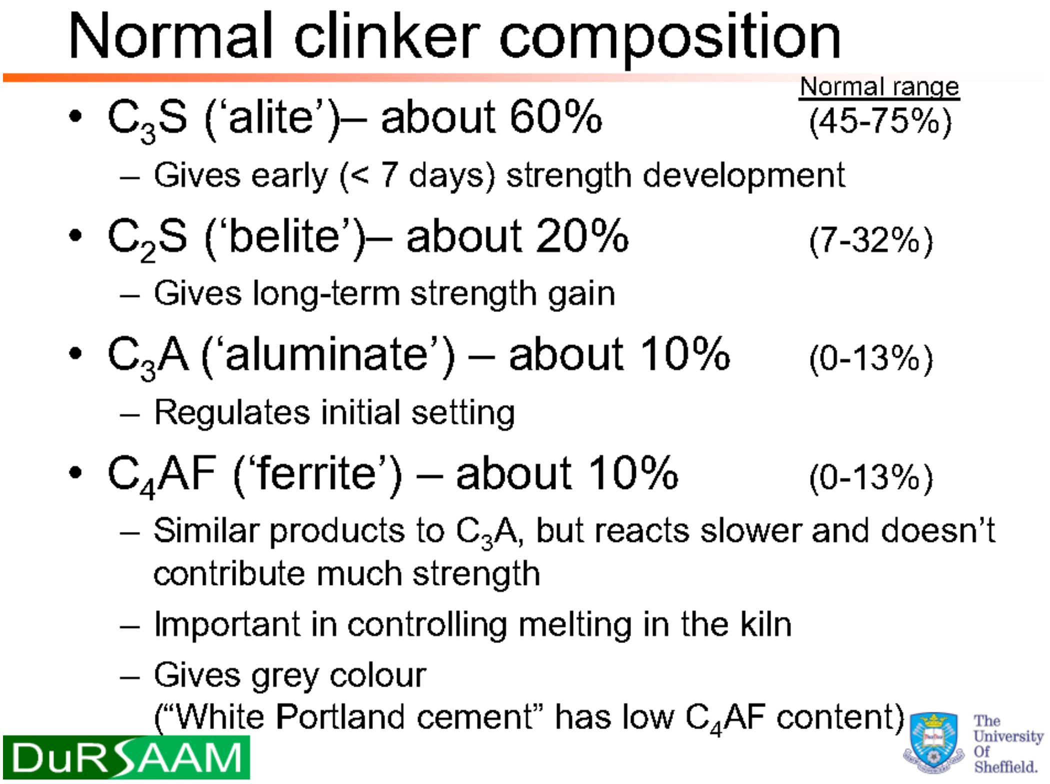
Making cement

- Limestone: $CaCO_3$
- Clay/shale/sand/etc: supply Al_2O_3, SiO_2, Fe_2O_3
- Heat to ~1400°C in a rotary kiln

$$CaCO_3 \rightarrow CaO + CO_2$$

- Oxides combine to form clinker phases - http://www.youtube.com/watch?v=n-Pr1KTVSXo
- CO_2 emissions ~0.8 kg per kg cement
  - ~50% from fuel, ~50% from chemistry
- ~4 Gt cement produced worldwide p.a.

→ ~8% of global human-derived CO_2



Normal clinker composition

Normal range

- C_3S (‘alite’)– about 60% (45-75%)
  - Gives early (< 7 days) strength development
- C_2S (‘belite’)– about 20% (7-32%)
  - Gives long-term strength gain
- C_3A (‘aluminate’) – about 10% (0-13%)
  - Regulates initial setting
- C_4AF (‘ferrite’) – about 10% (0-13%)
  - Similar products to C_3A, but reacts slower and doesn’t contribute much strength
  - Important in controlling melting in the kiln
  - Gives grey colour (“White Portland cement” has low C_4AF content)

The calcination process

- [Image deleted for copyright reasons]

See: P.C. Aitcin, Binders for Durable and Sustainable Concrete, Taylor & Francis, 2007

Phase diagram – CaO-Al_2O_3-SiO_2

- [Image deleted for copyright reasons]

See: Y. Waseda & J.M. Toguri, The Structure and Properties of
Oxide Melts, World Scientific, 1998

Effect of Fe on melting (liquidus)

- [Image deleted for copyright reasons]

See: A. Kondratiev & E. Jak, Fuel 80(2001):1989-2000

Cement hydration

- Mixing cement with water makes it react
  - Particles dissolve
  - Ions rearrange in solution phase
  - Solid hydrate phases solidify and give strength

- Reaction process is **hydration**, not drying
  - Water forms an essential part of the solid phases in hardened cement
  - Drying is very bad for fresh cement

  → slows or stops reactions, causes cracking and loss of strength

The important hydrate phases

- Calcium silicate hydrate (C-S-H)
  - Formed by hydration of C_3S and C_2S
  - Non-crystalline (amorphous/disordered)
  - Porous on nanometre length scale
  - No fixed chemical composition, but often written as approximately $1.6CaO \cdot SiO_2 \cdot 1.8H_2O$

    (you may also see it given as
    $3CaO \cdot 2SiO_2 \cdot 3H_2O$, which is similar)
  - Fills a lot of the space
    in hardened binders

See: I.G. Richardson, *Cement & Concrete Research* 29 (1999):1131-1147

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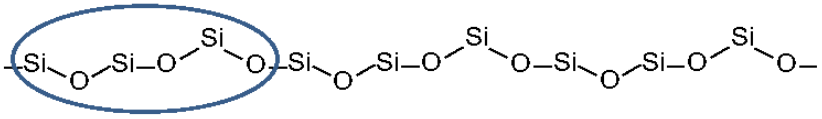
C-S-H(I) and C-S-H(II)

- Two main types of C-S-H exist (we think)
  - Differing in structure, C/S ratio and solubility
  - Based on structure of **tobermorite**: a crystalline, fibrous chain silicate mineral (rare in nature, found in N. Ireland)

  (C-S-H(II) resembles a different chain silicate: jennite, $Ca_9Si_6O_{18}(OH)_6 \cdot 8H_2O$)
  - Tobermorite is $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$ – C/S ratio 5/6 is lower than in C-S-H
  - ‘dreierketten’ structure (‘*drei*’ = 3) in kinked chains



  - Breaking some of the chains (removing Si sites) gives a disordered structure – this is C-S-H(I)

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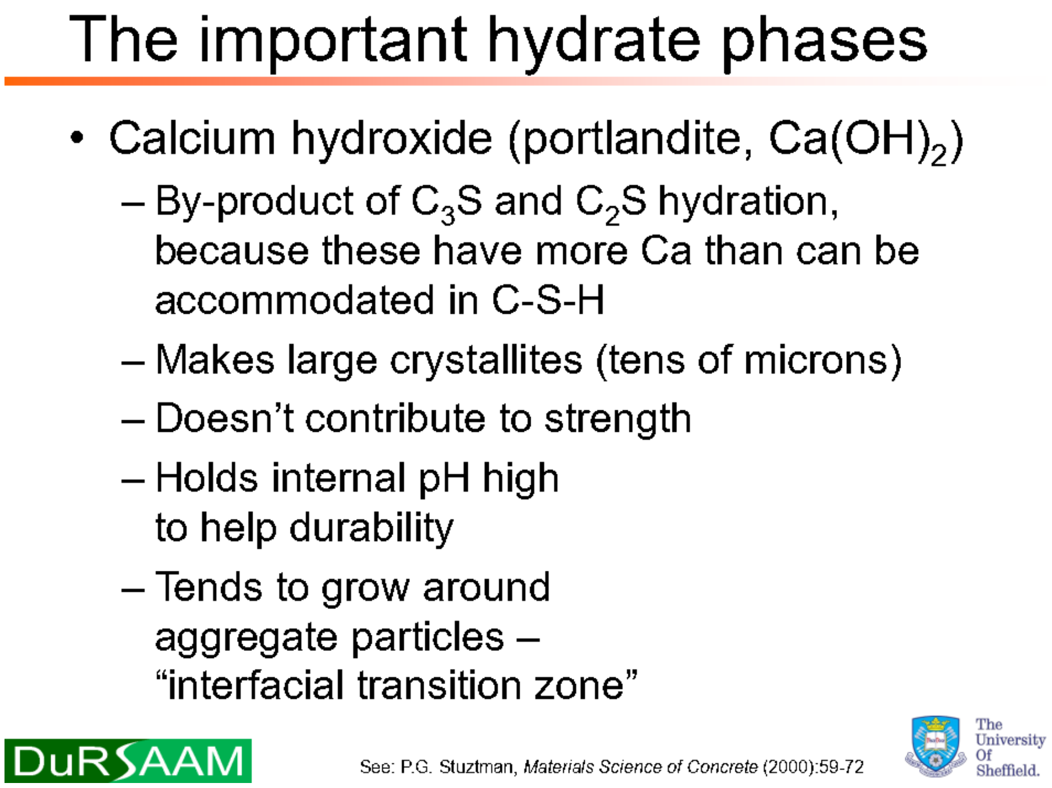
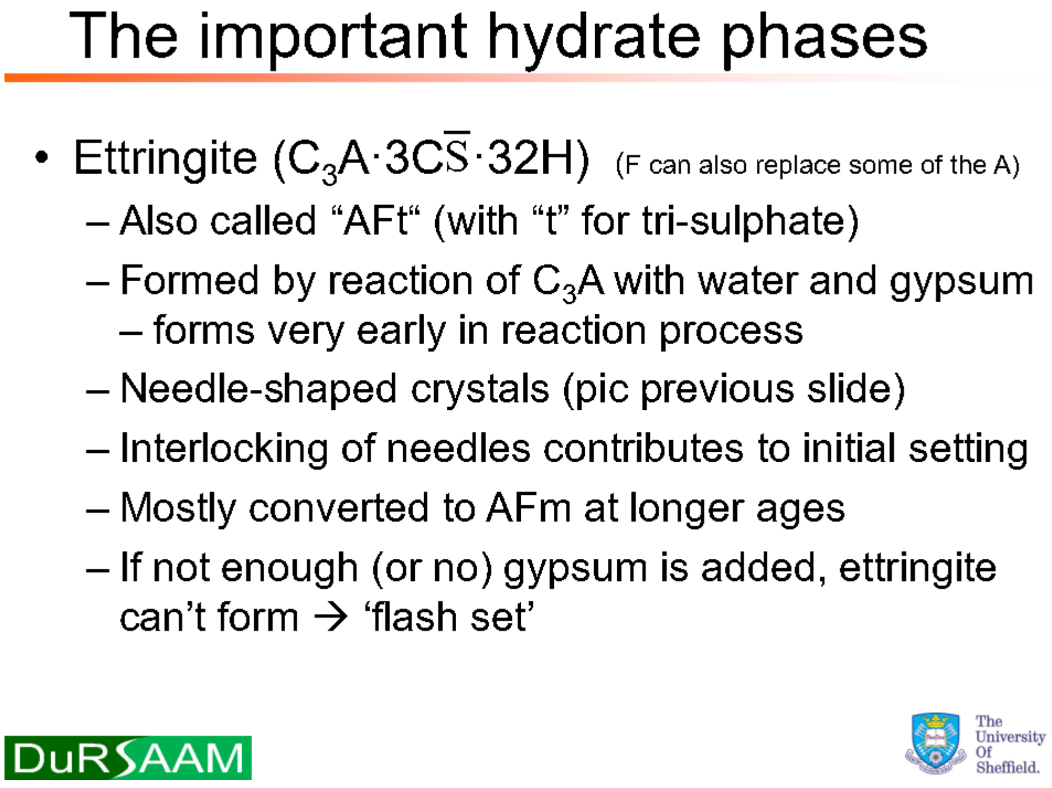


The important hydrate phases

- Calcium hydroxide (portlandite, $Ca(OH)_2$)
  - By-product of C_3S and C_2S hydration, because these have more Ca than can be accommodated in C-S-H
  - Makes large crystallites (tens of microns)
  - Doesn't contribute to strength
  - Holds internal pH high to help durability
  - Tends to grow around aggregate particles – "interfacial transition zone"

See: P.G. Stuztman, *Materials Science of Concrete* (2000):59-72



The important hydrate phases

- Ettringite ($C_3A\cdot3C\overline{S}\cdot32H$) (F can also replace some of the A)
  - Also called "AFt" (with "t" for tri-sulphate)
  - Formed by reaction of C_3A with water and gypsum – forms very early in reaction process
  - Needle-shaped crystals (pic previous slide)
  - Interlocking of needles contributes to initial setting
  - Mostly converted to AFm at longer ages
  - If not enough (or no) gypsum is added, ettringite can't form → 'flash set'

The important hydrate phases

- AFm phase (approximately $C_3A\cdot C\overline{S}\cdot n\mathrm{H}$)

  (or some of the sulphate can be replaced by carbonate and/or hydroxide)
  - ‘m’ for ‘monosulphate’
  - *n* usually 11-14
  - Forms more gradually during hydration
  - Ettringite can convert to AFm at later ages
  - Important phase, but can also cause durability problems (sulphate attack)

Seee: http://www.nanocem.org/fileadmin/nanocem_files/documents_viaFTP/TRANSCEND/posters/P13_project.pdf

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Reaction of phases over time

- Cement phases react at different rates – C_3S and C_3A fastest, some of the cement stays unreacted for a very long time

See: B. Lothenbach et al., *Cement and Concrete Research* 38 (2008) 848–860

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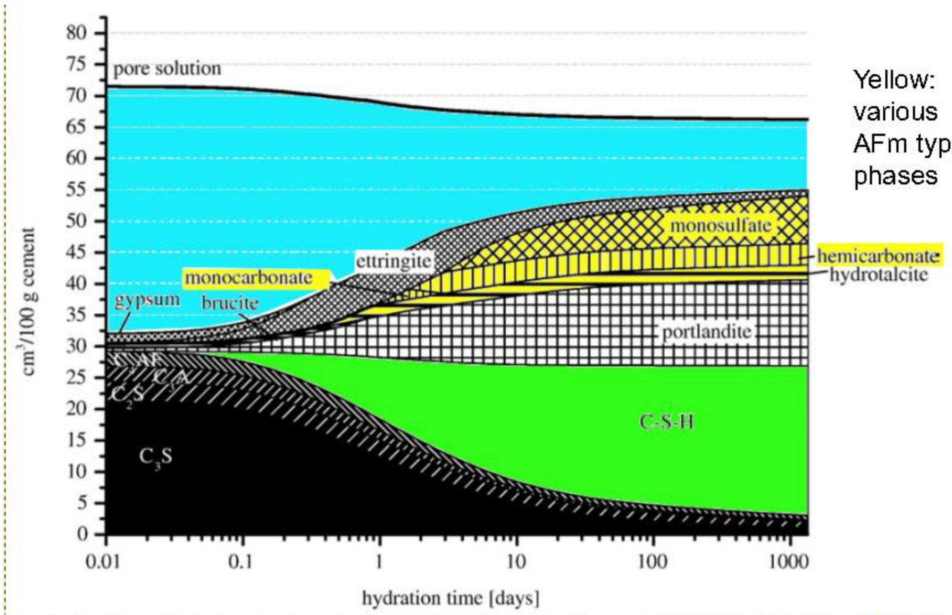
Formation of hydrate phases



Yellow: various AFm type phases

Image adapted from: B. Lothenbach et al., *Cement and Concrete Research* 38 (2008) 848–860

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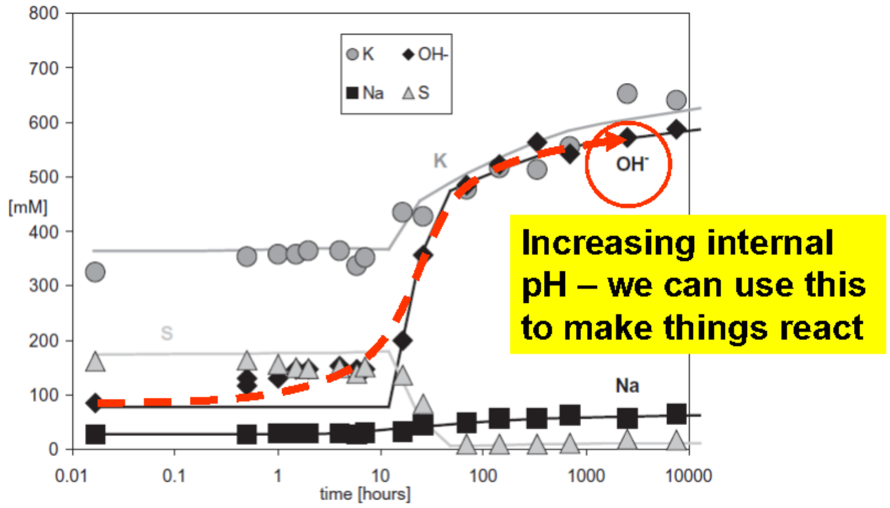
Pore fluid chemistry in hydrating cement



Increasing internal pH – we can use this to make things react

This plot is for plain Portland cement – 500 mM OH^- is pH 13.7 (!)

Image adapted from: B. Lothenbach, F. Winnefeld, Cement and Concrete Research 36 (2006) 209– 226

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Supplementary cementitious materials

- “SCMs” for short
- Any mineral component blended with cement that reacts to alter the properties of the binder
  - – Aggregates aren’t SCMs
  - – Organic admixtures aren’t SCMs
  - – Most SCMs are *pozzolans* (see next slide)
- Can be added to improve performance, improve sustainability, and/or reduce cost
  - – Sometimes may be able to do all of these at once..!

The pozzolanic reaction

- Blend cement with other sources of SiO_2, with or without additional Al_2O_3
  - – Waste or geological materials – cheap and low-CO_2
- These react with CH to form more C-S-H
  - – Fills pore spaces at longer age, refines pores
  - – Improves strength and durability

Approximately:

$$\mathbf{CH + \mathit{n}S + \mathit{x}A \rightarrow C\text{-}(A)\text{-}S\text{-}H} \quad (n \sim 1.6,\ 0 \leq x < 0.1)$$

- Pozzolanic reaction is usually slower than cement hydration
  - →Need cement hydration to generate high internal pH first
  - – Substitution by pozzolans usually reduces early strength

Slag

- Ground granulated* blast furnace slag
  - Abbreviated BFS, GGBFS, GBFS, or just ‘slag’

  (*or pelletised – but must be cooled rapidly)
- Calcium alumino-silicate glass
  - By-product of iron manufacturing (see next slide)
  - So useful that it’s not really ‘waste’ any more
  - Composition similar to clinker, but less Ca
- Reacts by a process similar to pozzolanic reaction to form C-S-H
  - Classified separately because it’s more reactive (and ‘better’) than normal pozzolans

Slag in iron-making

- Reduction of Fe_2O_3 to Fe, and purification
- $CaCO_3$ added to convert ore impurities to liquid slag
  - Impurities mainly silicates
  - Chemistry carefully controlled for pure Fe
- Rapid cooling of slag gives glassy structure
  - If slow-cooled, it crystallises → unreactive, used as aggregate in road-building

[Image deleted for copyright reasons]

See: http://www.chemguide.co.uk/inorganic/extraction/iron.html

Slag chemistry

- CaO (30-50%)
- SiO_2 (28-38%)
- Al_2O_3 (8-24%)
- MgO (1-18%)
- S^{2-} (0.5-2%)

  (changes redox environment in blended cement)

[Image deleted for copyright reasons]

C-S-A phase diagram modified with 10% MgO

Melilite group: $Ca_2(Mg,Al)[(Al,Si)(SiO_7)]$
e.g. åkermanite, $Ca_2Mg(Si_2O_7)$
gehlenite, $Ca_2Al(AlSiO_7)$

See: R. Snellings et al. Rev Mineralogy Geochem 74(2012):211-278

Slag reduces early strength, increases final strength

- [Image deleted for copyright reasons]

See: R. Snellings et al. Rev Mineralogy Geochem 74(2012):211-278

Main benefits: improved durability

Portland cement
(CEM I)

- [Image deleted for copyright reasons]

Portland cement
+ ~70% slag
(CEM III/B)

Curing duration (days)

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See: J.M. Ortega et al. Constr Build Mater 27(2012):176-183

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Fly ash (UK name: Pulverised fuel ash, PFA)

- Waste from coal-fired electricity generation
  - Mineral matter from within the coal particles
  - Mainly derived from clays, bits of carbonate minerals, etc., heated to ~1600°C+ as coal is burnt
  - When coal is burned, some of these impurities melt, go up out of the furnace with flue gases, and cool to form glassy particles

    (other parts go out the bottom → “bottom ash”)
  - Filters in the chimneys collect the ash

  (>500 million tonnes p.a. produced worldwide)
  - Generally fine (<100 μm) particles – size fraction <45 μm is the most reactive

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Understanding ash reactivity

- Fly ash is a mixture of glass and crystalline phases
  - Glass is mostly aluminosilicate, with Ca, Mg, K, Na, Fe
  - Main crystalline phases in siliceous (ASTM class F) FA are mullite ($3Al_2O_3{\cdot}2SiO_2$), quartz, and Fe oxides/spinels
  - Main crystalline phases in calcareous (ASTM class C) FA are CaO, MgO, $CaSO_4$, alkali sulfates, Fe_2O_3/Fe_3O_4, maybe C_3A or $C_{12}A_7$
  - Also can be some contamination with Cr, Hg, Cd, Zn etc.
- Not all fly ash is usable in concrete
  - If too much unburned carbon, can soak up important organic additives ('admixtures' – see later in semester)
  - Recent 'shortages' in UK & US relate to high percentage of off-specification ash being produced

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Particle morphology is important

- Particles mainly spherical
- Many are also hollow (wholly or partially)

[Image deleted for copyright reasons]

[Image deleted for copyright reasons]

S. Kumar & R. Kumar, Ceram Int 37(2011):533-541

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F. Goodarzi & H. Sanei, Fuel 88(2009):382-386

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Fly ash glass chemistry

- Interparticle heterogeneity
- Intraparticle heterogeneity
- Fe^{3+} sites (substitution for Al^{3+}?)
- Role of alkali metals
- Role of Ca^{2+}
- Aluminosilicate glass immiscibility

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How does fly ash react in cements?

- Mainly the pozzolanic reaction:

$$Ca(OH)_2 + xSiO_2 + yAl_2O_3 \rightarrow \text{C-(A)-S-H}$$

  - Forms Al-substituted C-S-H
  - Up to ~20% of Si in C-S-H can be replaced by Al within the tobermorite-like structure
  - Any extra reactive Al can also form calcium aluminate hydrate phases (AFm mostly)
- Reaction is fairly slow
  - Needs high OH^- concentration (generated by plenty of cement hydration) to really make it start reacting
  - After a few weeks, pH inside cement reaches ~13, which is enough to make fly ash start to dissolve
  - Some parts of the ash will never react

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Natural pozzolanic material (“P” in EN 197)

- Volcanic soils tend to have reactive components
- Basis of Roman concretes (as mentioned before)
  - original “pozzolan” was volcanic soil from Pozzuoli, Italy
- This behaves similarly to fly ash glasses in reacting with cement
  - Now widely used in Portland cement blends, but very variable in properties & performance
- Geologically altered (aged) pozzolans can also react, but usually slower than glassy (fresh) pozzolans
  - Partially crystallised (often into hydrous minerals) by geological processes – less reactive
  - Can be calcined for more reactivity (“Q” in EN 197)

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Compositions of reported natural pozzolans

- [Image deleted for copyright reasons]

Usually also:
~15% Al_2O_3,
~10% (CaO+MgO)

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See: R. Snellings et al. Rev Mineralogy Geochem 74(2012):211-278

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Calcined clay (Q in EN 197)

- Heat-treatment of clays at ~600-800°C gives a disordered, reactive phase
  - Kaolinite clay → metakaolin
  - Halloysite clay → metahalloysite (...&etc.)
- Highly reactive
- Al-rich (Si/Al~1)
- Pozzolanic
- Also makes AFm – e.g. in ternary blends with limestone ("LC3")

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Problem – particle shape

- Metakaolin particles are plate-shaped
  - High surface area
  - Take up a lot of water in a cement blend, make flow properties worse
  - Limits usage to ~20% in most blended cements
  - Flash calcination can reduce this problem
  - Valuable in refining pore network structure – increases durability of concretes
  - Ternary blends "LC3" in Cuba, India, China, etc. – with $CaCO_3$

[Image deleted for copyright reasons]

DuRSAAM B.B. Sabir et al., Cem Concr Compos 23(2001):441-454

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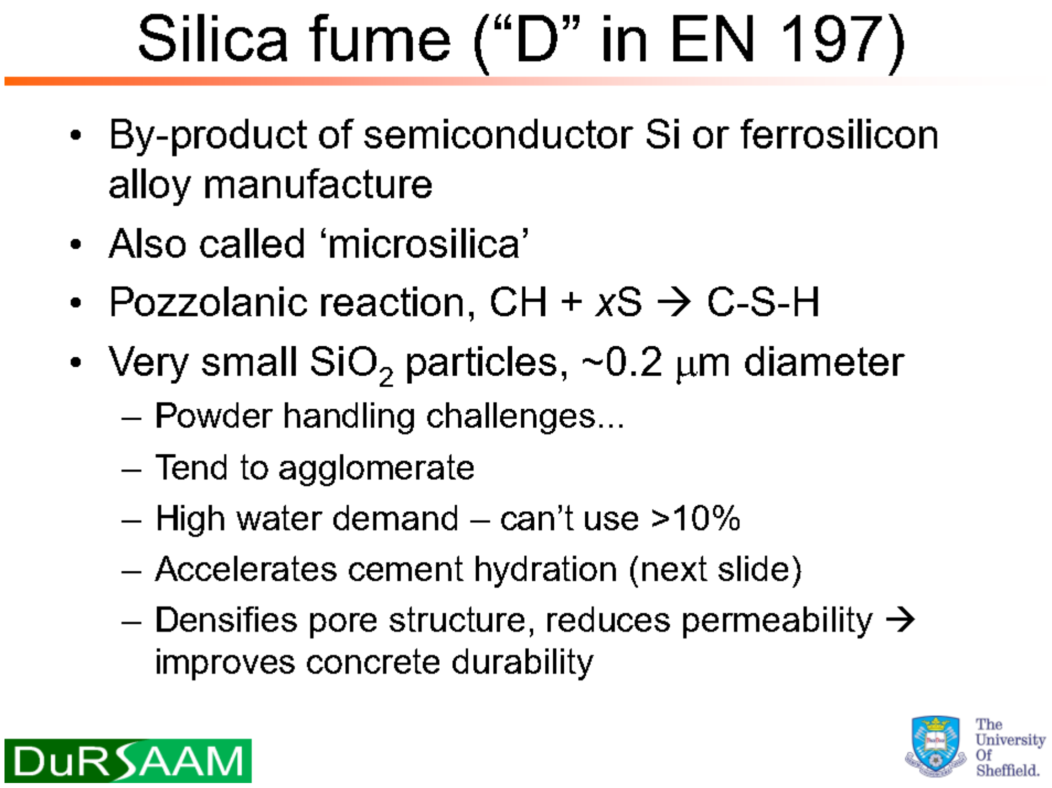
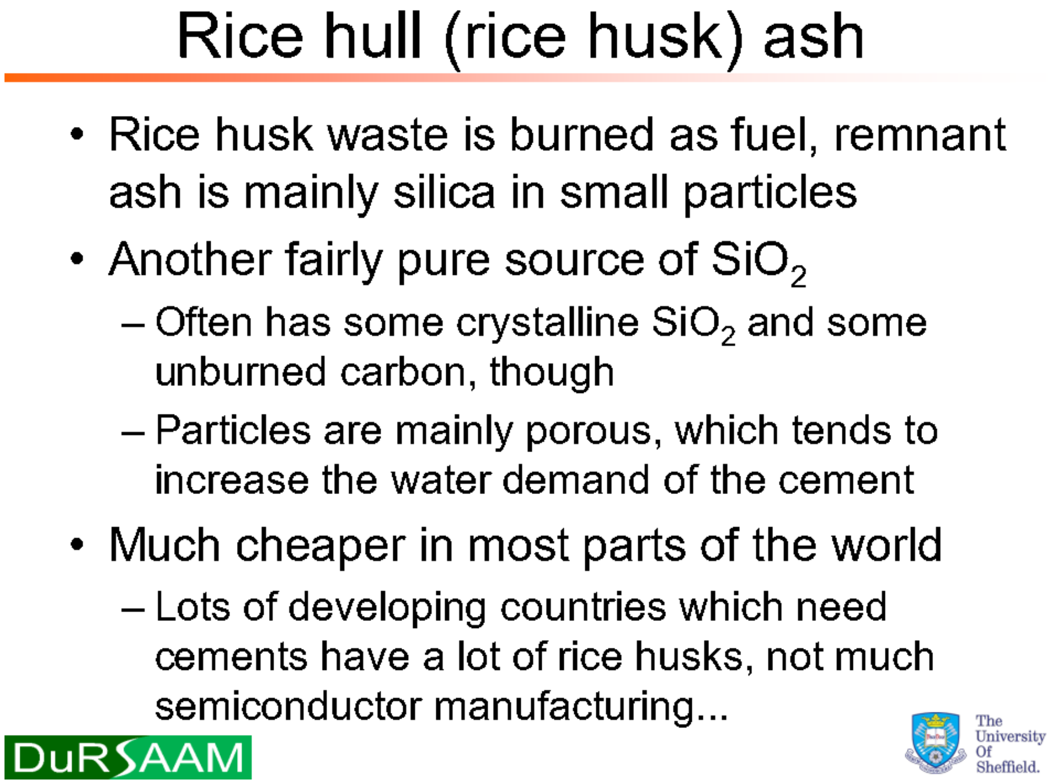


Silica fume (“D” in EN 197)

- By-product of semiconductor Si or ferrosilicon alloy manufacture
- Also called ‘microsilica’
- Pozzolanic reaction, CH + *x*S → C-S-H
- Very small SiO_2 particles, ~0.2 μm diameter
  - Powder handling challenges...
  - Tend to agglomerate
  - High water demand – can’t use >10%
  - Accelerates cement hydration (next slide)
  - Densifies pore structure, reduces permeability → improves concrete durability



Rice hull (rice husk) ash

- Rice husk waste is burned as fuel, remnant ash is mainly silica in small particles
- Another fairly pure source of SiO_2
  - Often has some crystalline SiO_2 and some unburned carbon, though
  - Particles are mainly porous, which tends to increase the water demand of the cement
- Much cheaper in most parts of the world
  - Lots of developing countries which need cements have a lot of rice husks, not much semiconductor manufacturing...

Limestone

- Calcium carbonate, $CaCO_3$
- Not technically a pozzolan, but can act in some similar ways to improve cements
- Used as an ingredient in the kiln, but can also add extra (unburned) limestone to cement
  - Usually very finely ground for reactivity
- Cheapest of all mineral admixtures
- Small amounts (<5%) can give improved properties
  - Makes extra AFm phases (monocarbonate)
  - Any more than this doesn't react – reduces strength
  - Synergy with metakaolin as mentioned previously

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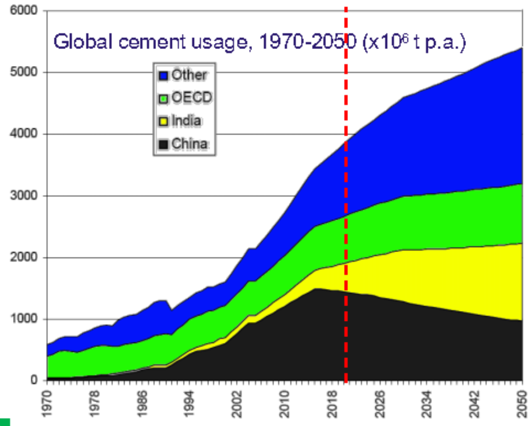
Sustainability in construction materials

- Cement manufacture causes ~8% of CO_2 emissions worldwide
- **~0.8** ton of CO_2 per **1** ton of cement
- Global market will double by 2050



Data: International Energy Agency, 2006

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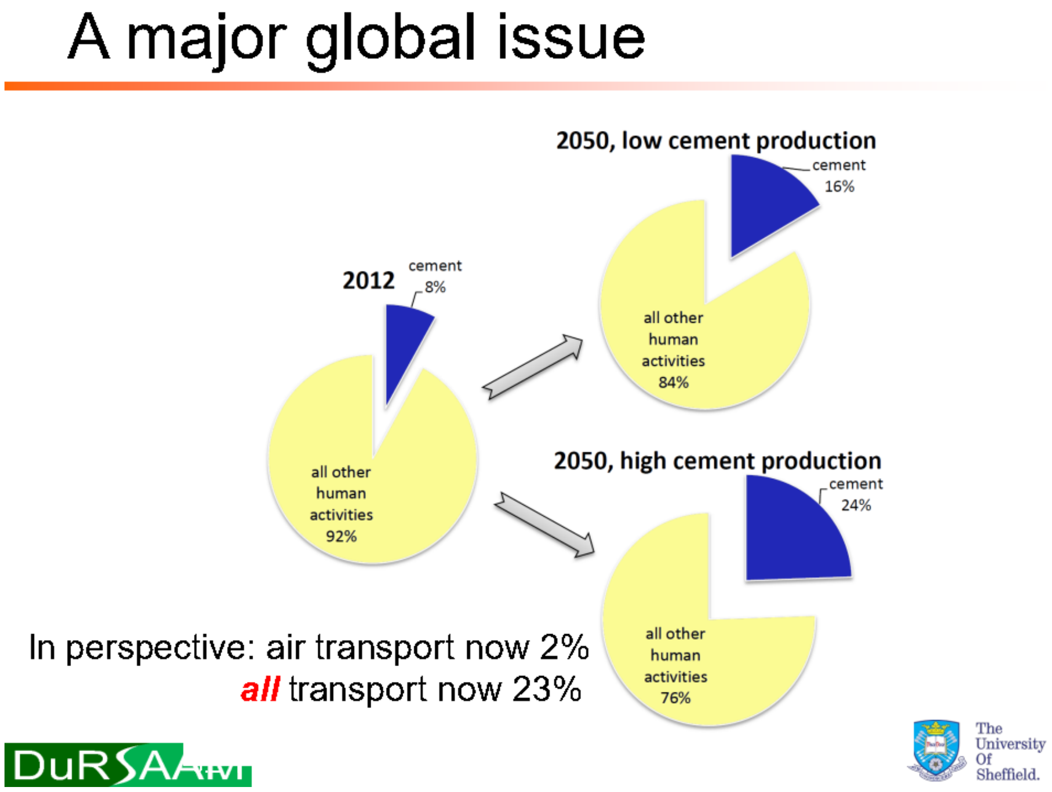
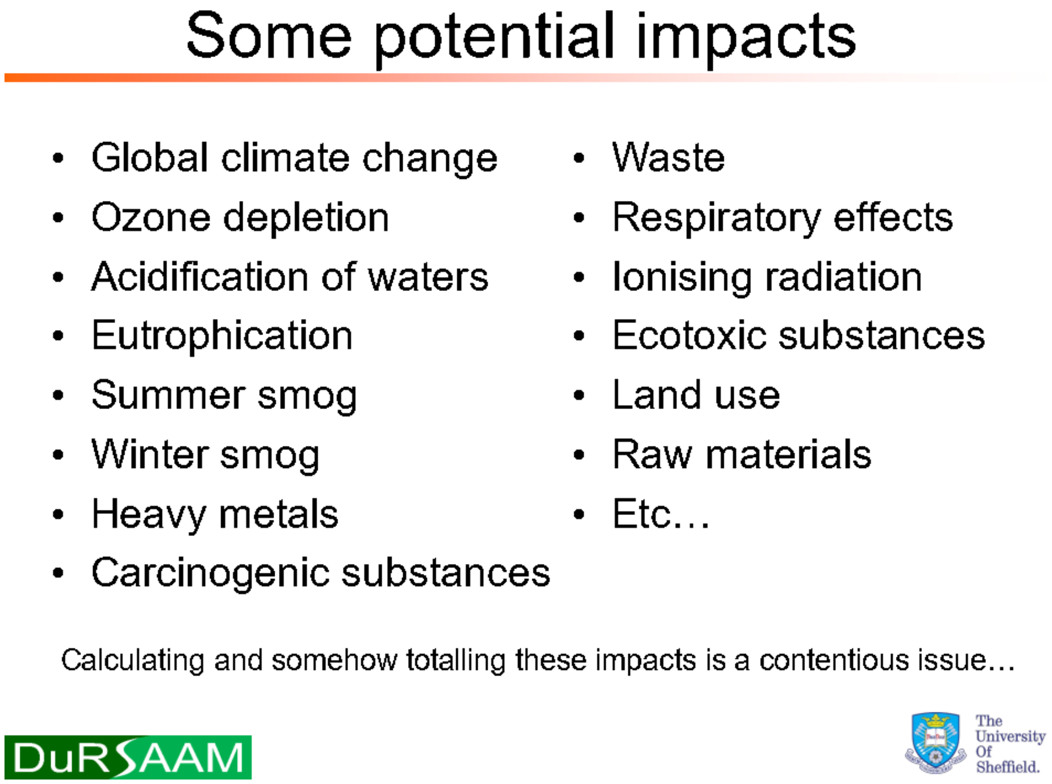


A major global issue

In perspective: air transport now 2%
all transport now 23%



Some potential impacts

- Global climate change
- Ozone depletion
- Acidification of waters
- Eutrophication
- Summer smog
- Winter smog
- Heavy metals
- Carcinogenic substances
- Waste
- Respiratory effects
- Ionising radiation
- Ecotoxic substances
- Land use
- Raw materials
- Etc…

Calculating and somehow totalling these impacts is a contentious issue…

Why is this important to engineers?

- To design a 'sustainable concrete', we need to define what we mean by 'sustainable'!
  - Just CO_2 emissions? Resource depletion? etc…
- Durability of concrete is very significant in a life-cycle analysis
  - But most life-cycle practitioners are essentially accountants, not specialists in a material
- Allocation of environmental impacts to wastes/by-products/secondary products is important
  - Can also be very controversial! (and philosophical)
  - Decisions made in this area – often by regulators - can determine the overall viability of new products/processes

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Shorter-term possibilities

- More efficient Portland cement processes
  - Kilns – newer 'dry process' is more efficient
  - Heat recovery, integration & recycling
  - Grinding
- Blended cements
- Alternative fuels for kilns
- Modification of clinker chemistry to reduce processing temperature
- ***Some (more mature) non-Portland cement binders***

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Limited scope for more direct efficiency gains…

- [Image deleted for copyright reasons]

See: http://www.wbcsdcement.org/pdf/technology/WBCSD-IEA_Cement%20Roadmap.pdf

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Longer-term possibilities

- ***Some (less-mature) non-Portland cement binders***
- Carbon capture and storage
- Oxygen-fired kilns
- Multi-cyclone precalciner kilns
- Fluidised bed kilns or other alternative calcination processes
- Advanced grinding technologies
- Alternative raw materials for cement kilns

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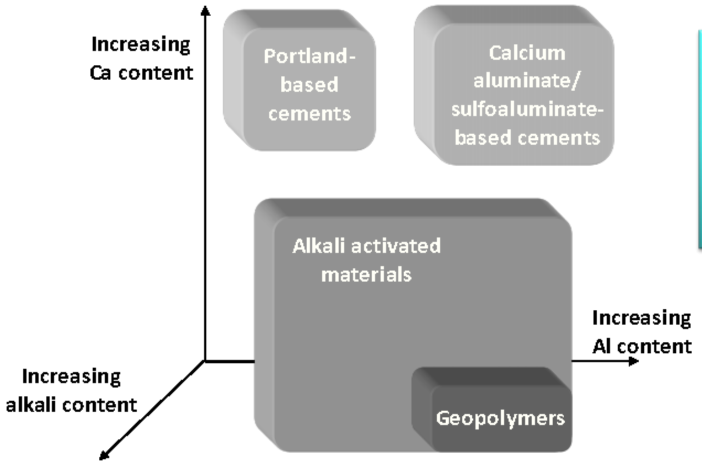
What is the answer?

- Portland cement production is already pretty efficient
  - Not much scope for further savings there
  - Blended cements are being developed further
  - Limitations on the availability of some of the blending components
- The way forward: a toolbox approach
  - The right cement for the right application
  - Portland and non-Portland cements
  - Clinker-based and non-clinker-based binders

Traditional and non-traditional cements



Increasing Ca content

Portland-based cements

Calcium aluminate/ sulfoaluminate-based cements

Alkali activated materials

Geopolymers

Increasing Al content

Increasing alkali content

Moving from a single universal cement to an array of cement types

Also supersulfated cements, Mg-based binders, and various others

See: JL Provis & JSJ van Deventer, State of the Art Report, RILEM TC 224-AAM, 2014

3. Alternative cements, what is available?

John Provis

In this chapter an overview is provided of different alternative cements, including alkali-activated binders. The basics are discussed of a set of 8 non-Portland cements which have been put forth as non-traditional cements.

Alternative cements – what is available?

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Non-Portland cements

- Useful in specific circumstances
- Can be more environmentally efficient
- Can give improved technical properties – particularly resistance to chemical attack
- Each produced in much lower volumes than Portland cement
- Some can be processed and placed using the same technology as Portland cement concretes
  - This is highly desirable – people don't like to replace familiar things with unfamiliar things!
- Most require some special attention in formulation and/or curing for good performance

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Alkali-activated cements

- Aluminosilicate materials + alkaline solution ("activator") – can use blast furnace slag, coal fly ash, natural pozzolans, calcined clays (see last lecture on blended cements for more info on these materials)
  - ~60-90% less CO_2 emissions than Portland cement
  - Main drawback: need for an alkaline solution
  - Commercial production in Eastern Europe, China, Australia, increasingly in UK/EU

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Alkali-activated binders - Why?

- Common SCMs (fly ash, slags, metakaolin etc.) can be used directly in alkali-activation
  - These are less reactive than clinker, so reaction with water is slow

  → Chemical activation needed

- High-volume blended cements can use PC clinker as activator – but it is not optimised for this task!
  - Clinker components & gypsum balanced to give optimal rheology, reaction & strength when used alone
  - If another material dominates, this is no longer optimal

→ Why not use a purpose-designed alkali activator instead?

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Versatility of alkali activation

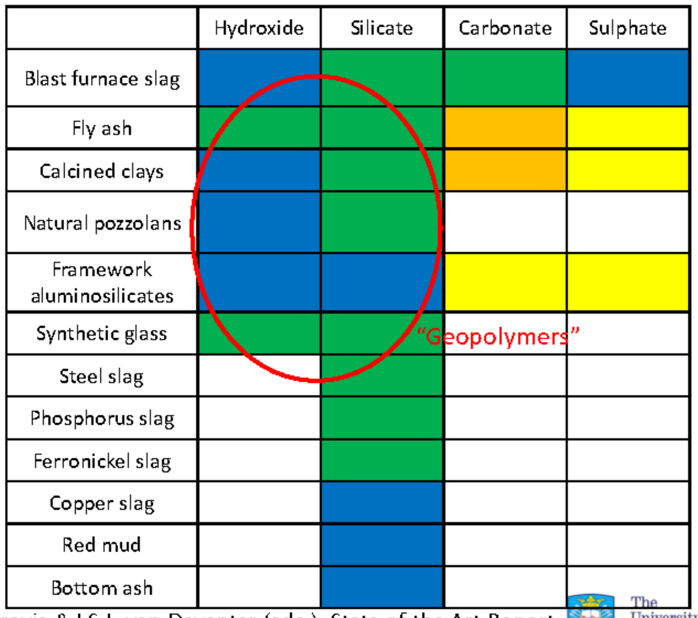
Green desirable

Blue acceptable

Yellow requires blending with clinker

Orange poor

White Little or no information



	Hydroxide	Silicate	Carbonate	Sulphate
Blast furnace slag	🟦	🟩	🟩	🟦
Fly ash	🟩	🟩	🟧	🟨
Calcined clays	🟦	🟩	🟧	🟨
Natural pozzolans	🟦	🟩		
Framework aluminosilicates	🟦	🟦	🟨	🟨
Synthetic glass	🟩	🟩		
Steel slag		🟩		
Phosphorus slag		🟩		
Ferronickel slag		🟩		
Copper slag		🟦		
Red mud		🟦		
Bottom ash		🟦		

J.L. Provis & J.S.J. van Deventer (eds.), State of the Art Report of RILEM TC 224-AAM, 2014

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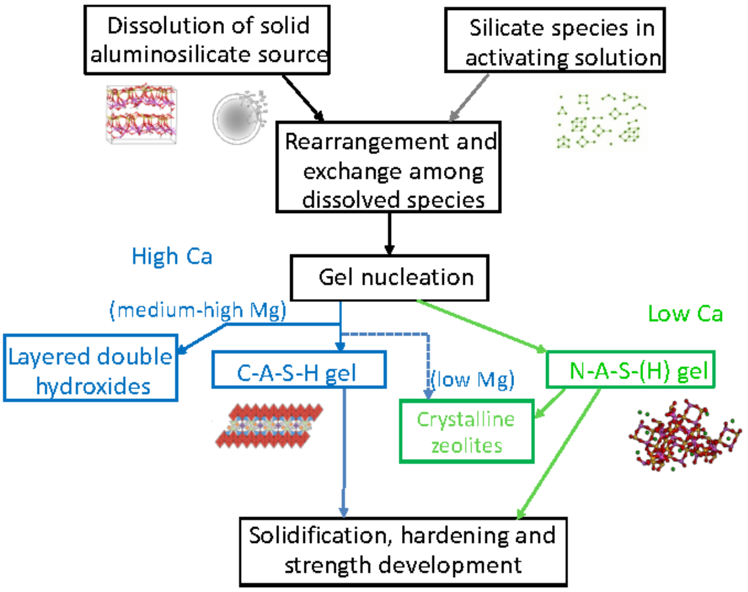
Two basic types of material

- High-calcium and low-calcium (“geopolymer”) AAMs
- Classified together because reaction process is similar
  - Interaction of an alkali source (usually liquid) with an aluminosilicate powder
- Binding phases can be very different, depending on calcium content/availability
- Sometimes (with high Ca) gives C-S-H type phases, sometimes very different products (N-A-S-H)

How does the reaction happen?



Dissolution of solid aluminosilicate source

Silicate species in activating solution

Rearrangement and exchange among dissolved species

Gel nucleation

High Ca

(medium-high Mg)

Layered double hydroxides

C-A-S-H gel

(low Mg)

Crystalline zeolites

Low Ca

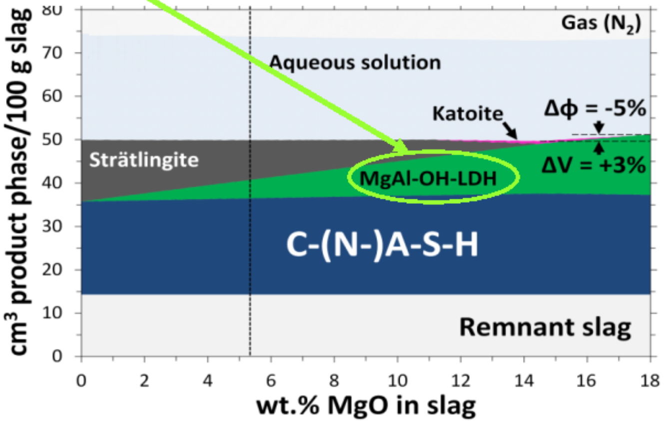
N-A-S-(H) gel

Solidification, hardening and strength development

J.L. Provis & S.A. Bernal, *Annu. Rev. Mater. Res.*, 2014, 44: 299–327

Phase assemblage controlling durability

MgAl layered double hydroxides give resistance to carbonation, and restrict chloride ingress



R.J. Myers et al. *Applied Geochemistry*, 61(2015): 233-247

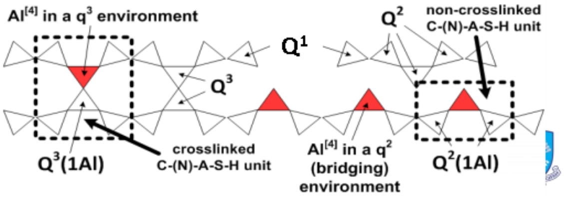
Gel chemistry – C-A-S-H gel

- Alkali activation with more calcium – main binder product is Al-substituted C-S-H (C-A-S-H) type gel:

  $$(0.6\text{-}1.6)CaO\cdot(0\text{-}0.3)Al_2O_3\cdot SiO_2\cdot(1.0\text{-}1.6)H_2O$$

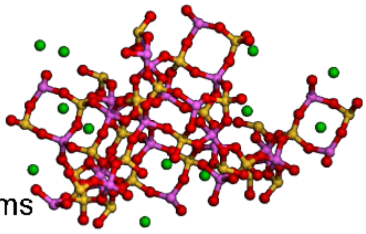
  - Compared to PC hydration products: Lower C/S ratio (PC has 1.6), higher Al content (PC usually has <0.04)
  - Alkalis can be sorbed on gel, or free in the pore solution
  - Secondary phases can include hydrotalcite, zeolites (or N-A-S-(H)), AFm phases
  - Bound water gives strong space-filling effects
  - Can also be cross-linked tobermorite-type structures (Q^3)

R.J. Myers et al. *Langmuir* 29(2013):5294-5306



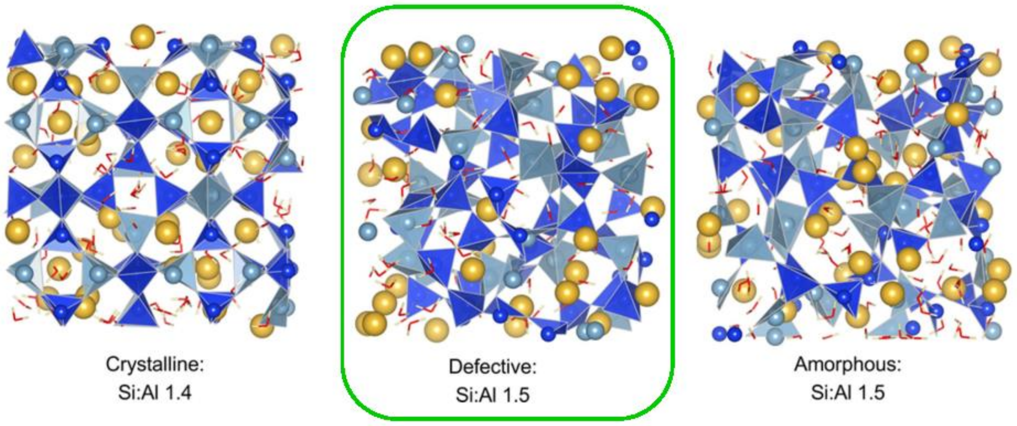
Gel chemistry – N-A-S-(H) gel

- Alkali activation with low calcium gives, as the main binding product, a 'geopolymer' (N-A-S-(H)) gel: $Na_2O \cdot Al_2O_3 \cdot (2\text{-}6)SiO_2 \cdot (0\text{-}0.5)H_2O$
  - Highly crosslinked (Q^4) framework structure – similar to a zeolite ("pre-zeolitic"?)
  - Little chemically bound water – almost of the water is held in pores not in the gel itself
    - This is good for fire resistance – don't need to destroy the gel to remove water
    - But - tends to give high permeability
  - Also generally has good acid and sulfate resistance
    - Low Ca content means usual mechanisms observed in PC aren't a problem



R.J. Myers et al. *Langmuir* 29(2013):5294–5306;
J.L. Provis et al. *Cem Concr Res* 42(2012):855–864

Modelling N-A-S-(H)



Crystalline:
Si:Al 1.4

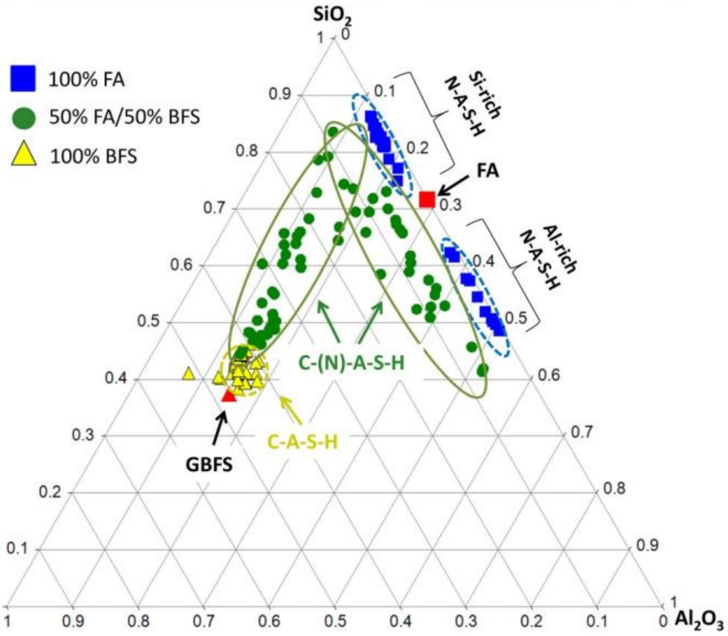
Defective:
Si:Al 1.5

Amorphous:
Si:Al 1.5

Partially disordered – not fully amorphous – structure gives the best match to experimental results

F. Lolli et al. *ACS Appl. Mater. Interf.* 10(2018): 22809–20

Different gels can co-exist in one sample



S.A. Bernal, J.L. Provis, *J. Am. Ceram. Soc.*, *97*(**2014**):997–1008
(data from Ph.D. thesis, I. Ismail)

Some of the reactions...

(note – not written balanced!)

- Alkali-activation of aluminosilicates
  - NS + AS + H → N-A-S-(H)
  - NH + AS → N-A-S-(H) (lower Si/Al ratio)

(S/A ratio can be ~2-6; N-A-S-(H) gel and/or zeolites)

- Alkali-activation of slag
  - NS (or NH) + C-A-S (slag) + H → C-(N)-A-S-H
  - Nc + C-A-S (slag) + H → Cc + C-(N)-A-S-H
  - Mg + Al from slag + OH^- → hydrotalcite
    (layered Mg-Al hydroxide/carbonate)
- Low heat of reaction (~10-50% cf. Portland cement)

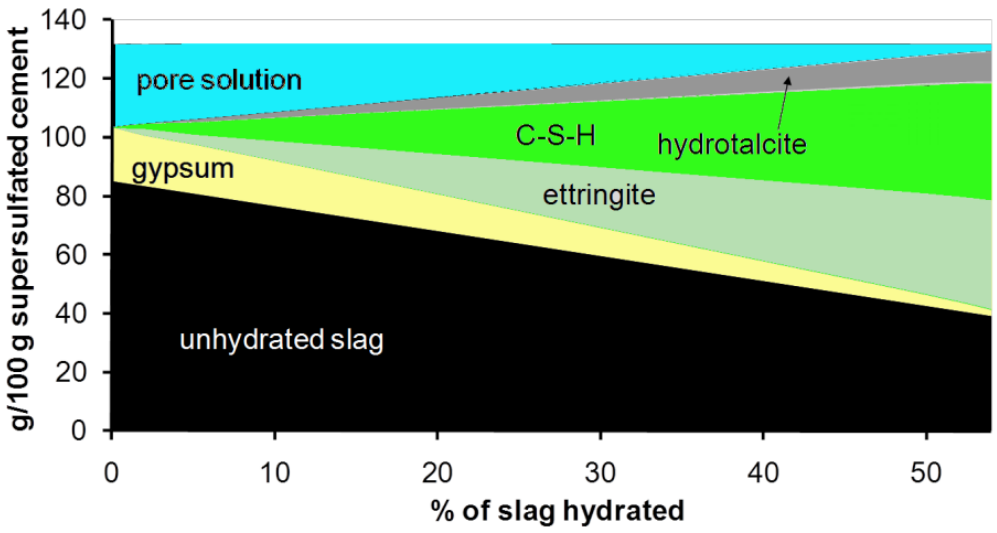
Current/ongoing issues

- Workability control – organic admixtures used in Portland cement don't work well
- Needs careful curing to keep water in
- Understanding steel corrosion chemistry
- Controlling shrinkage
- Standards environment restrictive
- Competing with an extremely successful commodity product!

Supersulphated cement

- BFS + calcium sulfate (hydrous or anhydrous) + ~5% Portland cement clinker – almost AAM chemistry?
- Developed in Germany ~1909, based on high-Al (~14% Al_2O_3) slags
  - Al levels of slags dropped ~1960s, the cements stopped working so well, standards were withdrawn
  - Now coming back into use, standards have been rewritten and approved in EU
- C-S-H, ettringite, hydrotalcite as main binding phases
  - Pore solution pH lower than Portland cement
  - Low heat of hydration
  - Large ettringite needles

Phase evolution in supersulphated cement



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M.C.G. Juenger et al. Cem Concr Res 41(2011):1232-1243

The University Of Sheffield.

Properties

- Fairly long initial setting times
- Somewhat slower strength development, but 28-day strengths similar to Portland cement
- Careful curing is very important
  - Not suited to heat curing, because ettringite degrades at high temperatures
- Very good sulphate resistance
  - Ettringite can't be further attacked by sulphates
- Low porosity – generally good durability
- Very low CO_2 emissions
- Drawbacks: limited availability of the correct slags

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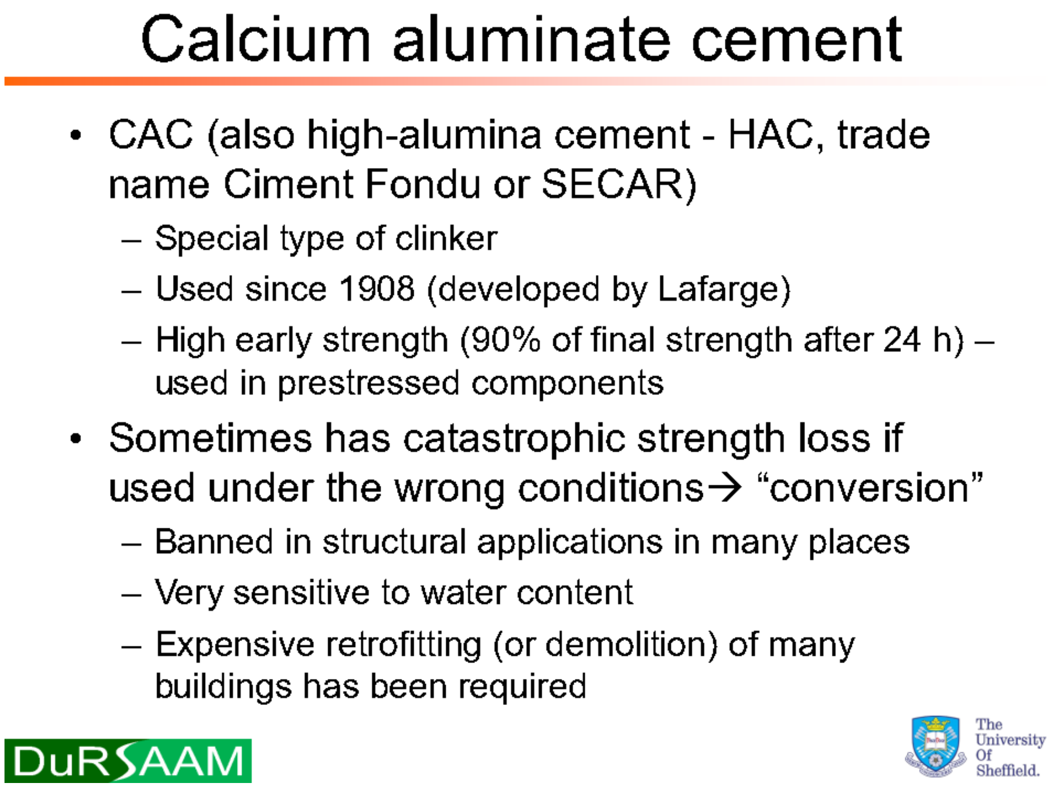
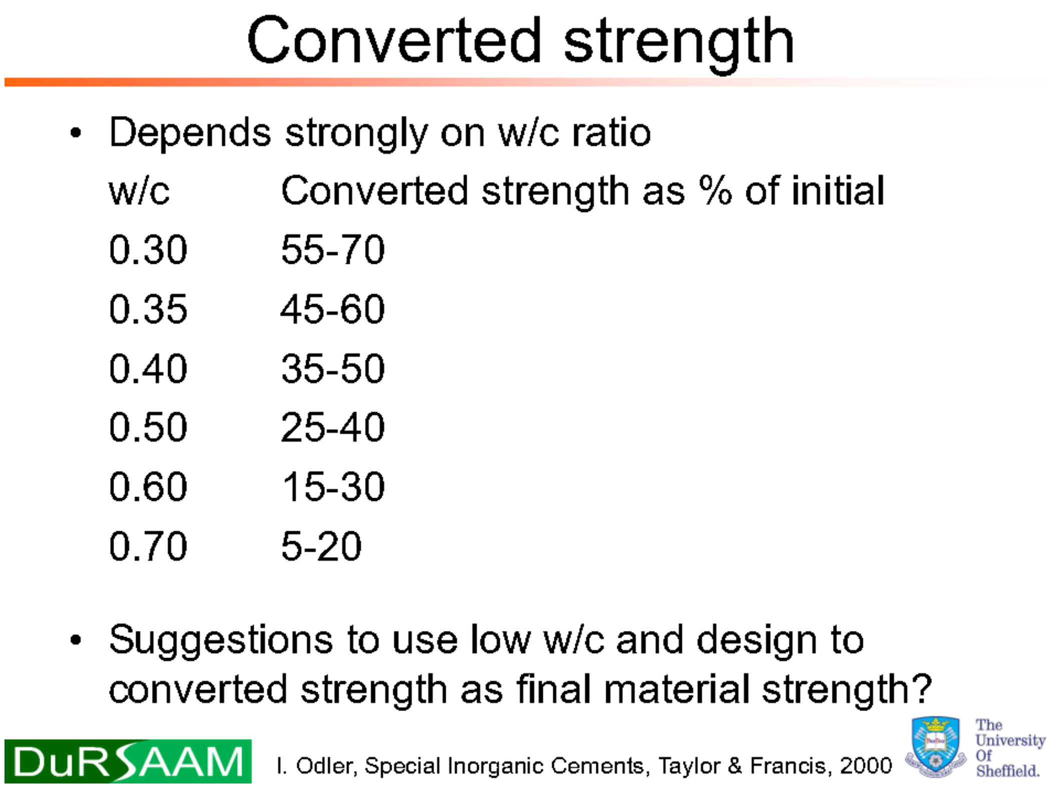


Calcium aluminate cement

- CAC (also high-alumina cement - HAC, trade name Ciment Fondu or SECAR)
  - Special type of clinker
  - Used since 1908 (developed by Lafarge)
  - High early strength (90% of final strength after 24 h) – used in prestressed components
- Sometimes has catastrophic strength loss if used under the wrong conditions→ “conversion”
  - Banned in structural applications in many places
  - Very sensitive to water content
  - Expensive retrofitting (or demolition) of many buildings has been required



Converted strength

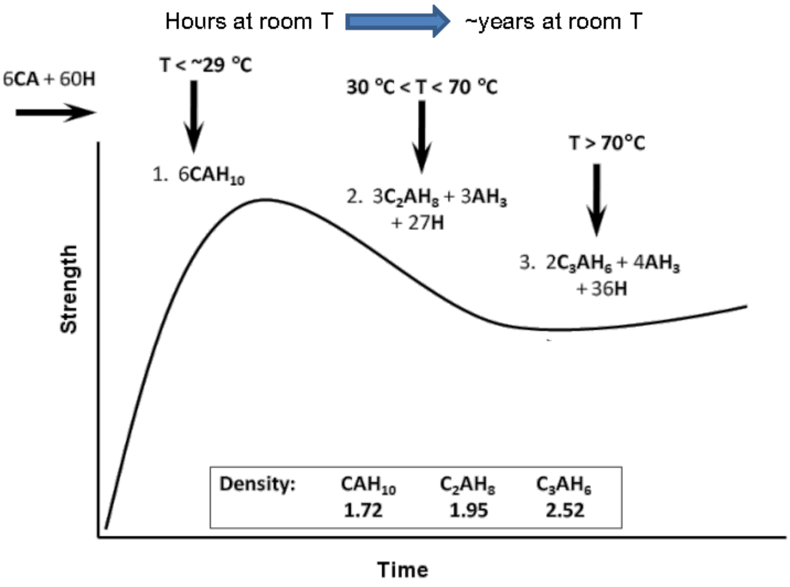
- Depends strongly on w/c ratio

w/c	Converted strength as % of initial
0.30	55-70
0.35	45-60
0.40	35-50
0.50	25-40
0.60	15-30
0.70	5-20

- Suggestions to use low w/c and design to converted strength as final material strength?

I. Odler, Special Inorganic Cements, Taylor & Francis, 2000

Conversion as a function of time or temperature



- Strength and volume both change

M.C.G. Juenger et al. Cem Concr Res 41(2011):1232-1243

Warm, wet environments make it worse

- Stepney School swimming pool roof structural beams

Useful in some specific applications

- Refractory cements (up to 1800°C)
- Rapid-hardening mortars
- Pipes
- Flooring
- Used in many cement blends
- Potentially lower CO_2 emissions than Portland cement (lower Ca content)
- Bauxite is generally more expensive than most cement ingredients
  - not ideal for bulk concreting

Calcium sulphoaluminate cement

- Very popular in China – ‘Third Cement Series’ (TCS) – not so widely used elsewhere
- Clinkers based on the phase ye’elimite, $C_4A_3\overline{S}$
  - Generally together with belite, with or without C_4AF
  - Made from limestone, silica, bauxite and $CaSO_4$ - or replace some of these by wastes for lower cost
  - Fe in some bauxites leads to C_4AF component
- Interground with gypsum
- Cements are rapid-hardening, high-strength, can be designed to expand upon hydration
- Moderate pore solution pH
- Processed at slightly lower T than PC clinker

Phase assemblage

[Image deleted for copyright reasons]

See: F. Winnefeld, B. Lothenbach, Cem Concr Res 40(2010):1239-1247

Adjustable

- Varying expansion depending on gypsum added (and water)
- Enables self-stressing concrete production
  - Reducing cracking during drying shrinkage
  - Pipes, water towers, runways, etc.
- Also used in floor screeds and other niche applications
- Lower CO_2 emissions: made using $CaSO_4$ and lower production temperature
  - Can use some waste materials (i.e. red mud)

Carbonation-curing cements

- New high-profile development, e.g. “Solidia Cement” and competitors
- Produce a mixture of CS and C_3S_2, react with water and high-pressure CO_2
- Binder product phases are silica gel and $CaCO_3$
  - C-S-H isn’t stable at such high CO_2 concentrations
- Mostly useful for precasting – need to apply the CO_2 from a cylinder, can’t just pour concrete of this type

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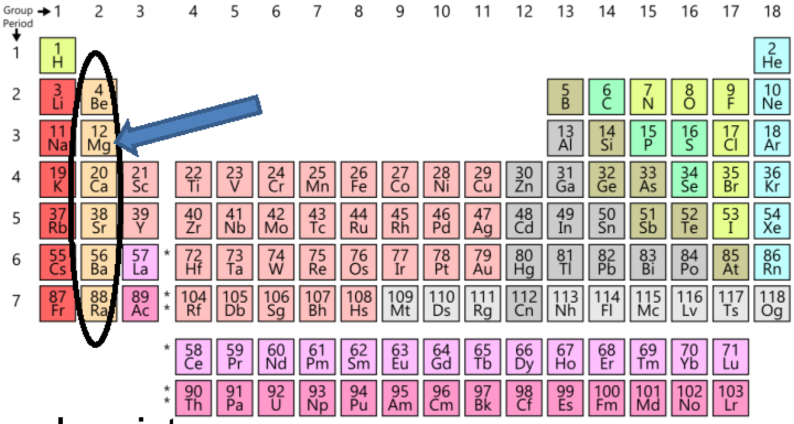
Magnesium-based

- Usual:
  - **Ca**
  - Si
  - Al
  - S



- Need:
  - Suitable chemistry
    - Low temperature formation of strong minerals
    - Water resistant?
  - Cheap and readily available

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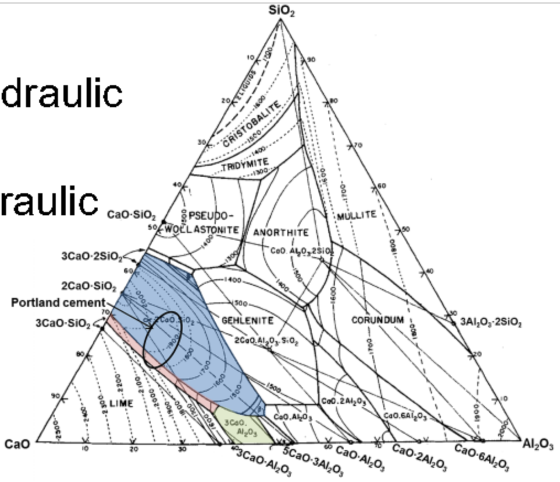
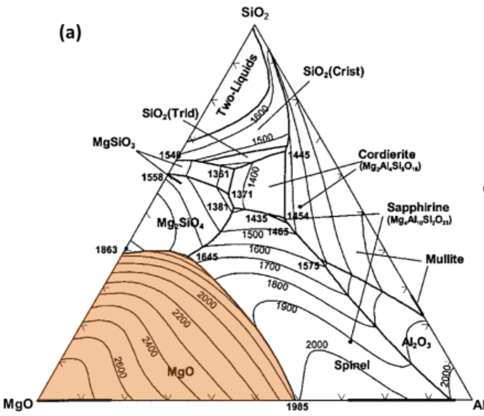
Magnesium-based

- $CaO-Al_2O_3-SiO_2$
  - Several naturally hydraulic regions
  - Others 'latently' hydraulic





- $MgO-Al_2O_3-SiO_2$
  - MgO only

S.A. Walling & J.L. Provis, Chem Rev 116(2016) 4170-4204

Magnesium phosphate cement

- Acid-base chemistry
- MgO + soluble acid phosphate
- Originally designed as refractory cements
  - Initially a sprayable composition
  - Quick setting, so began to be sold as rapid-repair cements by early 1970's

FebSET 45

Can drive over it after 45 minutes
Can be used down to temperatures of -20°C

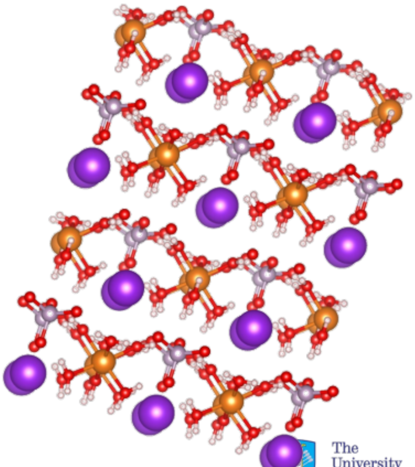
https://www.everbuild.co.uk/product/febset-45/

Magnesium phosphate cement

- Acid-base chemistry

e.g. $MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O$

Struvite-K



[Image deleted for copyright reasons]

A.S. Wagh & S.Y. Jeong, J Am Ceram Soc 86(2003):1838-1844

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Magnesium phosphate cement

- Form a crystalline binder – need correct stoichiometry to get desired products
  - Unreacted MgO issues?
  - Phosphate efflorescence
- Also substitute for both Mg and K sites
  - Replace some Mg^{2+} with Ca^{2+} (but reaction is very fast) or Fe^{2+} (but reaction is very slow)
  - Replace some K^+ with Na^+, Cs^+, or H^+
- Workability control can be challenging
  - Not really proposed for use in large-scale concreting
  - Binds to steel

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Magnesium silicate cement

- First seen as a degradation product in sea walls and from sulfate attack:

  C-S-H + $MgSO_4 \rightarrow CaSO_4 + SiO_2 + Mg(OH)_2 \rightarrow CaSO_4$ + M-S-H
- Interest in 1980's as a refractory binder
- Cement interest mid 2000's in China
  - MgO + silica fume + industrial by-products
- High water demand and expensive precursors
- Chemistry not well described in the scientific literature
  - Appears to be a type of poorly crystalline serpentine / phyllosilicate (e.g. lizardite / talc)

Magnesium silicate cement

- "Novacem" (Imperial College spin-off) – high publicity, no longer produced, but interesting anyway
  - "carbon negative cement"
- Binding gel is magnesium silicate hydrate (M-S-H), similar to C-S-H
  - M/S ratio lower than C/S ratio of C-S-H, strength and stability generally lower
- Carbonates by CO_2 uptake from the atmosphere – gains strength from $MgCO_3$ formation
- Salts added to increase internal RH
  - Aided formation of $MgCO_3{\cdot}3H_2O$
- Related to this: "Reactive magnesia" cements

Magnesium oxychloride cement

- Main binder phase $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, but many other phases exist
- Wide range of filler materials
  - Granite, sawdust, ivory dust
- Variants use sulphate instead of chloride, or zinc instead of magnesium – this can enhance the water resistance
  - Magnesium oxysulfate
  - Cupric oxychloride
  - Zinc oxychloride

[Image deleted for copyright reasons]

http://www.lehvoss.de/images/PICT0188.JPG

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Magnesium oxychloride cement

- Renewed interest
  - Lower CO_2 (disputed)
  - Use of local natural resource (usually MgCl brine)
- Qinghai salt lakes (China)
- Dead sea (Israel / Jordan) →
- Salt lake (Utah)

- Fire resistance (~35% hydrated water by weight)
  - MgO refractory, high melting temperature

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Image from Wikimedia commons

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Magnesium oxychloride cement

- Niche uses:
  - Temporary oil-well cements
  - Stabilising salt mines
  - Dry-wall (replacing gypsum)
  - Industrial flooring

[Image deleted for copyright reasons]

Endlager Asse II: Aktueller Stand der Arbeiten zur Stabilisierung und sicheren Schließung; BfS (2010)

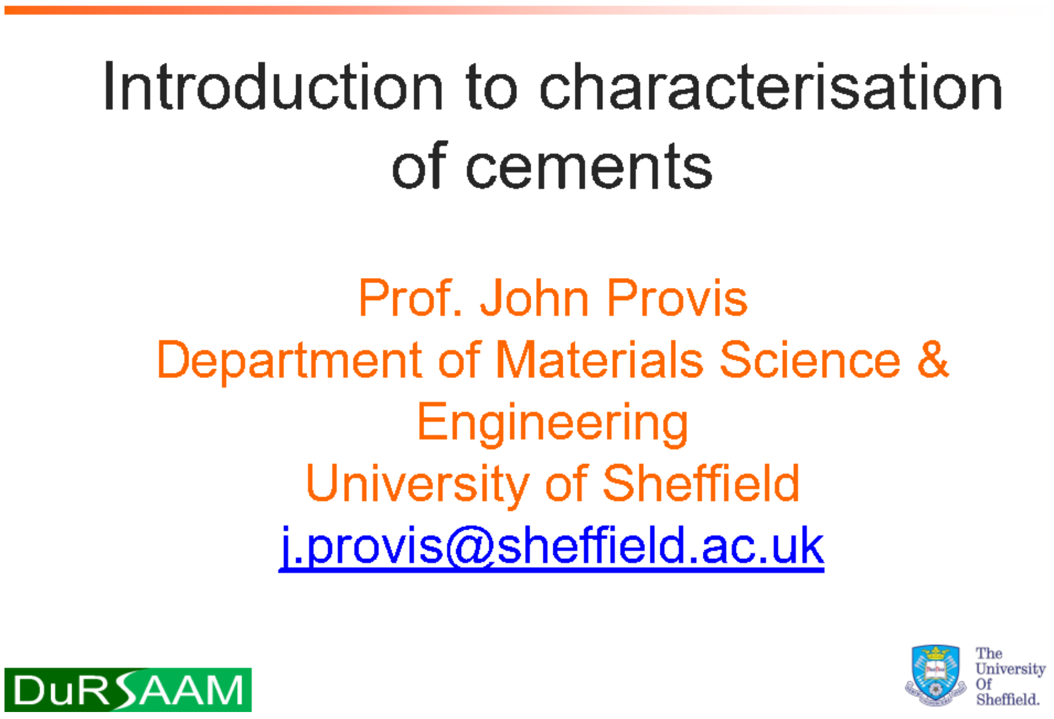
[Image deleted for copyright reasons]

https://www.eurolit.gr/magnesite.html

4. Cement characterisation

John Provis

In this chapter an introduction is provided to the characterisation of cements. Typically a combination of techniques are used to characterize the cement powder by means of experimental testing. Various techniques are discussed in terms of principles of the test method and characterized binder properties.



Introduction to characterisation of cements

Prof. John Provis
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What do you need to know?

- There are many analytical tools which are available, and each gives different information
- It is very rare, in modern materials science, to get important results using only one technique
  - Combining techniques will give you more information
  - Approach the same question from different angles
- It is **essential** to understand the techniques you use
  - Even if a technician is running the instrument for you, you need to know what they do, and why
  - Know the limitations of your data – what can it not tell you? Why?

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Comments on testing…

"It is very important to understand the philosophy of testing. Only people ignorant of the true situation regard a test result as an accurate portrayal of the property tested. Unfortunately, this tends to include many people in authority such as specifiers, controllers, and legal people."

(KW Day, J Aldred & B Hudson, *Concrete Mix Design, Quality Control and Specification*, 4th ed. 2014, CRC Press)

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Testing cement powders

- When producing any industrial product, it is essential to provide reliable performance
- For materials used in construction, and the oil industry, this is a major safety consideration

Deepwater Horizon

[Images deleted for copyright reasons]

http://www.eoearth.org/files/142601_142700/142603/dispersants6_globalwarming.jpg

http://www.thetimes.co.uk/tto/multimedia/archive/00269/NM294402_a_269855c.jpg

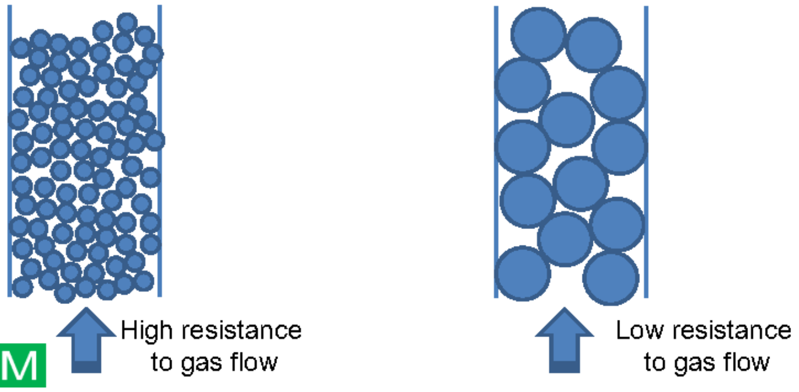
Earthquake, China, 2008 – Schools built with 'fake cement' http://www.mcclatchydc.com/2008/05/21/38020_angry-parents-protest-collapse.html?rh=1

Main initial acceptance tests

- Composition – does it contain the correct components?
  - Wet chemical (or XRF) and Bogue analysis
  - Increasingly, XRD for quality control
- Particle size – will it react at the correct speed?
  - Blaine fineness
  - Gas sorption and BET method for surface area
  - Laser granulometry

Blaine fineness

- Measure the flow of a gas through a packed bed of particles
  - This relates to the particle size – smaller particles have smaller inter-particle spaces, which give more resistance to gas flow



High resistance to gas flow

Low resistance to gas flow

The Blaine apparatus

http://www.controls-group.com/backend/prodotti/img_upload/img_big/1203191126100_1_62_I0041_a_62_I0041_c.jpg

- [Image deleted for copyright reasons]

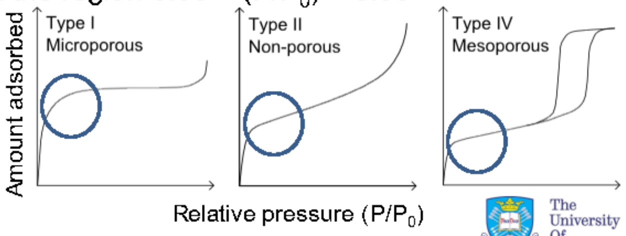
Assumptions in the Blaine method

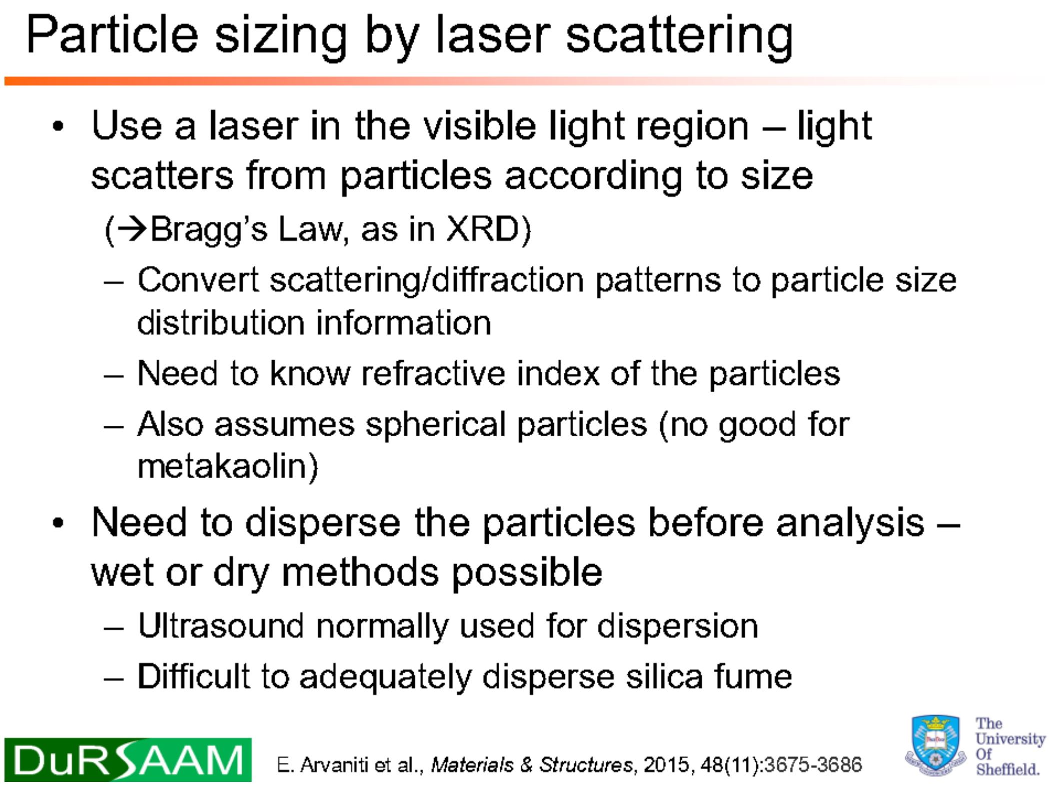
- The equation used in Blaine calculations (Carman-Kozeny eqn.) is only true for single-sized spheres
  - Calculate a surface area from comparison to a known reference material – assume similar shapes
  - Cementitious powders are never single-sized, and rarely spheres (only fly ash has spherical particles)
  - Use empirical correction factors to work-around problems
- Neglects any internal surface area
  - Fly ash has hollow particles, and sponge-like unburned carbon particles – very high actual surface area, but not seen in Blaine method

E. Arvaniti et al., *Materials & Structures*, 2015, 48(11):3675-3686

Nitrogen sorption (BET method)

- Brunauer-Emmett-Teller (*J. Am. Chem. Soc, 1938)*
  → calculation of surface area from gas sorption
- Usually use N_2 as probe gas, sometimes Ar or H_2O (but H_2O is difficult for cements)
- At low T (liquid N_2), the gas condenses on the surface of a solid sample with increasing pressure
  - Assumed to form a monolayer first – and identify the point at which the monolayer is complete from the sorption isotherm
  - Can use this assumption to calculate surface area from the amount of gas condensation in the region $0.05 < (P/P_0) < 0.35$
  - P_0 is the saturation pressure of the gas – which is 1 atm for N_2 at 77 K (normal test conditions)

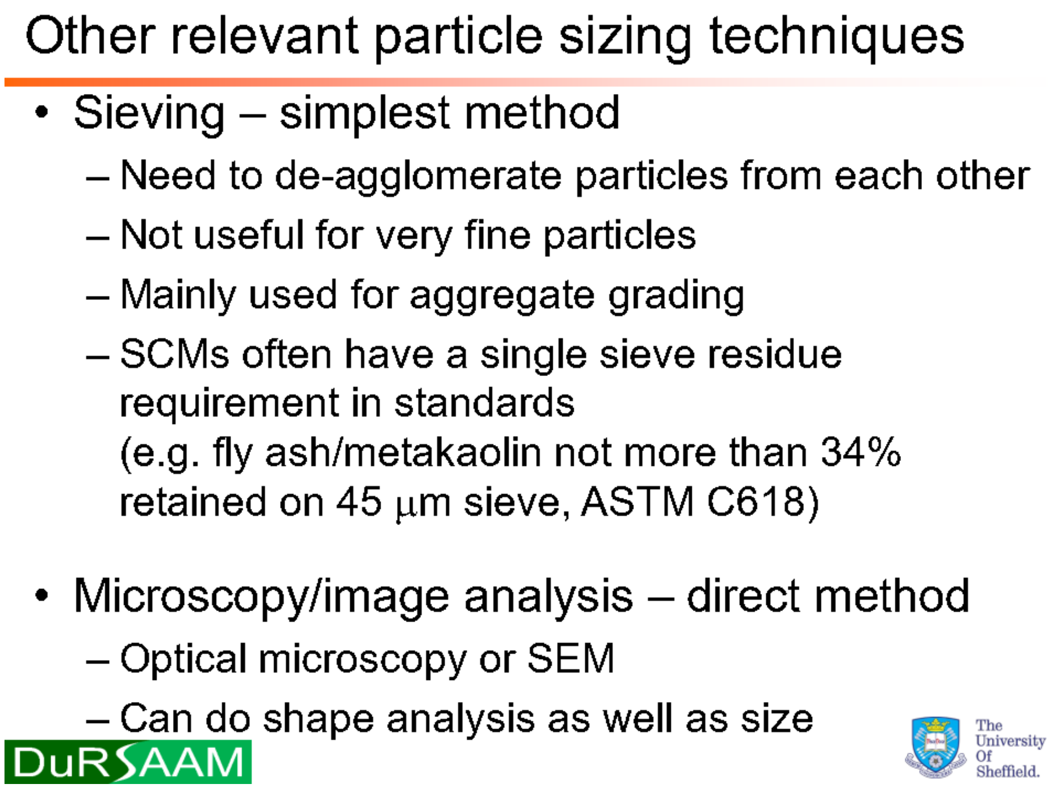




Particle sizing by laser scattering

- Use a laser in the visible light region – light scatters from particles according to size
  (→Bragg's Law, as in XRD)
  - Convert scattering/diffraction patterns to particle size distribution information
  - Need to know refractive index of the particles
  - Also assumes spherical particles (no good for metakaolin)
- Need to disperse the particles before analysis – wet or dry methods possible
  - Ultrasound normally used for dispersion
  - Difficult to adequately disperse silica fume

E. Arvaniti et al., *Materials & Structures*, 2015, 48(11):3675-3686



Other relevant particle sizing techniques

- Sieving – simplest method
  - Need to de-agglomerate particles from each other
  - Not useful for very fine particles
  - Mainly used for aggregate grading
  - SCMs often have a single sieve residue requirement in standards
    (e.g. fly ash/metakaolin not more than 34% retained on 45 μm sieve, ASTM C618)
- Microscopy/image analysis – direct method
  - Optical microscopy or SEM
  - Can do shape analysis as well as size

Example of size and shape analysis by scanning electron microscopy - metakaolin

Shape

Normal MK

Flash MK

[Image deleted for copyright reasons]

Size

R. San Nicolas et al. *Applied Clay Science* 83(2013):253-262

Hydration/reaction - measuring by heat release

- Most important reactions in cement hydration are exothermic (release heat)
  - True for PC and almost all alternative cements

→cumulative heat released is a good way of measuring the extent of hydration/reaction

- Can ideally see distinct peaks for each process in the reaction sequence

- Two main ways to do this:
  - Isothermal calorimetry
  - Semi-adiabatic calorimetry

Isothermal calorimetry (ICC)

- Hold a sample at constant temperature
  - – T-controlled metal block, or oil or water bath
- Measure heat released by sample
  - – Measure voltage, calibrate to convert to heat flow
  - – Report either differential or cumulative data
- Sample size up to a few grams
  - – (new instruments ~200 g for concrete testing)
- Difficult to measure very early stages
  - – Internal or external mixing?

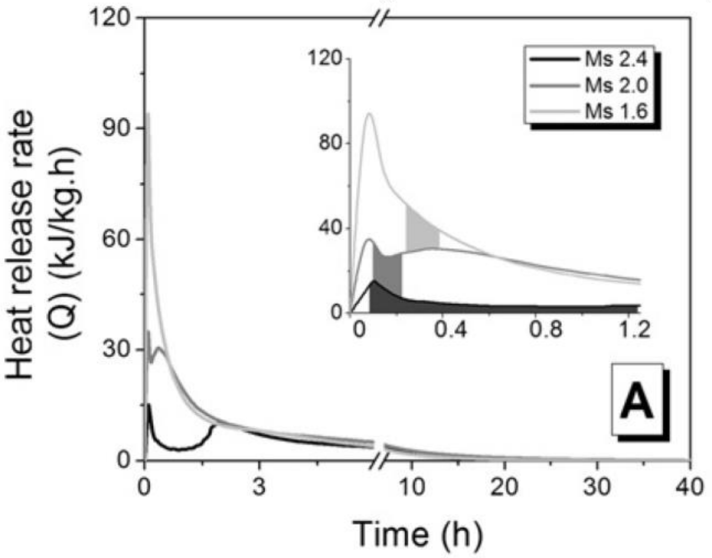
C_3S hydration measured by ICC

- [Image deleted for copyright reasons]

J.W. Bullard et al. Cem Concr Res 41(2011):1208-1223

Alkali-activation of BFS

Shading – Vicat initial & final setting times



S.A. Bernal et al. *Cem Concr Compos* 33(2011):46-54

Semi-adiabatic calorimetry

- Measure temperature inside a (mostly insulated) sample as a function of time
  - Use this to describe rate of reaction
- Advantages
  - Represents conditions inside large concrete blocks
  - Can use much larger samples than ICC
- Disadvantages
  - Can't convert directly to heat evolution
  - Reactions all happen at different temperatures - activation energy effects can be significant
  - Temperature can change by as little as a few °C, or as much as >30°C, depending on sample setup

Example of data for PC hydration

- [Image deleted for copyright reasons]

http://www.cptechcenter.org/t2/documents/10PracticalSACTTCC-NCC9-23-08_000.pdf

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Main materials science techniques

- Mechanical properties testing
- Microscopy
  - Looking at arrangements of phases in space: optical microscopy, SEM, TEM
- Diffraction
  - Looking at arrangements of atoms (crystal structures)
- Spectroscopy
  - Looking at bonds between atoms: FTIR
  - Looking at local environments of atoms: NMR

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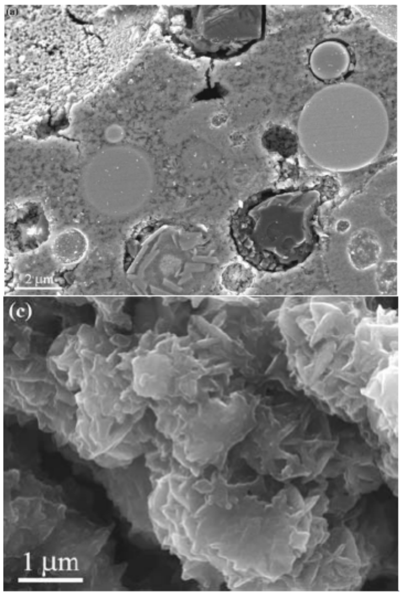
Mechanical properties testing

- Strength (compressive, flexural, tensile)
- Hardness (Vickers, nanoindentation)
- Standard procedures for testing each particular type of material
  - The standards describe specimen geometry, test equipment, rate of application of load, etc.
  - Always test by a standard method – or you won't be able to compare with other people's results
  - Always test a 'representative' number of specimens (the standards say how many to use), and report mean and standard deviation

Scanning electron microscopy

- Scan an electron beam across the surface of a sample
  - Can measure backscattered electrons (BSE)
  - Showing structures in a polished surface), or...
  - Can measure secondary electrons (SE)
  - showing topography of a surface



R.R. Lloyd et al. *J. Mater. Sci.* 44(2009):620

Transmission electron microscopy

- Measure electrons travelling through a very very thin sample
  - Highest resolution of all of these techniques
  - Sample preparation can be very difficult, beam can also damage the sample
  - Interpretation of images can also be difficult

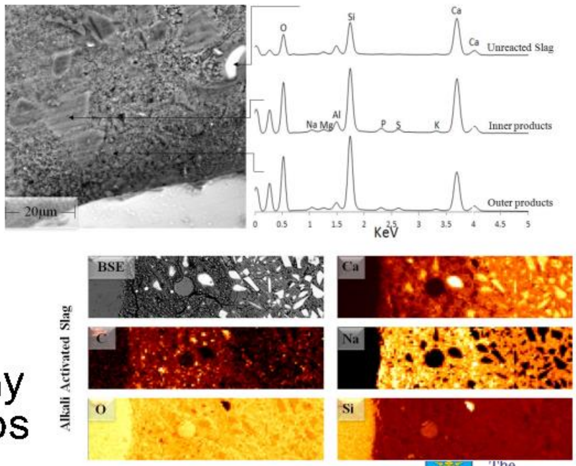
http://www.ccber.ucsb.edu/research/esau/topics-of-study/microscopes/electron_microscope.jpg

See: I.G. Richardson, *Cem. Concr. Compos.* 22(2000):97-113

Elemental compositions

- SEM and TEM can be coupled with energy-dispersive X-ray spectroscopy (EDS or EDX)
- Gives composition at one position in the sample
- Definition of 'one position' depends on the instrument setup
- Or can collect at many points and make maps

R. San Nicolas & J.L. Provis, *Frontiers in Materials*, 2015, 2, #70



Elemental correlation mapping

Al/Ca vs Si/Ca

Shows all Si-Al-Ca phases, but different AFm phases all in one point

●

[Image deleted for copyright reasons]

CEM I

LS-MK blend

★

■

▲

●

★ AFm

▲

M. Antoni et al. *Cement and Concrete Research* 42 (2012) 1579–1589

Elemental correlation mapping

S/Ca vs Al/Ca

[Image deleted for copyright reasons]

Shows Al/Ca ratio of C-A-S-H, distinguishes AFt, and can separate different AFm phases from each other

(plots are for cement being attacked by an external sulfate source, presented in terms of depth from the surface, showing AFm conversion to AFt as the paste is damaged)

W. Kunther et al. *Cement and Concrete Research* 44 (2013) 77–86

Diffraction

- X-ray diffraction (XRD) most commonly used in lab analysis of cements
  - Can also use neutrons (on a dedicated beamline), or electrons (in a TEM)
  - All work on the same principle – Bragg's Law
  - Gives a 'fingerprint' for a crystal structure

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http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/imgqua/bragglaw.gif

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What to do with this...?

- Identify phases – search/match in databases
  - Commercial: ICDD Powder Diffraction File (PDF)
  - Free online: http://rruff.geo.arizona.edu/AMS/amcsd.php
  - Sometimes it's easy... Single phase, simple crystal structures (NaCl here)

[Image deleted for copyright reasons]

http://universe-review.ca/I13-04-XRD.jpg

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- Complex phase mixtures in most cements
- Each phase has a ‘fingerprint’ in XRD
- Not very helpful for C-S-H or N-A-S-H, though

A diversion – what is “amorphous”?

- [Image deleted for copyright reasons]

C. Meral et al. Cem Concr Res 41(2011):696-710

Spectroscopy - NMR

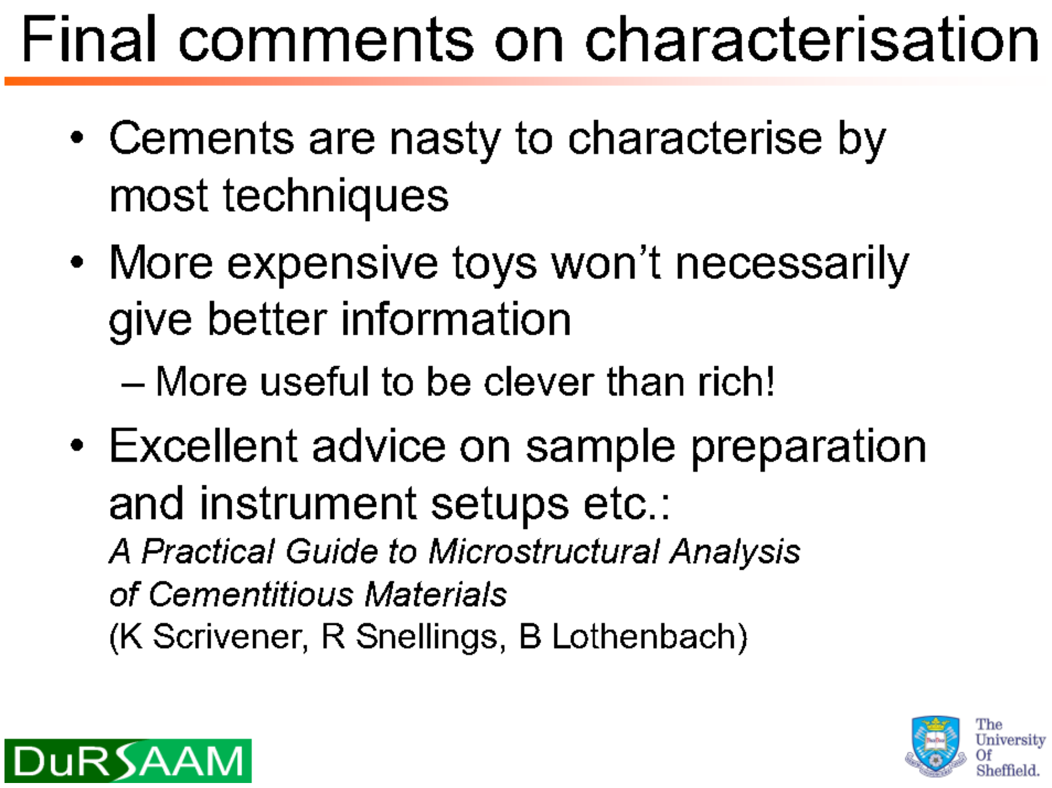
- Nuclear magnetic resonance (NMR)
  - Needs a nucleus with a non-zero spin – selective for specific isotopes

    i.e. Can see ^{29}Si (~4% of all Si), not ^{28}Si (~96%), similarly can see ^{13}C (1.1%) but not ^{12}C (98.9%)

    → can use this to selectively 'label' the parts of a molecule/structure that you want to see
- Relatively easy for liquid samples
  - More difficult for solids; need to spin the sample very rapidly (>5 kHz) to get sharp peaks

How it works (in very simplified form)

- Measures density of electrons around a nucleus
  - response to a (pulsed) magnetic field – 'resonance'
- Compare against a reference compound to say whether an element in your sample has more or less electron density
  - This tells about chemical bonding environments
  - Neighbouring atoms either donate or withdraw electron density from the atom of interest
- In cements, most useful for analysis of H, Al, Si
  - Still possible but trickier: Mg, O, Na, K
  - Very difficult to get useful information: S, C, Ca
  - Tends to get messed up by Fe – broadens the spectra



Final comments on characterisation

- Cements are nasty to characterise by most techniques
- More expensive toys won't necessarily give better information
  - – More useful to be clever than rich!
- Excellent advice on sample preparation and instrument setups etc.:
  A Practical Guide to Microstructural Analysis of Cementitious Materials
  (K Scrivener, R Snellings, B Lothenbach)

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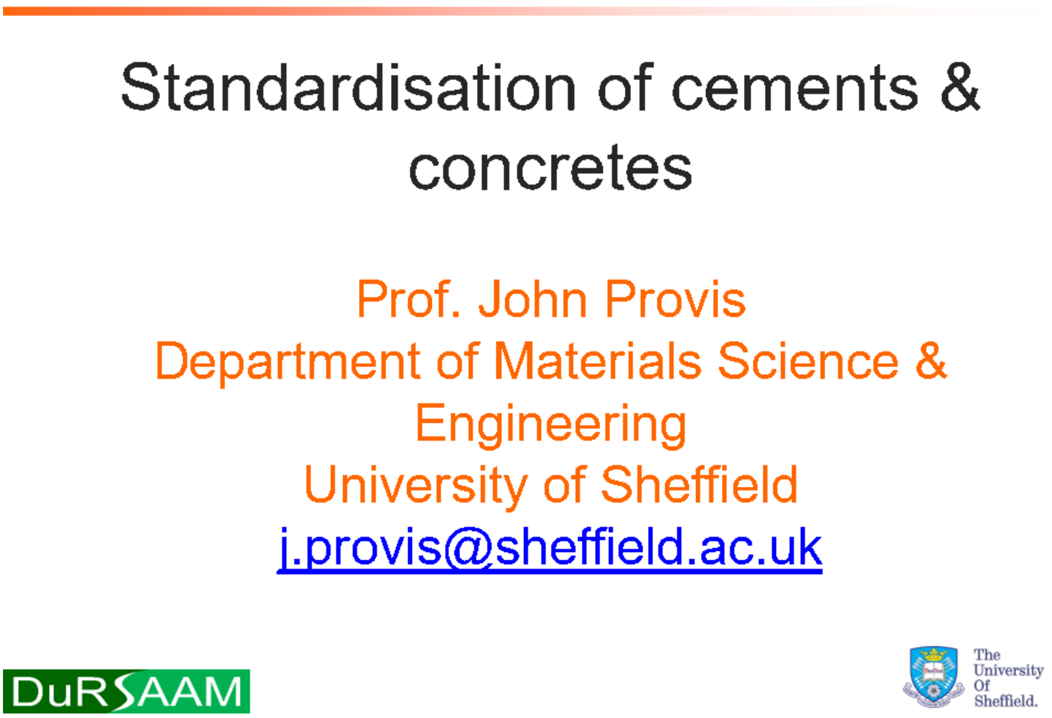
5. Standardisation of cements and concretes

John Provis

In the construction sector standards and product certification are often applicable. When using novel binder and concrete technologies, existing standards might not always be fully applicable or adapted yet. Nevertheless, though new concrete technologies might be out of scope of existing standards, this does not prevent that they can be already used to some respect. A discussion in this respect is given in this chapter.



Standardisation of cements & concretes

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Standardisation of cement & concrete

- IMPORTANT NOTE: The majority of tables and extracts from standards documents within this set of slides are too small to read all the details. This is intentional – I don't want you to sit memorising these tables!

  → Understand the significance of the things that are in them, rather than the exact numbers/details.

- Note also that every time you use a standard in your professional work, you should obtain the newest version of it to ensure that it hasn't changed.

European approach to specifying cement/concrete

- A family tree of standards
- Controlled by cement and concrete industry
- Cascading set of requirements for materials to be used in concrete
  - Hopefully not conflicting with each other..!
  - Many testing methods are integrated into material standards

Types of Portland cement

- British & European Standard BS EN 197-1
- 27 sub-types of cement, 5 categories:
  - – CEM I Portland cement (≥95% Portland clinker)
  - – CEM II Portland-composite cement (65-94% Portland + 1 pozz./limestone)
  - – CEM III Blastfurnace cement (5-64% Portland + slag)
  - – CEM IV Pozzolanic cement (45-89% Portland + 1 pozz.)
  - – CEM V Composite cement (20-64% Portland + slag + 1 other SCM)

Note also: USA uses different types (ASTM Types I-V)

Cements standards

- Prescriptive standards – 27 different types of cement are listed in the standard (EN 197-1)

[Image deleted for copyright reasons]

Allowed certain combinations of SCMs

- [Image deleted for copyright reasons]

See: http://www.cemnet.com/content/uploads/images/3994c1c4-8914-4e83-805f-aface7eef086.jpg

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Each is also given a strength class

- 28 d compressive strength, mortar with ratio 3:1 sand:cement, w/c 0.50, 40 mm pseudo-cubes*

*produced as 40x40x160 mm prisms, broken in flexion then ends tested as 'cubes'

L: Low
N: Normal
R: Rapid (high early strength)

- Full name of product includes cement type and strength class – e.g. CEM II/B-V 42.5 N

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Concrete classes

- ‘Strength classes’ also defined for concretes, based on 28-day cube & cylinder strengths
  - E.g. C40/50 : 40 MPa cylinder, 50 MPa cube @28d
- ‘Exposure classes’ are used to describe the environments in which concretes are used – each environment type is defined
- Each country in Europe then has rules about which cement types, and which minimum cement contents and strength grades, can be used in each exposure class

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Assume high strength, low w/c → good durability

- Define maximum w/c ratio, minimum strength class, minimum cement content for each type of exposure – *assumed* to give sufficient performance

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e.g. UK national standard BS 8500-1

How can a new material be used..?

- Add it to the EN standard?
  - Extremely slow
  - Standards committees controlled by producers of existing materials
  - National appendix (or guideline) is a way into this
- European Technical Assessments
  - Product-based specifications, funded by producers of the new product, issued by national approved authorities
  - Products are deemed to be acceptable across EU
- National specification (e.g. UK “PAS” system)
  - Publicly Available Specification – not legally a standard
- Outside the standard? Alternative applications…

Target the right application

- Specialty products often have purpose-written, performance-based standards
  - Roof tiles
  - Masonry blocks
  - Paving slabs
  - Tile grouts
  - Etc…
- Waste immobilisation
  - Nuclear waste industry in the UK only requires 0.7 MPa @ 28 d, but has a lot of other requirements instead of strength

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ASTM approach to standards

- Prescriptive standards
  - ASTM C150 – Portland cement (defines 5 types of cement)
  - ASTM C595 – Blended hydraulic cements
- Performance-based standard
  - ASTM C1157 – ‘Standard Performance Specification for Hydraulic Cement’

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ASTM C150

- Prescriptive standard for cement composition, defines clinker composition (next slide)
  - Contrast to BS EN approach, where clinker composition is barely described beyond ‘it is Portland cement clinker’

ASTM cement types → [Image deleted for copyright reasons]
(would all be classified
as CEM I in UK/EU)

ASTM C1157

- [Image deleted for copyright reasons]

Comments on C1157

- Pure performance-based standard
  - Very few prescriptive requirements
- Not yet really trusted in practice
- Seen as a way forward for alternative cements – we want to follow a similar route
  - Main question: are the tests any good? – see last two lectures…
  - Useless to base a standard on tests that don't apply to the materials we want to test… see lectures on testing methods!

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Standardisation of AAMs

- A recent example, **PAS 8820:2016 (BSI)** – *"Construction materials – Alkali-activated cementitious material and concrete – Specification"*
- World-first, UK standardisation process for alkali-activated materials
  - Performance-based specification for alkali-activated cements and concretes ("AACMs")
  - Testing methods, quality criteria, etc.
  - Bagged cement, ready-mix concrete, precast elements

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The PAS 8820 approach

- Performance based specification
- 'AACM' binder chemistry described very broadly
  - Minimal prescription required to avoid overlap with BS EN 197-1 cement classes → no more than 5% PC
- Following established UK practice where possible
- Basic philosophy – design a 'reference concrete' to the BS 8500 exposure class regulations, and test in parallel
  - Reference should have chemistry as close as possible to the AACM (i.e. maximum use of same SCMs)
  - Specified suite of durability tests, same for both materials
  - AACM concrete must perform at least as well as the concrete of known (assumed?) good performance

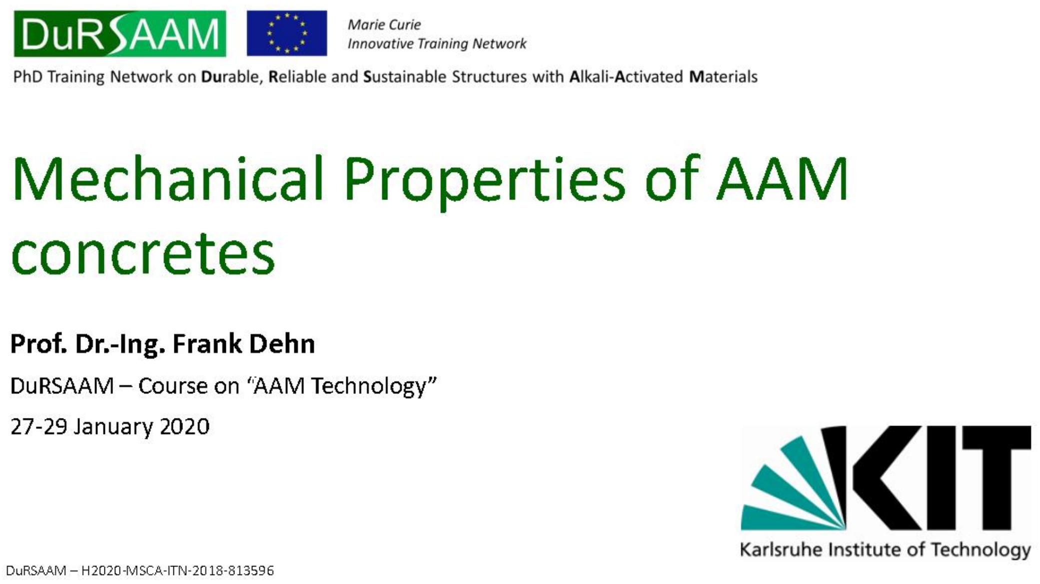
Where does this lead?

- Intended to be a very conservative approach
- Conformity & identity testing required – strength & flow
- Tests follow established methods where possible
  - Most require adaptation for application to AACMs
- For all concretes:
  - ASR (RILEM AAR-3)
  - freeze-thaw (HETEK/Borås)
  - sulfate including permeability (ASTM C1012 & BS EN 12390-8)
- For reinforced concretes, also: (*non-accelerated tests*)
  - carbonation (DD CEN/TS 12390-10)
  - chloride ingress (DD CEN/TS 12390-11)

6. Mechanical Properties of AAM concretes

Frank Dehn

Given the somewhat different chemical composition of AAM concretes, it is of interest to look into its mechanical performance, and to compare it with relationships provided in existing standards for traditional concrete. This chapter looks into typical strength parameters for concrete, as well as their development over time. Also long-term sustained stress, resulting in creep strains, is discussed.



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Innovative Training Network

PhD Training Network on **Du**rable, **R**eliable and **S**ustainable Structures with **A**lkali-**A**ctivated **M**aterials

Mechanical Properties of AAM concretes

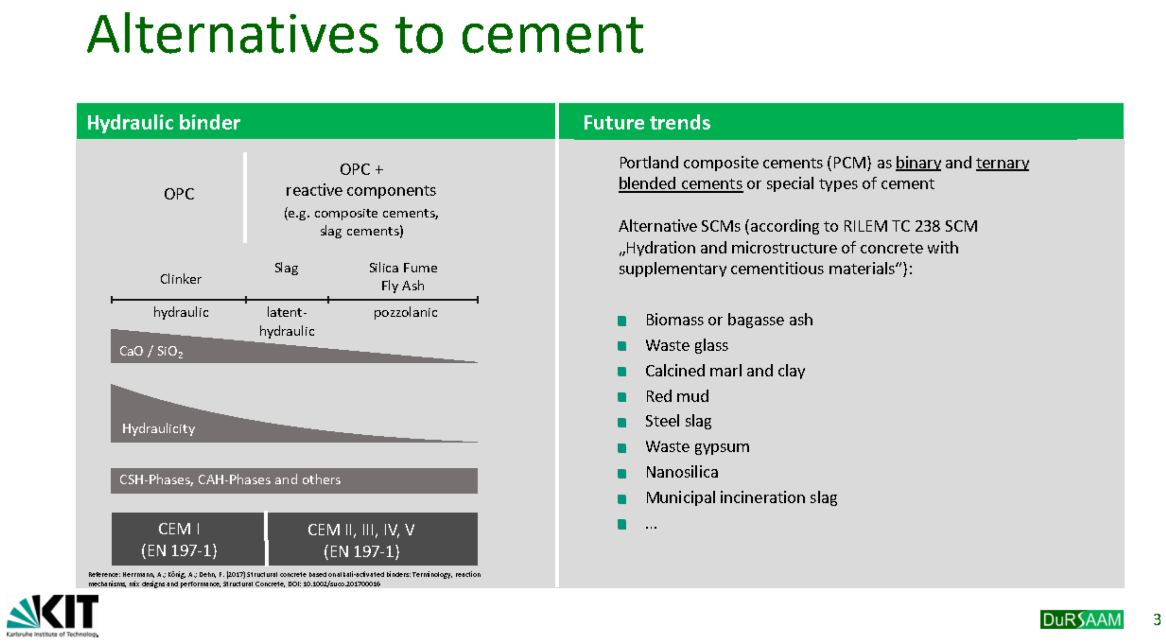
Prof. Dr.-Ing. Frank Dehn

DuRSAAM – Course on "AAM Technology"

27-29 January 2020

Karlsruhe Institute of Technology

DuRSAAM – H2020-MSCA-ITN-2018-813596



Alternatives to cement

Hydraulic binder

OPC	OPC + reactive components (e.g. composite cements, slag cements)

Clinker | Slag | Silica Fume
Fly Ash

hydraulic | latent-hydraulic | pozzolanic

CaO / SiO_2

Hydraulicity

CSH-Phases, CAH-Phases and others

CEM I
(EN 197-1)

CEM II, III, IV, V
(EN 197-1)

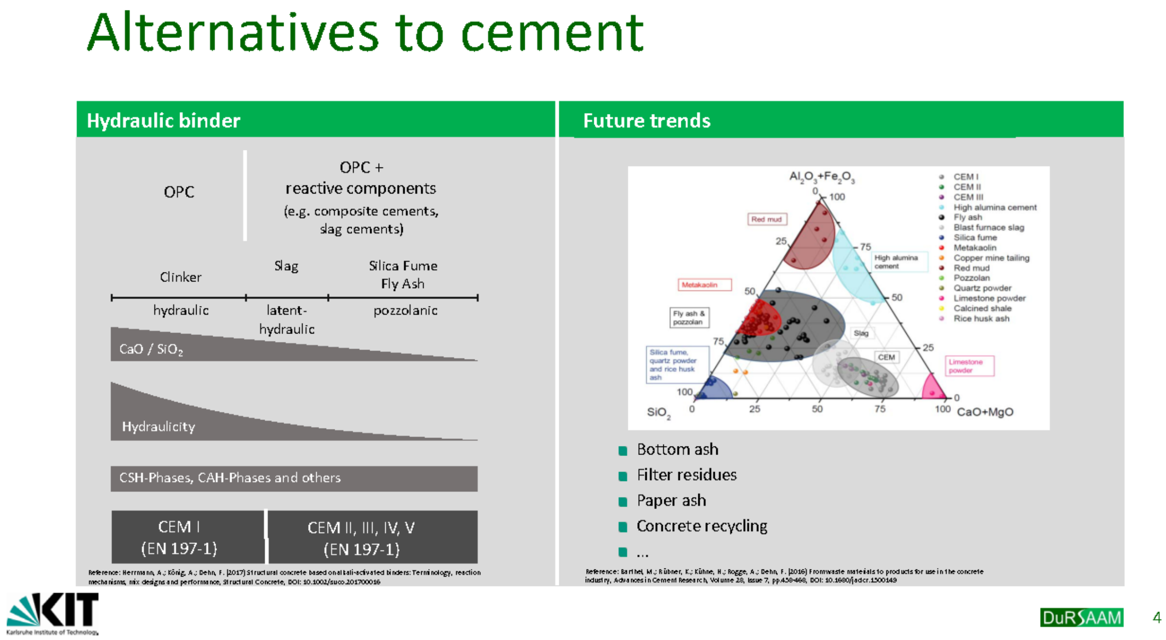
Reference: Herrmann, A.; König, A.; Dehn, F. (2017) Structural concrete based on alkali-activated binders: Terminology, reaction mechanisms, mix designs and performance, Structural Concrete, DOI: 10.1002/suco.201700016

Future trends

Portland composite cements (PCM) as binary and ternary blended cements or special types of cement

Alternative SCMs (according to RILEM TC 238 SCM „Hydration and microstructure of concrete with supplementary cementitious materials“):

- Biomass or bagasse ash
- Waste glass
- Calcined marl and clay
- Red mud
- Steel slag
- Waste gypsum
- Nanosilica
- Municipal incineration slag
- …



Alternatives to cement

Hydraulic binder

OPC	OPC + reactive components (e.g. composite cements, slag cements)

Clinker | Slag | Silica Fume
Fly Ash

hydraulic | latent-hydraulic | pozzolanic

CaO / SiO_2

Hydraulicity

CSH-Phases, CAH-Phases and others

CEM I
(EN 197-1)

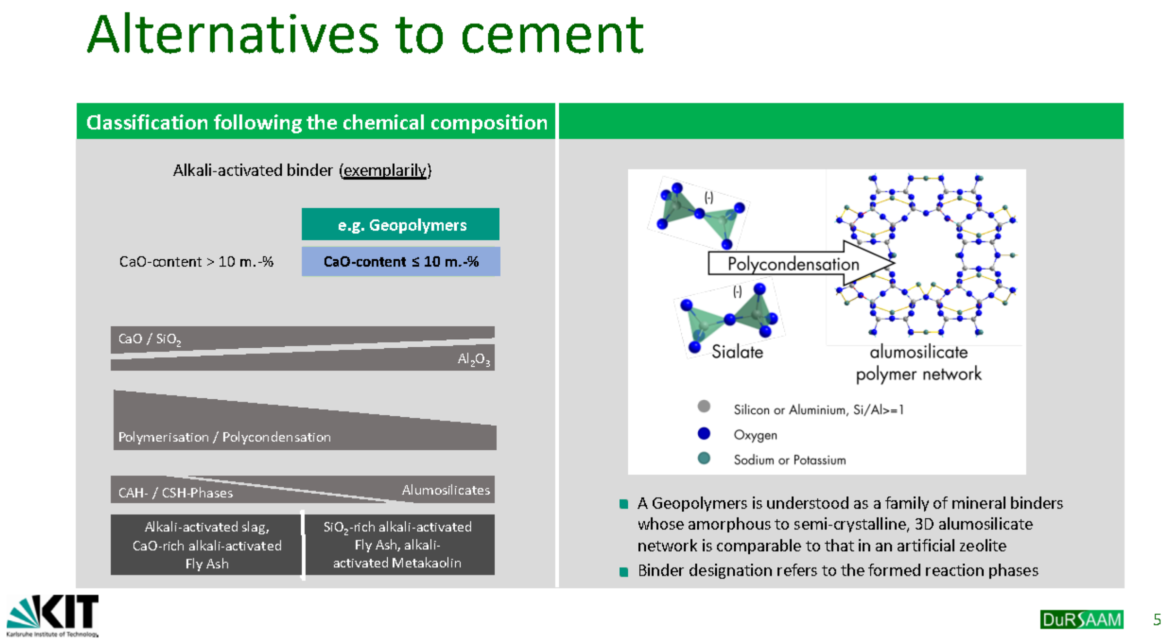
CEM II, III, IV, V
(EN 197-1)

Reference: Herrmann, A.; König, A.; Dehn, F. (2017) Structural concrete based on alkali-activated binders: Terminology, reaction mechanisms, mix designs and performance, Structural Concrete, DOI: 10.1002/suco.201700016

Future trends

- Bottom ash
- Filter residues
- Paper ash
- Concrete recycling
- …

Reference: Barthel, M.; Rübner, K.; Kühne, H.; Rogge, A.; Dehn, F. (2016) From waste materials to products for use in the concrete industry, Advances in Cement Research, Volume 28, Issue 7, pp.458-468, DOI: 10.1680/jadcr.1500149



Alternatives to cement

Classification following the chemical composition

Alkali-activated binder (exemplarily)

e.g. Geopolymers

CaO-content > 10 m.-%

CaO-content ≤ 10 m.-%

CaO / SiO$_2$

Al$_2$O$_3$

Polymerisation / Polycondensation

CAH- / CSH-Phases

Alumosilicates

Alkali-activated slag, CaO-rich alkali-activated Fly Ash

SiO$_2$-rich alkali-activated Fly Ash, alkali-activated Metakaolin

● Silicon or Aluminium, Si/Al>=1

● Oxygen

● Sodium or Potassium

- A Geopolymers is understood as a family of mineral binders whose amorphous to semi-crystalline, 3D alumosilicate network is comparable to that in an artificial zeolite
- Binder designation refers to the formed reaction phases

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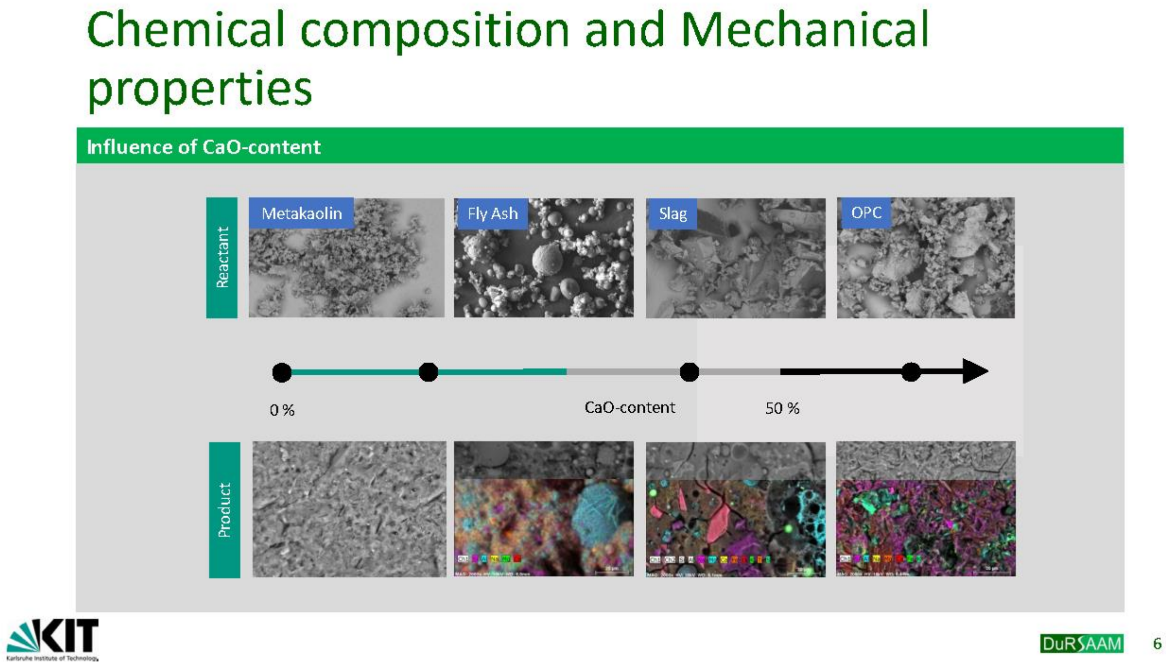

Chemical composition and Mechanical properties

Influence of CaO-content

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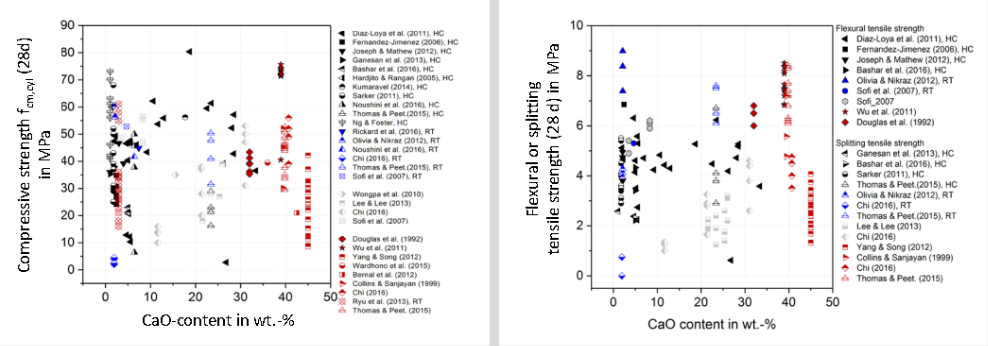
Chemical composition and Mechanical properties

Influence of CaO-content on compressive strength $f_{cm,cyl}$ and tensile strength f_{ct}



➔ No correlation between CaO content and compressive strength or tensile strength

Using existing standards for cement-based concrete

Recall for cement-based concrete classification

„In this Model Code, concrete is classified on the basis of its ***compressive strength*** *[obtained at a concrete age of 28 days]. Design is based on a grade of concrete which corresponds to a specific value of its characteristic compressive strength f_{ck}"*

Fib Model Code 2010, bulletin 65

CXX = Class of concrete, such as $f_{ck}(28\ days) = XX\ MPa$

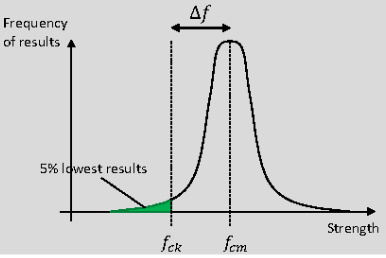
Existing classes:

C12, C16, C20, C25, C30, C35, C40, C45,
C50, C60, C70, C80, C90, C100, C110, C120

$$f_{cm} = f_{ck} + \Delta f$$

mean value of compressive strength

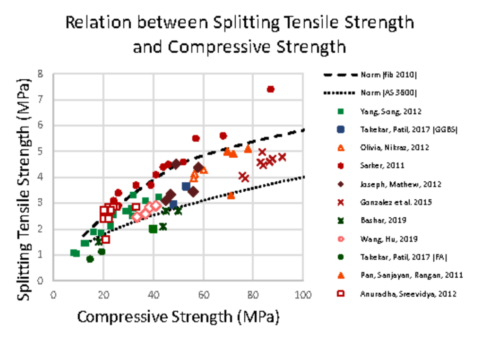
specific characteristic compressive strength



Using existing standards for cement-based concrete

Relation between tensile strength f_{ct} and compressive strength $f_{cm,cyl}$

Relation between Splitting Tensile Strength and Compressive Strength



Tensile Strength for fib (2010)

$f_{ct} = 0.3\,(f_{ck})^{2/3}$ for concrete grades $\leq C50$

$f_{ct} = 2.12\,\ln(1 + 0.1\,(f_{ck} + \Delta f))$ for concrete grades $> C50$

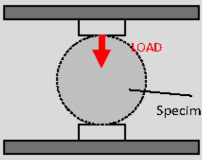
Tensile Strength for AS 3600 (2018)

$f_{ct} = 0.36\sqrt{f_{ck}}$

Splitting Tensile Strength

$f_{ct} = 0.9\,f_{ct.sp}$

(for both standards)



- Existing standards for tensile strength can be adapted to predict AAM tensile strength

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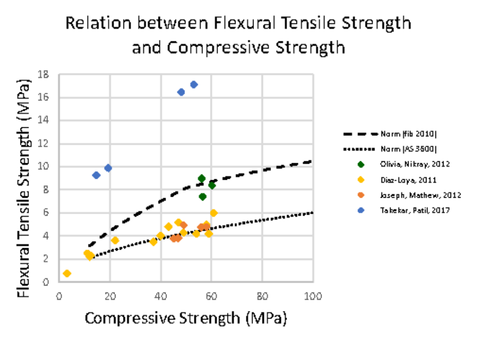
Using existing standards for cement-based concrete

Relation between tensile strength f_{ct} and compressive strength $f_{cm,cyl}$

Relation between Flexural Tensile Strength and Compressive Strength



Tensile Strength for fib (2010)

$f_{ct} = 0.3\,(f_{ck})^{2/3}$ for concrete grades $\leq C50$

$f_{ct} = 2.12\,\ln(1 + 0.1\,(f_{ck} + \Delta f))$ for concrete grades $> C50$

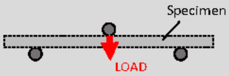
Tensile Strength for AS 3600 (2018)

$f_{ct} = 0.36\sqrt{f_{ck}}$

Flexural Tensile Strength

$f_{ct} = 0.5\,f_{ct.sp}$ (fib Model code)

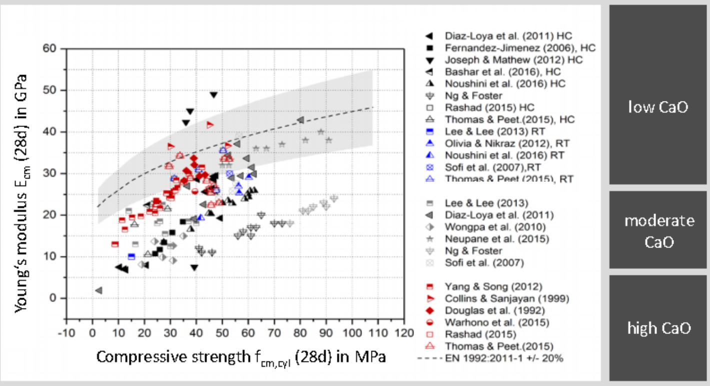
$f_{ct} = 0.6\,f_{ct.sp}$ (AS 3600)



- Existing standards for tensile strength can be adapted to predict AAM tensile strength

Using existing standards for cement-based concrete

Relation between Young's modulus E_{cm} and compressive strength $f_{cm,cyl}$



$$E_{ci} = E_{c0}\alpha_E\left(\frac{f_{ck} + \Delta f}{10}\right)^{1/3}$$

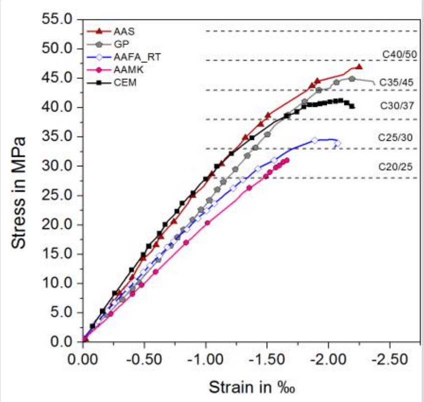
Δf: 8 MPa
E_{c0}: 21.5 GPa

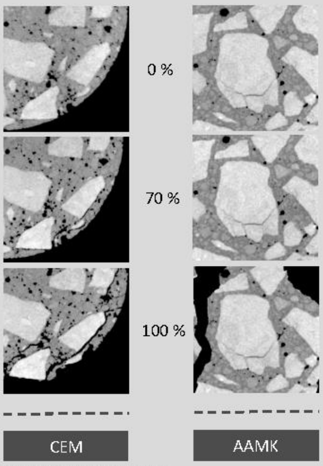
Type of aggregates	α_E
Basalt, dense limestone	1.2
Quartzite	1.0
Limestone	0.9
Sandstone	0.7

- Young's modulus is globally largely under-estimated for AAM concretes

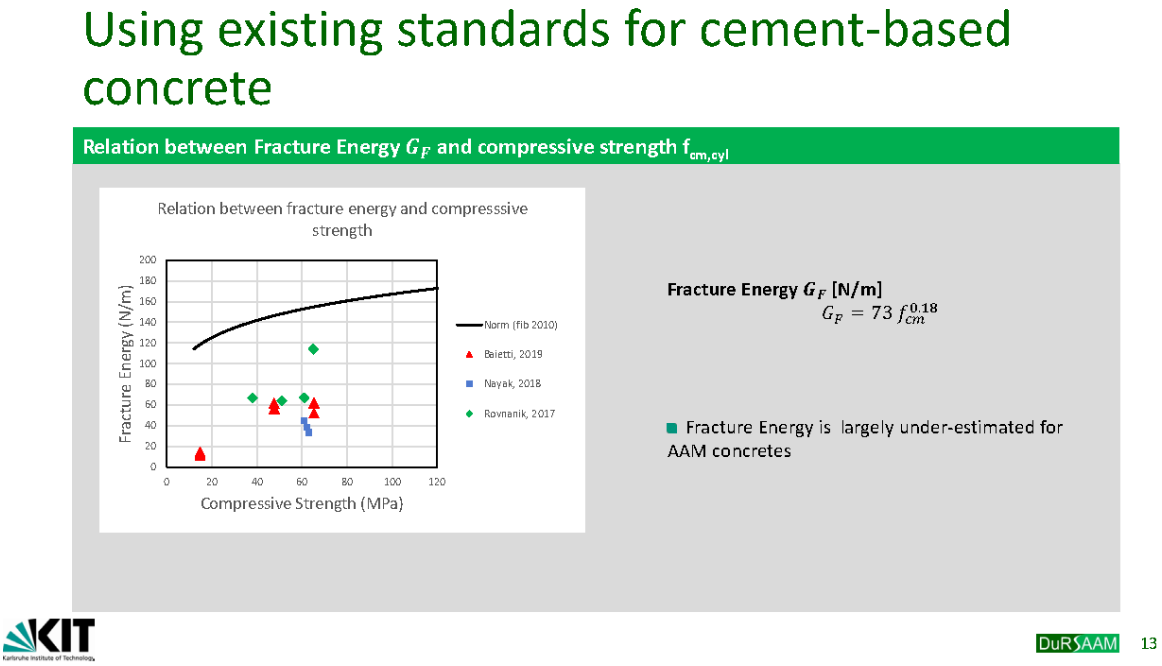
Using existing standards for cement-based concrete

Stress/Strain behaviour of AAC / GP





- Cracks not located at the same place:
  - -CEM: matrix-aggregates bond
  - -AAM: aggregates



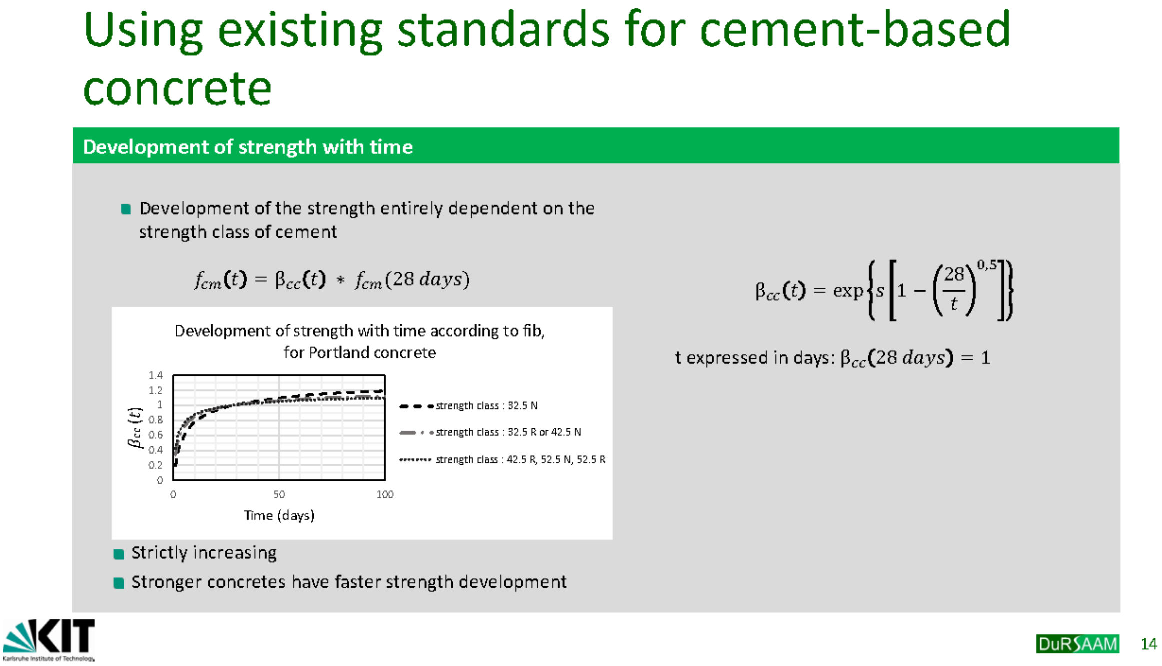
Using existing standards for cement-based concrete

Relation between Fracture Energy G_F and compressive strength $f_{cm,cyl}$

Fracture Energy G_F [N/m]

$$G_F = 73\, f_{cm}^{0.18}$$

- Fracture Energy is largely under-estimated for AAM concretes



Using existing standards for cement-based concrete

Development of strength with time

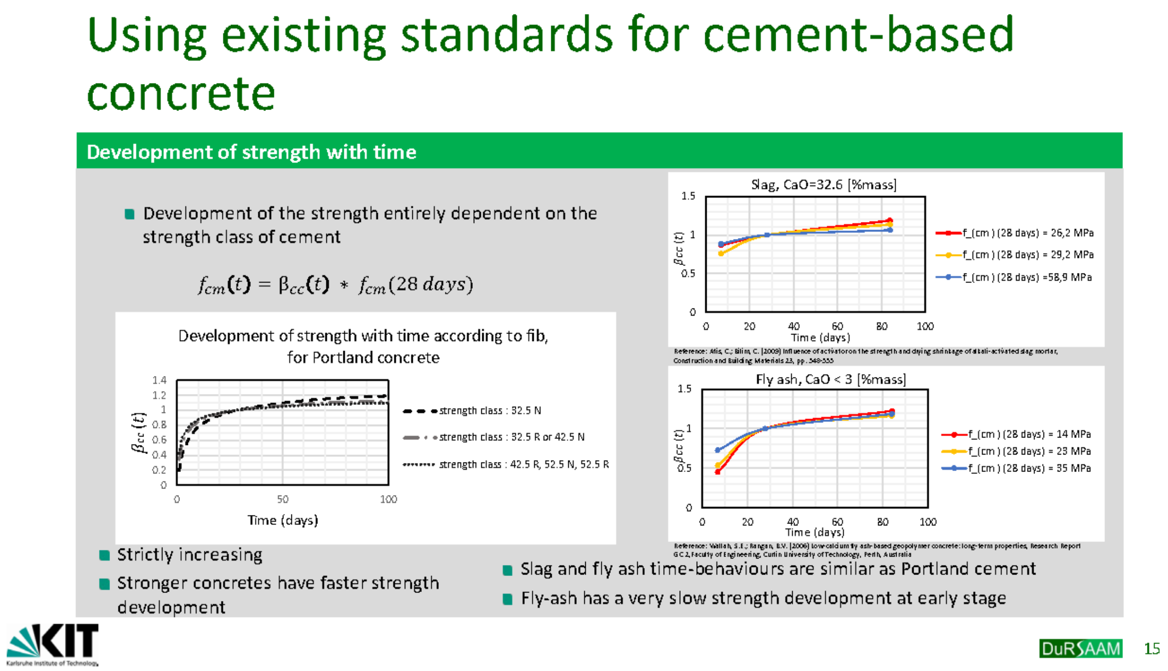
- Development of the strength entirely dependent on the strength class of cement

$$f_{cm}(t) = \beta_{cc}(t) * f_{cm}(28\ days)$$

- Strictly increasing
- Stronger concretes have faster strength development

$$\beta_{cc}(t) = \exp\left\{s\left[1 - \left(\frac{28}{t}\right)^{0,5}\right]\right\}$$

t expressed in days: $\beta_{cc}(28\ days) = 1$



Using existing standards for cement-based concrete

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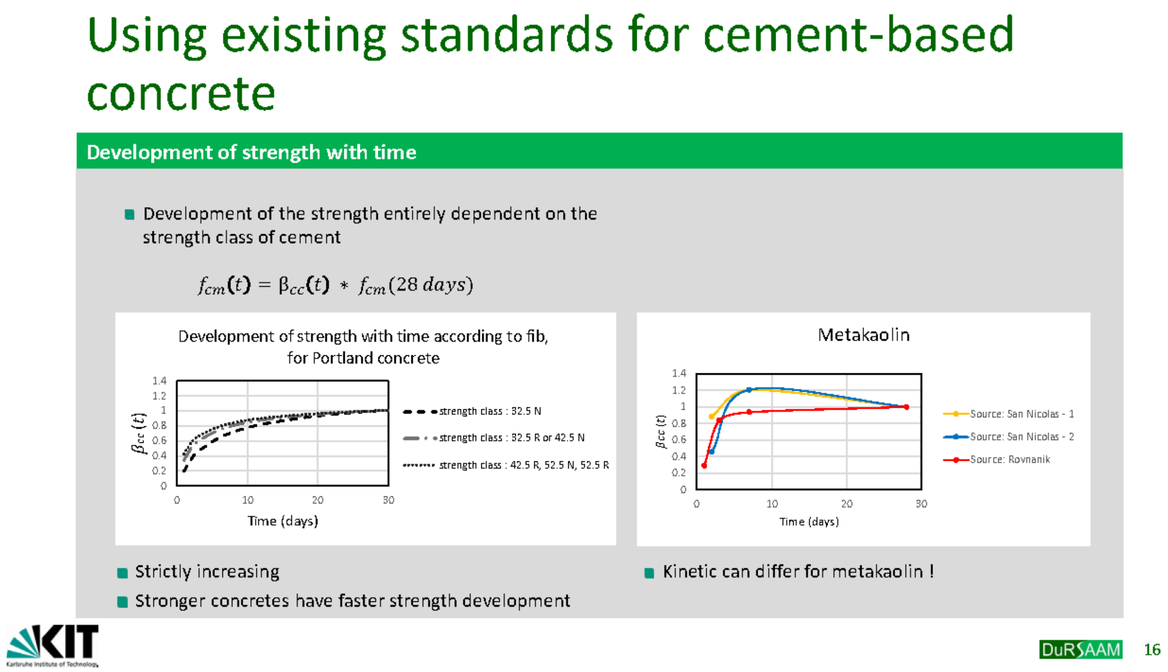
$$f_{cm}(t) = \beta_{cc}(t) \ * \ f_{cm}(28\ days)$$

Reference: Atis, C.; Bilim, C. (2009) Influence of activator on the strength and drying shrinkage of alkali-activated slag mortar, Construction and Building Materials 23, pp. 548-555

Reference: Wallah, S.E.; Rangan, B.V. (2006) Low-calcium fly ash-based geopolymer concrete: long-term properties, Research Report GC 2, Faculty of Engineering, Curtin University of Technology, Perth, Australia

- Strictly increasing
- Stronger concretes have faster strength development

- Slag and fly ash time-behaviours are similar as Portland cement
- Fly-ash has a very slow strength development at early stage



Using existing standards for cement-based concrete

Development of strength with time

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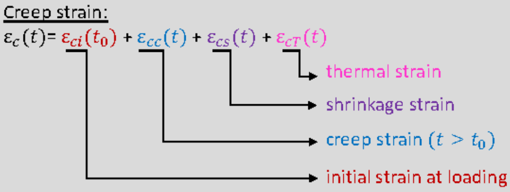
$$f_{cm}(t) = \beta_{cc}(t) \ * \ f_{cm}(28\ days)$$

- Strictly increasing
- Stronger concretes have faster strength development

- Kinetic can differ for metakaolin !

Using existing standards for cement-based concrete

Creep: strain generated by the application of the load



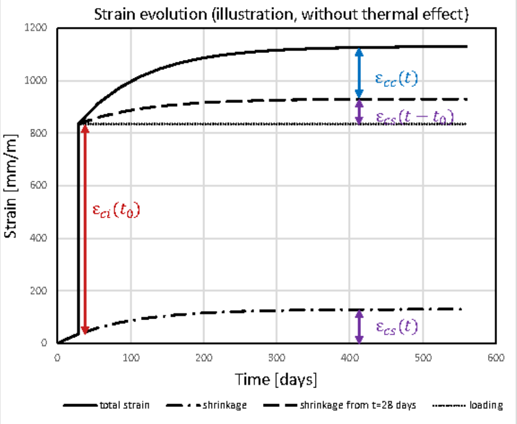
Creep strain:

$\varepsilon_c(t) = \varepsilon_{ci}(t_0) + \varepsilon_{cc}(t) + \varepsilon_{cs}(t) + \varepsilon_{cT}(t)$

- $\varepsilon_{cT}(t)$ → thermal strain
- $\varepsilon_{cs}(t)$ → shrinkage strain
- $\varepsilon_{cc}(t)$ → creep strain ($t > t_0$)
- $\varepsilon_{ci}(t_0)$ → initial strain at loading

Creep coefficient:

$$\varphi_c(t, t_0) = \frac{\varepsilon_{cc}(t, t_0)}{\varepsilon_{ci}(t_0)}$$



Using existing standards for cement-based concrete

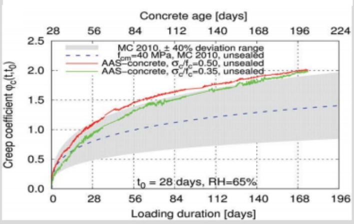
Creep: strain generated by the application of the load

Comparison Model Codes / AAM

Creep coefficient:

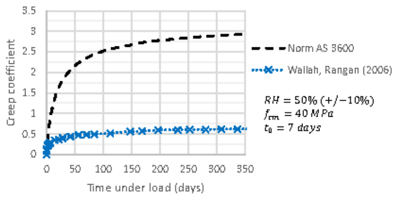
$$\varphi_c(t, t_0) = \frac{\varepsilon_{cc}(t, t_0)}{\varepsilon_{ci}(t_0)}$$

Creep coefficient for a slag (CaO=40.3%mass])



Reference: Ma, J.; Dehn, F., Shrinkage and creep behavior of an alkali-activated slag concrete *Structural Concrete*. 2017;18:801-810. https://doi.org/10.1002/suco.201600147

Creep coefficient for a fly ash, class F



Reference: Wallah, S.E., Rangan, B.V.: Low-Calcium Fly Ash-Based Geopolymer Concrete: Long-Term Properties, Curtin University of Technology, Research Report GC2 (2006)

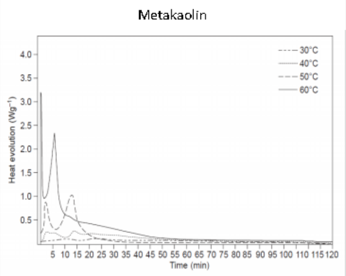
Using existing standards for cement-based concrete

Sum up: can we use standards for cement-based concrete to AAM?

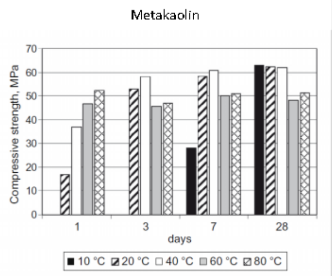
Mechanical Property	Correlation with f_{cm} given by standards
Tensile Strength f_{ct}	Standards adapted
Young's modulus E	No real correlation
Fracture Energy G_F	Small correlation, standard largely underestimate the value
Development of strength $f_{cm}(t)$	• Slag & Fly Ash: development similar as with cement • Metakaolin: different kinetic
Creep	New norm to create

Other physical insights

Temperature effect: Metakaolin


Metakaolin

Reference: Muñiz-Villarreal, M.S. (2011) The effect of temperature on the geopolymerization process of a metakaolin-based geopolymer, Material Letters 65 (2011), 995-998

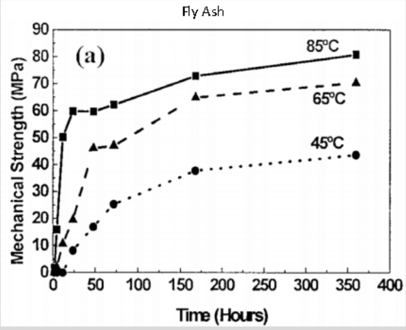

Metakaolin

Reference: Rovnanik, P. (2010) Effect of curing temperature on the development of hard structure of metakaolin-based geopolymer, Construction and Building Materials 24 (2010), 1176-1183

- Increasing the temperature increases the kinetic speed
  - Lower setting time
  - Faster strength development
  - Lower 28-day compressive strength

Other physical insights

Temperature effect: Fly Ash



Reference: Palomo, A. (2004) Alkali activation of fly ashes: a NMR study of the reaction products, J Am Ceram Soc, 87, 1141-1145

- Here, increasing the temperature increases also the kinetic speed
    - Lower setting time
    - Faster strength development
    - **Bigger** 28-day compressive strength
    - ➔ Curing plays a crucial role for Fly Ash

Other physical insights

Others

- Properties related to non-static loading:
    - Fatigue
    - Impact

} Few investigations on the subjects

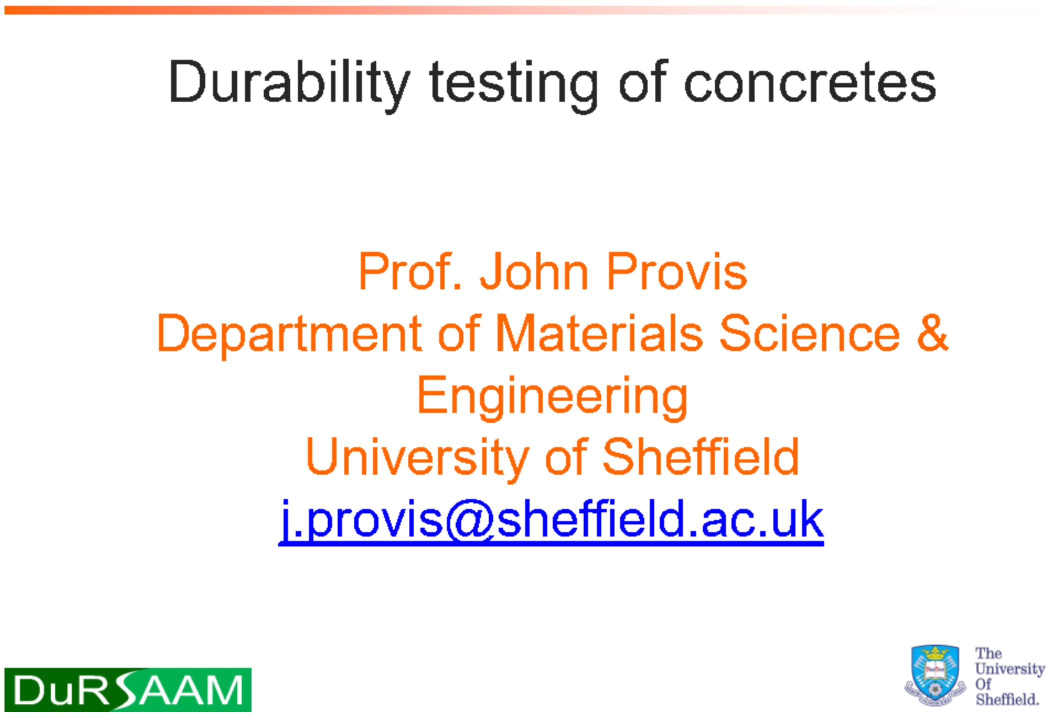
- Transport phenomena
    - Permeation
    - Diffusion
    - Capillary suction

} Related to durability properties

7. Durability testing of concretes

John Provis

In view of the service life of concrete structures, it is important that concretes are made durable. Different durability issues can become apparent in (reinforced) concrete. It is important to also understand how the durability of concrete is tested, so to understand if test methods remain suited to verify the durability behaviour of AAM concrete.



Durability testing of concretes

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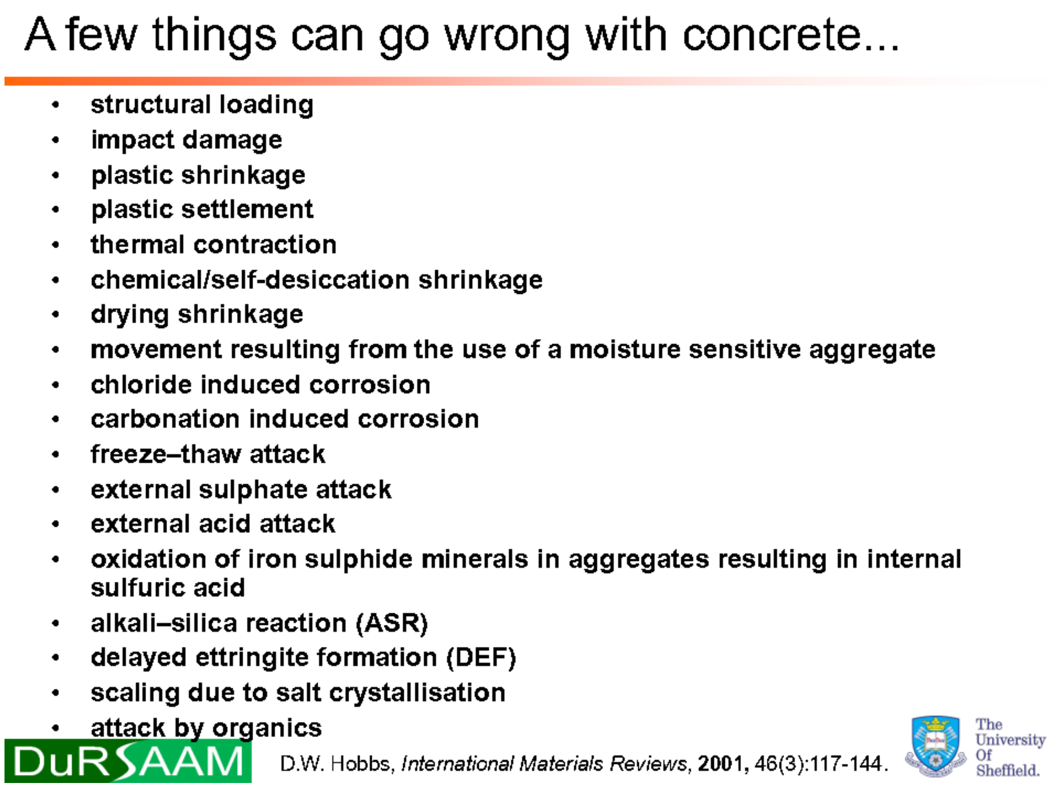
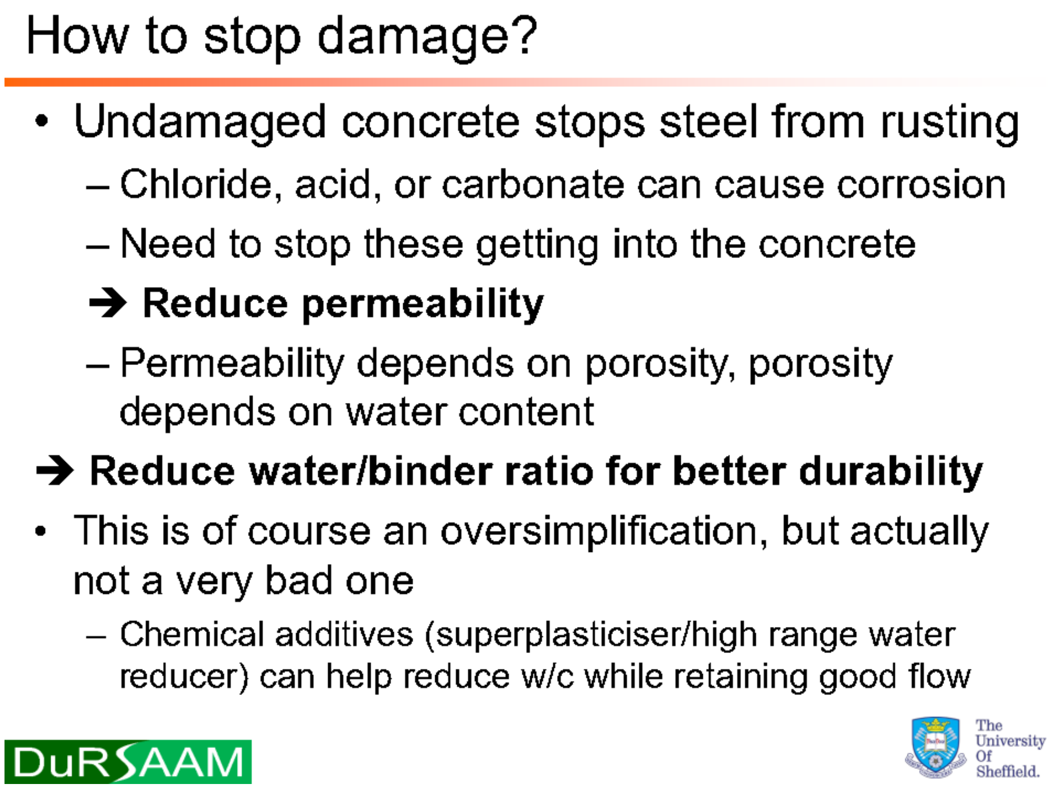


A few things can go wrong with concrete...

- structural loading
- impact damage
- plastic shrinkage
- plastic settlement
- thermal contraction
- chemical/self-desiccation shrinkage
- drying shrinkage
- movement resulting from the use of a moisture sensitive aggregate
- chloride induced corrosion
- carbonation induced corrosion
- freeze–thaw attack
- external sulphate attack
- external acid attack
- oxidation of iron sulphide minerals in aggregates resulting in internal sulfuric acid
- alkali–silica reaction (ASR)
- delayed ettringite formation (DEF)
- scaling due to salt crystallisation
- attack by organics

D.W. Hobbs, *International Materials Reviews*, **2001**, 46(3):117-144.



How to stop damage?

- Undamaged concrete stops steel from rusting
  - Chloride, acid, or carbonate can cause corrosion
  - Need to stop these getting into the concrete
  - ➔ **Reduce permeability**
  - Permeability depends on porosity, porosity depends on water content

➔ **Reduce water/binder ratio for better durability**

- This is of course an oversimplification, but actually not a very bad one
  - Chemical additives (superplasticiser/high range water reducer) can help reduce w/c while retaining good flow

Transport-related durability

- Key issue here is usually chloride
  - Chloride exposure doesn't affect the binder chemistry very much, but makes steel rust
  - A little bit of binding of Cl^- in AFm phases, but no damage to C-S-H or other hydrates
- Chloride permeability is assumed in many cases to be the key factor limiting concrete service life
  - Particularly in North America & northern Europe – salts applied to concrete for de-icing
  - Marine conditions are also problematic
- Need to understand how, and how rapidly, the chloride will move through the pore network of the material

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What helps to keep chloride out?

- Dense binder
  - Low water/cement ratio
  - Lots of C-S-H
  - Refined pore structure (small, tortuous pores)
- Pozzolanic reactions really help this in the long term
  - Producing more C-S-H from portlandite (portlandite doesn't restrict chloride movement)
  - Extra AFm phases help a little, but not as much as C-S-H

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Chloride corrosion

- Cold and warm environments
- Steel rusts, expands, cracks concrete

http://www.efcweb.org/efcweb_media/Bilder/WP11/KorroMeer.jpg

[Images deleted for copyright reasons]

http://www.buildreport.com.au/news/2003_03_spalling_01.jpg

Testing chloride penetration

- Simplest methods – “ponding” tests
  - Make a concrete cylinder or slab, put a pool of chloride solution (usually NaCl) on top, and wait
  - After several months (6-24), measure how far the chloride has travelled into the material
- Advantage – generally very accurate
- Disadvantage – very very slow
  - Need to get answers faster than this
  - Use electricity to force chloride to move faster, and use this to calculate material parameters (diffusion coefficient)

Rapid Chloride Permeability Test

- ASTM C1202 – apply a voltage and measure current passed by the specimen in 6 h, use this as a measure of permeability

http://www.concrete.org/FAQ/files/082006-figure1.png

But what is it really measuring?

- Charge passed depends on multiple factors:
  - Partly due to chloride moving in to the specimen
  - Partly due to dissolved ions in the pore solution moving under the applied electric field
- Test is actually a *resistivity/conductivity* test
  - Measuring the electrical properties of the specimen, and assuming that this relates to chloride diffusion
- For materials with similar chemistry, this can be true
  - Changing chemistry will change pore fluid conductivity
  - Test can't be used to compare materials with different chemistry, but is useful for ***quality control*** of one material
  - Resistivity tests sometimes used non-destructively in the field, but can have errors from temperature or humidity

Better methods are becoming available

- Becoming more popular – hybrid methods
  - E.g. NordTest NTBuild 492 (recommended as an EN standard by an EU project)
  - Use electrical acceleration of chloride migration, but measure actual chloride depth at end of test
- Give the advantage of a 24-hour testing time, but without needing to assume things about the resistivity of the material
  - Can compare different types of cements
  - More reproducible (RCPT test has a ±42% error margin according to ASTM standard)
- But all use fully saturated (underwater) material – no splashing/drying effects

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Sulphate attack on Portland cement

- Internal sulphate attack
  - Sulphates present within concrete causing phase evolution after a long time
- External sulphate attack (more common)
  - Sulphates from the environment entering material and causing phase changes
- In both cases, AFm → AFt conversion is the key mechanism
  - External $MgSO_4$ also causes decalcification of C-S-H to form M-S-H and gypsum
- Result is expansion and cracking
- Use slag blends or low-C_3A clinker to resist it

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Causes severe cracking

http://static7.theconstructor.org/wp-content/uploads/2010/04/image55.png http://www.understanding-cement.com/sulfate.html

http://www.cementaid.ie/about.html

http://www.isse.org.uk/index.php/survey/salt-analysis-side

Testing sulphate resistance

- Immerse the concrete in a sulphate-rich solution (usually 5% Na_2SO_4)
  - Measure specimen length regularly
- Testing for conversion of AFm to AFt phases, which causes expansion
  - Not enough to fully explain expansion, but important

[Image deleted for copyright reasons]

W. Kunther et al., Cement and Concrete Research 46 (2013) 23–29

Sulphate-resistant cements

- Low C_3A content, or high slag in PC blend
  - Favour formation of C-S-H rather than AFm phases, so don't expand

[Image deleted for copyright reasons]

DuRSAAM W. Kunther et al., Cement and Concrete Research 46 (2013) 23–29

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Thaumasite sulphate attack

- Relatively rare worldwide, important in UK conditions
- Needs cool (4-10°C), wet conditions, with both carbonate and sulphate
- Thaumasite: $Ca_3Si(OH)_6(SO_4)(CO_3)\cdot 12H_2O$
  - C-S-H converted to thaumasite becomes 'mush'
  - No strength at all – soft

https://www.youtube.com/watch?v=AFRYPVHRjLw

[Images deleted for copyright reasons]

Buried sample
3 years exposure

http://www.sheffield.ac.uk/polopoly_fs/1.142963!/file/05.pdf
http://www.sheffield.ac.uk/cmru/research/thaumasite/index

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Alkali-aggregate (alkali-silica) reactions

- Portland cement contains a small quantity of alkalis (Na and K)
  - Remains in the pore solution upon hydration
  - Pore solution pH is very high
- If the aggregate is unreactive (e.g. quartz), this is fine
- If the aggregate contains reactive (e.g. glassy, opal etc.) components, it can be attacked by the pore solution
  - Chemical reaction at the aggregate surface

Alkali-silica reaction products

- Makes an expansive, white silicate gel product

[Images deleted for copyright reasons]

Abdelrahman et al. *Constr Build Mater* 95(2015):406

https://www.vdz-online.de/en/services/research-and-technology/concrete-and-constituents/asr-alkali-silica-reaction/alkali-kieselsaeure-reaktion/

How is it identified?

- Reaction of alkalis with silica from aggregates causes concrete to expand
- Characteristic ‘map-cracking’ on surface

http://www.fhwa.dot.gov/pavement/concrete/reactive/v02issue02.cfm http://fsel.engr.utexas.edu/research/iac-rcbeams/index.cfm

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Alkali-aggregate testing

- Test the aggregate, the cement, or both?
- Which test?
  - Appendix X1.3 of ASTM C33 lists 8 different methods for combinations of cement, SCM and siliceous aggregates (plus 3 more for carbonate aggregates)
- UK approach follows BRE Digest 330 (4 parts)
  - Limits on alkali content of concrete based on aggregate reactivity classification (low/normal/high) from rock type
  - Concrete prism test (similar to ASTM method below) if uncertain – 12 months duration
  - Most cements sold in the UK are low-alkali – if not, need to calculate concrete alkali content (some complexity…)
  - Blending with slag or pozzolans helps protect from damage

Testing alkali-aggregate reaction quickly?

- ASTM C1260, mortar bars in 40 g/L NaOH at 80°C, measure expansion at 16 days
- Because alkali concentration is so high, there is no influence from the alkalis in the cement
  - Really only an aggregate test, arguably not related to cement properties at all?
  - Well known to give false positives – extremely aggressive test
- Advantage is that it is fast, and widely used – but used far beyond its scope, e.g. for cement testing…

[Image deleted for copyright reasons]

https://www.fhwa.dot.gov/publications/research/infrastructure/pavements/concrete/06133/002.cfm

Testing both aggregate and cement?

- ASTM C1293 – concrete prism test
  - Extra alkali added into the cement (double the limit of 0.60% Na_2Oe), then store at 38°C for 1 year (to show excessive expansion), or 2 years (to show no expansion problems) → **Slow**
  - Can also test the use of pozzolans or slag to reduce expansion – but alkali levels are artificially high anyway
- Considered the most reliable test, but also very slow

http://www.fhwa.dot.gov/pavement/concrete/reactive/issue01.cfm

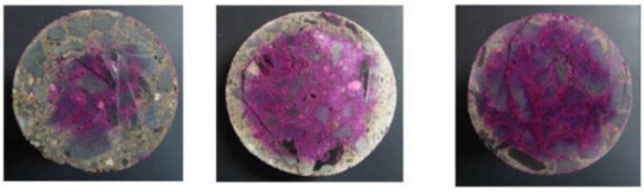
Carbonation testing

- Interaction with atmospheric CO_2 can cause problems – CO_2 acts as an acid

  $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$, portlandite consumed
  - Reduces the alkalinity (pH) of the cement, which can induce corrosion of the steel reinforcing
  - Extreme cases of carbonation can also show damage (decalcification) in C-S-H phases
  - Happens fastest at intermediate humidity (~65%) or under wet-dry cycling
- Generally want to measure the depth of CO_2 penetration into the concrete
  - Rate of ingress under natural conditions is ~mm/yr, so use higher CO_2 concentrations to accelerate the test

Measuring carbonation

- Phenolphthalein is a useful indicator of pH change
  - Pink when conditions are alkaline (pH >12)
  - Colourless when pH drops below 9
  - Colour change corresponds well to 'danger levels' for alkalinity in concrete leading to steel corrosion
- Measure depth of CO_2 ingress after exposure to elevated concentration, and scale this to predict performance in natural conditions
  - This is the main limitation on concrete service life in many warm climate areas without marine exposure



S.A. Bernal et al. *Cement & Concrete Research*, 41(2011):1-8

Freeze-thaw damage

- Very similar mechanisms for bricks, concrete, and porous building stones
- When it freezes, water expands ~9%
  - salt makes this worse – more dramatic volume change
  - external surface of the material is damaged/removed

http://www.expertsmind.com/questions/density-of-water-in-relation-to-temperature-30125050.aspx

http://www.petercox.com/penetrating-damp.php

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http://www.concrete-experts.com/pages/ft.htm

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Freeze-thaw testing

- Many tests, none universally accepted
- Samples usually cylinders or slabs
- Freeze-thaw cycle repeatedly (e.g. +4/-18°C every 4 h, or +20/-18°C every 24 h)
  - Tens to hundreds of cycles used
  - Measure changes in elastic modulus, dimensions, mass (material scaled from surface)
  - Sometimes just give a visual rating of damage
- Tests are generally very harsh cf. normal UK environmental conditions

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How to protect? – Air entrainment

- Put appropriately sized bubbles (< 1 mm, a few % by volume, well spaced) into concrete
  - Gives the water space to expand into as it freezes

[Image deleted for copyright reasons]

https://ca.gcpat.com/en/news/blog/gcp-labs-analyze-concrete-optimize-performance

Activities of RILEM TC 247-DTA (2012-9)

- Analyse available durability testing methods applied to alkali-activated materials (AAMs) in key areas:
  - Chloride
  - Sulfate
  - Carbonation
  - Freeze-thaw/frost-salt
  - ASR
- Generate recommendations for which test methods should be applied to AAMs
- Round-robin test – **19** labs, **12** countries returned results
- All testing the 'same' concretes
  - Same mix designs, same precursors, same activator chemistry

J.L. Provis et al., *Materials & Structures* 52(2019):#99; G.J.G. Gluth et al., *Materials & Structures* under review

Underlying question

- Testing the tests – not specifically the materials – so mix designs are not intended to be "optimised"
- 2 mix designs for GGBFS, 2 for fly ash, 1 for metakaolin
  - Targeting one of expected good performance, one of expected less-good performance

→ Can the tests, as specified in existing standards, distinguish a 'good' from a 'less good' AAM?

J.L. Provis et al., *Materials & Structures* 52(2019):#99
G.J.G. Gluth et al., *Materials & Structures* under review

Chloride - all mixes @ 28 d

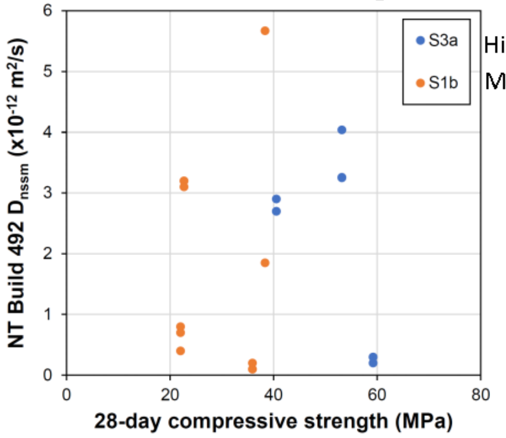
Mix	NT Build 443 D_{nss} ($x10^{-12}$ m^2/s)		NT Build 492 D_{nssm} ($x10^{-12}$ m^2/s)	
	Mean	Range	Mean	Range
S1b	0.66	0.62 – 0.69	1.80	0.1 – 5.67
S3a	1.12	0.95 – 1.2	2.25	0.3 – 4.04
FA2	45.9	42 – 67	34.1	25.3 – 46.0
FA8	79	39 – 99	61.4	32.8 – 86.2
MK	77	59 – (>95)	117.0	79.1 – 163.8

- **NT Build 492 (migration) within-lab reproducibility is generally better than ±15% across 2 or 3 samples**
- **Ranking of 'good' and 'less good' mixes not in agreement with expectations from strength and mix design for slag mixes**
  - NT Build 443 (ponding) shows lower-strength S1b with less chloride ingress cf. higher-strength S3a – paste volume is determining factor?
- **ASTM C1202 RCPT gave very scattered results – not recommended**

J.L. Provis et al., *Materials & Structures* 52(2019):#99
G.J.G. Gluth et al., *Materials & Structures* under review

Can we relate durability to strength?

No direct correlation between chloride migration and compressive strength for two alkali-activated slag concretes



Higher-strength concrete

Moderate-strength concrete

To be investigated further in new RILEM TC CAM (chair: A. Castel, UTS)

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J.L. Provis et al., *Materials & Structures* 52(2019):#99
G.J.G. Gluth et al., *Materials & Structures* under review

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Brief summary of other TC findings

- Accelerated carbonation at 1% CO_2 gave mostly the same rank order of samples as natural carbonation
  - Alkali washout important for outdoor carbonation, rate is reduced cf. sheltered conditions
- Sulfate damage in all tests with Na_2SO_4 is limited, $MgSO_4$ is more aggressive
  - Difficult to set 'zero' point for length measurement
- ASR tests show no problems of inducing reaction in unreactive aggregates
  - Some expansion can be induced with very reactive aggregates, as expected for any concrete/mortar
- Freeze-thaw and frost-salt tests require more work, but salt effects are important

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G.J.G. Gluth et al., *Materials & Structures*, under review;
F. Winnefeld et al., *Materials & Structures*, in preparation

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General comments on testing AAMs

- Be careful with curing regimes
  - When changing binder chemistry, are the specified curing conditions still optimal (or even relevant?)
- Be careful with sample pre-conditioning
  - Blended cements can crack under the harsh drying regimes specified for pure OPC
- Be careful with differential ageing of specimens in long-duration tests
- Look at precision statements of the tests

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Concluding comments

- We need to be very careful when applying standardised testing methods
  - many of them are actually testing quite different things compared to what they claim to test

  → **must understand what the test is really testing!**
- Test methods vary in usefulness and applicability
  - Usually, the fastest methods are the least accurate
- It is worthwhile to use multiple methods to test important parameters
- Some tests are mainly useful for quality control between batches in a production run, not as an absolute measure of the properties of a material

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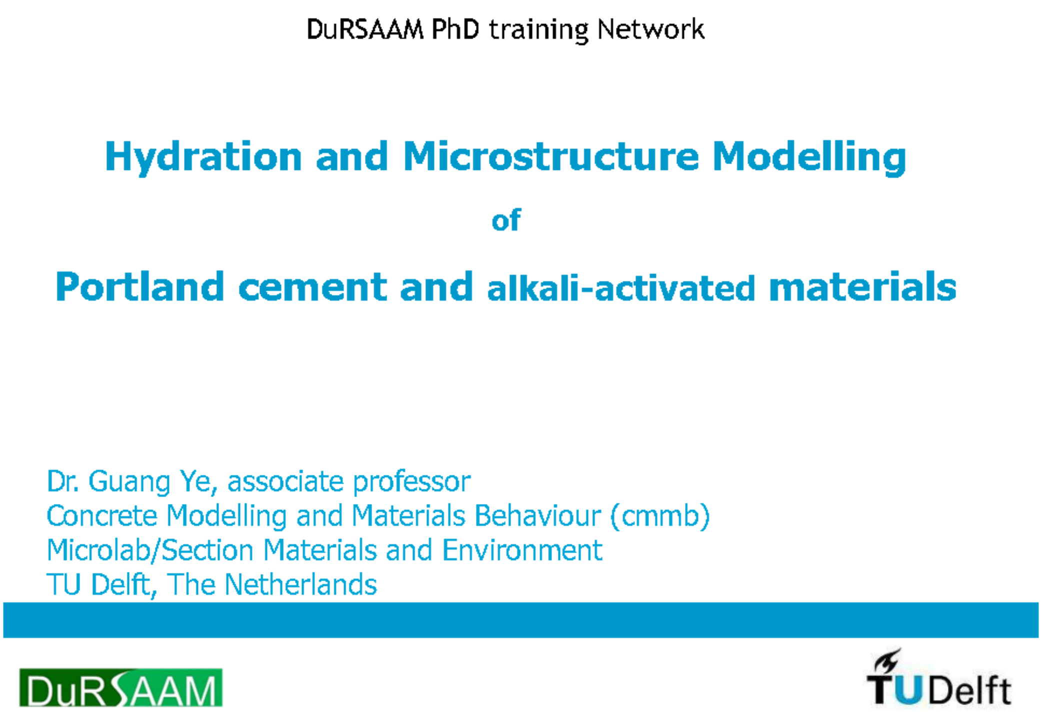
8. Modelling of AAM concretes

Guang Ye

In this chapter the hydration mechanisms and the resulting microstructure of concrete is considered, looking especially on how to model this. Both Portland cement and alkali-activated materials are considered.



DuRSAAM PhD training Network

Hydration and Microstructure Modelling

of

Portland cement and alkali-activated materials

Dr. Guang Ye, associate professor
Concrete Modelling and Materials Behaviour (cmmb)
Microlab/Section Materials and Environment
TU Delft, The Netherlands

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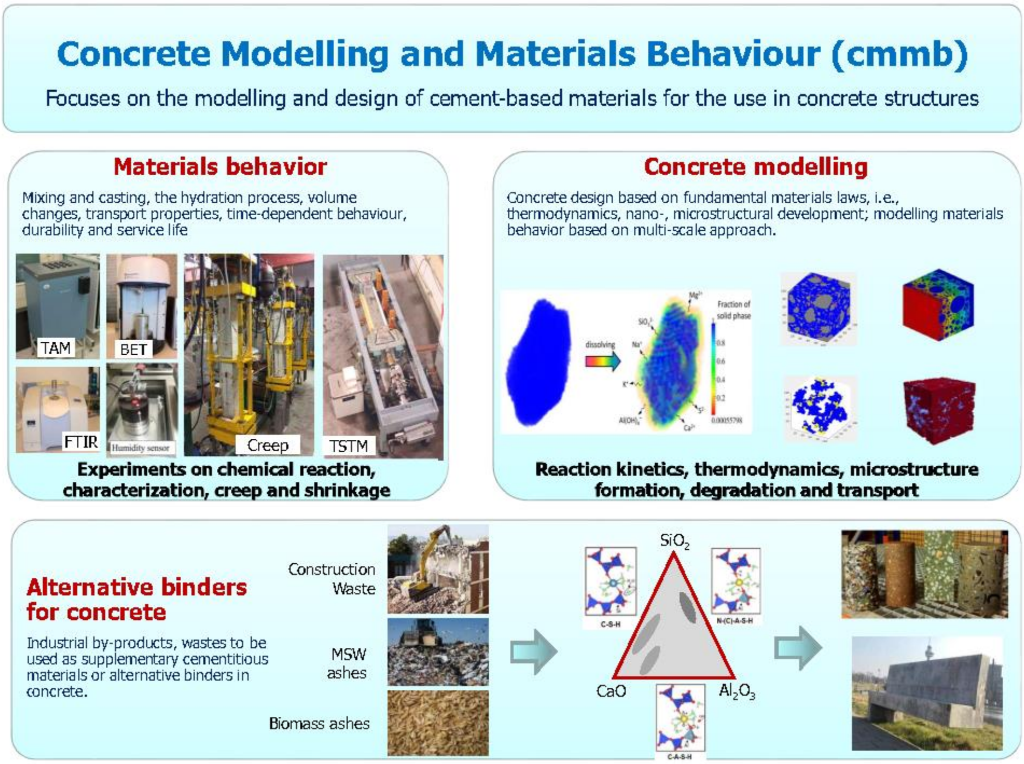


Concrete Modelling and Materials Behaviour (cmmb)

Focuses on the modelling and design of cement-based materials for the use in concrete structures

Materials behavior

Mixing and casting, the hydration process, volume changes, transport properties, time-dependent behaviour, durability and service life

Experiments on chemical reaction, characterization, creep and shrinkage

Concrete modelling

Concrete design based on fundamental materials laws, i.e., thermodynamics, nano-, microstructural development; modelling materials behavior based on multi-scale approach.

Reaction kinetics, thermodynamics, microstructure formation, degradation and transport

Alternative binders for concrete

Industrial by-products, wastes to be used as supplementary cementitious materials or alternative binders in concrete.

Goal of this lecture

- ❑ To provide basic knowledge on modelling of reaction process and microstructure formation of Portland cement paste and alkali-activated materials
- ❑ To introduce cement hydration and microstructure model **HYMOSTRUC3D** and alkali-activated materials model **GeoMicro3D**

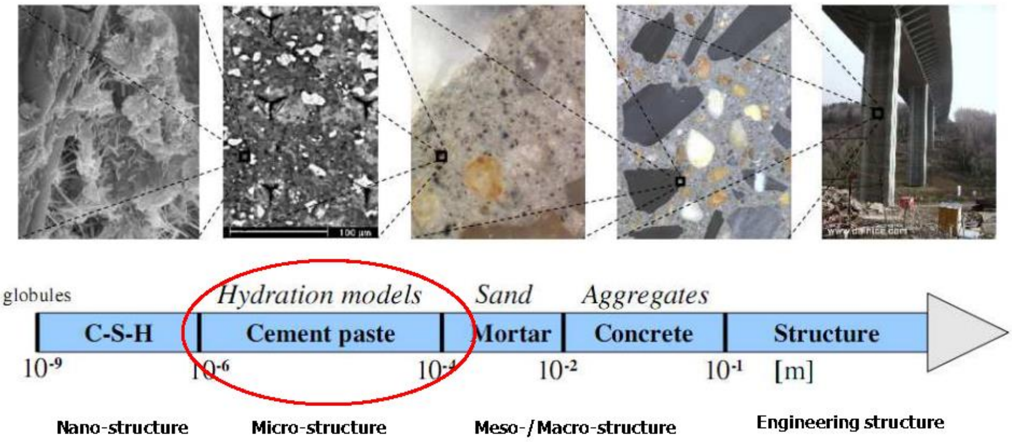
Outline of the lecture

- Introduction
- Cement hydration and microstructure models
- Numerical framework for alkali-activated materials

Introduction

02 September 2025

Multi-scale features of concrete



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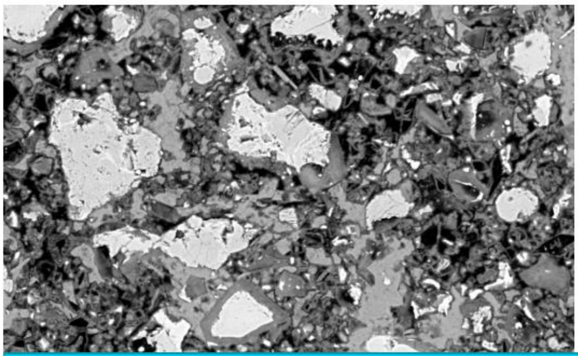
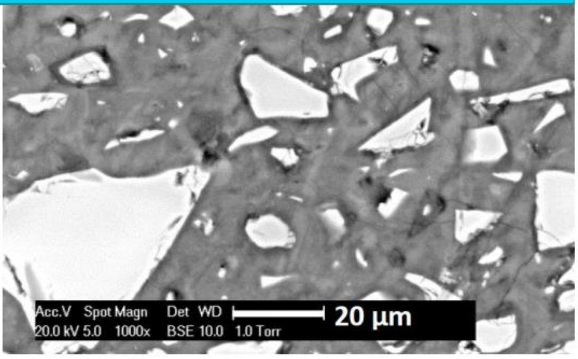


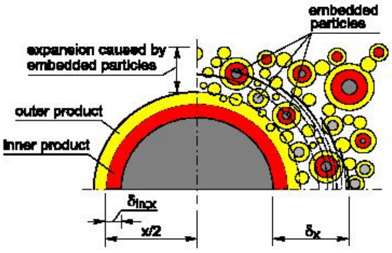
OPC paste viewed under BSE

Is it possible to simulate the microstructure?

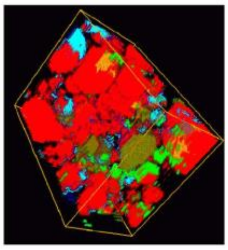


Alkali-activated slag view under BSE

Cement hydration models - history



HYMOSTRUC (van Breugel)
1991



CEMHYD3D (Bentz)
1994

µic (Shashank)
2008

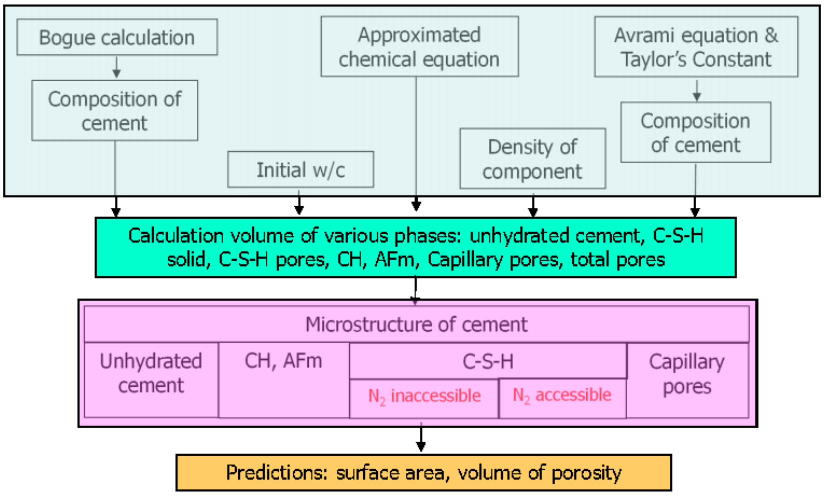
Modelling Cement Hydration and Microstructure Formation

02 September 2029

What are we going to simulate?

- What kind of phases are present? ← Chemical reaction
- How much of each phase is present? ← Reaction kinetics
- What is the shape and length scale of each phases and how the phases are connected? ← Nucleation and growth

Jenning’s approach (1986)



Bogue calculation

Composition of cement

Initial w/c

Approximated chemical equation

Density of component

Avrami equation & Taylor’s Constant

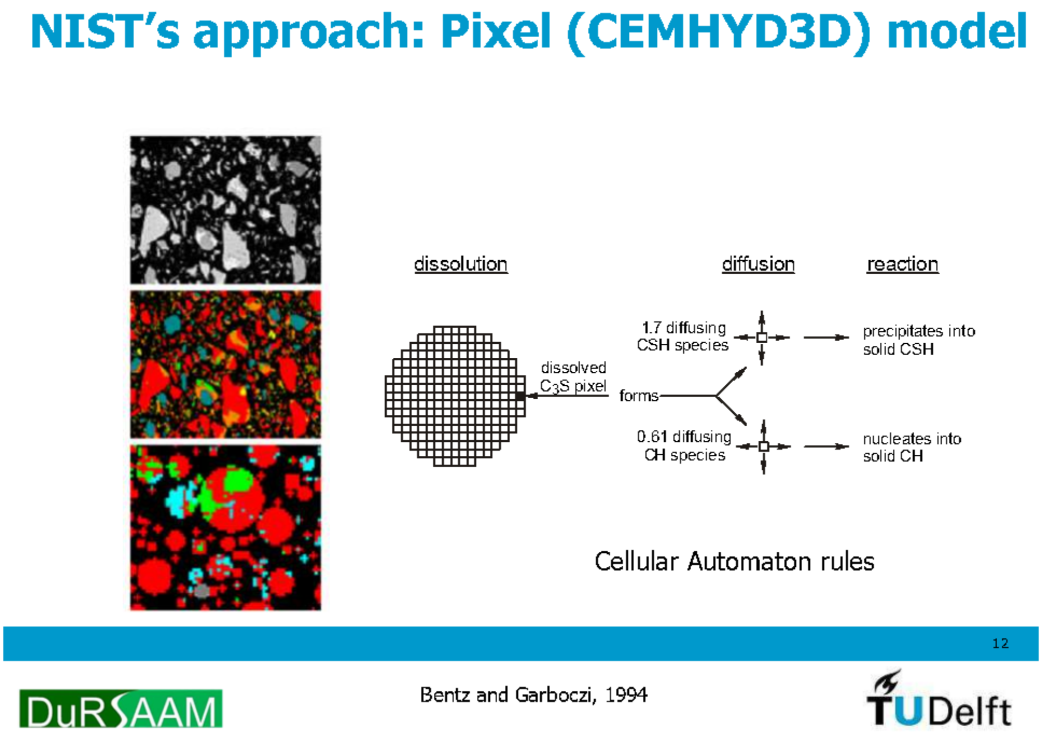
Composition of cement

Calculation volume of various phases: unhydrated cement, C-S-H solid, C-S-H pores, CH, AFm, Capillary pores, total pores

Microstructure of cement

Unhydrated cement	CH, AFm	C-S-H		Capillary pores
		N_2 inaccessible	N_2 accessible	

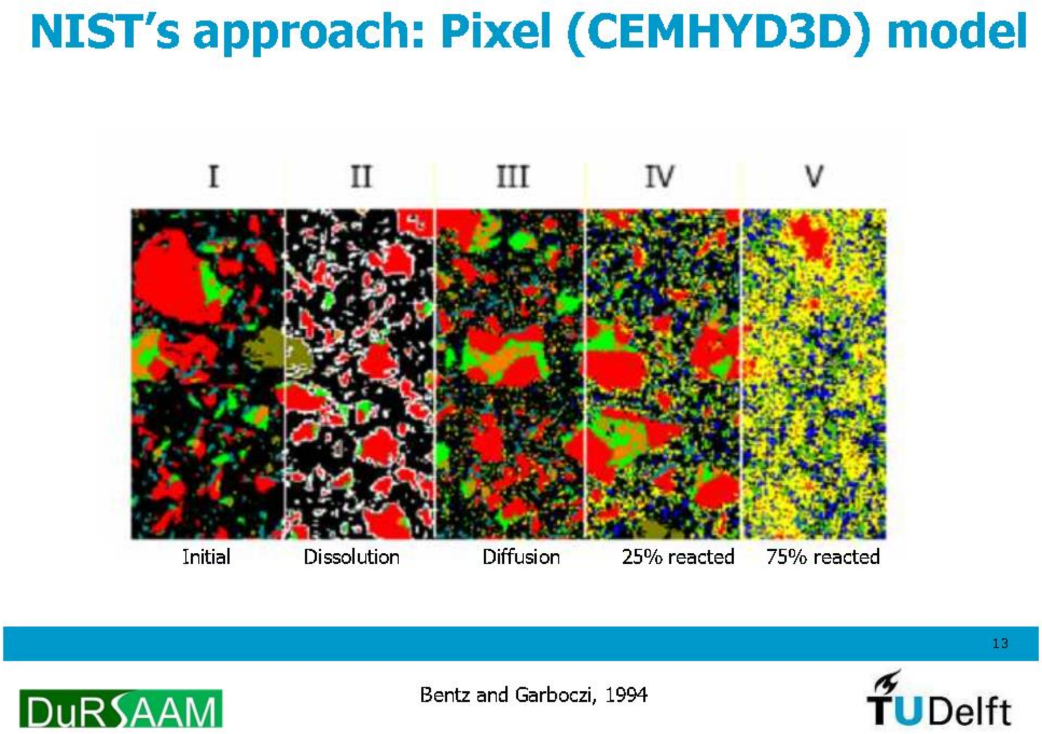
Predictions: surface area, volume of porosity



NIST's approach: Pixel (CEMHYD3D) model

Cellular Automaton rules

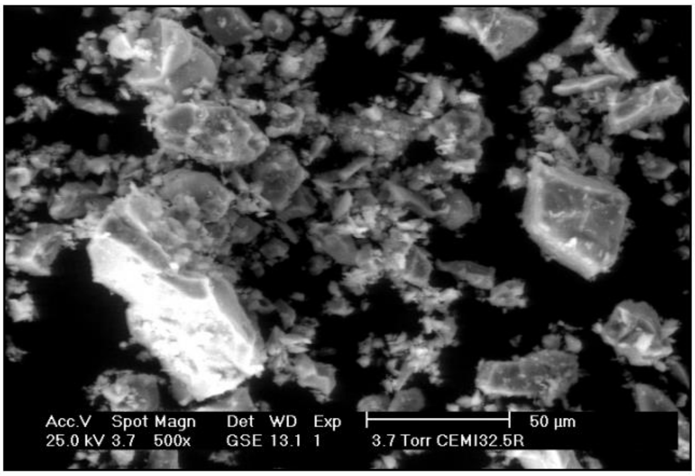
Bentz and Garboczi, 1994



NIST's approach: Pixel (CEMHYD3D) model

Bentz and Garboczi, 1994

Cement particles – shape and size distribution



- CEMI 42.5 N
- Size:
  Max: ~50 µm
  Min: ~ 0.5 µm
- Irregular

02 September 2014

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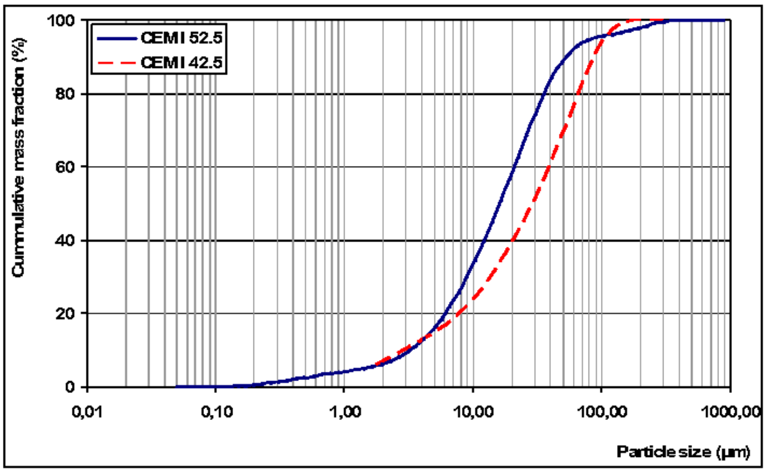
Cement particles – shape and size distribution



Based on laser analysis

02 September 2015

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Cement chemical composition

The principal oxides in clinker of Portland cement clinker

analyte (Oxide)	weight (%)
CaO	**64.4**
SiO_2	**20.36**
Al_2O_3	**4.96**
Fe_2O_3	**3.17**
K_2O	0.64
Na_2O	0.14
SO_3	2.57
MgO	2.09
TiO_2	0.35
Mn_2O_3	0.14
P_2O_5	0.18
LOI	0.88
free CaO	*0.6*
total	99.7

A example of CEMI 42.5N

Cement chemical composition

Main constituents

- Tricalcium silicate $3CaO{\cdot}SiO_2$ (C_3S) → Alite
- Dicalcium silicate $2CaO{\cdot}SiO_2$ (C_2S) → Belite
- Tricalcium aluminates $3CaO{\cdot}Al_2O_3$ (C_3A)
- Calcium ferroaluminate $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ (C_4AF).
- Gypsum $CaSO_4{\cdot}2H_2O$ ($C\underline{S}H_2$)

Bogue equation [Taylor 1989]

- $C_3S = 4.07\ CaO - (7.60\ SiO_2 + 6.72\ Al_2O_3 + 1.43\ Fe_2O_3 + 2.85\ SO_3)$
- $C_2S = 2.87\ SiO_2 - 0.754\ C_3S$
- $C_3A = 2.65\ Al_2O_3 - 1.69\ Fe_2O_3$
- $C_4AF = 3.04\ Fe_2O_3$

Stoichiometry of cement hydration

(1) Reactions of C_3S and C_2S:

$C_3S+5.3H \rightarrow C_{1.7}SH_4+1.3CH$

$C_2S+4.3H \rightarrow C_{1.7}SH_4+0.3CH$

(2) Reactions of C_3A and C_4AF (depends on actual content of gypsum and AFt):

a. If gypsum is present:

$C_3A+3C\bar{S}H_2+26H \rightarrow C_6A\bar{S}_3H_{32}$

$C_4AF+3C\bar{S}H_2+30H \rightarrow C_6A\bar{S}_3H_{32}+CH+FH_3$

b. If gypsum is used up and AFt is present:

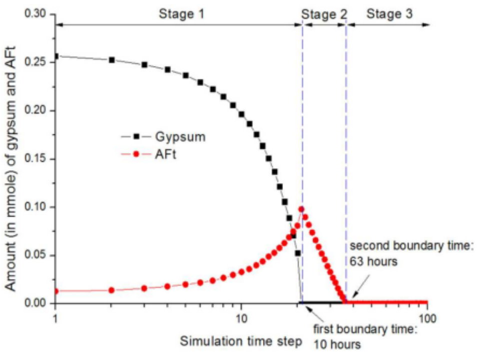
$2C_3A+C_6A\bar{S}_3H_{32}+4H \rightarrow 3C_4A\bar{S}H_{12}$

$2C_4AF+C_6A\bar{S}_3H_{32}+12H \rightarrow 3C_4A\bar{S}H_{12}+2CH+2FH_3$

c. If gypsum is used up and AFt is used up:

$C_3A+6H \rightarrow C_3AH_6$

$C_4AF+10H \rightarrow C_3AH_6+CH+FH_3$



Degree of hydration

Degree of hydration $\alpha(t)$ [-], is defined as the ratio of the amount of cement that has reacted at time *t* relative to the original amount of cement

$$\alpha(t)=\frac{amount\ of\ cement\ that\ has\ reacted\ at\ time\ t}{total\ amount\ of\ cement\ at\ time\ t=0}$$

02 September 2019

Degree of hydration – experiments

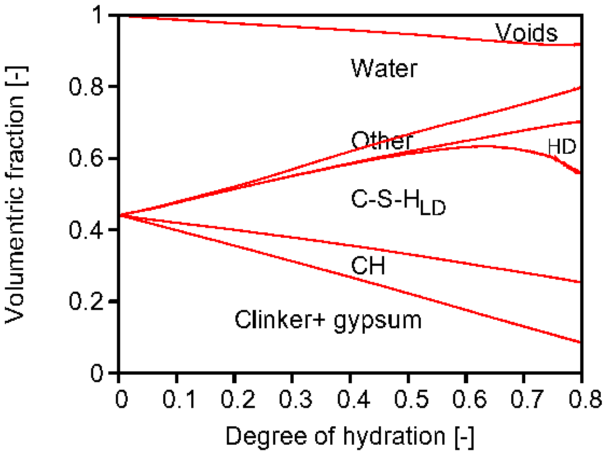
$$\alpha(t) = \frac{Q(t)}{Q_{pot}} \approx \frac{W_n(t)}{W_{n,pot}}$$

That depends on the accuracy of Q_{pot} of $W_{n,pot}$

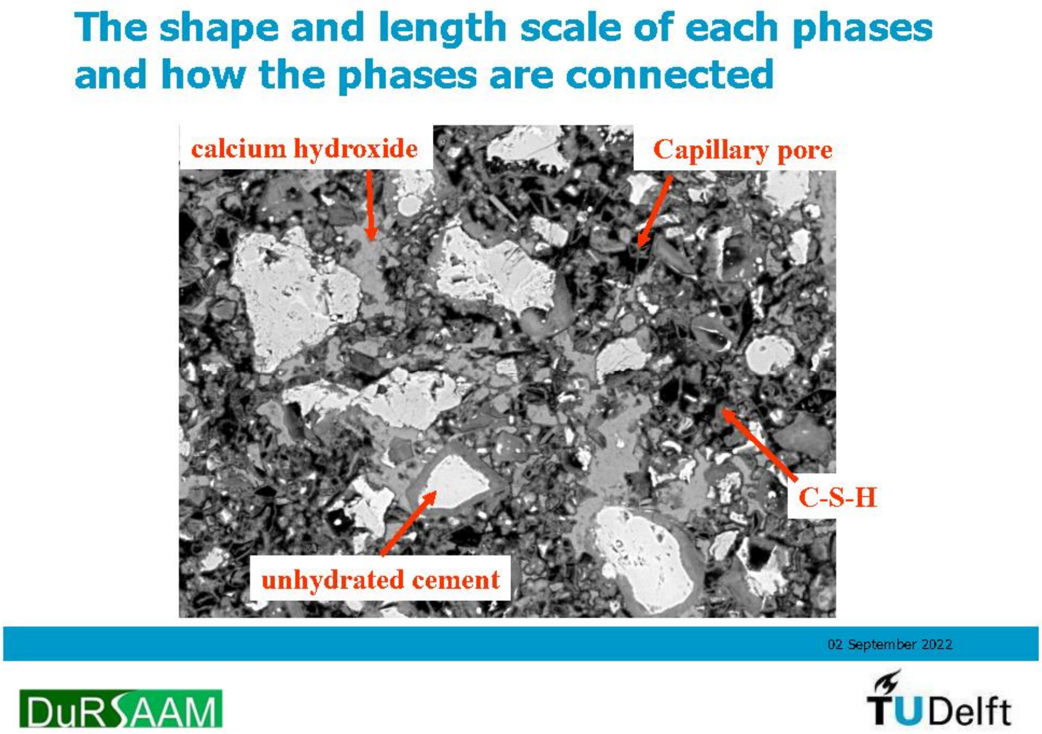
$Q(t)$, total heat release at time t (Cal)
Qpot, potential total heat (Cal/1g cement)
W_n (t), Non-evaporable water at hydration time t (g)
$W_{n, pot}$, potential Non-evaporable water content (g/1g cement)

02 September 2020

What and how much of the phases ?



02 September 2021



The shape and length scale of each phases and how the phases are connected

02 September 2022

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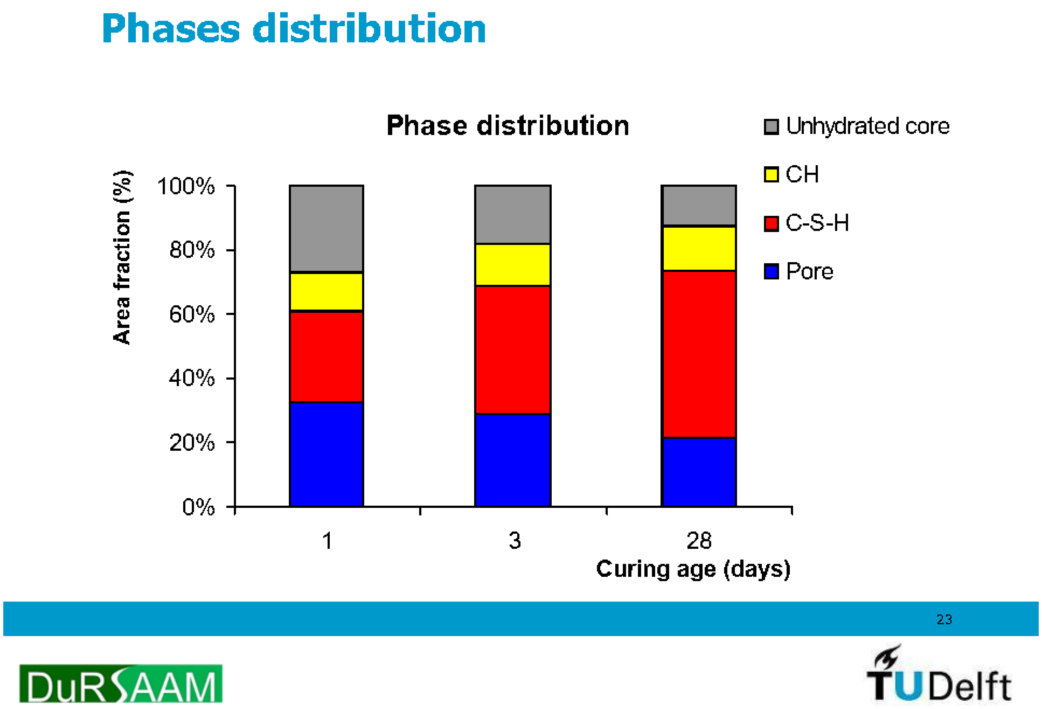

Phases distribution

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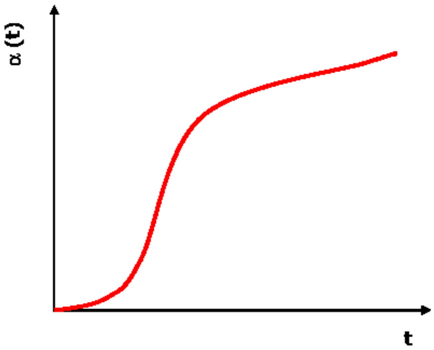
Hydration and microstructure modeling of Portland cement

- **Hydration kinetics: particle kinetics, particle kinetics, integrated kinetics**
- **3D Microstructure building up**

Modelling of hydration and kinetics

Overall kinetics models (I)

– **Avrami:** $\alpha(t) = 1 - e^{-(k_A t)^n}$



Features:

- Fits well on nucleation and growth mechanism

- No particle size distribution information and mineral composition

Modelling of hydration and kinetics

Overall kinetics models (II)

- Taylor (1987)

$$\alpha_{(t)} = 1 - \exp\left[-k_2 (t/24 - k_3)^{k_1}\right]$$

Where:

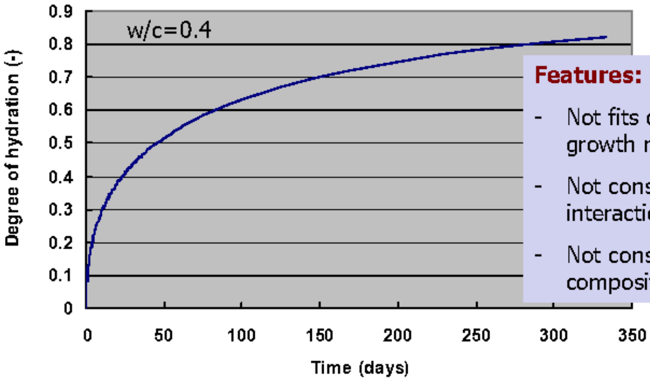
- K1, k2 and k3 are three characteristic parameters (dimensionless), list in table
- t = hydration time (in hour)

k1	k2	k3
0.46	0.12	0

Modelling of hydration and kinetics

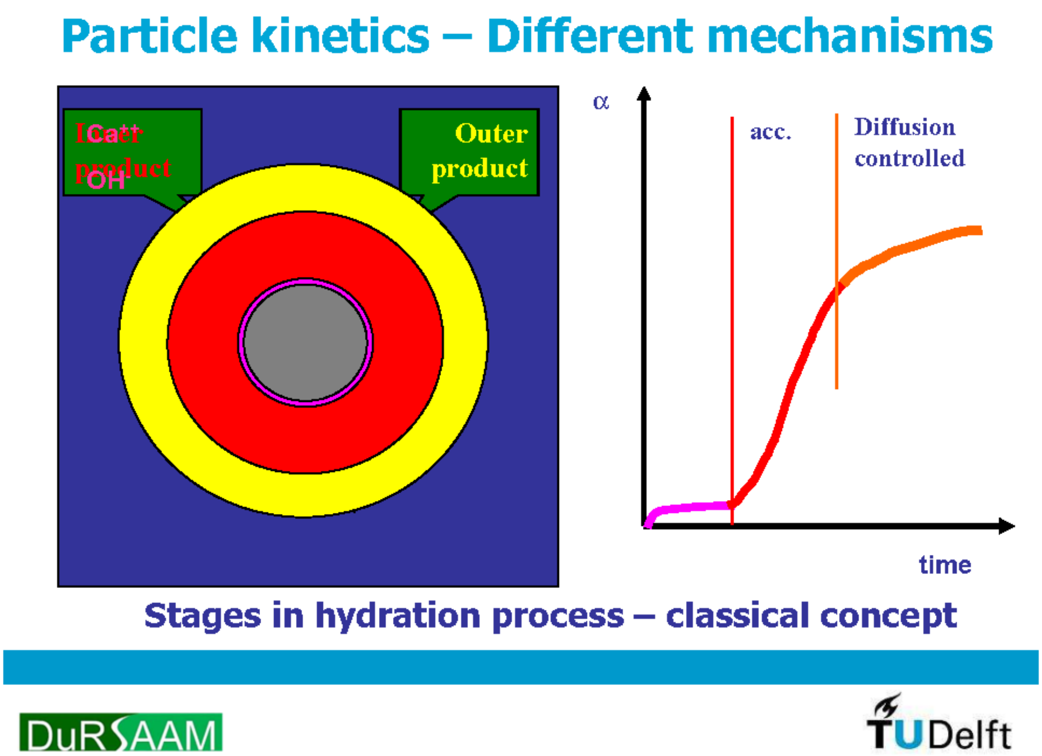
➢ Overall kinetics models (II)

- Taylor (1987)



Features:

- Not fits on nucleation and growth mechanism
- Not consider the particles interaction,
- Not consider the mineral composition



Particle kinetics – Different mechanisms

Stages in hydration process – classical concept

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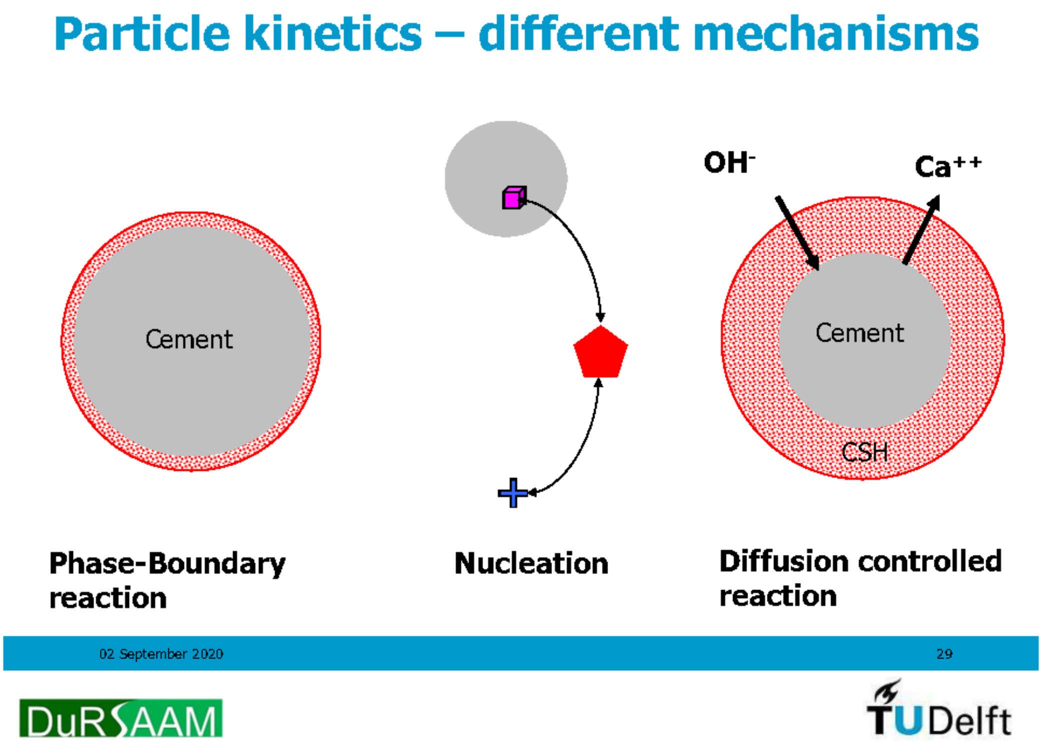

Particle kinetics – different mechanisms

Phase-Boundary reaction

Nucleation

Diffusion controlled reaction

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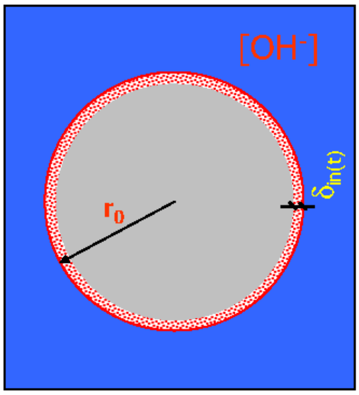
Particle kinetics – different mechanisms

Phase-Boundary reaction



For **a spherical particle** with radius r_0=x/2 of the reactant and penetration depth $\delta_{in}(t)$, the degree of hydration is:

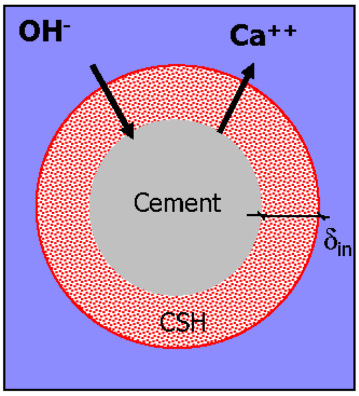
$$\alpha_{x;\delta_{in}} = 1 - \left[1 - \frac{\delta_{in;x}(t)}{r_0}\right]^3$$

the penetration depth $\delta_{in}(t)$ is

$$\delta_{in;x}(t) = k \times t = r_0 \times \left[1 - (1 - a_{x;\delta_{in;x}})^{\frac{1}{3}}\right]$$

Particle kinetics – different mechanisms

Diffusion controlled reaction



- Jander

$$[1-(1-a_x)^{\frac{1}{3}}]^N = \frac{2.k.t}{r_0^2}$$

- Ginstling and Brownshtein

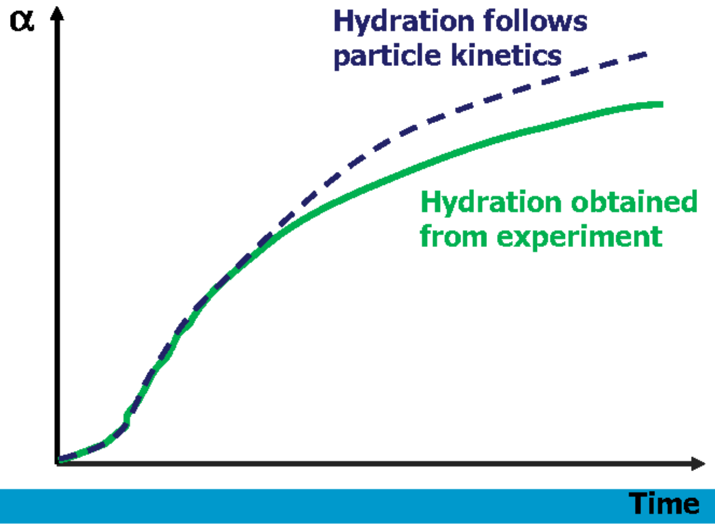
$$[1-\frac{2a_x}{3}]-(1-a_x)^{\frac{2}{3}} = k.t$$

- Carter

$$[1+(v-1)\times a_x]^{\frac{2}{3}} + (v-1)\times(1-a_x)^{\frac{2}{3}} - v = k.t$$

v, the ratio of the v. of the reaction products relative to that of the dissolved part of the reactant

Particle kinetics – there is a limitation



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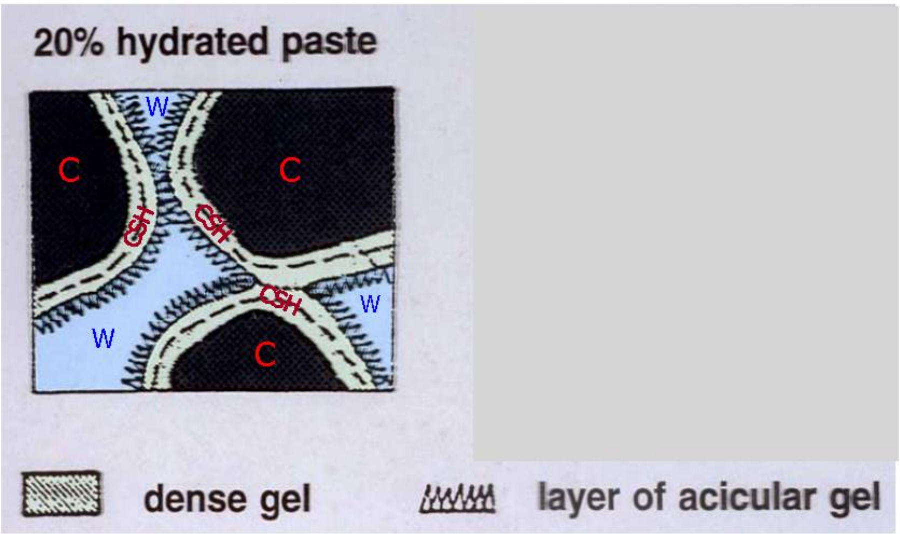
Particle interaction– Schematic



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Crar ju & Maso (1984)

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Chemical reaction affected by physical contact between hydrating cement particles

Interaction between hydration kinetics and microstructural development

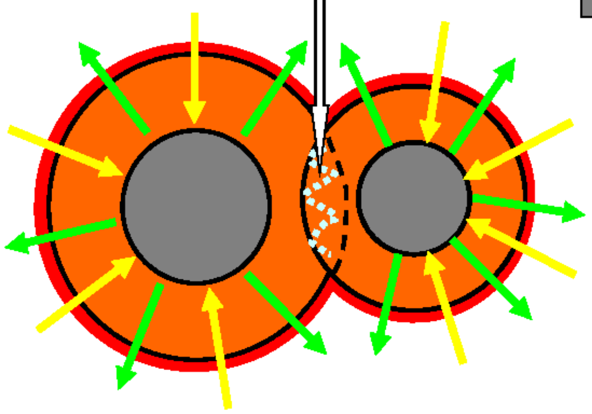
Integrated kinetics model

Overlap volume:

To be redistributed at the periphery of hydrating particles

🟧 **Gel**

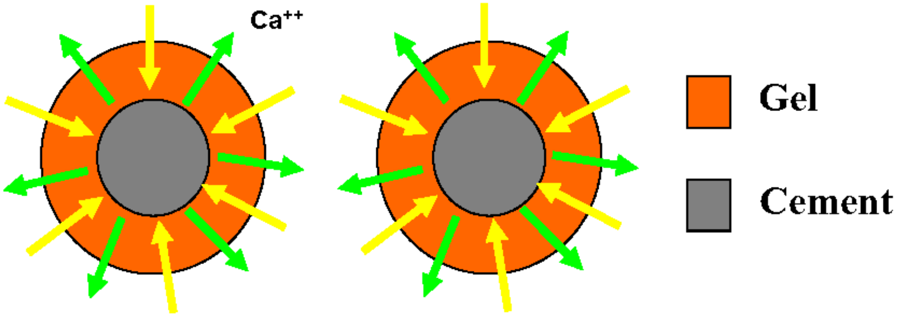
⬛ **Cement**



Particles interaction – Conceptual

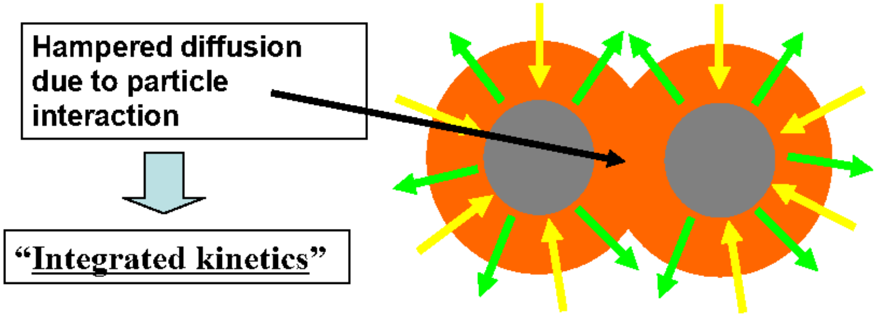
After Jennings et al (1986)

Two hydrating cement particles - apart



Diffusion-controlled hydration of individual grains

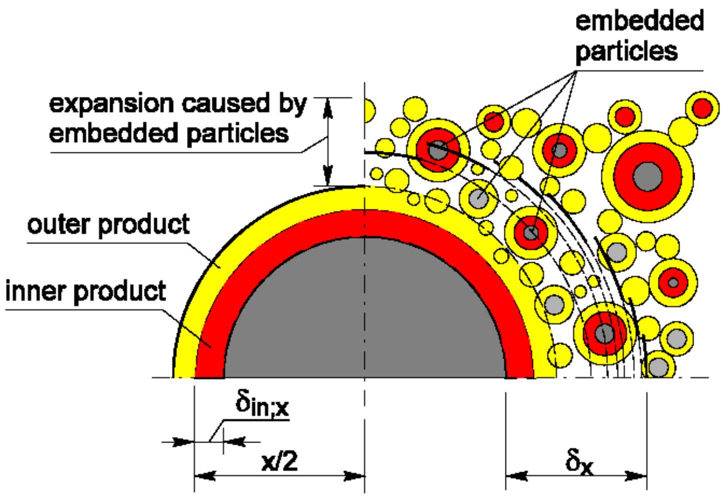
Two hydrating cement particles - overlap



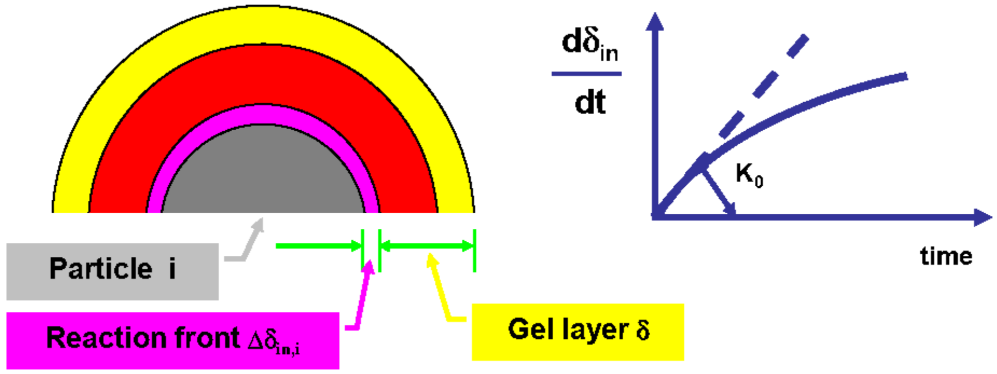
Hampered diffusion due to particle interaction

"Integrated kinetics"

HYMOSTRUC is an integrated kinetics model



Particle interaction due to outward growth, van Breugel 1991



Basic rate formula:

$$\frac{d\delta_{in,i}}{dt} = K_0 * \Omega_1 * \Omega_2 * \Omega_3 * F_1 * F_2 * \left\{\frac{\delta(\alpha_i)}{\delta_{tr}}\right\}^{\lambda}$$

Rate of penetration of reaction front in particle i

$$\frac{d\delta_{in,i}}{dt} = K_0 * \Omega_1 * \Omega_2 * \Omega_3 * F_1 * F_2 * \left\{\frac{\delta(\alpha_i)}{\delta_{tr}}\right\}^{\lambda}$$

K_0 = basic rate factor: function of C_3S content

$\Omega_{1,2,3}$ = factors allowing for state of water in the system

1. water withdrawal mechanism
2. amount of water
3. distribution of water in pore system

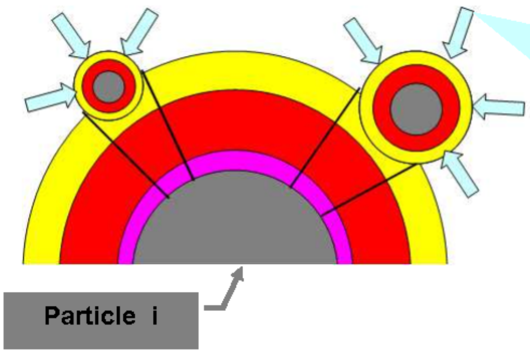
$F_{1,2}$ = factors allowing for effects of temperature

1. Arrhenius function
2. Coarseness of pore structure

δ_{tr} = transition thickness: phase-boundary → diffusion

α_i = degree of hydration of particle i

$$\frac{d\delta_{in,i}}{dt} = K_0 * \boxed{\Omega_1} * \Omega_2 * \Omega_3 * F_1 * F_2 * \left\{\frac{\delta(\alpha_i)}{\delta_{tr}}\right\}^{\lambda}$$

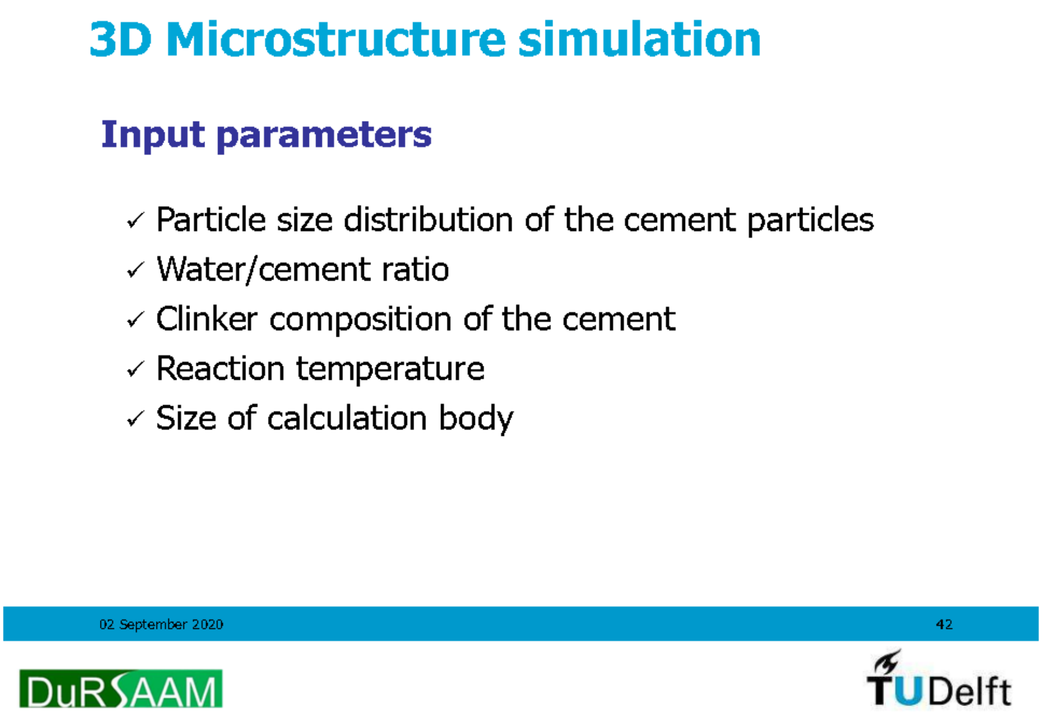


Ω_1 accounts for water consumption by embedded cement particles

↓

Reduction of the rate of hydration of particle i

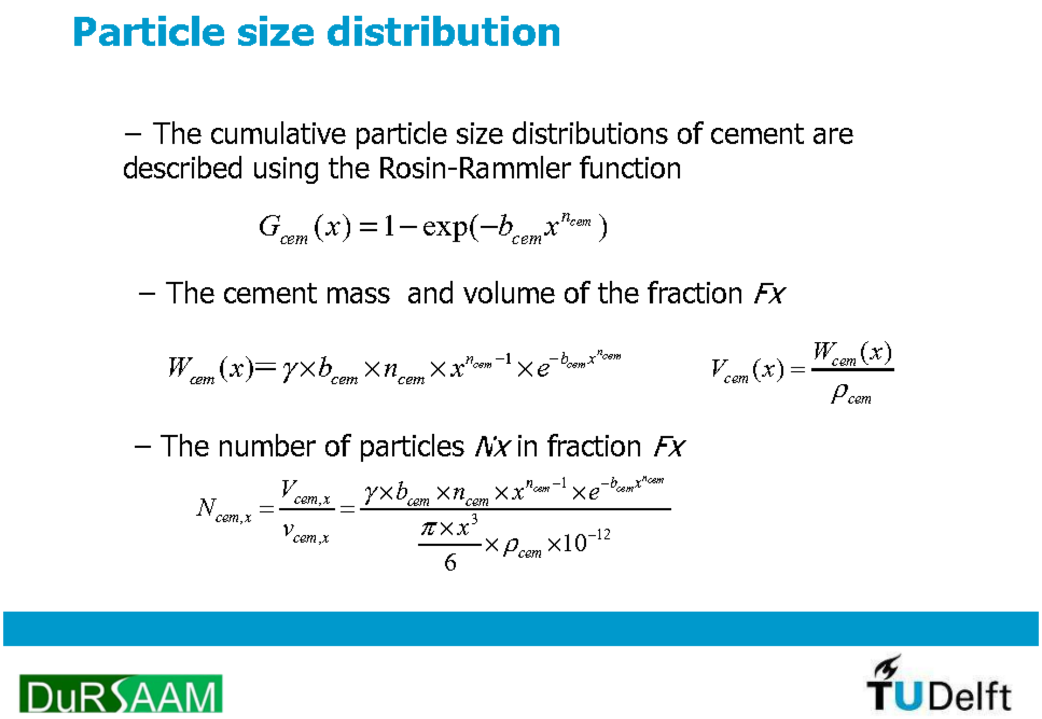
Principle of water withdrawal mechanism



3D Microstructure simulation

Input parameters

- ✓ Particle size distribution of the cement particles
- ✓ Water/cement ratio
- ✓ Clinker composition of the cement
- ✓ Reaction temperature
- ✓ Size of calculation body



Particle size distribution

– The cumulative particle size distributions of cement are described using the Rosin-Rammler function

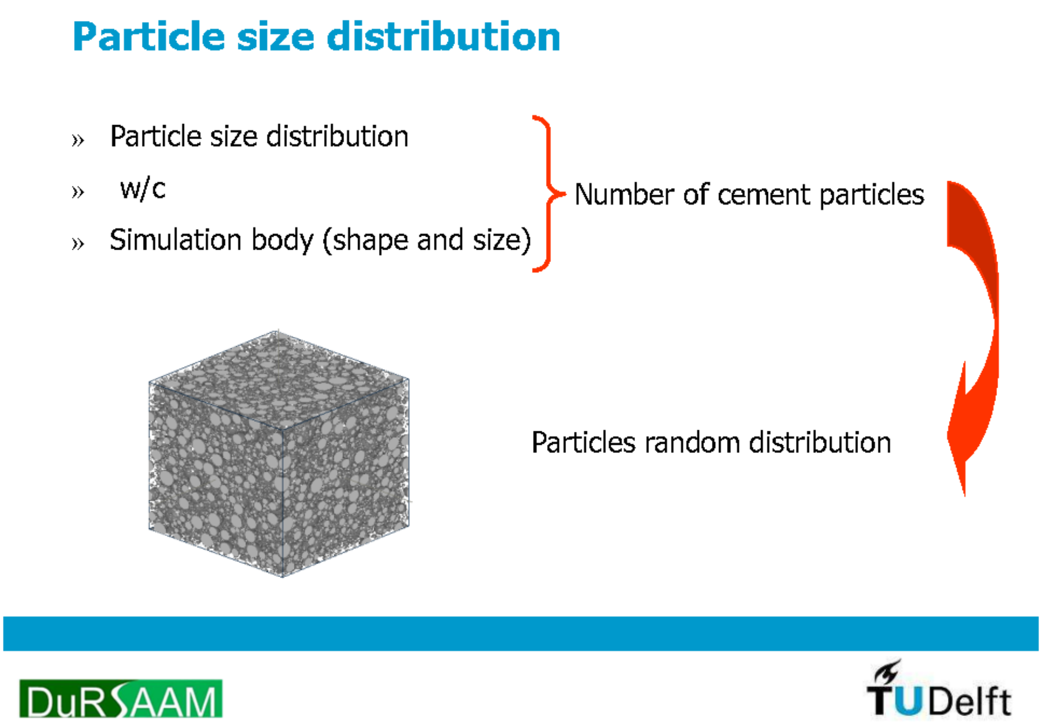
$$G_{cem}(x) = 1 - \exp(-b_{cem} x^{n_{cem}})$$

– The cement mass and volume of the fraction *Fx*

$$W_{cem}(x) = \gamma \times b_{cem} \times n_{cem} \times x^{n_{cem}-1} \times e^{-b_{cem} x^{n_{cem}}} \qquad V_{cem}(x) = \frac{W_{cem}(x)}{\rho_{cem}}$$

– The number of particles *Nx* in fraction *Fx*

$$N_{cem,x} = \frac{V_{cem,x}}{v_{cem,x}} = \frac{\gamma \times b_{cem} \times n_{cem} \times x^{n_{cem}-1} \times e^{-b_{cem} x^{n_{cem}}}}{\frac{\pi \times x^3}{6} \times \rho_{cem} \times 10^{-12}}$$

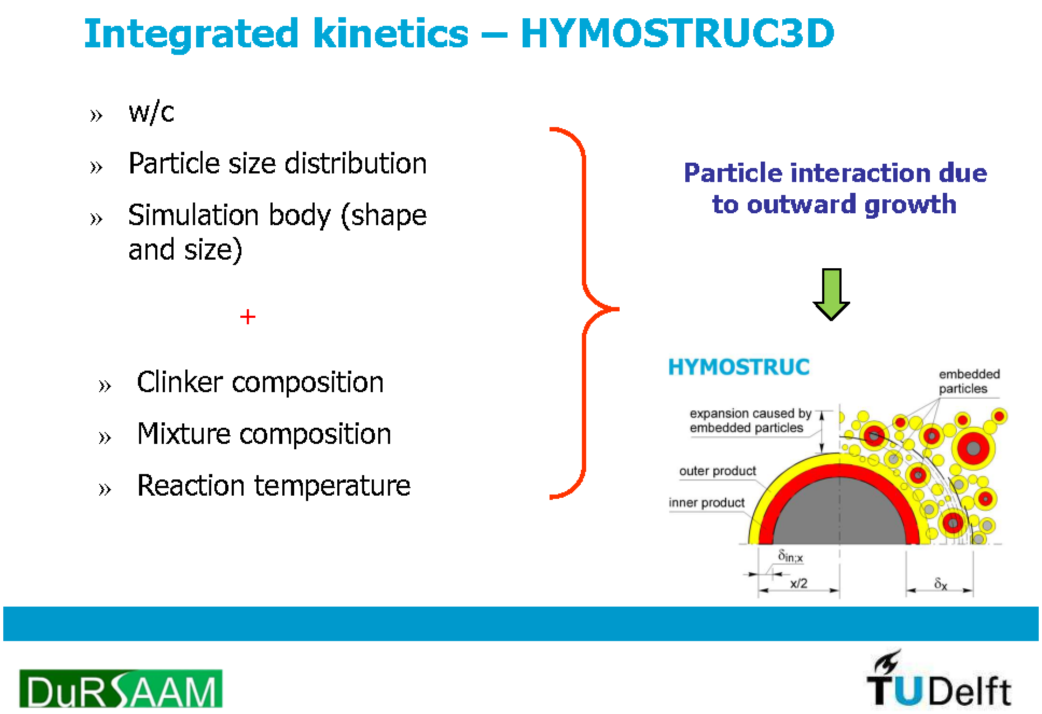


Particle size distribution

- Particle size distribution
- w/c
- Simulation body (shape and size)

Number of cement particles

Particles random distribution



Integrated kinetics – HYMOSTRUC3D

- w/c
- Particle size distribution
- Simulation body (shape and size)

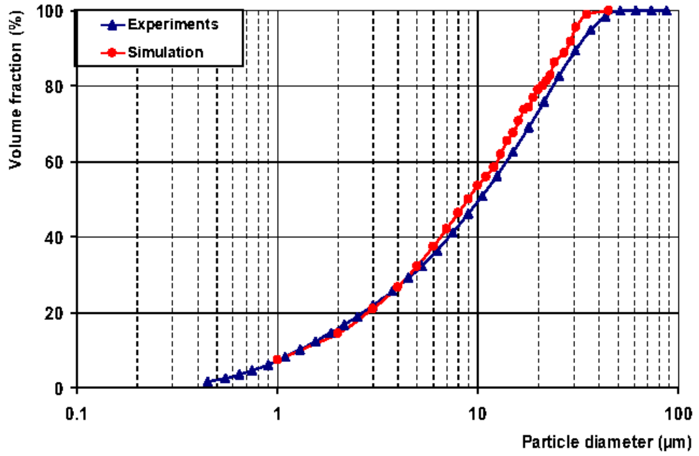
\+

- Clinker composition
- Mixture composition
- Reaction temperature

Particle interaction due to outward growth

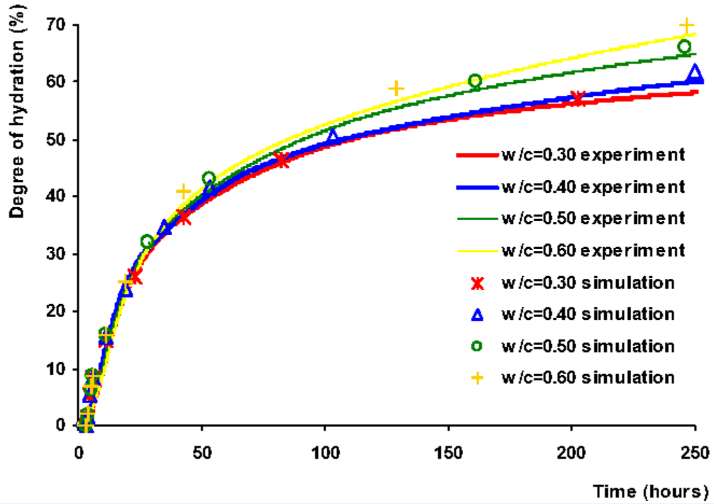
3D Microstructure simulation

Check the particle size distribution with experiments

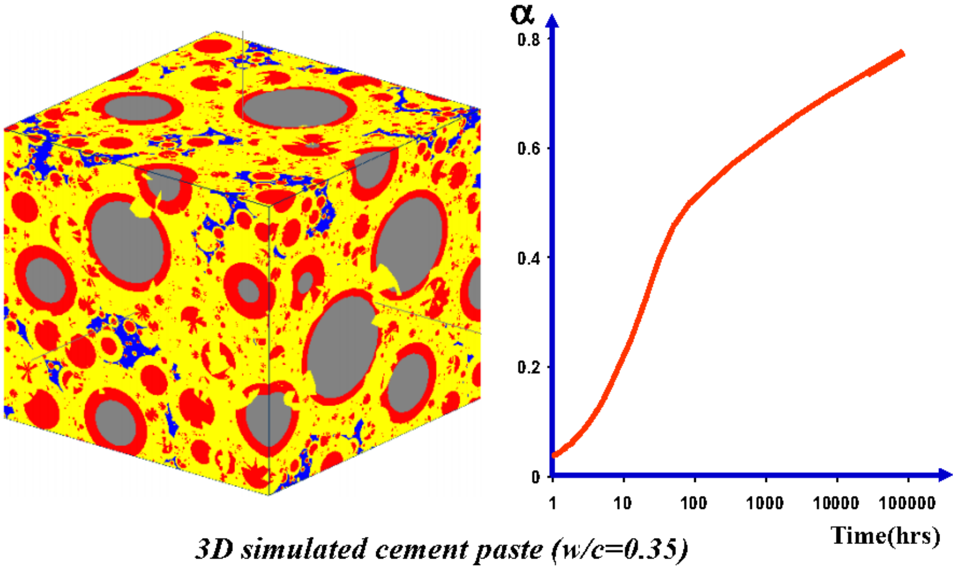


3D Microstructure simultion

Check predicted degree of hydration with experiments

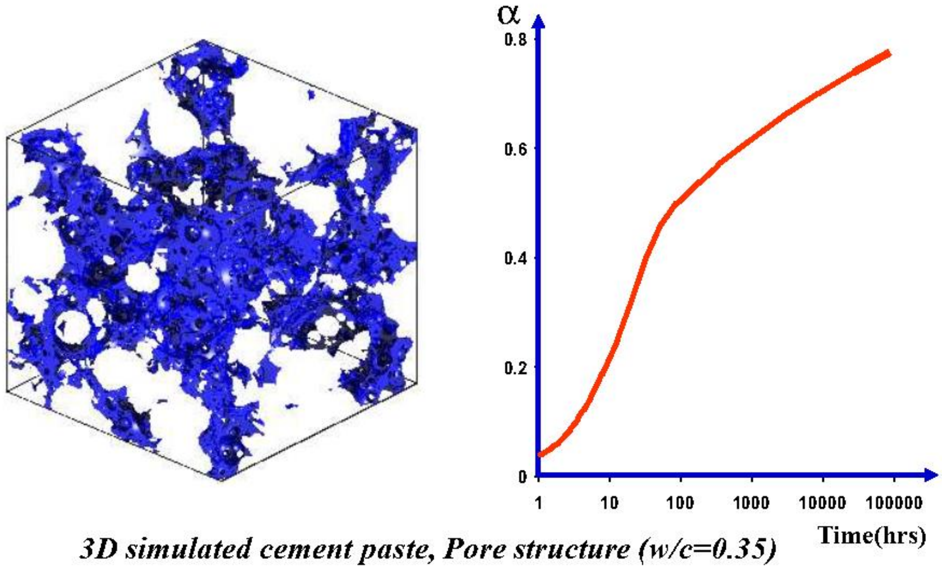


Microstructure simulation

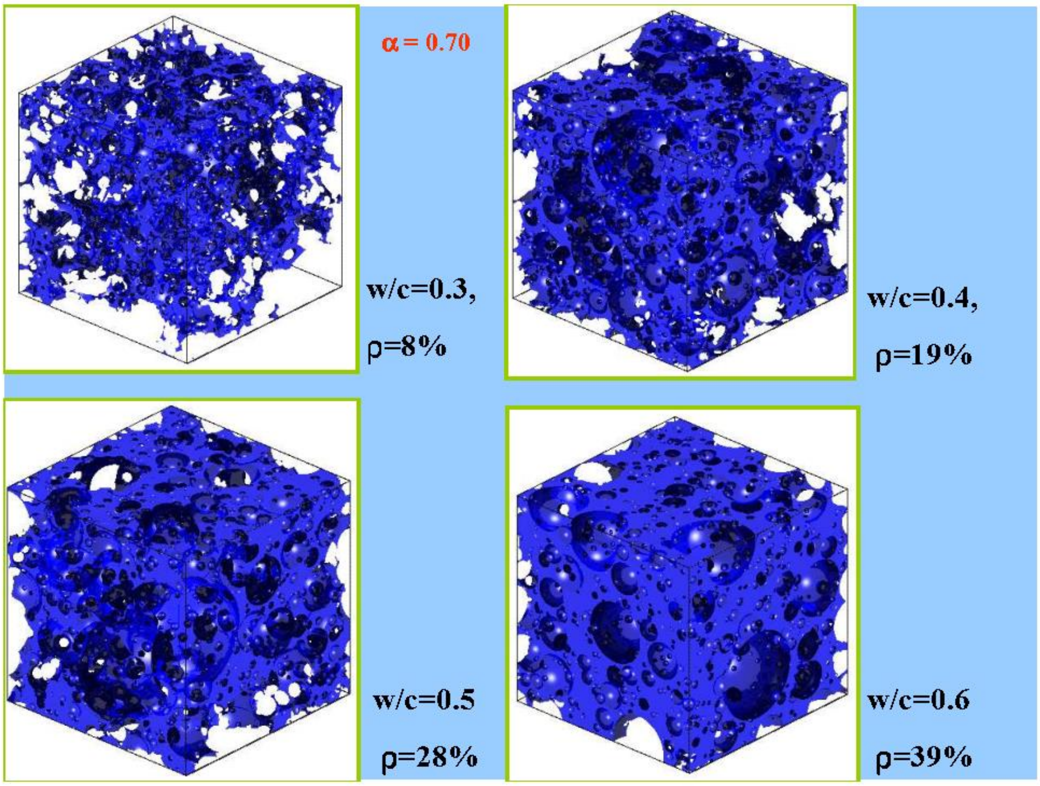


3D simulated cement paste (w/c=0.35)

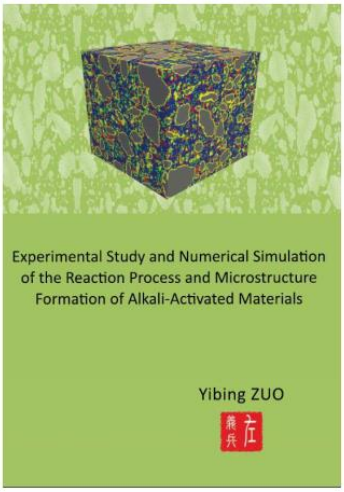
Microstructure simulation



3D simulated cement paste, Pore structure (w/c=0.35)



Reaction and Microstructure Simulation of Alkali-activated Materials (AAM)



Experimental Study and Numerical Simulation of the Reaction Process and Microstructure Formation of Alkali-Activated Materials

Yibing ZUO

https://doi.org/10.4233/uuid:193a4016-5fc7-401b-babe-722ff6a95a6c

Comparison between AAM and OPC

	AAM	OPC
Binder	aluminosilicate precursors, such as slag, fly ash …(reactivity/amorphous content)	ordinary Portland cement (C_3S, C_2S..)
Liquid	alkaline activator, such as sodium hydroxide, sodium silicate …(nature and concentration)	water
Reaction products	high-Ca AAM: C-(N-)A-S-H, Ht, C_4AH_{19}, C_3AH_6, C_2ASH_8 … low-Ca AAM: N-A-S-H, zeolites such as hydroxysodalite, zeolite P, Na-chabazite …	C-S-H, CH, AFt, AFm
Microstructure formation	heterogeneous (sodium hydroxide), homogeneous (sodium silicate)	heterogeneous

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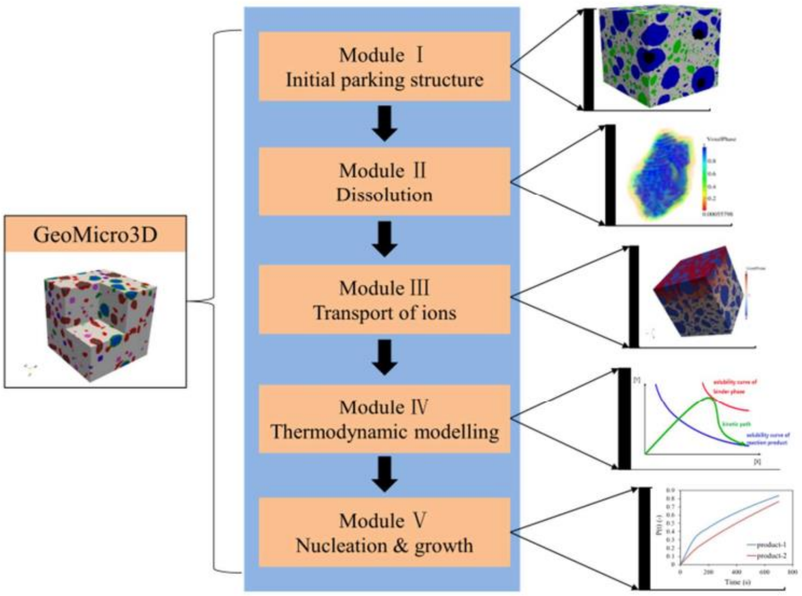
Reaction and Microstructure simulation - GeoMicro3D

- Modelling Scheme



GeoMicro3D

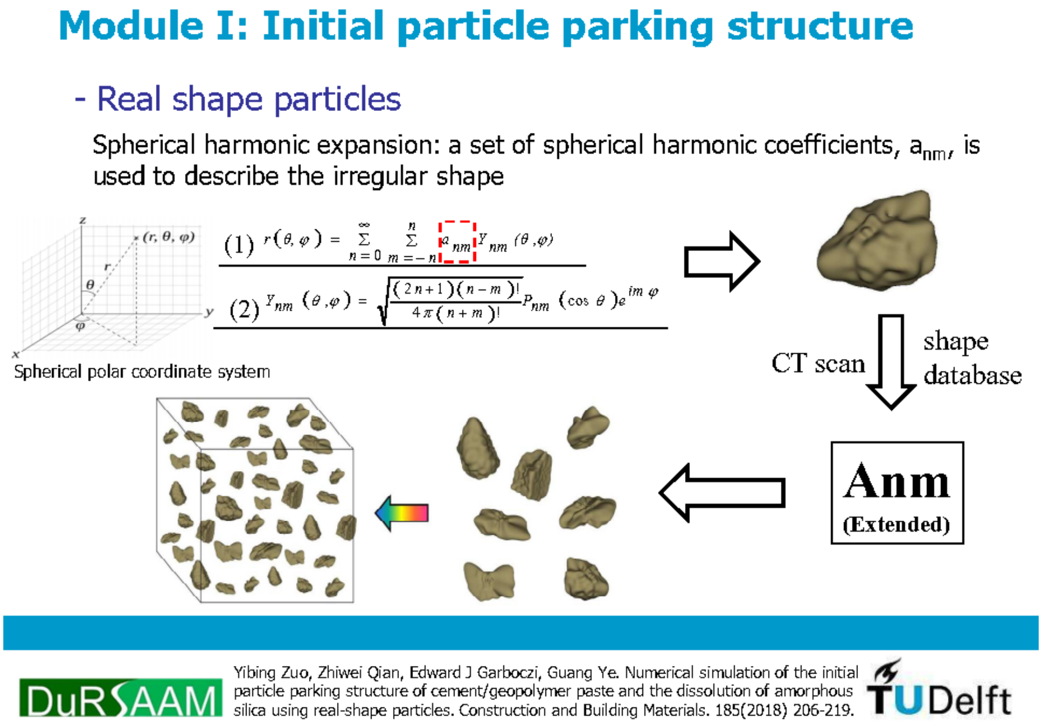
Module I
Initial parking structure

Module II
Dissolution

Module III
Transport of ions

Module IV
Thermodynamic modelling

Module V
Nucleation & growth



Module I: Initial particle parking structure

- Real shape particles

Spherical harmonic expansion: a set of spherical harmonic coefficients, a_{nm}, is used to describe the irregular shape

$$(1)\ r(\theta, \varphi) = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \boxed{a_{nm}} Y_{nm}(\theta, \varphi)$$

$$(2)\ Y_{nm}(\theta, \varphi) = \sqrt{\frac{(2n+1)(n-m)!}{4\pi(n+m)!}} P_{nm}(\cos\theta) e^{im\varphi}$$

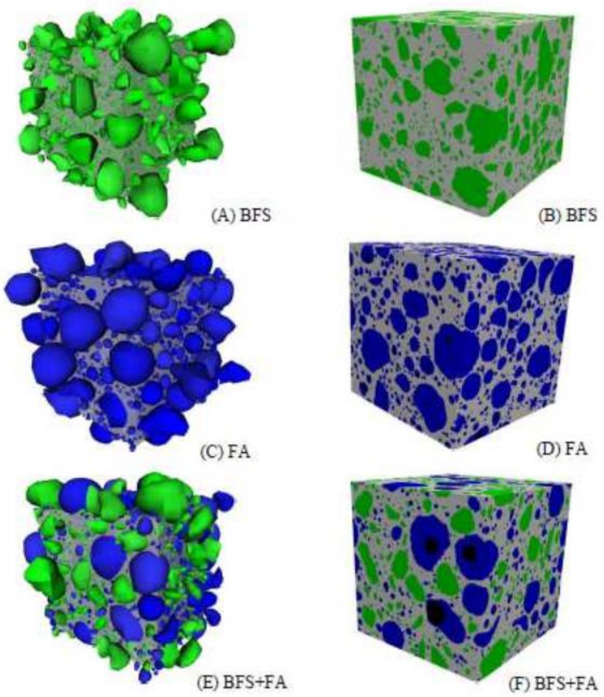
Spherical polar coordinate system

CT scan

shape database

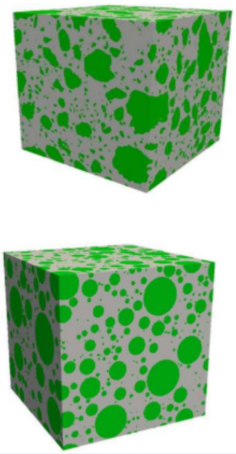
Anm
(Extended)

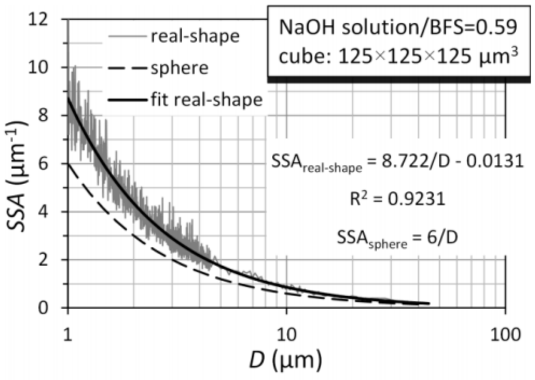
Yibing Zuo, Zhiwei Qian, Edward J Garboczi, Guang Ye. Numerical simulation of the initial particle parking structure of cement/geopolymer paste and the dissolution of amorphous silica using real-shape particles. Construction and Building Materials. 185(2018) 206-219.



Module I: Initial particle parking structure

- Real shape particles, and spherical particles of BFS





Databased of BFS was taken from E.J. Garboczi

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Yibing Zuo, Zhiwei Qian, Edward J Garboczi, Guang Ye. Numerical simulation of the initial particle parking structure of cement/geopolymer paste and the dissolution of amorphous silica using real-shape particles. Construction and Building Materials. 185(2018) 206-219.

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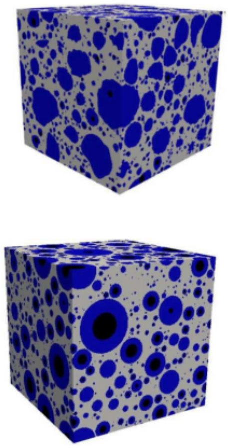
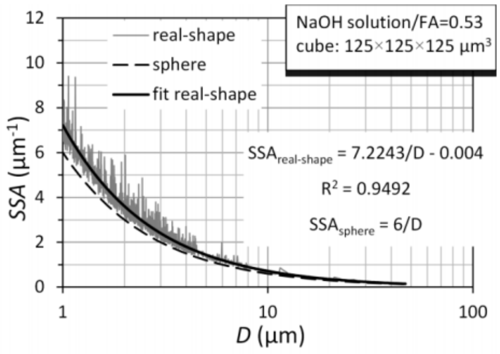
Module I: Initial particle parking structure

- Real shape particles, and spherical particles of fly ash





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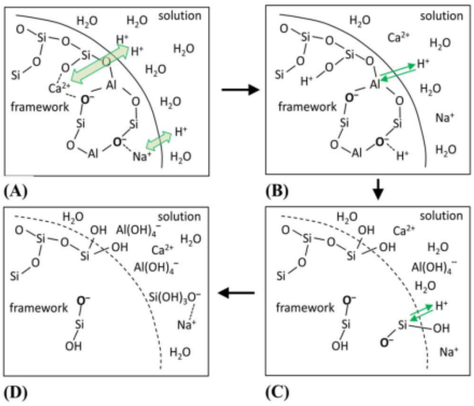
Module II: Dissolution

- Dissolution of Al, Si, Ca…from precursor



Schematic illustration of the dissolution of aluminosilicate glass (P. Duxson, J.L. Provis)

(A) Alkali and alkali-earth metal elements are initially dissolved from the surface through metal/proton exchange reactions.

(B) The hydrolysis of Al-O bonds starts

(C) The bonds of Si-O start to break

(D) Tetrahedrally coordinated Al and Si in the framework are released into the solution

---

Module II: Dissolution

According to transition state theory, the dissolution rate of glass can be described by

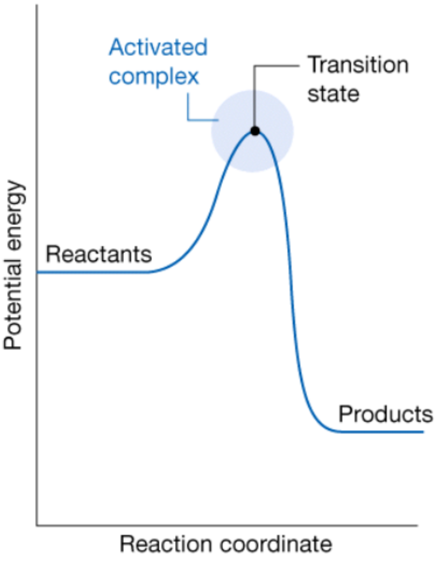
$$r = r_+\left(1 - exp\left(-\frac{A^*}{\sigma RT}\right)\right)$$

- σ the ratio of the rate of dissolution of the *activated complex*
- A*, the chemical affinity

$$A^* = -RTln\left(\frac{IAP}{K_{sp}}\right)$$

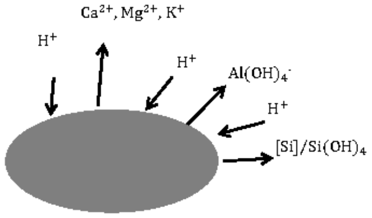
IAP - the ion activity product
Ksp - the solubility product

$$r = r_+\left(1 - \left(\frac{IAP}{K_{sp}}\right)^{1/\sigma}\right)$$



E.H. Oelkers, General kinetic description of multioxide silicate mineral and glass dissolution, Geochim. Cosmochim. Acta, 65 (2001) 3703-3719.

Module II: Dissolution



$$SiO_2 + 2OH^- \leftrightarrow H_2O + SiO_3^{2-} \qquad LogK_{sp,Si} = 2.09$$

$$Al_2O_3 + 2OH^- \leftrightarrow H_2O + 2AlO_2^- \qquad LogK_{sp,Al} = 0.55$$

$$CaO + H_2O \leftrightarrow 2OH^- + Ca^{2+} \qquad LogK_{sp,Ca}=4.58$$

$$\downarrow$$

$$IAP_{Si} = \frac{a_{SiO_3{}^{2-}} * \ a_{H_2O}}{a_{OH^-} \ * \ a_{OH^-}}$$

$$IAP_{Al} = \frac{a_{AlO_2{}^-} * a_{AlO_2{}^-} * \ a_{H_2O}}{a_{OH^-} \ * a_{OH^-}}$$

$$IAP_{Ca} = \frac{a_{Ca^{2+}} * \ a_{OH^-} \ * a_{OH^-}}{a_{H_2O}}$$

$$r_{Si} = r_{+,Si}\left(1 - \left(\frac{IAP_{Si}}{K_{sp,Si}}\right)^{1/\sigma}\right)$$

$$r_{Al} = r_{+,Al}\left(1 - \left(\frac{IAP_{Al}}{K_{sp,Al}}\right)^{1/\sigma}\right)$$

$$r_{Ca} = r_{+,Ca}\left(1 - \left(\frac{IAP_{Ca}}{K_{sp,Ca}}\right)^{1/\sigma}\right)$$

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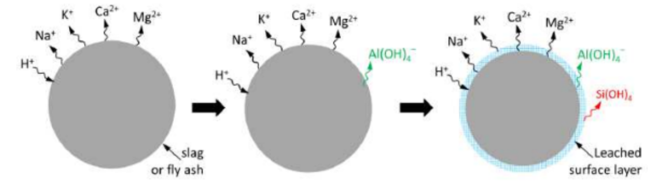
Module II: Dissolution

- Depression of dissolution rate by aluminium species:



(A) release of modifying elements (B) release of Al (C) release of Si

-The initially released Al species were absorbed to the leached surface layer and **slowed down the dissolution of fly ash** in the sodium hydroxide activated fly ash system

The depression of the dissolution rate of quartz is related to **the adsorption of $Al(OH)^{4-}$ at silanol sites on the surface of quartz** (Bickmore et al):

$$r_{Si,with}=r_{Si,without}(1-\theta_{Al})$$

$$\theta_{Al} = \frac{bC_{Al}}{(1+bC)(1+kNBO/T)}\theta_{Al,max}$$

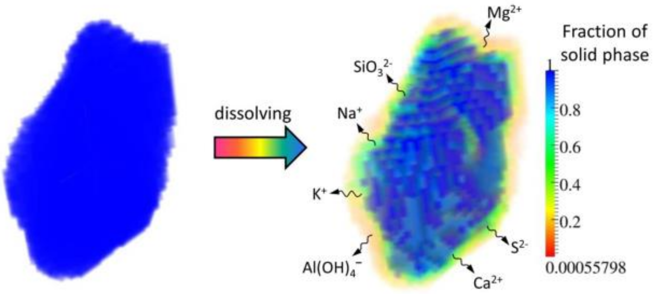
$$r_{Si} = r_{+,Si}\left(1 - \left(\frac{IAP_{Si}}{K_{sp,Si}}\right)^{1/\sigma}\right)(1-\theta_{Al})$$

θ_{Al} is the fraction of the quartz surface that is passivated

$$\theta_{Al,max} = -0.177pH + 3.23$$

Module II: Dissolution

- Implementation by LB – dissolution amount



Dissolved amount of elements at one lattice Boltzmann time step: $\Delta n_{X,i} = r_{X,i} T_0 L_0{}^2$

The total dissolved amount: $\Delta N_X = \sum_{i=1}^{6} \Delta n_{X,i}$

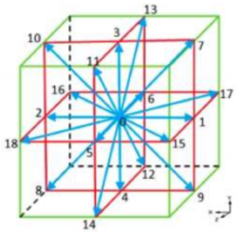
Module III: Transport

- Transport of aqueous ions: LB approach

☐ At the microscopic level, a fluid made up of particles can move randomly in all directions as a result of collisions of particles with other particles. The probability of these particles' position in the physical space is dynamically described by the continuous Boltzmann equation:

$$\frac{\partial f}{\partial t} + \xi \cdot \frac{\partial f}{\partial x} + F \cdot \frac{\partial f}{\partial u} = \Omega(f)$$

$$\Omega(f) = -\frac{1}{\tau}\left(f - f^{eq}\right)$$



Module III: Transport

- Transport of aqueous ions: LB approach

- ☐ By discretizing the physical space with regular lattice nodes, the lattice Bhatager-Gross-Krook (BGK) equation can be:

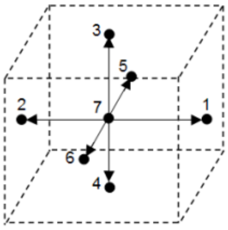
$$f_j(x+e_j\delta t,t+\delta t)=f_j(x,t)-\frac{\delta t}{\tau}[f_j(x,t)-f_j^{eq}(x,t)]+\omega_j\delta tS$$

Where, f and f^{eq} is the non-equilibrium and equilibrium particle distribution function respectively. δt is the time step, ϵj is the microscopic velocity at location x at time t and in velocity direction j, and wj is the weighting factor in the velocity direction j. S is the source term to consider the influence of dissolution.

$$f_j^{eq}=\omega_j F$$

Ion concentration F in the lattice node:

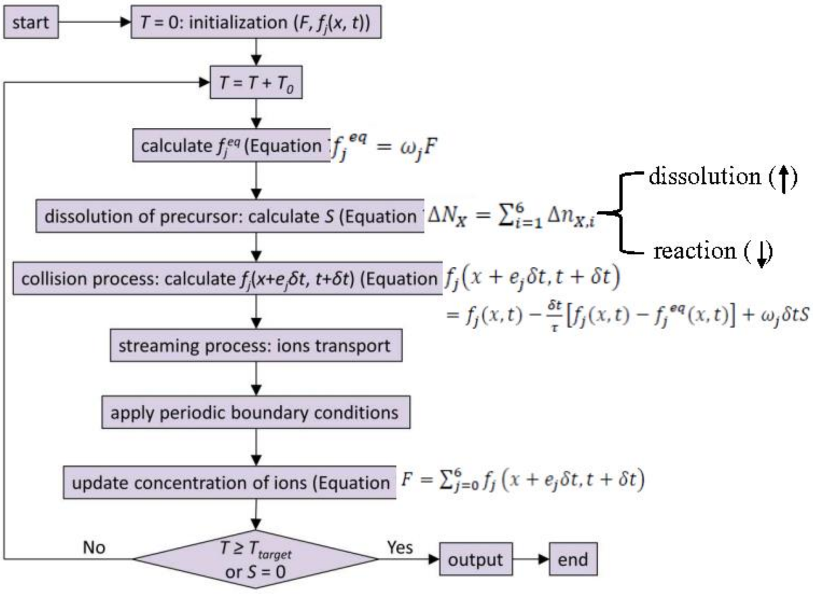
$$F=\textstyle\sum_{j=0}^{6} f_j\left(x+e_j\delta t,t+\delta t\right)$$ for D3Q7



D3Q7

Module III: Transport

- Transport of aqueous ions: LB approach



start

T = 0: initialization (F, $f_j(x,t)$)

$T=T+T_0$

calculate f_j^{eq} (Equation $f_j^{eq}=\omega_j F$

dissolution of precursor: calculate S (Equation $\Delta N_X=\sum_{i=1}^{6}\Delta n_{X,i}$

dissolution (↑)

reaction (↓)

collision process: calculate $f_j(x+e_j\delta t, t+\delta t)$ (Equation $f_j\left(x+e_j\delta t,t+\delta t\right)=f_j(x,t)-\frac{\delta t}{\tau}[f_j(x,t)-f_j^{eq}(x,t)]+\omega_j\delta tS$

streaming process: ions transport

apply periodic boundary conditions

update concentration of ions (Equation $F=\sum_{j=0}^{6} f_j\left(x+e_j\delta t,t+\delta t\right)$

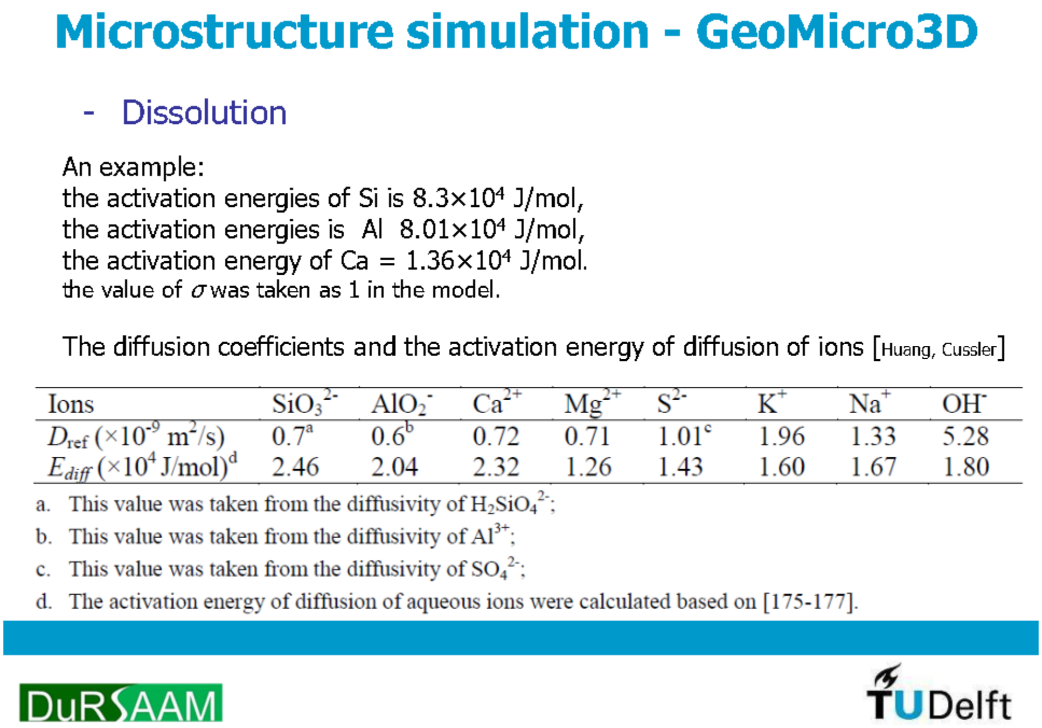
No

$T\geq T_{target}$ or $S=0$

Yes

output

end



Microstructure simulation - GeoMicro3D

- Dissolution

An example:
the activation energies of Si is 8.3×10^4 J/mol,
the activation energies is Al 8.01×10^4 J/mol,
the activation energy of Ca = 1.36×10^4 J/mol.
the value of σ was taken as 1 in the model.

The diffusion coefficients and the activation energy of diffusion of ions [Huang, Cussler]

Ions	SiO_3^{2-}	AlO_2^-	Ca^{2+}	Mg^{2+}	S^{2-}	K^+	Na^+	OH^-
D_{ref} ($\times10^{-9}$ m^2/s)	0.7^a	0.6^b	0.72	0.71	1.01^c	1.96	1.33	5.28
E_{diff} ($\times10^4$ J/mol)^d	2.46	2.04	2.32	1.26	1.43	1.60	1.67	1.80

a. This value was taken from the diffusivity of $H_2SiO_4^{2-}$;
b. This value was taken from the diffusivity of Al^{3+};
c. This value was taken from the diffusivity of SO_4^{2-};
d. The activation energy of diffusion of aqueous ions were calculated based on [175-177].

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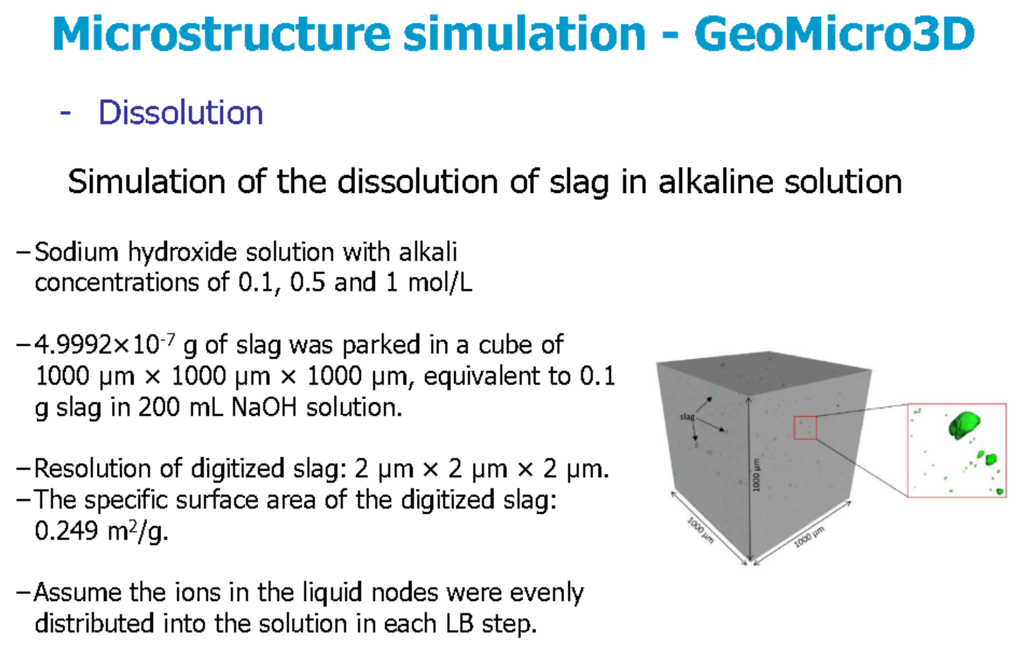


Microstructure simulation - GeoMicro3D

- Dissolution

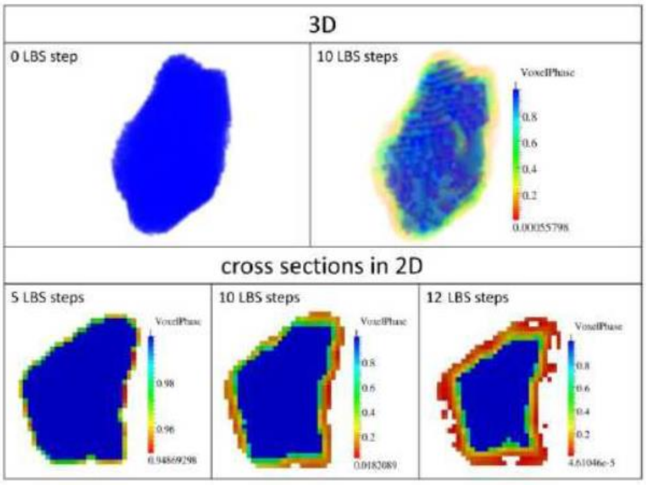
Simulation of the dissolution of slag in alkaline solution

- Sodium hydroxide solution with alkali concentrations of 0.1, 0.5 and 1 mol/L
- 4.9992×10^{-7} g of slag was parked in a cube of 1000 µm × 1000 µm × 1000 µm, equivalent to 0.1 g slag in 200 mL NaOH solution.
- Resolution of digitized slag: 2 µm × 2 µm × 2 µm.
- The specific surface area of the digitized slag: 0.249 m^2/g.
- Assume the ions in the liquid nodes were evenly distributed into the solution in each LB step.

Microstructure simulation - GeoMicro3D

- Dissolution

Simulation of the dissolution of slag in alkaline solution

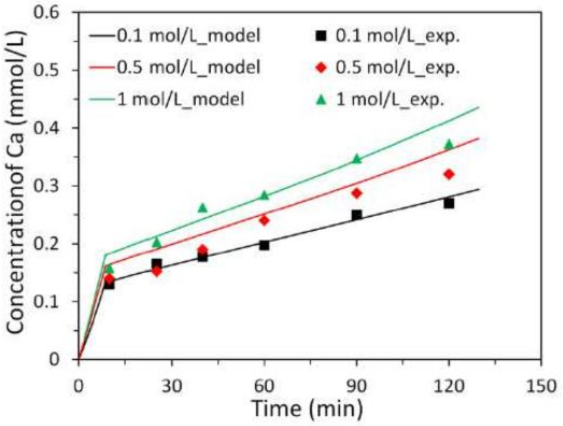


Progressing dissolution front as a function of lattice Boltzmann simulation

Microstructure simulation - GeoMicro3D

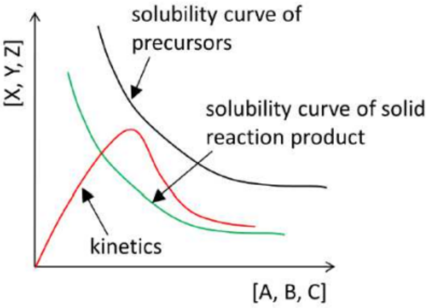
- Dissolution

Simulation of the dissolution of slag in alkaline solution – Ca concentration



Module IV: Chemical reaction

- Thermodynamic modelling



- When aluminosilicate precursors are contacted with an alkaline activator, their constituents start to dissolve, → an increase of the concentrations of aqueous ions in solution (red curve, kinetics).

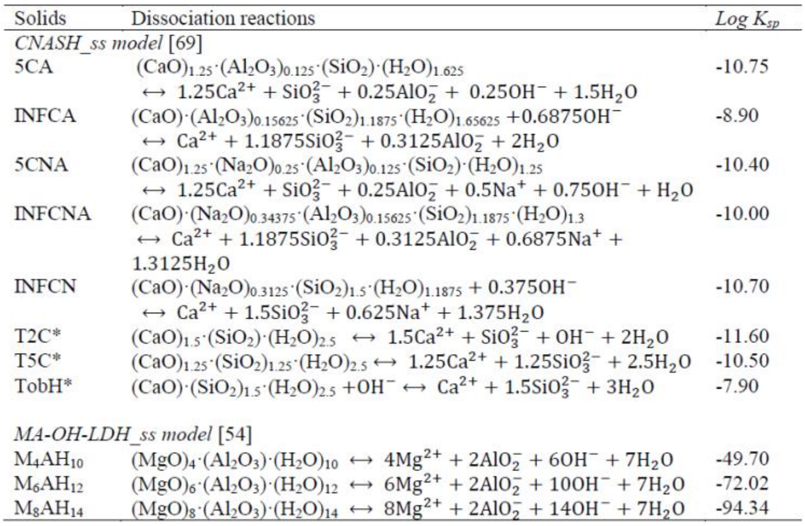
- When the concentrations of the aqueous ions increase to a certain level, the solution is saturated or supersaturated, → precipitate and form solid reaction products.

- Two kinds of thermodynamic interactions:
    1. Between the precursors and the solution, continuously releasing elements into solution.
    2. Between the solution and the solid reaction products, leading to growth of the solid reaction products.

Module IV: Chemical reaction

- Thermodynamic modelling for C-(N-)A-S-H gel in AA-slag

Chemical reactions and solubility products (Log Ksp) at 25 °C and 1 bar for C-(N-)A-S-H and hydrotalcite-like phases (Myers, Bernal and Provis, CCR 66 (2014) 27-47)



Solids	Dissociation reactions	*Log K_{sp}*
CNASH_ss model [69]		
5CA	$(CaO)_{1.25}\cdot(Al_2O_3)_{0.125}\cdot(SiO_2)\cdot(H_2O)_{1.625} \leftrightarrow 1.25Ca^{2+} + SiO_3^{2-} + 0.25AlO_2^- + 0.25OH^- + 1.5H_2O$	-10.75
INFCA	$(CaO)\cdot(Al_2O_3)_{0.15625}\cdot(SiO_2)_{1.1875}\cdot(H_2O)_{1.65625} + 0.6875OH^- \leftrightarrow Ca^{2+} + 1.1875SiO_3^{2-} + 0.3125AlO_2^- + 2H_2O$	-8.90
5CNA	$(CaO)_{1.25}\cdot(Na_2O)_{0.25}\cdot(Al_2O_3)_{0.125}\cdot(SiO_2)\cdot(H_2O)_{1.25} \leftrightarrow 1.25Ca^{2+} + SiO_3^{2-} + 0.25AlO_2^- + 0.5Na^+ + 0.75OH^- + H_2O$	-10.40
INFCNA	$(CaO)\cdot(Na_2O)_{0.34375}\cdot(Al_2O_3)_{0.15625}\cdot(SiO_2)_{1.1875}\cdot(H_2O)_{1.3} \leftrightarrow Ca^{2+} + 1.1875SiO_3^{2-} + 0.3125AlO_2^- + 0.6875Na^+ + 1.3125H_2O$	-10.00
INFCN	$(CaO)\cdot(Na_2O)_{0.3125}\cdot(SiO_2)_{1.5}\cdot(H_2O)_{1.1875} + 0.375OH^- \leftrightarrow Ca^{2+} + 1.5SiO_3^{2-} + 0.625Na^+ + 1.375H_2O$	-10.70
T2C*	$(CaO)_{1.5}\cdot(SiO_2)\cdot(H_2O)_{2.5} \leftrightarrow 1.5Ca^{2+} + SiO_3^{2-} + OH^- + 2H_2O$	-11.60
T5C*	$(CaO)_{1.25}\cdot(SiO_2)_{1.25}\cdot(H_2O)_{2.5} \leftrightarrow 1.25Ca^{2+} + 1.25SiO_3^{2-} + 2.5H_2O$	-10.50
TobH*	$(CaO)\cdot(SiO_2)_{1.5}\cdot(H_2O)_{2.5} + OH^- \leftrightarrow Ca^{2+} + 1.5SiO_3^{2-} + 3H_2O$	-7.90
MA-OH-LDH_ss model [54]		
M_4AH_{10}	$(MgO)_4\cdot(Al_2O_3)\cdot(H_2O)_{10} \leftrightarrow 4Mg^{2+} + 2AlO_2^- + 6OH^- + 7H_2O$	-49.70
M_6AH_{12}	$(MgO)_6\cdot(Al_2O_3)\cdot(H_2O)_{12} \leftrightarrow 6Mg^{2+} + 2AlO_2^- + 10OH^- + 7H_2O$	-72.02
M_8AH_{14}	$(MgO)_8\cdot(Al_2O_3)\cdot(H_2O)_{14} \leftrightarrow 8Mg^{2+} + 2AlO_2^- + 14OH^- + 7H_2O$	-94.34

Module IV: Chemical reaction

- Thermodynamic model for the N-A-S-H gel in AA-Fly ash

Chemical reactions and solubility products (Log Ksp) at 25 °C and 1 bar for N-(C-)A-S-H

Solids	Dissociation reactions	$Log\ K_{sp}$
NASH_1-1[a]	$(Na_2O)_{0.5}\cdot(Al_2O_3)_{0.5}\cdot(SiO_2)_1\cdot(H_2O)_1 + 2OH^-$ $\leftrightarrow SiO_3^{2-} + AlO_2^- + Na^+ + 2H_2O$	-6.51
NASH_2-1	$(Na_2O)_{0.5}\cdot(Al_2O_3)_{0.5}\cdot(SiO_2)_2\cdot(H_2O)_1 + 4OH^-$ $\leftrightarrow 2SiO_3^{2-} + AlO_2^- + Na^+ + 3H_2O$	-8.01
NASH_3-1	$(Na_2O)_{0.5}\cdot(Al_2O_3)_{0.5}\cdot(SiO_2)_3\cdot(H_2O)_1 + 6OH^-$ $\leftrightarrow 3SiO_3^{2-} + AlO_2^- + Na^+ + 4H_2O$	-9.51
NASH_4-1	$(Na_2O)_{0.5}\cdot(Al_2O_3)_{0.5}\cdot(SiO_2)_4\cdot(H_2O)_1 + 8OH^-$ $\leftrightarrow 4SiO_3^{2-} + AlO_2^- + Na^+ + 5H_2O$	-11.01
NCASH_1-0.1	$(Na_2O)_{0.05}\cdot(CaO)_{0.45}\cdot (Al_2O_3)_{0.5}\cdot(SiO_2)_1\cdot(H_2O)_1 + 2OH^-$ $\leftrightarrow SiO_3^{2-} + AlO_2^- + 0.45Ca^{2+} + 0.1Na^+ + 2H_2O$	-8.51
NCASH_2-0.1	$(Na_2O)_{0.05}\cdot(CaO)_{0.45}\cdot (Al_2O_3)_{0.5}\cdot(SiO_2)_2\cdot(H_2O)_1 + 4OH^-$ $\leftrightarrow 2SiO_3^{2-} + AlO_2^- + 0.45Ca^{2+} + 0.1Na^+ + 3H_2O$	-10.01
NCASH_3-0.1	$(Na_2O)_{0.05}\cdot(CaO)_{0.45}\cdot (Al_2O_3)_{0.5}\cdot(SiO_2)_3\cdot(H_2O)_1 + 6OH^-$ $\leftrightarrow 3SiO_3^{2-} + AlO_2^- + 0.45Ca^{2+} + 0.1Na^+ + 4H_2O$	-11.51
NCASH_4-0.1	$(Na_2O)_{0.05}\cdot(CaO)_{0.45}\cdot (Al_2O_3)_{0.5}\cdot(SiO_2)_4\cdot(H_2O)_1 + 8OH^-$ $\leftrightarrow 4SiO_3^{2-} + AlO_2^- + 0.45Ca^{2+} + 0.1Na^+ + 5H_2O$	-13.01

a. The first and second number after N(C)ASH represent the molar ratio of Si/Al and Na/Al in the solid solution member, respectively.

Module IV: Chemical reaction

- Degree of reaction

The degree of reaction of slag or fly ash ($\alpha(t)$) can be calculated as the ratio of cumulative heat release at time t ($Q(t)$) to the total heat release ($Q_{\max}$)

$$\alpha(t) = \frac{Q(t)}{Q_{max}}$$

$Q_{(t)}$ can be described using an exponential function as follows

$$Q(t) = Q_{max}\exp(-(\frac{\lambda}{t})^{\beta})$$

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Module IV: Chemical reaction

- Implementation

- GEM-Selektor V3 was used for performing thermodynamic calculations
- The CEMDATA07 thermodynamic database was used as the basis thermodynamic database
- The thermodynamic models for the C-(N-)A-S-H gel, N-A-S-H gel and hydrotalcite-like phase, and the thermodynamic data for zeolite phases are added to the basis thermodynamic database for thermodynamic modelling of the reactions in AAMs.

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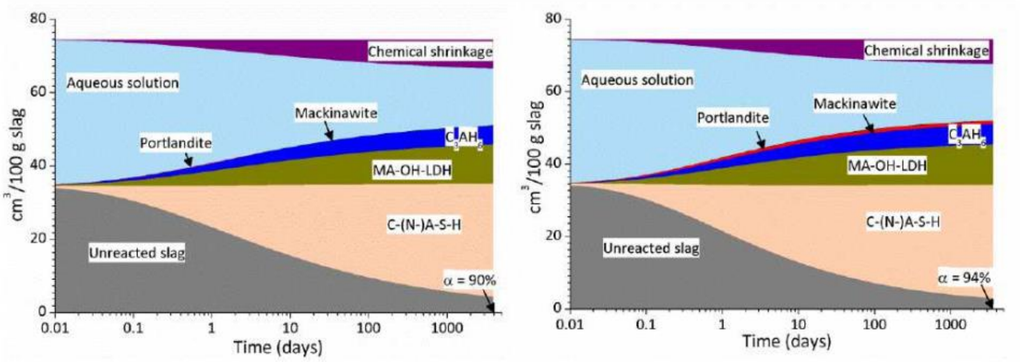
Module IV: Chemical reaction

- Implementation

Example of AA-Slag



(A) BFS_N4S0 (B) BFS_N6S0

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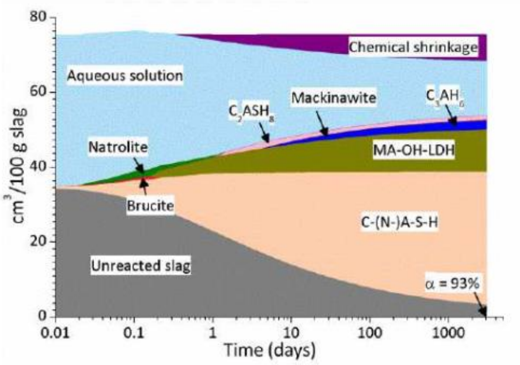
Module IV: Chemical reaction

- Implementation

Example of AA-Slag



(C) BFS_N6S5.4

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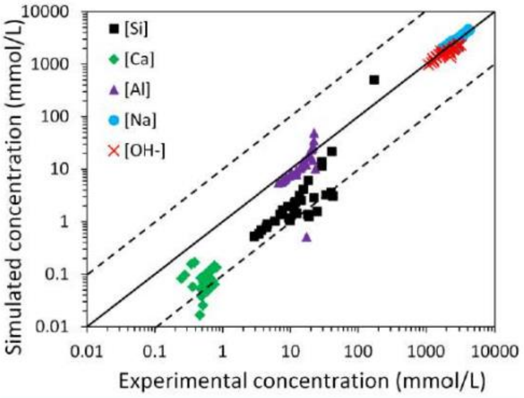
Module IV: Chemical reaction

- Implementation

Example of AA-Slag



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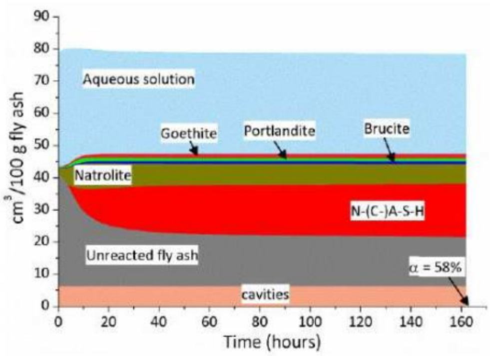
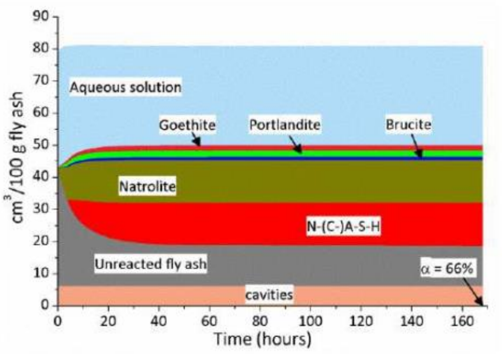
Module IV: Chemical reaction

- Implementation

Example of AA-Fly ash



(A) FA_N6.2S0T60

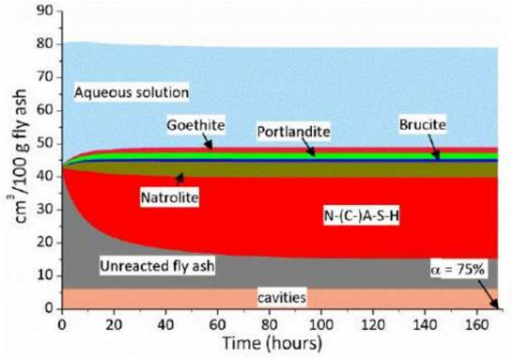


(B) FA_N9.3S0T60

Module IV: Chemical reaction

- Implementation

Example of AA-Fly ash



(C) FA_N9.3S9T60

Module V: Nucleation and growth

- Simulation of the nucleation

The probability P(t) that at least one critical nucleus has formed in a time interval Δt

$$P(\Delta t)=1-\exp\,(-J\cdot V\cdot \Delta t)$$

where V is the solution volume within which the nucleus forms and J is the nucleation rate

$$J(S) = A \cdot S \cdot \exp(-\frac{B}{ln^2 S})$$

where A is the kinetic parameter, S is the supersaturation ratio and B is the thermodynamic parameter of nucleation.

Module V: Nucleation and growth

- Simulation of the nucleation

The thermodynamic parameter B for heterogeneous nucleation is expressed with the following equation

$$B = \frac{4}{27}\frac{c^3 \cdot v^2 \cdot \gamma_{ef}^3}{k_B^3 \cdot T^3}$$

where c is a shape factor ((36п)1/3 for spheres and 6 for cubes), v is the molecular volume of the phase, kB is the Boltzmann constant and T is the absolute temperature. γef is the effective interfacial energy, where γef = ψγ with activity factor 0 < ψ < 1. For homogeneous nucleation ψ = 1.

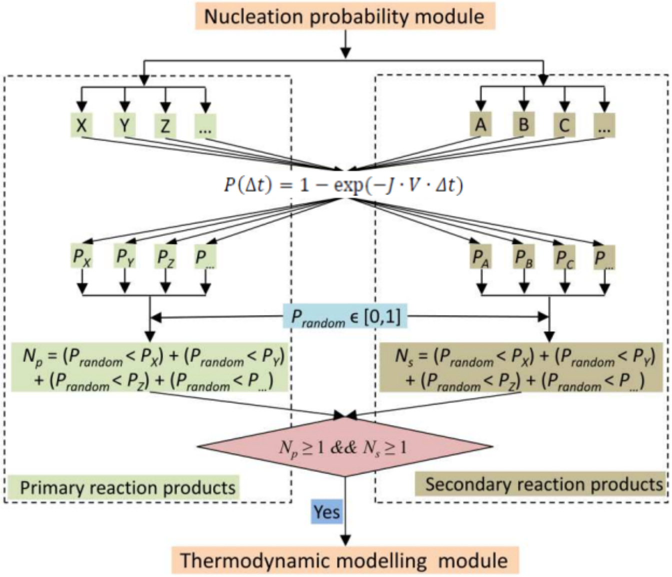
The interfacial energy is calculated using the following equation

$$\gamma = \beta_N \cdot k_B \cdot T \cdot \frac{1}{v^{2/3}} \cdot \ln(\frac{1}{N_a \cdot v \cdot c^*})$$

where β_N is a numerical factor (β_N = 0.514 for spherical nuclei), N_a is Avogadro's number and c^* is the molar solubility.

Module V: Nucleation and growth

- Flowchart of nucleation probability module



1) Calculate the nucleation probabilities, P_X, P_Y and P_Z for primary reaction products and P_A, P_B and P_C for secondary reaction products.

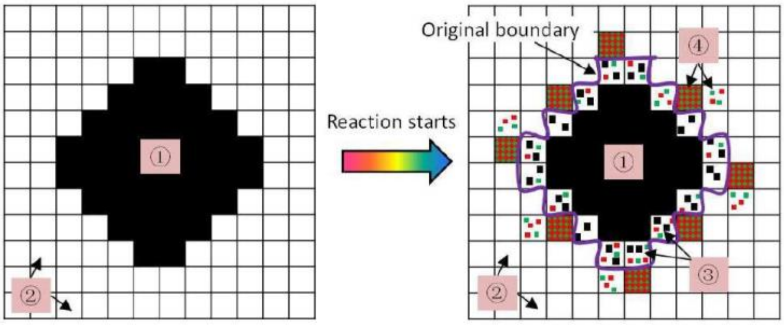
2) Generate a random probability $0 \leq P_{random} \leq 1$.

3) Calculate the numbers (i.e. N_p and N_s) of primary reaction products and secondary reaction products that are predicted to nucleate, respectively.

4) If $N_p \geq 1$ and $N_s \geq 1$, then the thermodynamic modelling module is called.

Module V: Nucleation and growth

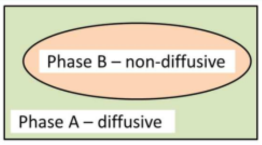
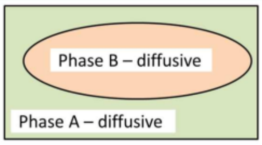
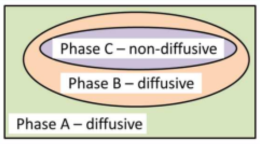
- Diffusivity of ions through lattice nodes



Schematic representation of the diffusion of ions through different lattice nodes in 2D. In the graph black, white, red and green represent precursor, solution, primary reaction products and secondary reaction products, respectively. ① and ② represent precursor and solution nodes, respectively. ③ represents nodes where precursor may dissolve and reaction products may precipitate, and ④ represents nodes that are completely or partially filled with reaction products.

Module V: Nucleation and growth

- Diffusivity of ions through lattice nodes (voxel)

Model-I	**Model-II**	**Model-III**
		
$D_{medium} = D_A(1-\phi_B)^{5/3}$	$\left(\frac{D_B - D_{medium}}{D_B - D_A}\right)\left(\frac{D_A}{D_{medium}}\right)^{1/3}$ $= 1 - \emptyset_B$	$D_{BC} = D_B(1-\phi_C)^{5/3}$ $\left(\frac{D_{BC} - D_{medium}}{D_{BC} - D_A}\right)\left(\frac{D_A}{D_{medium}}\right)^{1/3}$ $= 1 - \emptyset_{BC}$
where D_A, D_B, D_{BC} and D_{medium} are the diffusivities of ions in phase A, phase B, phases BC and the medium, respectively. φ_B is the volume fraction of phase B in the medium, φ_C is the volume fraction of phase C in the phases B and C. φ_{BC} is the volume fraction of phases B and C in the medium		

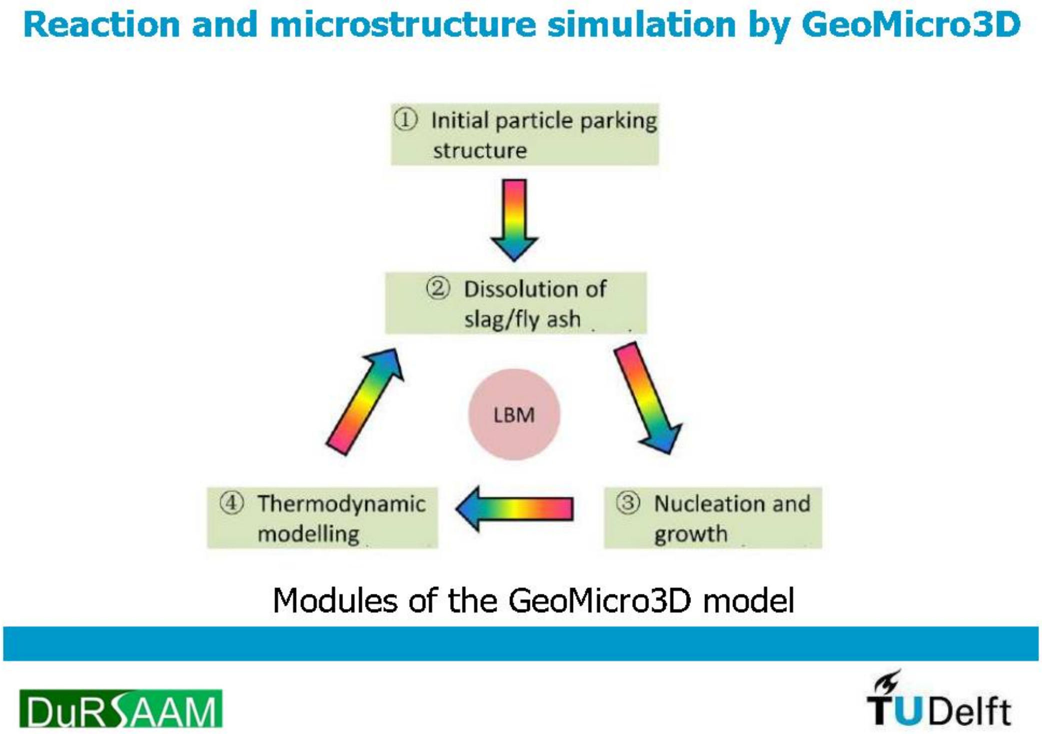
Module V: Nucleation and growth

- The primary reaction products, i.e. the C-(N-)A-S-H gel and the N-A-S-H gel, are diffusive for ions.
- The secondary reaction products, i.e. crystalline phases, are non-diffusive for ions.

Relative diffusivity of ions through the C-S-H gel

Ions	Relative diffusivity	Ref.
Cl^-	0.0025	[E. Garboczi]
H_2O	0.001	[S. Kamali-Bernard]
Electron	0.00775	[H. Ma]

Description of the lattice node	**Selection of the model**
Contains one diffusive phase, i.e. solution, and one non-diffusive phase, i.e. slag or/and secondary reaction products	Model-I
Contains two diffusive phases, i.e. solution and primary reaction products	Model-II
Contains one non-diffusive phase, i.e. slag or/and secondary reaction products, and two diffusive phases, i.e. solution and primary reaction products	Model-III



Reaction and microstructure simulation by GeoMicro3D

① Initial particle parking structure

② Dissolution of slag/fly ash

LBM

③ Nucleation and growth

④ Thermodynamic modelling

Modules of the GeoMicro3D model

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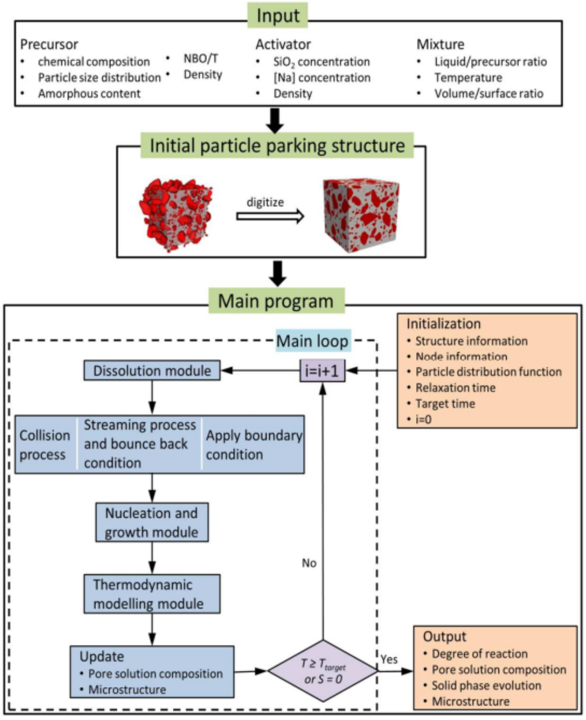
The overall flowchart of the GeoMicro3D model.



Reaction and microstructure simulation by GeoMicro3D

- An example of simulation of alkali-activated slag

Simulation parameters

- Mixture

Sample	Precursor	Na2O	SiO2	*Msb*	Curing temperature
BFS_N4S0	slag	4	0	0	20 °C
BFS_N6S0	slag	6	0	0	20 °C
BFS_N6S5.4	slag	6	5.4	0.93	20 °C

water-to-slag ratio = 0.4

- Diffusivities of ions in solution and activation energy of diffusion of ions

Ions	SiO_3^{2-}	AlO_2^-	Ca^{2+}	Mg^{2+}	S^{2-}	K^+	Na^+	OH^-
D_{ref} ($\times 10^{-9}$ m^2/s)	0.7[a]	0.6[b]	0.72	0.71	1.01[c]	1.96	1.33	5.28
E_{diff} ($\times 10^4$ J/mol)[d]	2.46	2.04	2.32	1.26	1.43	1.60	1.67	1.80

a. This value was taken from the diffusivity of $H_2SiO_4^{2-}$;

b. This value was taken from the diffusivity of Al^{3+};

c. This value was taken from the diffusivity of SO_4^{2-};

d. The activation energy of diffusion of aqueous ions were calculated based on [175-177].

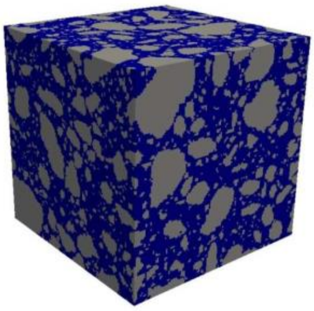
- Kinetic parameter A

	C(N)ASH_ss	M_4AH_{10}	M_6AH_{12}	M_8AH_{14}	C_3AH_6	C_2ASH_8	CH	Natrolite
A (m^{-3}s^{-1})	4.24×10^7	4.71×10^{-26}	4.71×10^{-51}	4.71×10^{-71}	27.6	0.101	4.71×10^9	9.62×10^3

Reaction and microstructure simulation by GeoMicro3D

- An example of simulation of alkali-activated slag

Simulation parameters

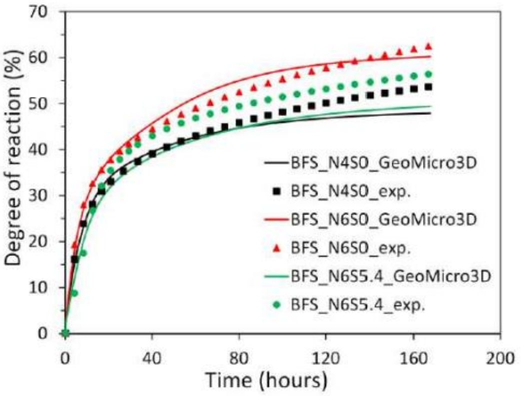


Simulated initial particle parking structure of slag in alkaline. In the graph, blue and gray represent activator and slag, respectively. The size of the cubic unit cell is 125 μm × 125 μm × 125 μm. The digitization resolution is 1 μm × 1 μm × 1 μm.

Reaction and microstructure simulation by GeoMicro3D

- Results

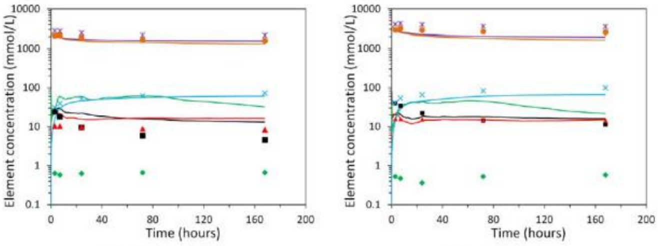
Degree of reaction



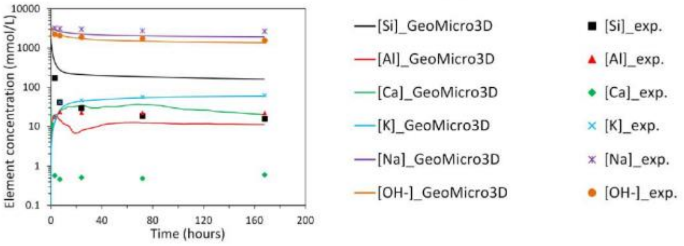
Reaction and microstructure simulation by GeoMicro3D

- Results

Pore solution chemistry



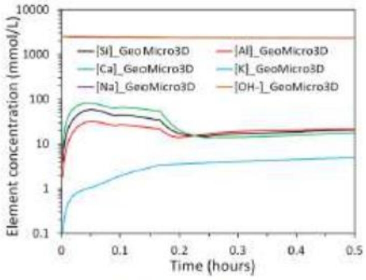
(A) BFS_N4S0 (B) BFS_N6S0



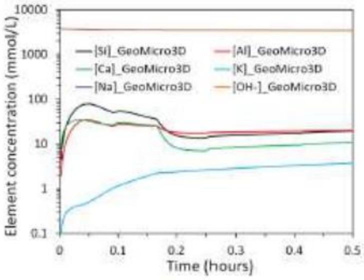
(C) BFS_N6S5.4

Reaction and microstructure simulation by GeoMicro3D

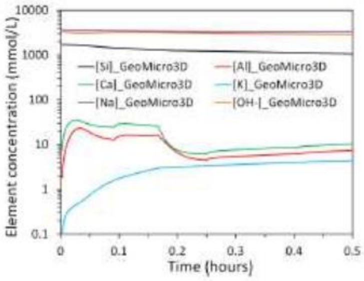
- Results



(A) BFS_N4S0



(B) BFS_N6S0

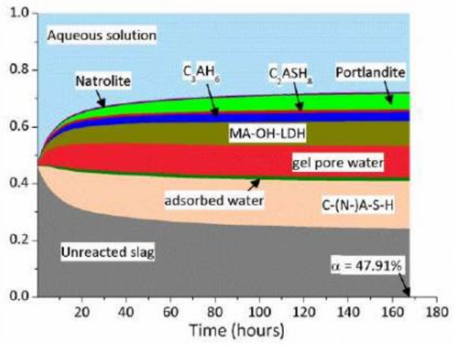


(C) BFS_N6S5.4

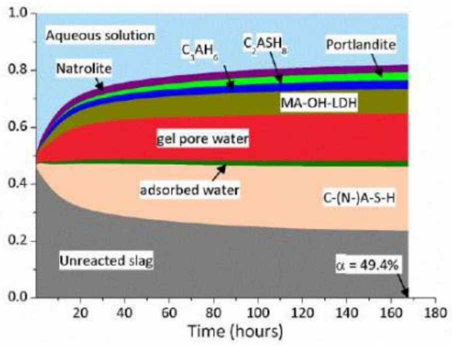
Reaction and microstructure simulation by GeoMicro3D

- Results

Volume evolution of phases



(A) BFS_N4S0, using GeoMicro3D



(E) BFS N6S5.4, using GeoMicro3D

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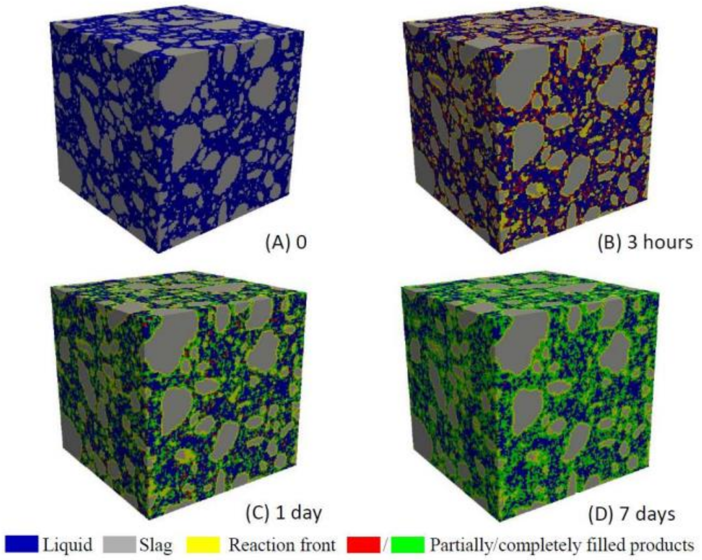
Reaction and microstructure simulation by GeoMicro3D

- Results

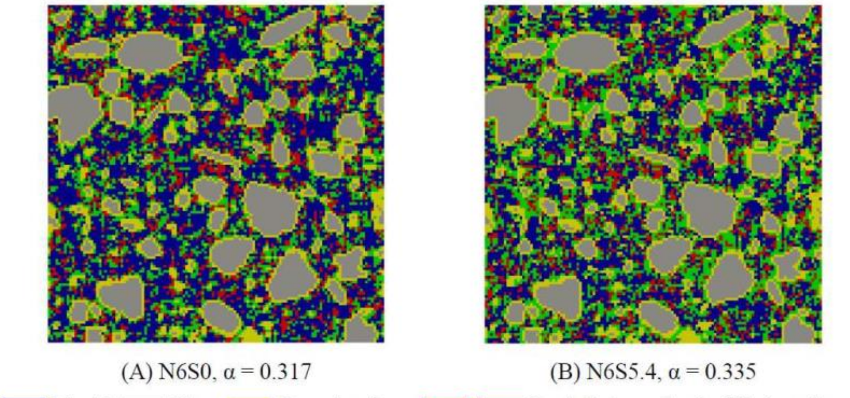
Microstructure development

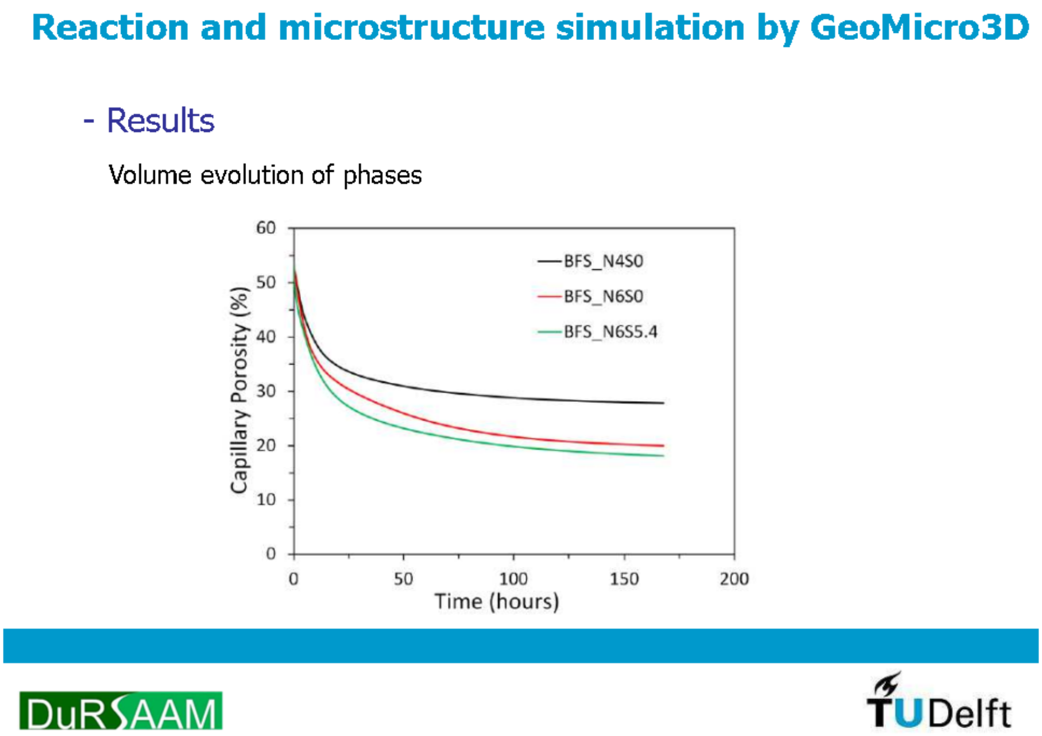


Reaction and microstructure simulation by GeoMicro3D

- Results

Microstructure development

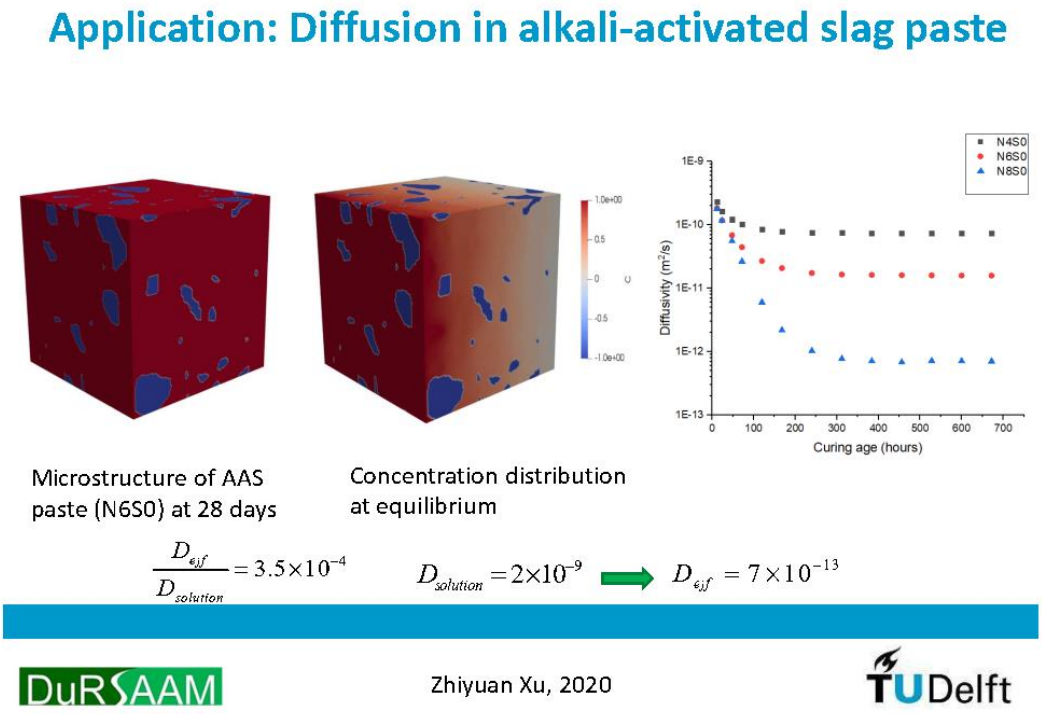




Reaction and microstructure simulation by GeoMicro3D

- Results

Volume evolution of phases



Application: Diffusion in alkali-activated slag paste

Microstructure of AAS paste (N6S0) at 28 days

Concentration distribution at equilibrium

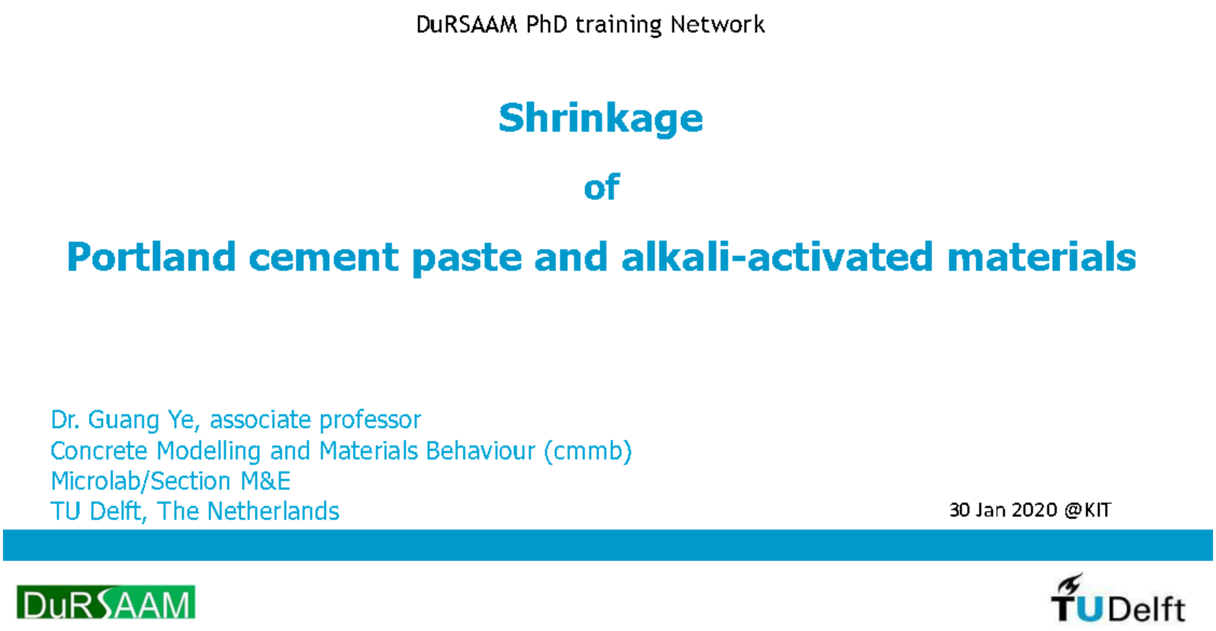
$$\frac{D_{eff}}{D_{solution}} = 3.5\times10^{-4} \qquad D_{solution} = 2\times10^{-9} \Longrightarrow D_{eff} = 7\times10^{-13}$$

Zhiyuan Xu, 2020

9. Shrinkage of AAM concretes

Guang Ye

AAM concrete by nature might sometimes be more sensitive to shrinkage and it is important to consider this in the mix design and curing conditions. In this chapter first a discussion is provided on different forms of shrinkage, how they can be characterized via testing and what can be done to mitigate excessive shrinkage. Secondly, this discussion is continued looking especially into autogenous shrinkage of AAM concrete.



DuRSAAM PhD training Network

Shrinkage

of

Portland cement paste and alkali-activated materials

Dr. Guang Ye, associate professor
Concrete Modelling and Materials Behaviour (cmmb)
Microlab/Section M&E
TU Delft, The Netherlands

30 Jan 2020 @KIT

DuRSAAM

TU Delft

Content

- Introduction of chemical shrinkage, autogenous shrinkage and dry shrinkage in cementitious materials
  - Mechanism
  - Test method
  - Mitigation
- Autogenous shrinkage of Alkali activated concrete
  - Mechanism
  - Test method
  - Cracking potential
  - Mitigation

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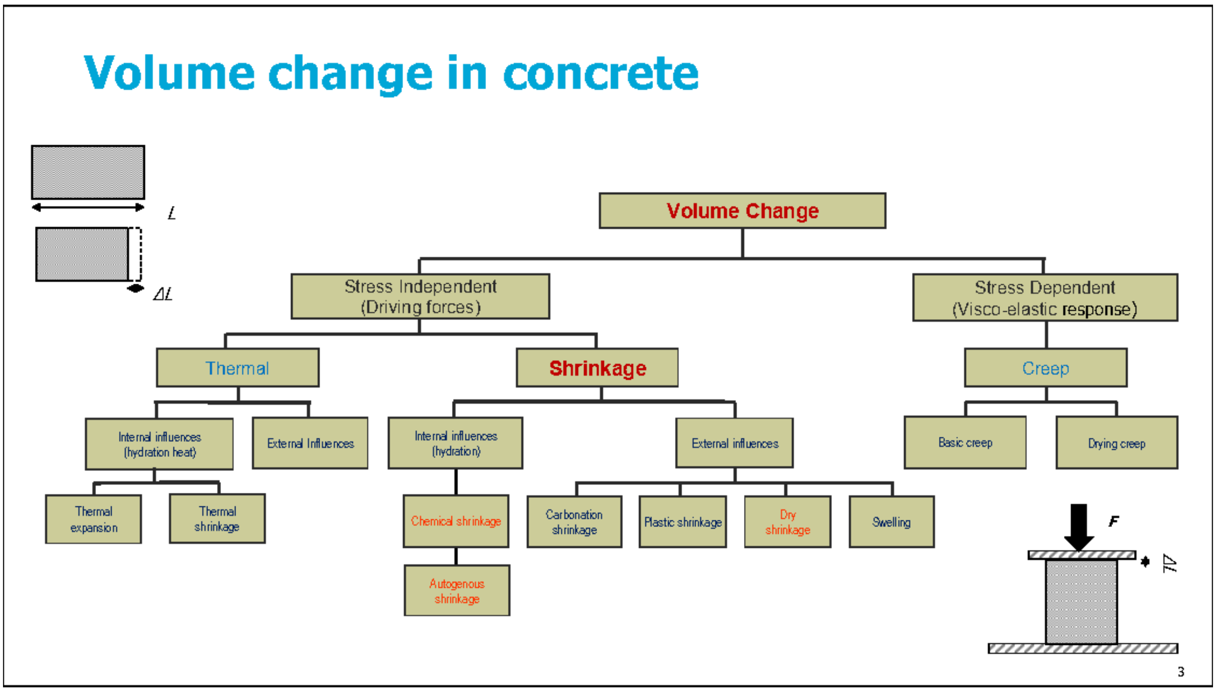
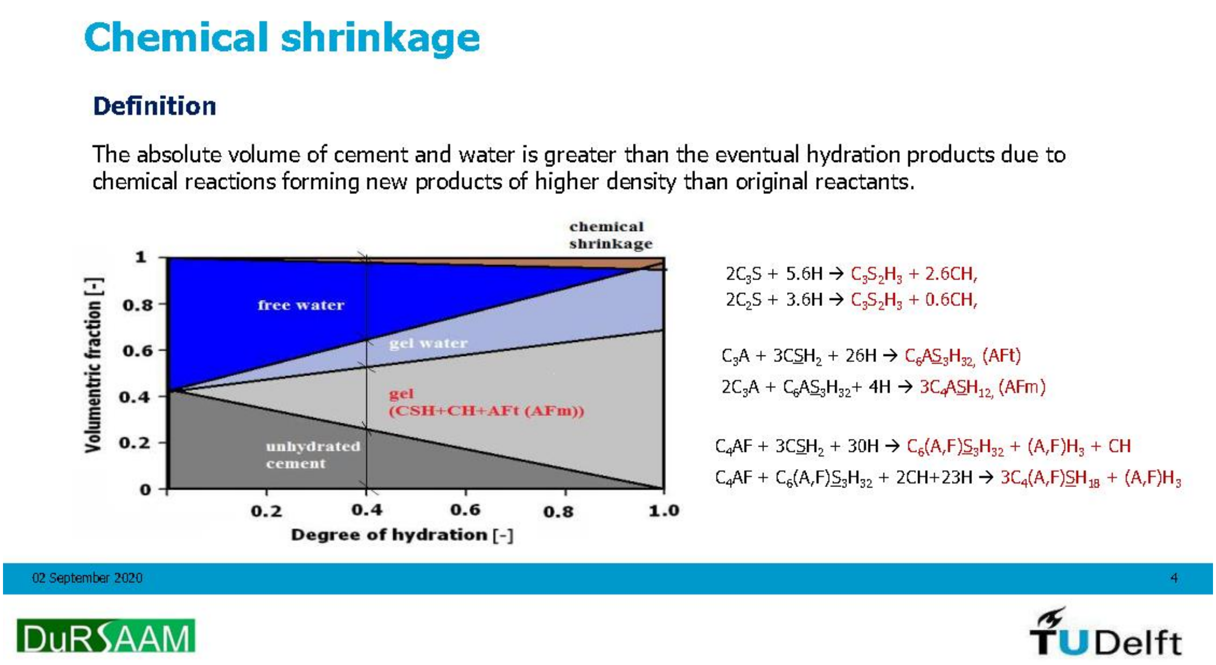
Volume change in concrete



- **Volume Change**
  - Stress Independent (Driving forces)
    - Thermal
      - Internal influences (hydration heat)
        - Thermal expansion
        - Thermal shrinkage
      - External Influences
    - **Shrinkage**
      - Internal influences (hydration)
        - Chemical shrinkage
          - Autogenous shrinkage
      - External influences
        - Carbonation shrinkage
        - Plastic shrinkage
        - Dry shrinkage
        - Swelling
  - Stress Dependent (Visco-elastic response)
    - Creep
      - Basic creep
      - Drying creep



Chemical shrinkage

Definition

The absolute volume of cement and water is greater than the eventual hydration products due to chemical reactions forming new products of higher density than original reactants.

$2C_3S + 5.6H \rightarrow C_3S_2H_3 + 2.6CH,$

$2C_2S + 3.6H \rightarrow C_3S_2H_3 + 0.6CH,$

$C_3A + 3C\underline{S}H_2 + 26H \rightarrow C_6A\underline{S}_3H_{32,}$ (AFt)

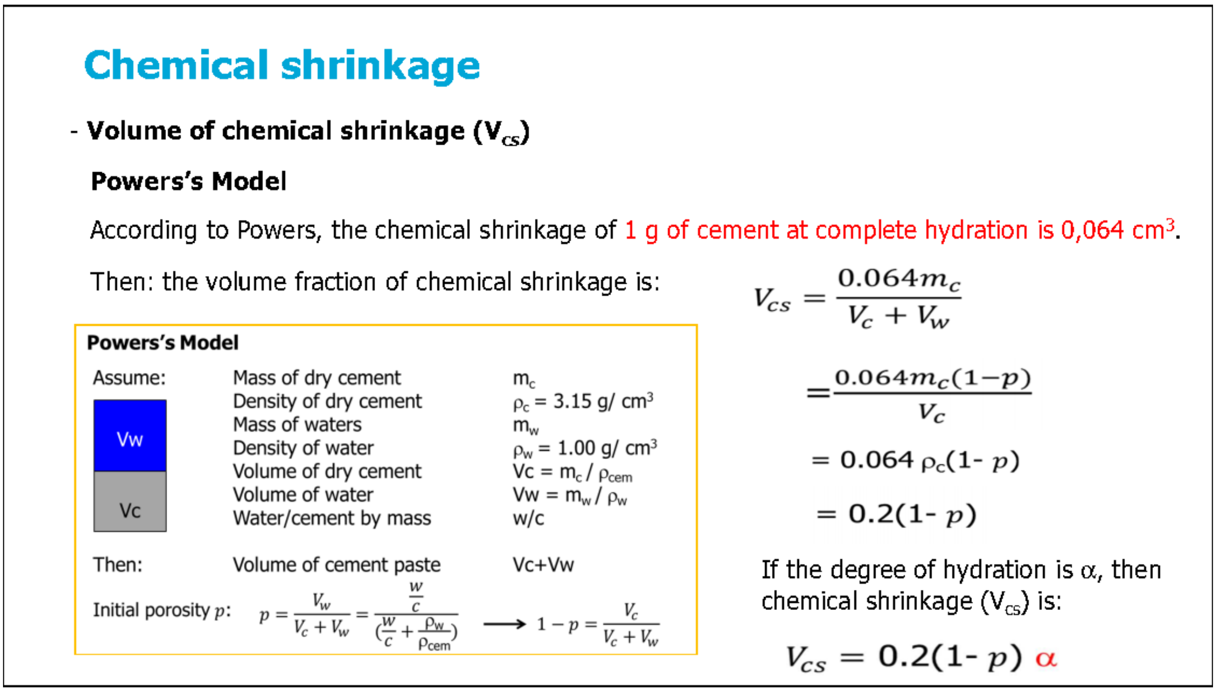
$2C_3A + C_6A\underline{S}_3H_{32} + 4H \rightarrow 3C_4A\underline{S}H_{12,}$ (AFm)

$C_4AF + 3C\underline{S}H_2 + 30H \rightarrow C_6(A,F)\underline{S}_3H_{32} + (A,F)H_3 + CH$

$C_4AF + C_6(A,F)\underline{S}_3H_{32} + 2CH + 23H \rightarrow 3C_4(A,F)\underline{S}H_{18} + (A,F)H_3$

02 September 2020 4

DuRSAAM TUDelft



Chemical shrinkage

- **Volume of chemical shrinkage (V_{cs})**

Powers's Model

According to Powers, the chemical shrinkage of 1 g of cement at complete hydration is 0,064 cm^3.

Then: the volume fraction of chemical shrinkage is:

Powers's Model

Assume:	Mass of dry cement	m_c
	Density of dry cement	$\rho_c = 3.15$ g/ cm^3
	Mass of waters	m_w
	Density of water	$\rho_w = 1.00$ g/ cm^3
	Volume of dry cement	$Vc = m_c / \rho_{cem}$
	Volume of water	$Vw = m_w / \rho_w$
	Water/cement by mass	w/c
Then:	Volume of cement paste	Vc+Vw

Initial porosity p: $p = \frac{V_w}{V_c + V_w} = \frac{\frac{w}{c}}{(\frac{w}{c} + \frac{\rho_w}{\rho_{cem}})} \longrightarrow 1 - p = \frac{V_c}{V_c + V_w}$

$$V_{cs} = \frac{0.064 m_c}{V_c + V_w}$$

$$= \frac{0.064 m_c (1-p)}{V_c}$$

$$= 0.064\, \rho_c (1-\, p)$$

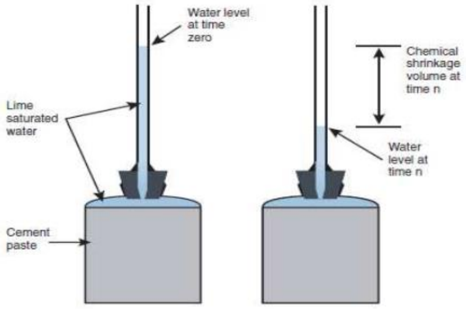
$$= 0.2(1-\, p)$$

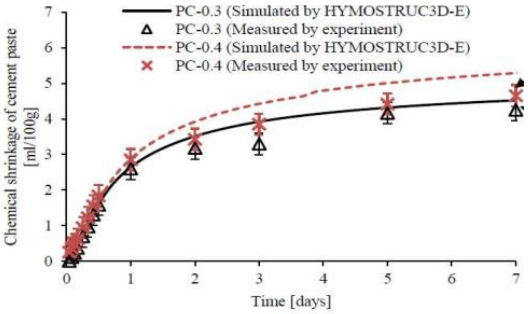
If the degree of hydration is α, then chemical shrinkage (V_{cs}) is:

$$V_{cs} = 0.2(1-\, p)\, \alpha$$

Chemical shrinkage

ASTM C1608 - Standard Test Method for Chemical Shrinkage of Hydraulic Cement Paste





Gao Peng 2018

Autogenous shrinkage

Introduction

Definition of autogenous shrinkage

By ASTM C1698-09 → The bulk strain of a sealed specimen of a cementitious mixture, not subjected to external forces and under constant temperature, measured from the time of final setting until a specified age.

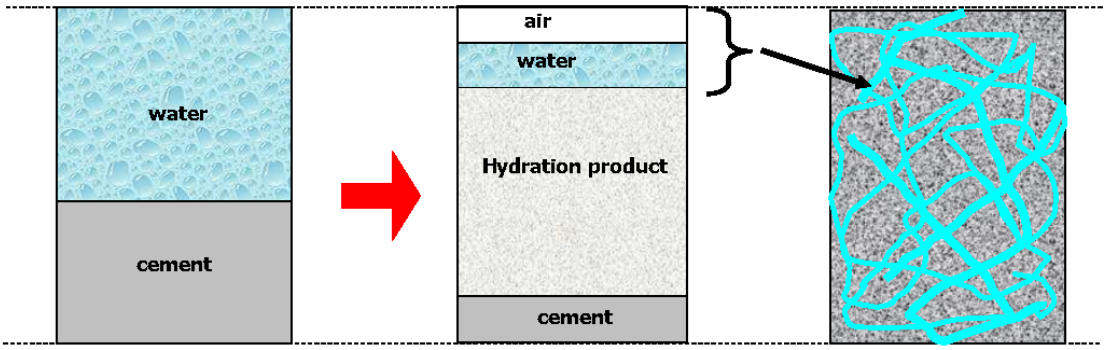
"final setting": i.e. time-zero of autogenous shrinkage occurs in standard.

"time-zero": the time which the concrete develops sufficient structure to enable tensile stress transfer through the concrete. (J. Weiss, 2002)

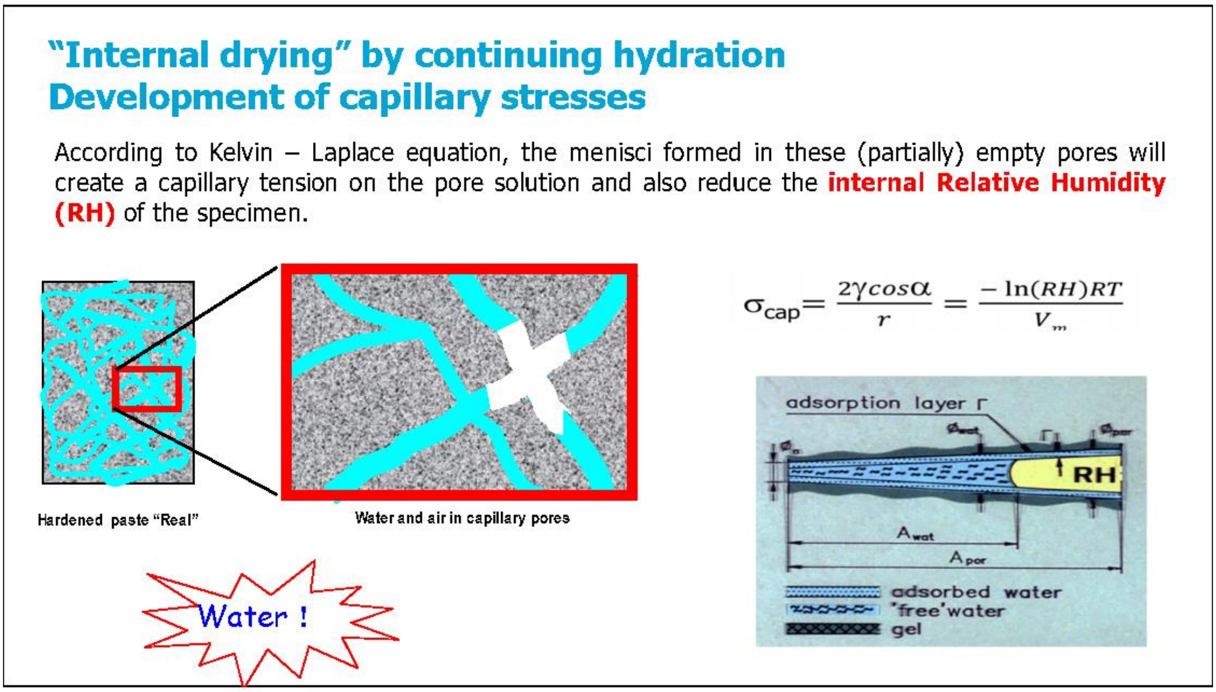
Autogenous shrinkage

Mechanism of autogenous shrinkage - Self-desiccation

- As a rigid network of hydration products forms (after final setting), chemical shrinkage leads to the creation of empty porosity and a reduction in the internal RH, this process is known as **self-desiccation**.
- Chemical shrinkage results in internal empty porosity, **not** in external volume changes



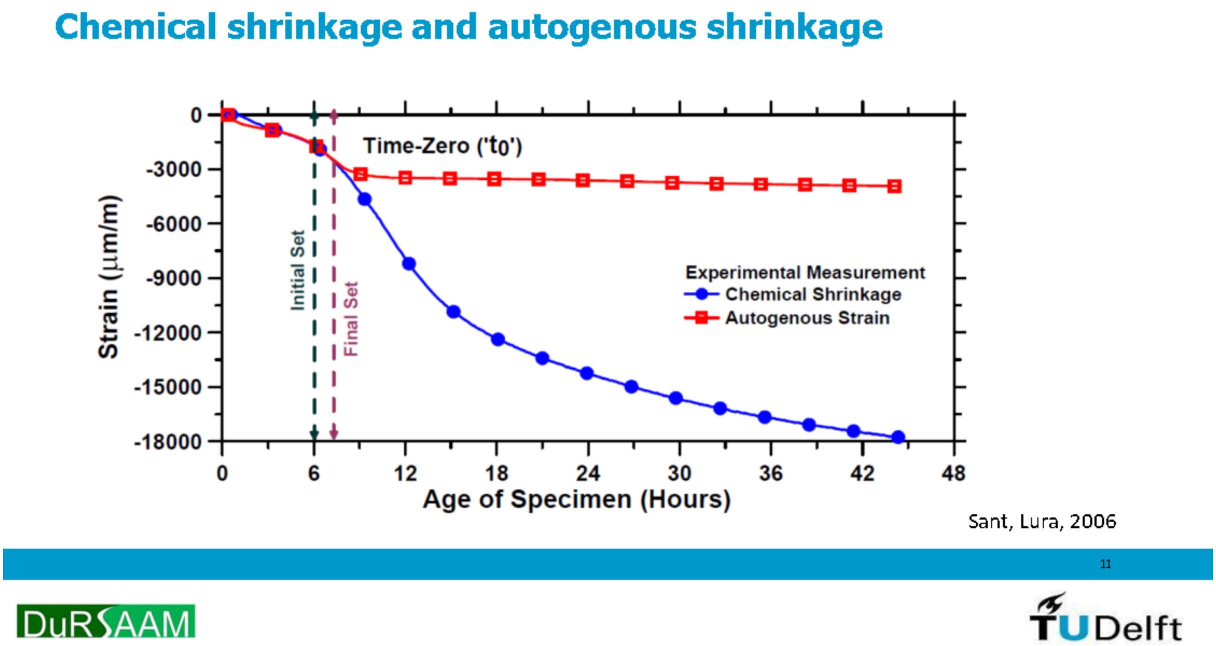
Fresh paste   Hardened paste schematic   Hardened paste "Real"



"Internal drying" by continuing hydration
Development of capillary stresses

According to Kelvin – Laplace equation, the menisci formed in these (partially) empty pores will create a capillary tension on the pore solution and also reduce the **internal Relative Humidity (RH)** of the specimen.

$$\sigma_{cap} = \frac{2\gamma\cos\alpha}{r} = \frac{-\ln(RH)RT}{V_m}$$



Chemical shrinkage and autogenous shrinkage

Sant, Lura, 2006

Autogenous shrinkage

Volume change of cement paste due to self-desiccation - macroscopy scale

Volume change:

$$\frac{\Delta V}{V} = \beta \left(\frac{R\ T}{M\ \upsilon_w} \ln\ RH \right)$$

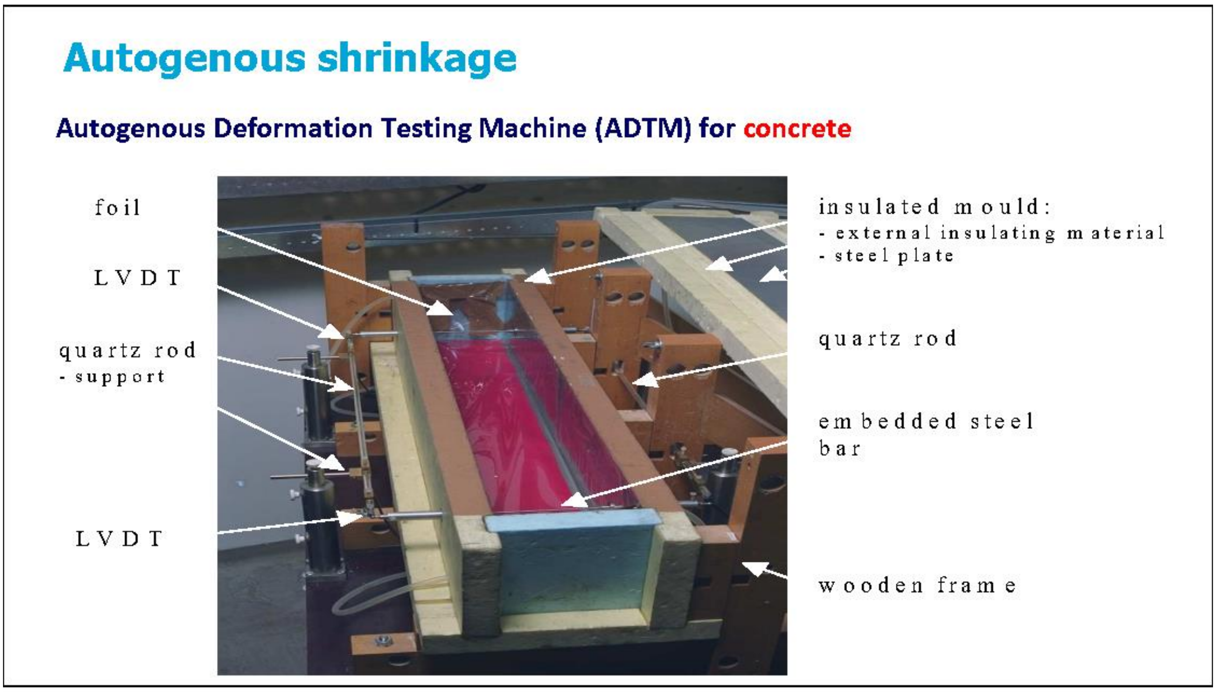
R	= universal gas constant: 8.13 J/mol	constant
T	= temperature in K	constant or variable
M	= molar weight of water	constant
υ_w	= specific volume of absorbed water	constant
RH	= relative humidity	changing with α
β	= compressibility coefficient of the specimen	changing with α

(α = degree of hydration)

Autogenous shrinkage

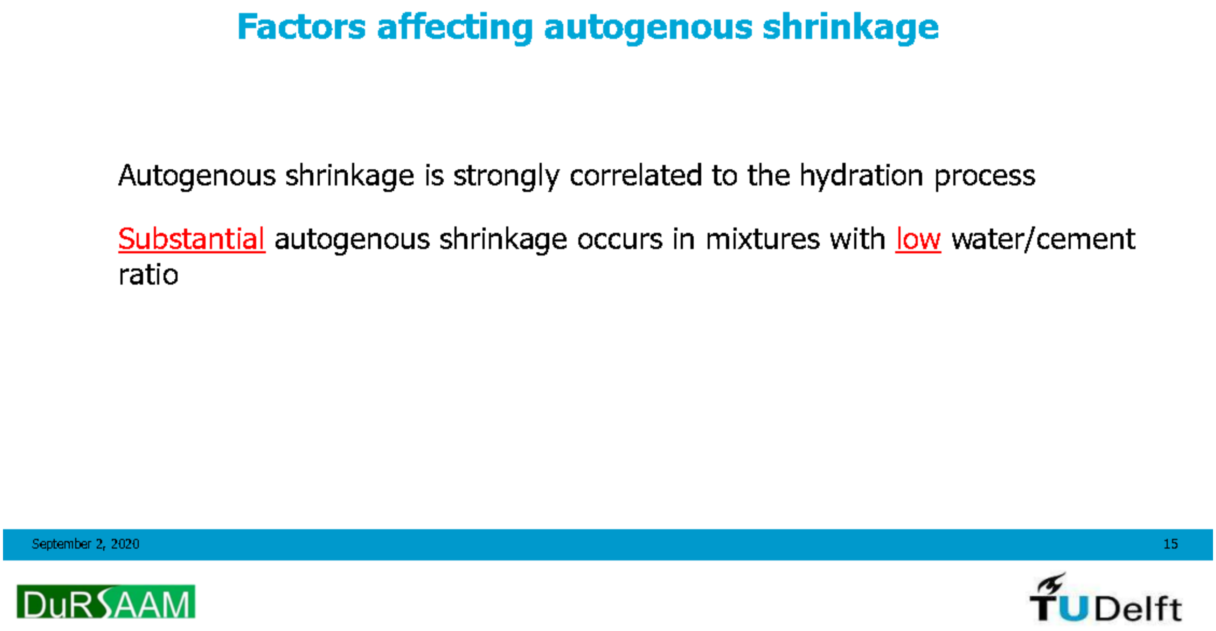
Early age autogenous shrinkage test for cement paste

- **ASTM C1698** standard originally developed by Jensen and Hansen.
- Three sealed corrugated moulds of 440 mm × Φ28.5 mm for each mix composition, T=20 ℃.



Autogenous shrinkage

Autogenous Deformation Testing Machine (ADTM) for concrete



Factors affecting autogenous shrinkage

Autogenous shrinkage is strongly correlated to the hydration process

Substantial autogenous shrinkage occurs in mixtures with low water/cement ratio

September 2, 2020

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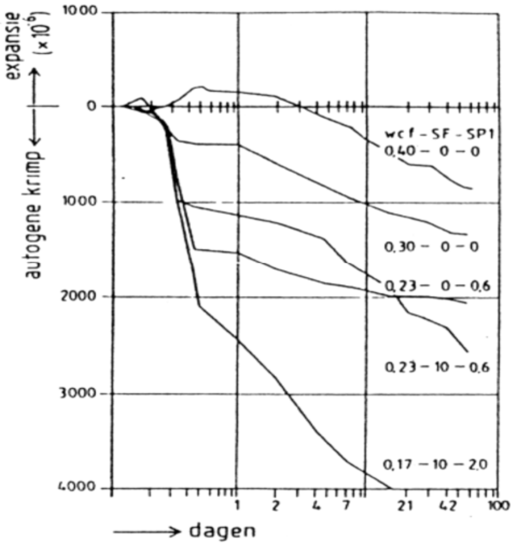
Water/cement ratio

Autogenous shrinkage of cement paste

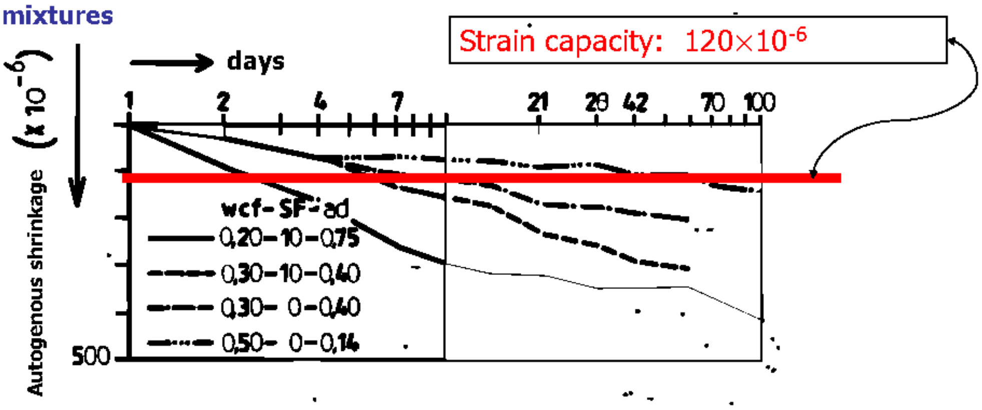
w/c	Silica ume
0.40	**0**
0.30	**0**
0.23	**0**
0.23	**10 %**
0.17	**10 %**

Tazawa e.a. 1992



Water/cement ratio

Concrete mixtures

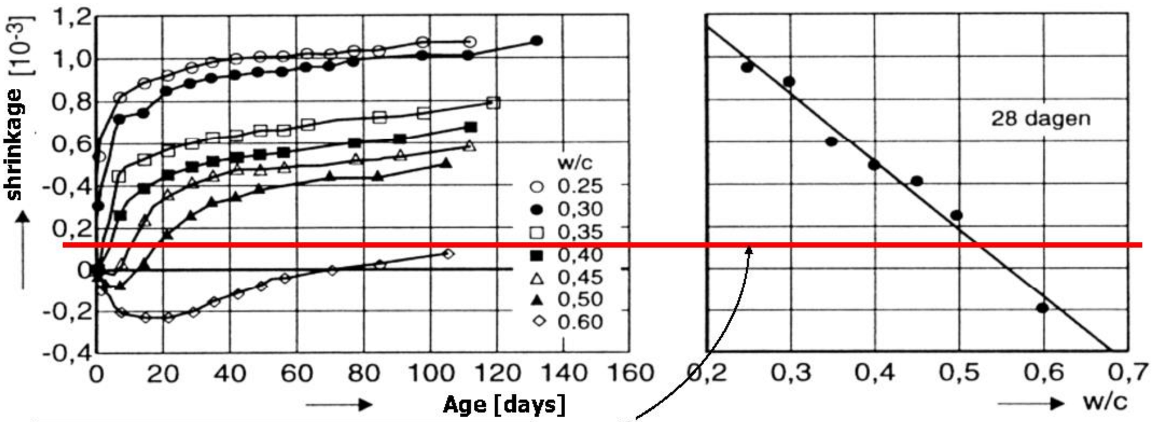


Strain capacity: 120×10^{-6}

Strain capacity concrete: 100×10^{-6} - 120×10^{-6}

Tazawa e.a. 1992

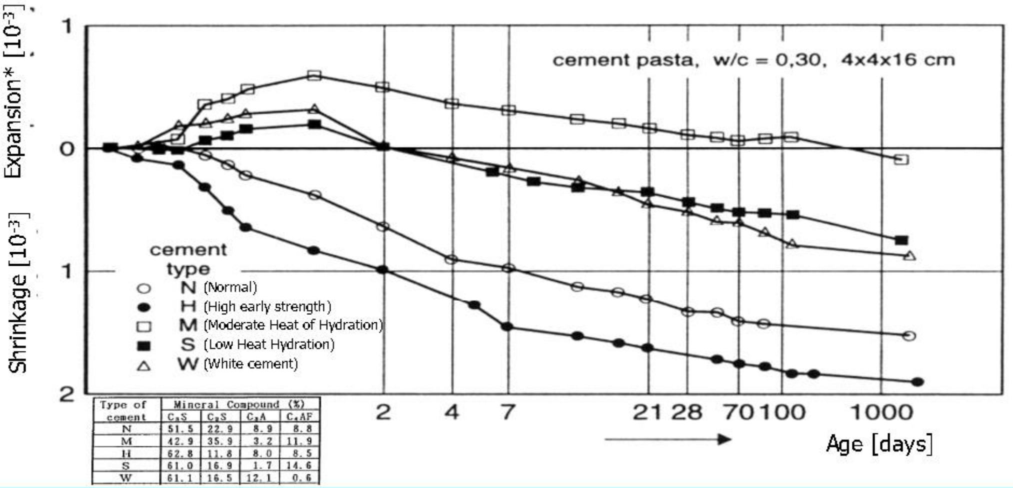
Effect w/c on autogenous shrinkage. w/c 0.25 to 0.60



Strain capacity: 120×10^{-6}

(Baroghel Bouny, 1996)

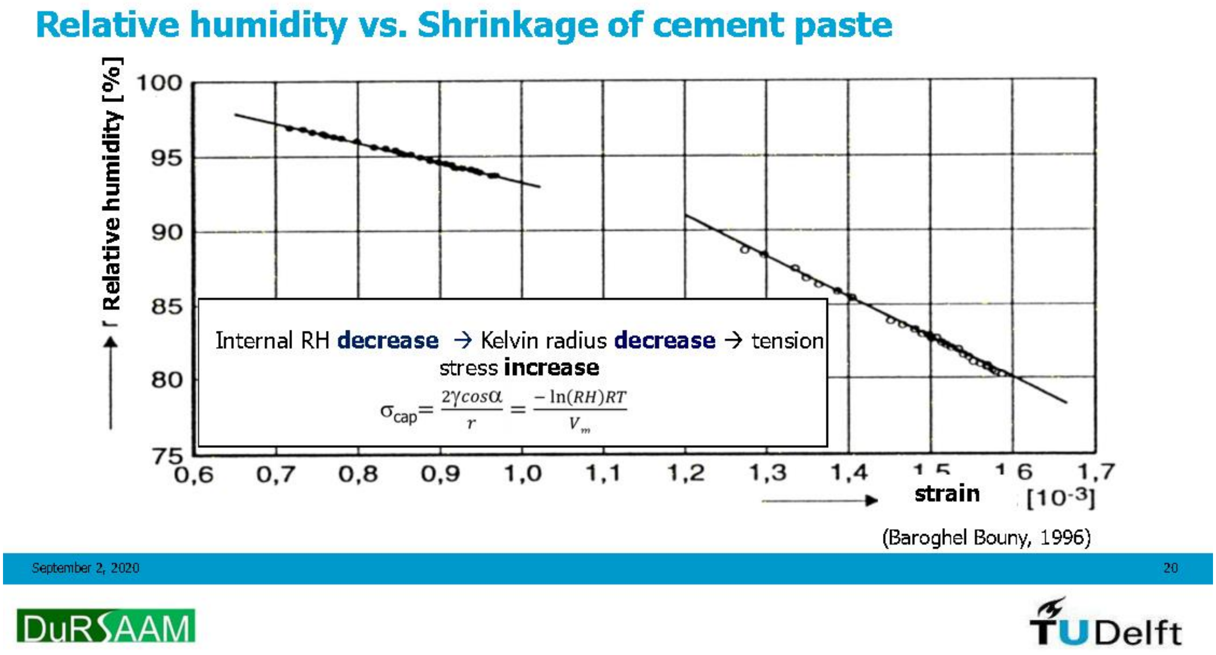
Effect cement type (cement paste. w/c 0.3)



Type of cement	Mineral Compound (%)			
	C_3S	C_2S	C_3A	C_4AF
N	51.5	22.9	8.9	8.8
M	42.9	35.9	3.2	11.9
H	62.8	11.8	8.0	8.5
S	61.0	16.9	1.7	14.6
W	61.1	16.5	12.1	0.6

Tazawa e.a. 1992

*A expansion might be due to the formation of expansive phases like ettringite or the re-absorption of the bleeding water.



Relative humidity vs. Shrinkage of cement paste

Internal RH **decrease** → Kelvin radius **decrease** → tension stress **increase**

$$\sigma_{cap} = \frac{2\gamma\cos\alpha}{r} = \frac{-\ln(RH)RT}{V_m}$$

(Baroghel Bouny, 1996)

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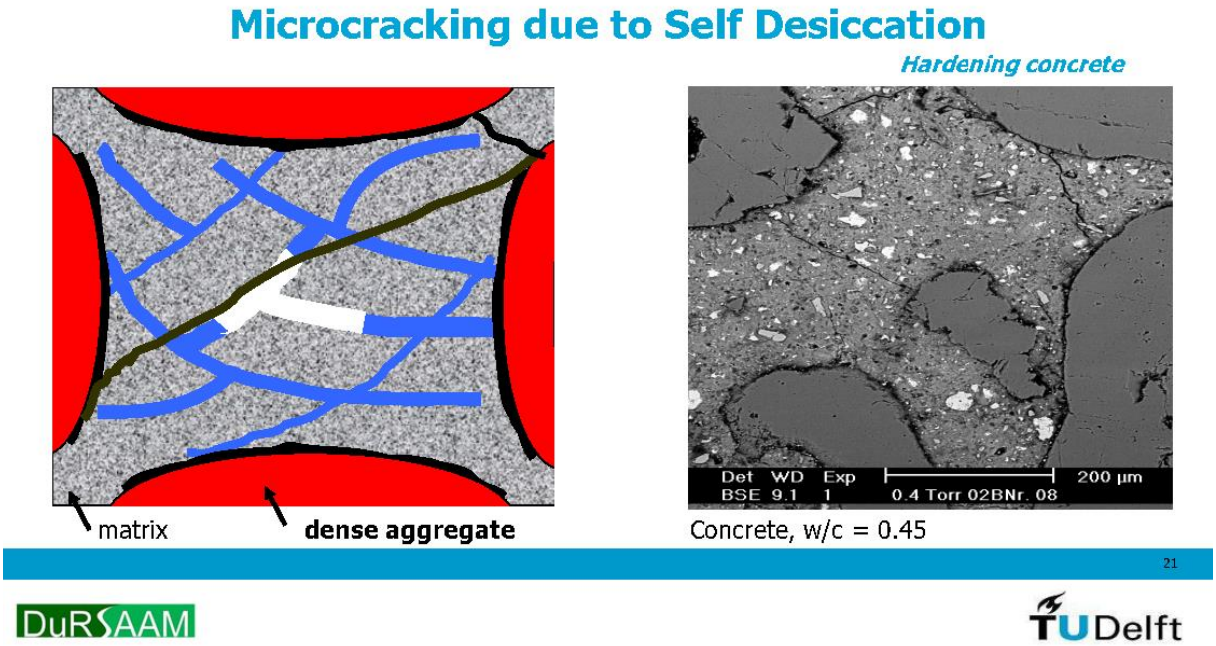

Microcracking due to Self Desiccation

Hardening concrete

Concrete, w/c = 0.45

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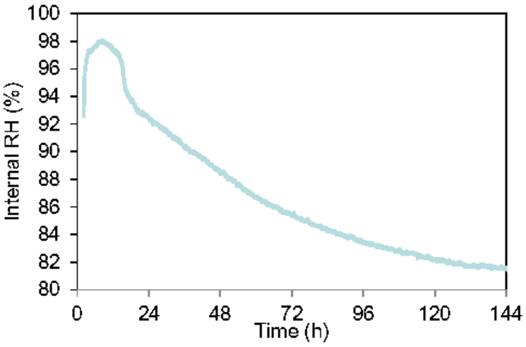
Relative Humidity can be measured

Improved hygrometer method

T (Air): 20 ± 0.1˚C

T (Water bath): 19.5 ± 0.1˚C

Avoid condensation on sensor at very early age



Cement pastes with w/c 0.28

Internal RH result is obtained since 1-2 hour after casting

*H Huang, G Ye, Examining the "time-zero" of autogenous shrinkage in high /ultra-high performance cement pastes, CCR 97 (2017), 107-114

Mitigating Autogenous shrinkage

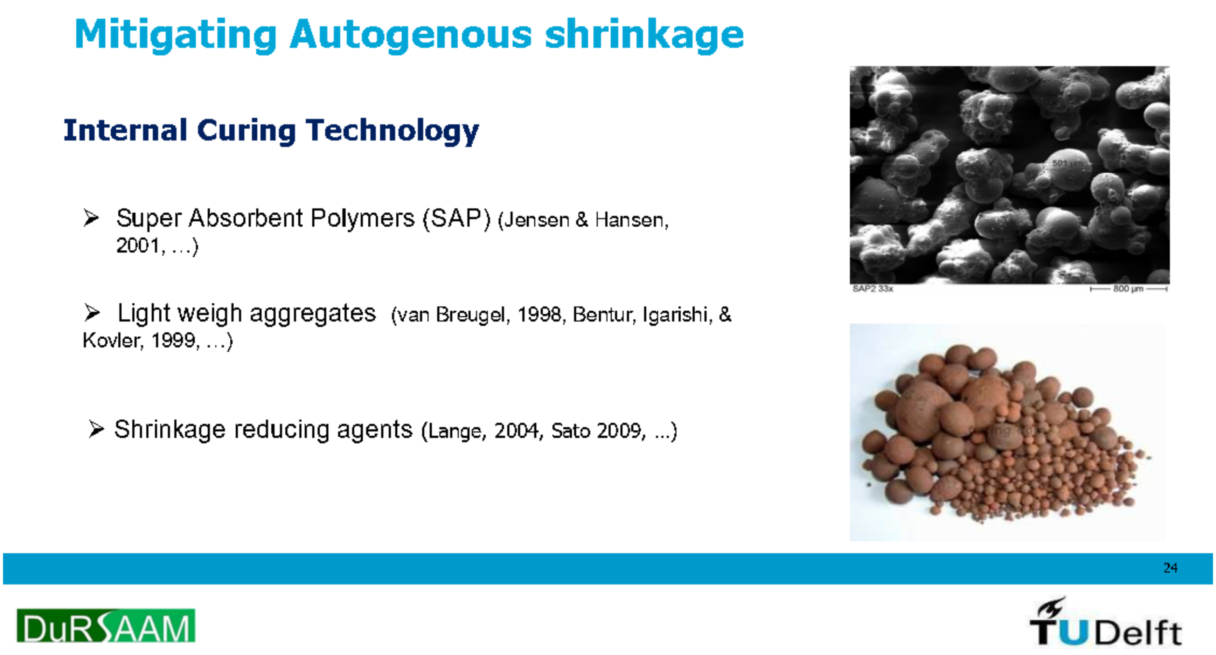
Possible solution to reduce autogenous shrinkage (AS)

Internal RH **decrease** → Kelvin radius **decrease** → tension stress **increase**

$$\sigma_{cap} = \frac{2\gamma cos\alpha}{r} = \frac{-\ln(RH)RT}{V_m}$$

Lower tension stress → bigger Kelvin radius → **higher internal RH**

Internal Curing Technology



Mitigating Autogenous shrinkage

Internal Curing Technology

- Super Absorbent Polymers (SAP) (Jensen & Hansen, 2001, …)
- Light weigh aggregates (van Breugel, 1998, Bentur, Igarishi, & Kovler, 1999, …)
- Shrinkage reducing agents (Lange, 2004, Sato 2009, …)

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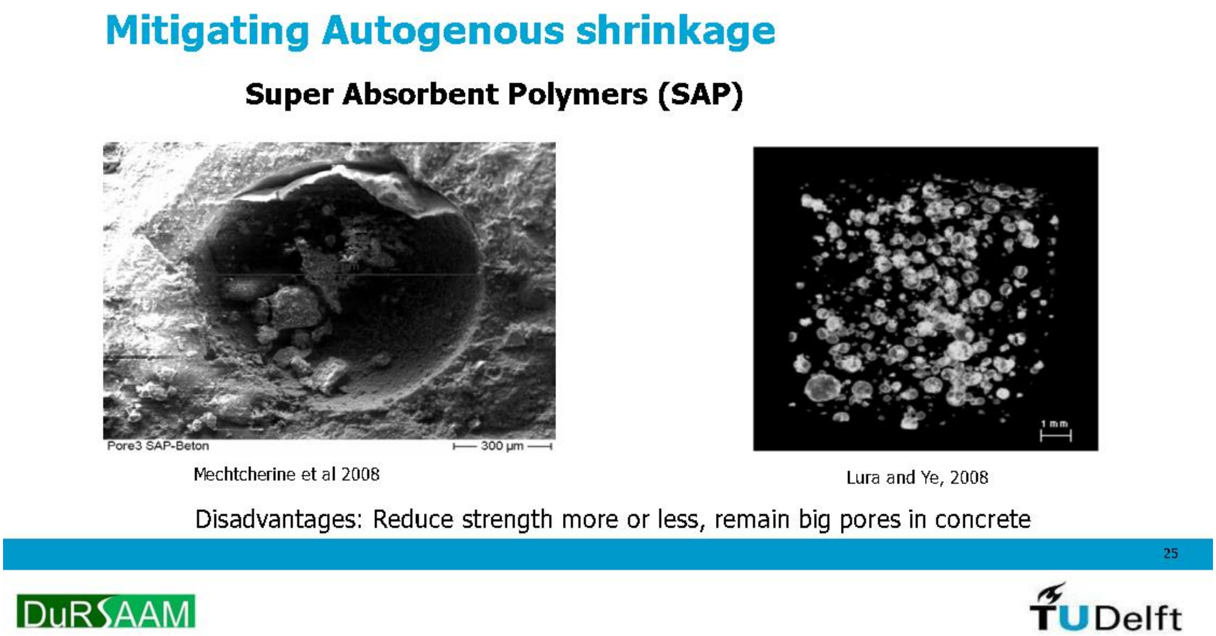

Mitigating Autogenous shrinkage

Super Absorbent Polymers (SAP)

Mechtcherine et al 2008

Lura and Ye, 2008

Disadvantages: Reduce strength more or less, remain big pores in concrete

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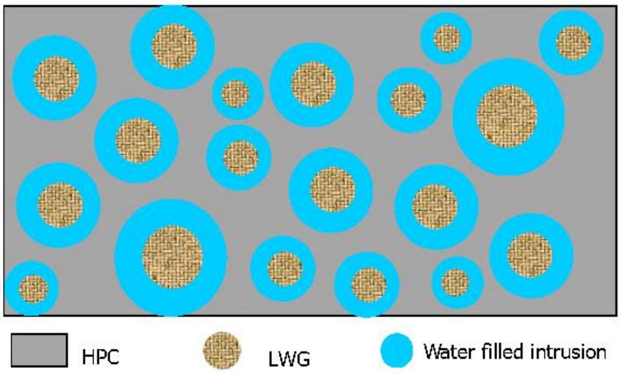
Mitigating Autogenous shrinkage

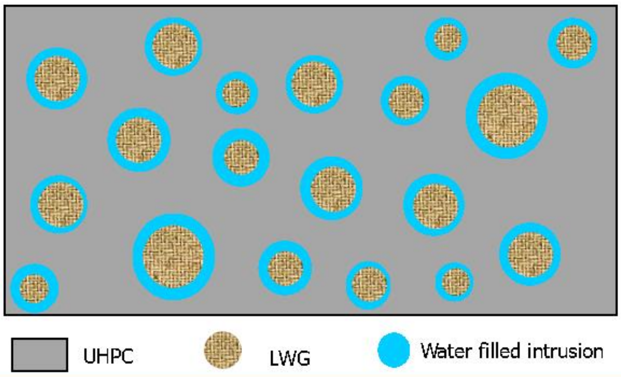
Light Weigh Aggregates (LWG) for HPC



After Bentz and Weiss, 2010

Mitigating Autogenous shrinkage

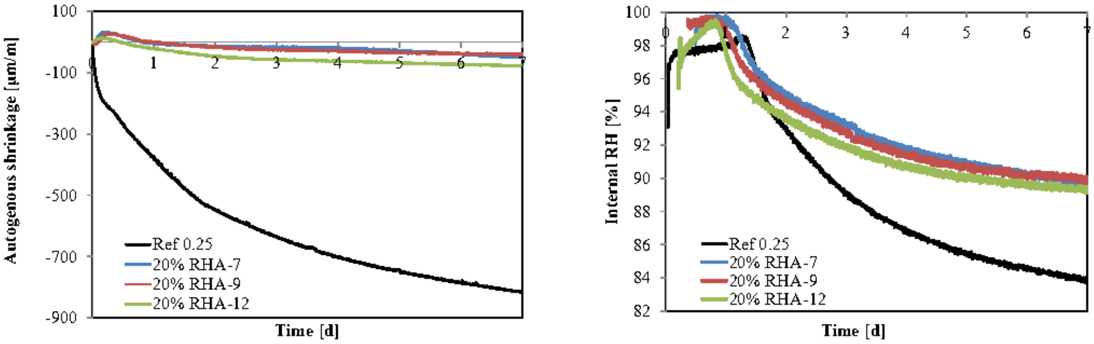
Light Weigh Aggregates (LWG) for UHPC



After Bentz and Weiss, 2010

Mitigating Autogenous shrinkage

Using RHA as an example on Mitigating the autogenous shrinkage

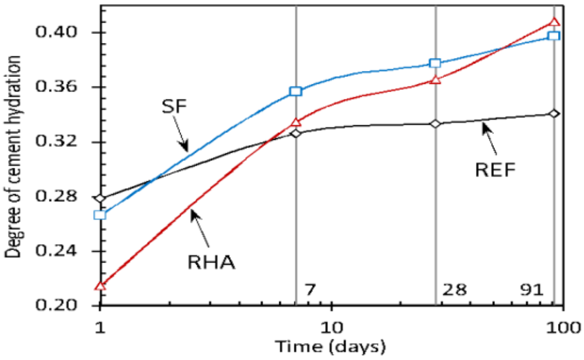


(a) (b)

Cement pastes incorporating RHA with different particle sizes (a) autogenous shrinkage since the onset of self-desiccation; (b) internal RH change since casting.

RHA can reduce the AS

Degree of hydration show the consequence of internal curing by RHA



- Curing temperature: 20°C
- The mean particle size of RHA: 5.6 µm
- The water to binder ratio: 0.18, by weight
- Cement replacement percentage: 20%

Tuan and Ye, 2012

Drying shrinkage

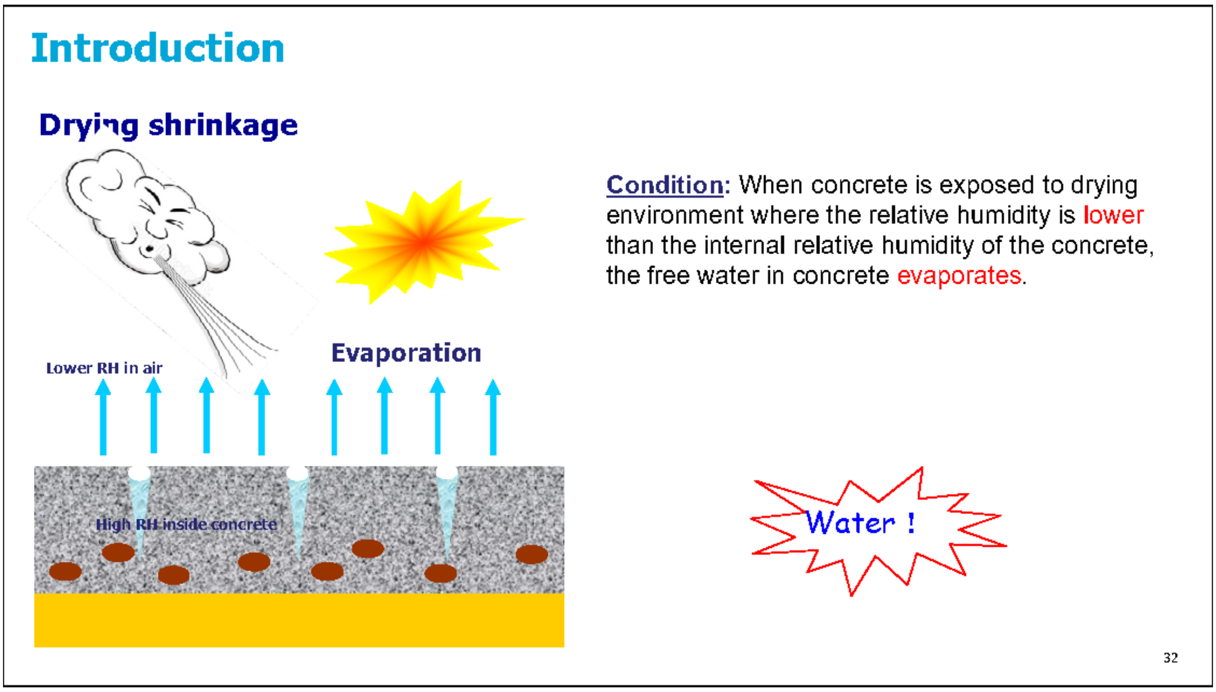
Introduction

Definition of drying shrinkage

- As the volume reduction that concrete suffers as a consequence of the moisture migration when exposed to a lower relative humidity environment than the initial one in its own pore system.

- Dry shrinkage is independent of applied loads

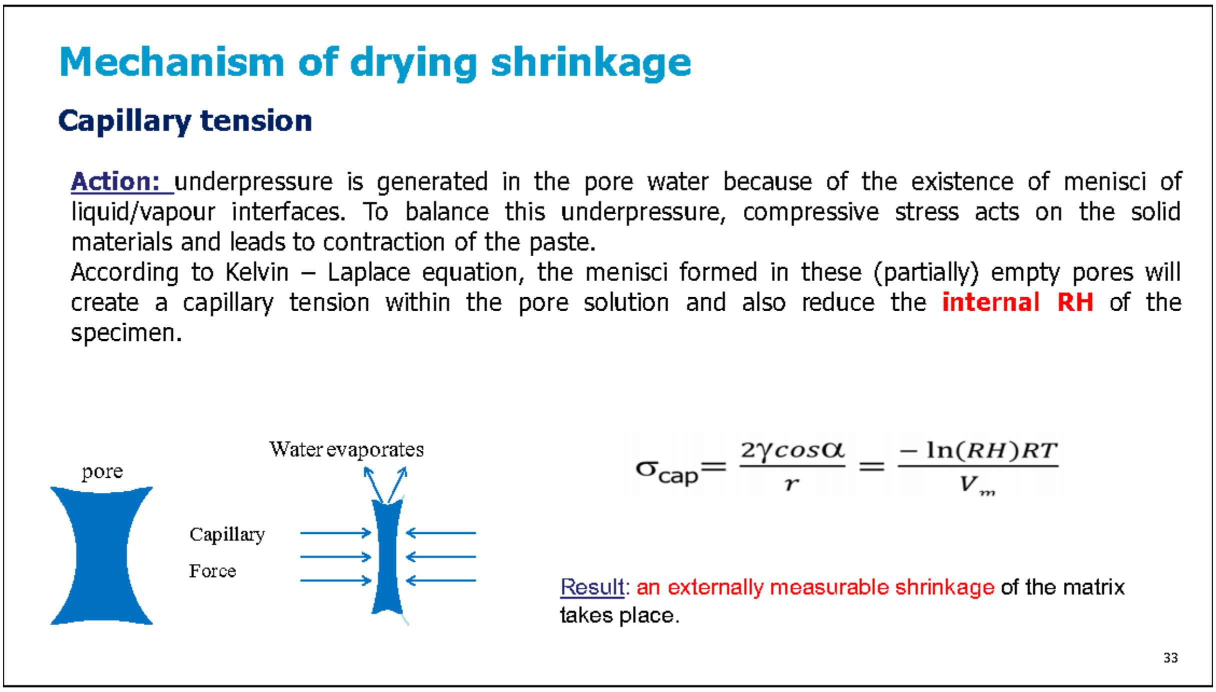
- Dry shrinkage is the time-dependent strain measured in an unloaded and unstrained specimen at constant temperature.



Introduction

Drying shrinkage

Condition: When concrete is exposed to drying environment where the relative humidity is lower than the internal relative humidity of the concrete, the free water in concrete evaporates.



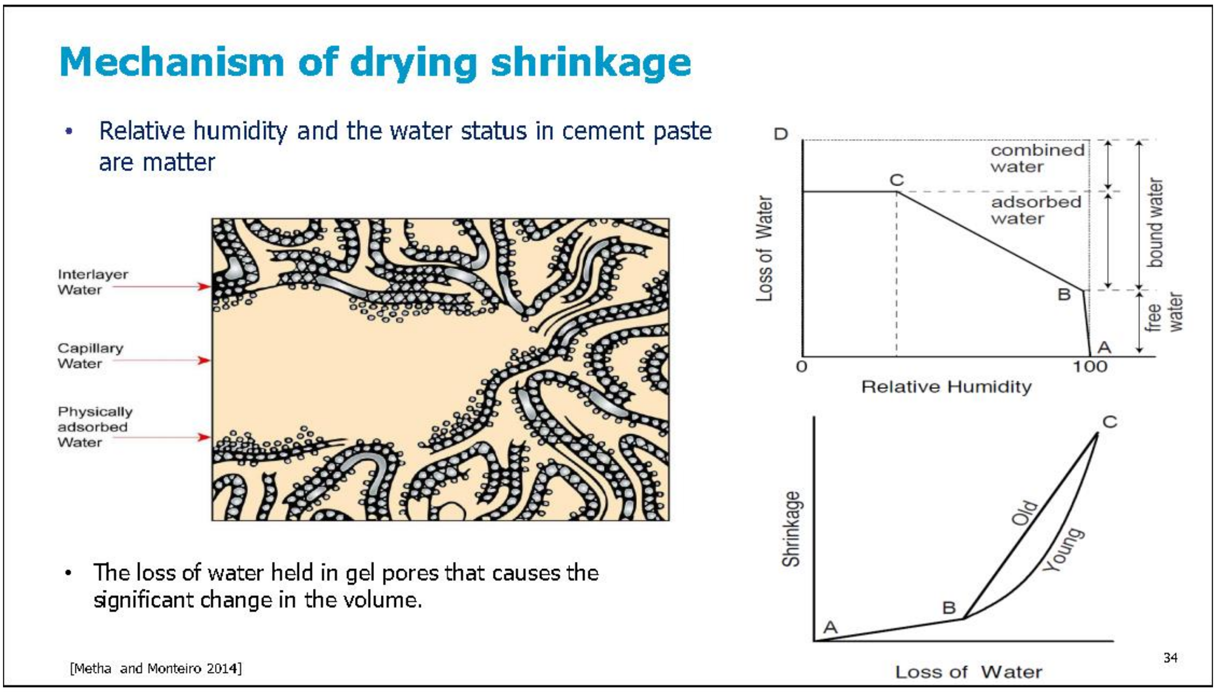
Mechanism of drying shrinkage

Capillary tension

Action: underpressure is generated in the pore water because of the existence of menisci of liquid/vapour interfaces. To balance this underpressure, compressive stress acts on the solid materials and leads to contraction of the paste.
According to Kelvin – Laplace equation, the menisci formed in these (partially) empty pores will create a capillary tension within the pore solution and also reduce the **internal RH** of the specimen.

$$\sigma_{cap} = \frac{2\gamma\cos\alpha}{r} = \frac{-\ln(RH)RT}{V_m}$$

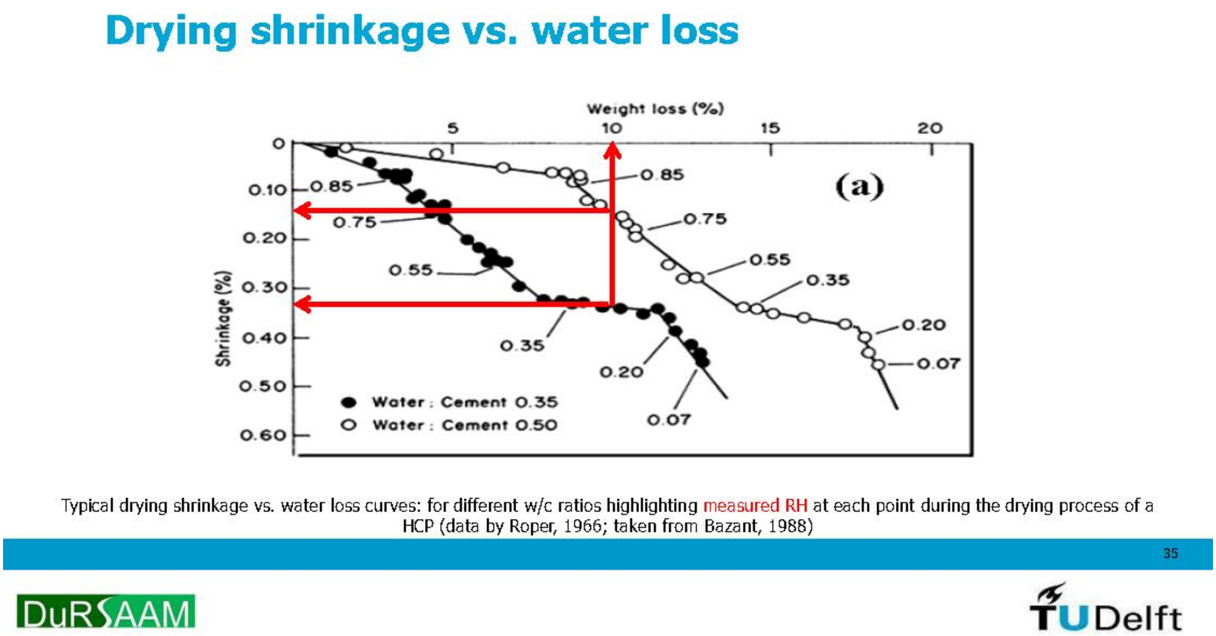
Result: an externally measurable shrinkage of the matrix takes place.



Mechanism of drying shrinkage

- Relative humidity and the water status in cement paste are matter
- The loss of water held in gel pores that causes the significant change in the volume.

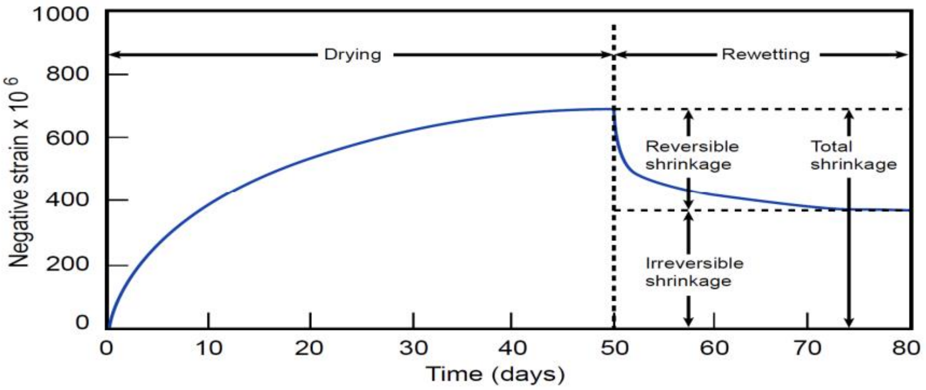
[Metha and Monteiro 2014]



Drying shrinkage vs. water loss

Typical drying shrinkage vs. water loss curves: for different w/c ratios highlighting measured RH at each point during the drying process of a HCP (data by Roper, 1966; taken from Bazant, 1988)

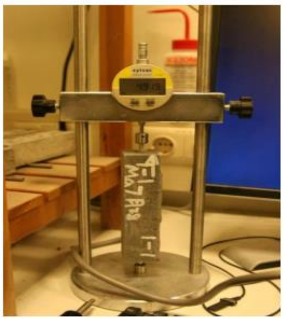
Reversibility



Moisture movement in concrete

[Metha and Monteiro 2014]

Drying shrinkage - Test method of cement mortar



- ASTM C175
- First 7 days sealed curing at 20 ℃
- Test was carried out in a room with 50% RH and 20 ℃

Comparator (accuracy 0.001mm)

The length and mass were monitored at regular time intervals.

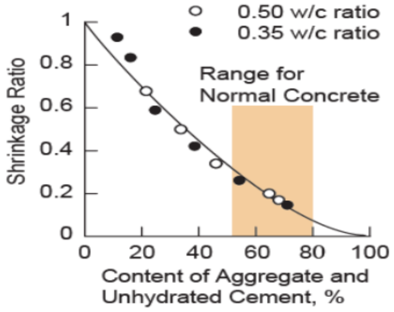
Factors affecting drying shrinkage

Materials and mix-proportion

Powers, 1961

$$\frac{S_c}{S_p} = (1-g)^n$$

S_c, shrinkage of concrete
S_p shrinkage of cement paste
g, the volume fraction of aggregate in concrete

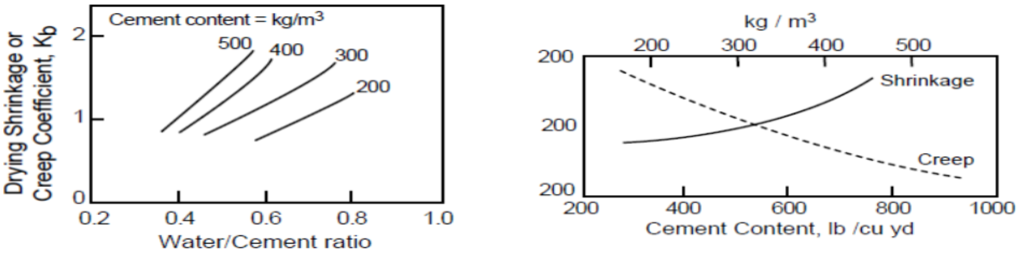


[Metha and Monteiro 2014]

Factors affecting drying shrinkage

Materials and mix-proportion

- Cement content and water/cement ratio



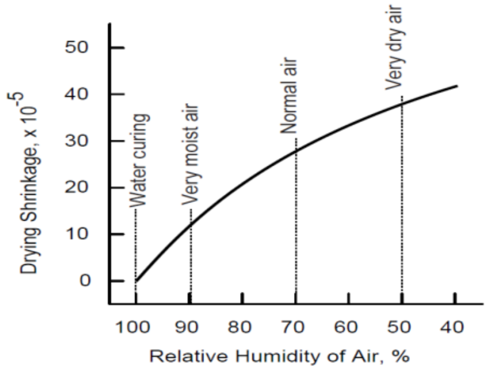
(a) (b)

Effect of water-cement ratio (a) and cement content (b) on dry shrinkage

[Metha and Monteiro 2014]

Factors affecting drying shrinkage

Humidity



Influence of the relative humidity on drying shrinkage

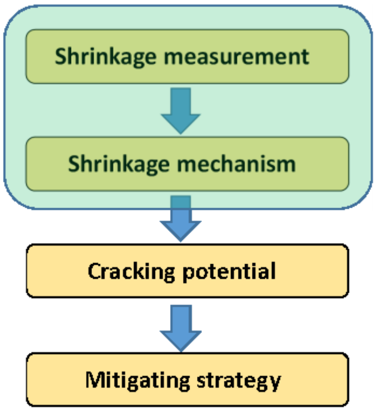
[Metha and Monteiro 2014]

Autogenous shrinkage and cracking potential

of

Alkali activated concrete

Contents



Shrinkage measurement

Shrinkage mechanism

Cracking potential

Mitigating strategy

Autogenous shrinkage mechanism

Raw Materials

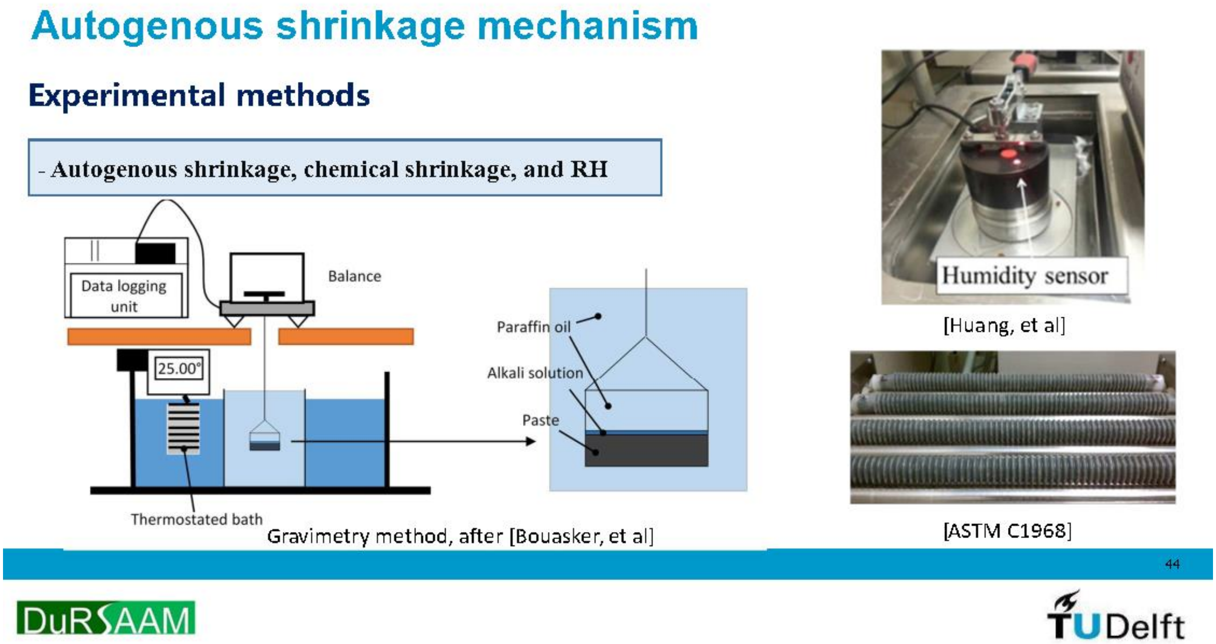
Chemical compositions of slag and fly ash measured with XRF

	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3	K_2O	TiO_2	Other	LOI
Slag	31.77	13.25	40.50	9.27	0.52	1.49	0.34	0.97	0.21	1.31
Fly ash	56.8	23.8	4.8	1.5	7.2	0.3	1.6	1.2	1.6	1.2

	D50
Slag	18.3 μm
Fly ash	48.1 μm

Mixture proportions of AAS pastes with and without MK

Mixture	Slag (g)	Fly ash (g)	SiO_2 (mol)	Na_2O (mol)	H_2O (g)
AAS	1000	-	1.146	0.76	384
AASF	500	500	1.146	0.76	384



Autogenous shrinkage mechanism

Experimental methods

- Autogenous shrinkage, chemical shrinkage, and RH

Gravimetry method, after [Bouasker, et al]

[Huang, et al]

[ASTM C1968]

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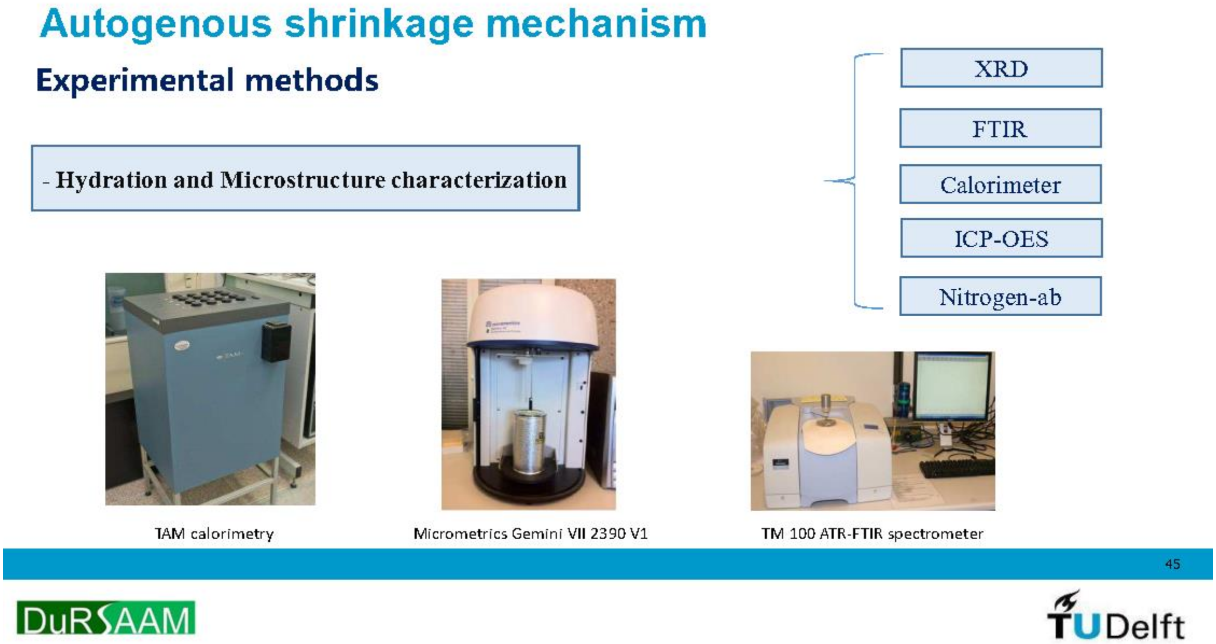

Autogenous shrinkage mechanism

Experimental methods

- Hydration and Microstructure characterization

- XRD
- FTIR
- Calorimeter
- ICP-OES
- Nitrogen-ab

TAM calorimetry

Micrometrics Gemini VII 2390 V1

TM 100 ATR-FTIR spectrometer

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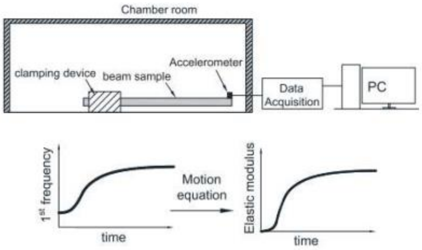
Autogenous shrinkage mechanism

Experimental methods

- Setting, compressive strength, flexural strength and elastic modulus

Automatic Vicat apparatus

E-modulus testing setup

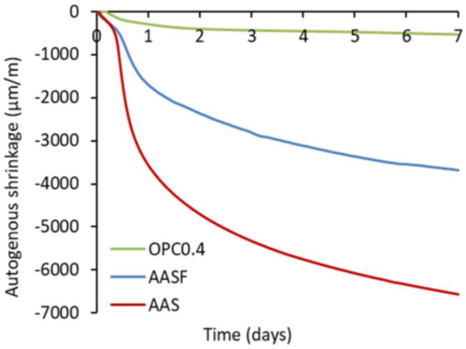


Autogenous shrinkage mechanism

Setting time & autogenous shrinkage

Vicat setting time of the pastes (min).

Mixture	AAS	AASF	OPC0.4
Initial setting	25	63	240
Final setting	35	103	340

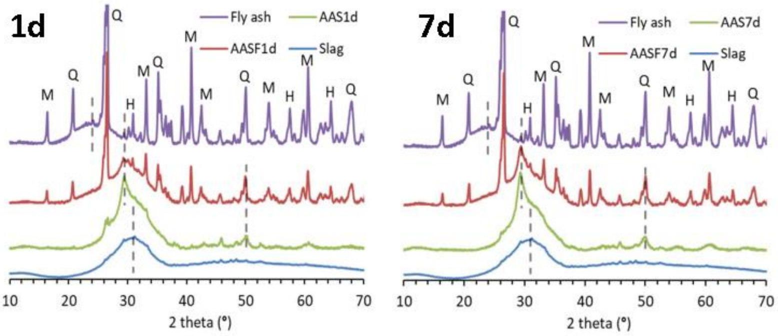


Autogenous shrinkage of AAS and AASF pastes in comparison with OPC paste.

Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107

Chapter 3 Autogenous shrinkage mechanism

Microstructure characterization



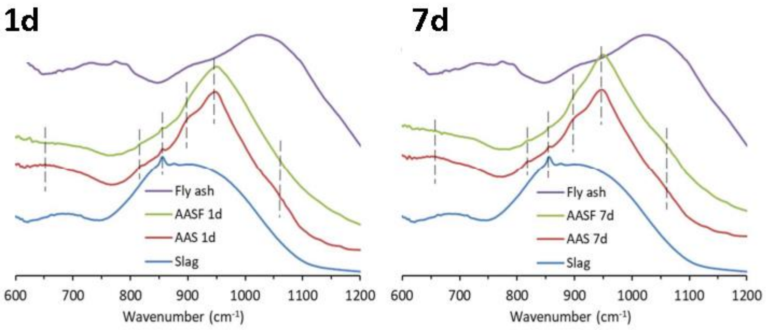
- Main reaction products: CASH gel
- Increases with time
- Decreases when slag is replaced by fly ash

XRD patterns. M, Q and H stand for mullite, quartz and hematite, respectively.

Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107

Autogenous shrinkage mechanism

Microstructure characterization



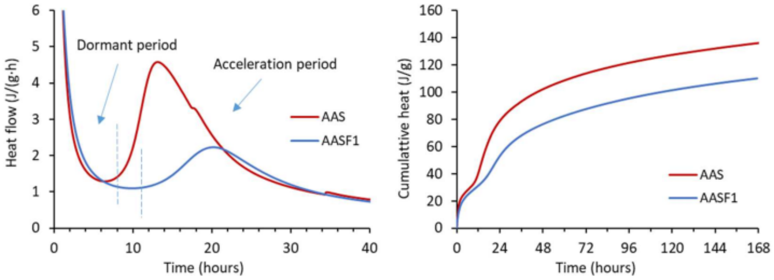
- 950, 900, 815, 660 cm^{-1} for CASH gels.
- Increases with time
- Decreases when slag is replaced by fly ash
- No NASH gel is detected.

FITR spectra

Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107

Autogenous shrinkage mechanism

Microstructure characterization



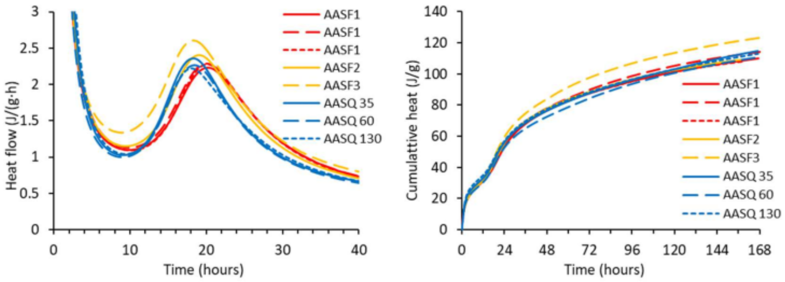
Heat flow and cumulative heat of AAS and AASF pastes

- Later acceleration period and lower heat release for AASF.
- Fly ash lower reactivity

Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107

Autogenous shrinkage mechanism

Microstructure characterization



Heat flow and cumulative heat of AASF pastes made from fly ashes ordered in different batches and AASQ pastes where fly ash is replaced by quartz with different particle sizes.

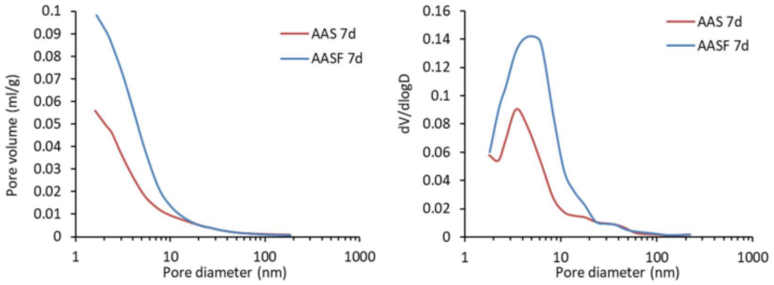
Role of fly ash?

- Little difference from quartz…

Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107

Autogenous shrinkage mechanism

Microstructure characterization



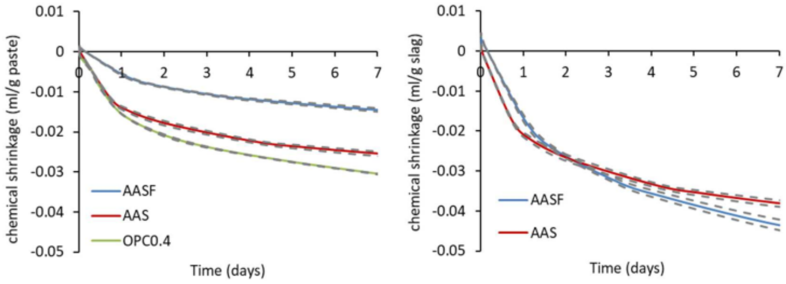
Pore size distribution of for AAS and AASF

- The presence of fly ash induces a coarser pore structure.

Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107

Autogenous shrinkage mechanism

Chemical shrinkage

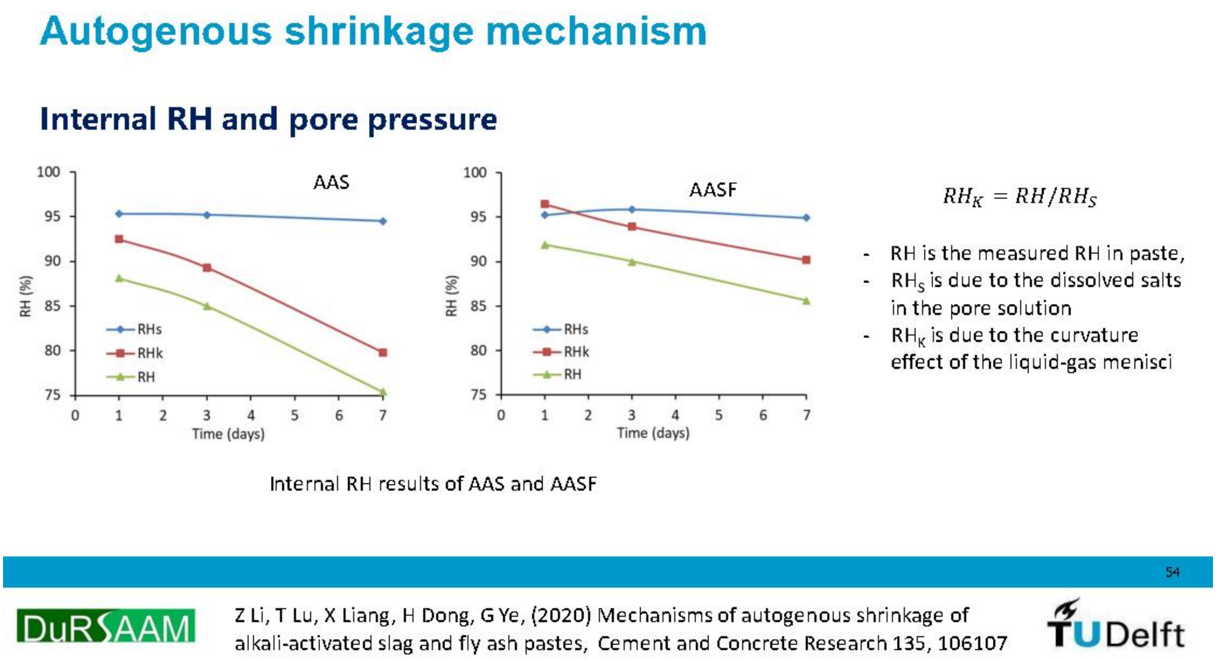


(a) (b)

(a) Chemical shrinkage of AAS and AASF pastes in comparison with that of OPC paste, in ml per gram of paste and (b) chemical shrinkage of AAS and AASF paste in ml per gram of slag.

- The presence of fly ash induces a lower chemical shrinkage.
- In the unit of mass of slag, the two chemical shrinkages are similar.

Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107



Autogenous shrinkage mechanism

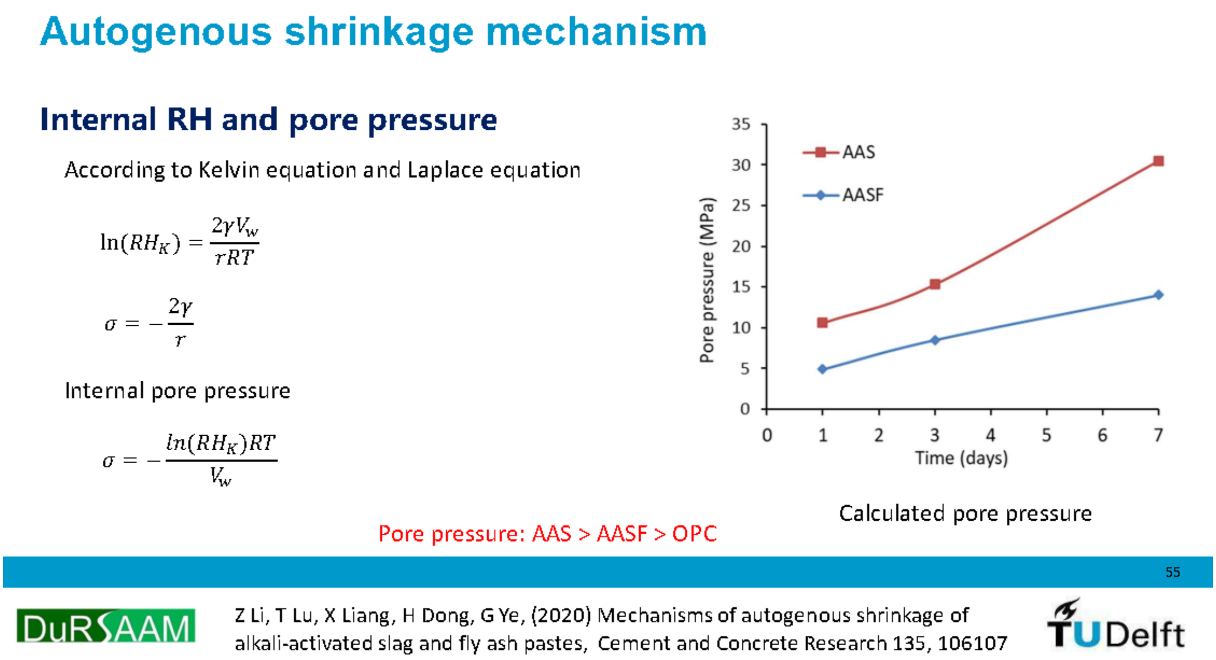
Internal RH and pore pressure

Internal RH results of AAS and AASF

$$RH_K = RH/RH_S$$

- RH is the measured RH in paste,
- RH_S is due to the dissolved salts in the pore solution
- RH_K is due to the curvature effect of the liquid-gas menisci

Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107



Autogenous shrinkage mechanism

Internal RH and pore pressure

According to Kelvin equation and Laplace equation

$$\ln(RH_K) = \frac{2\gamma V_w}{rRT}$$

$$\sigma = -\frac{2\gamma}{r}$$

Internal pore pressure

$$\sigma = -\frac{ln(RH_K)RT}{V_w}$$

Calculated pore pressure

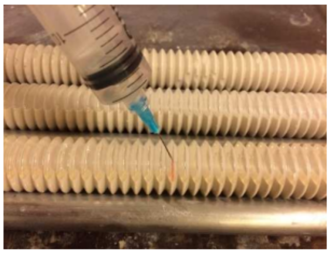
Pore pressure: AAS > AASF > OPC

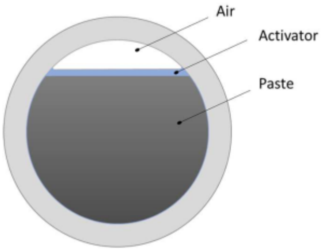
Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107

Autogenous shrinkage mechanism

Internal RH and pore pressure

Is pore pressure the only driving force of autogenous shrinkage?

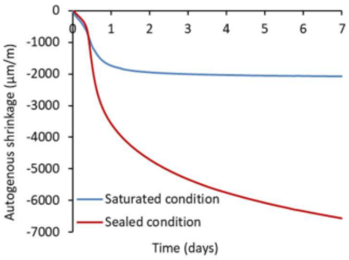




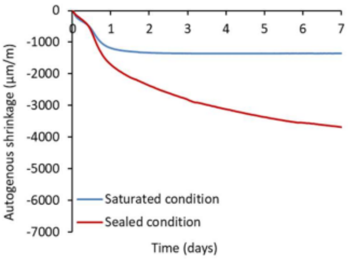
Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107

Autogenous shrinkage mechanism

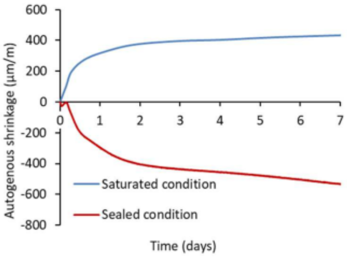
Shrinkage under saturated condition



AAS



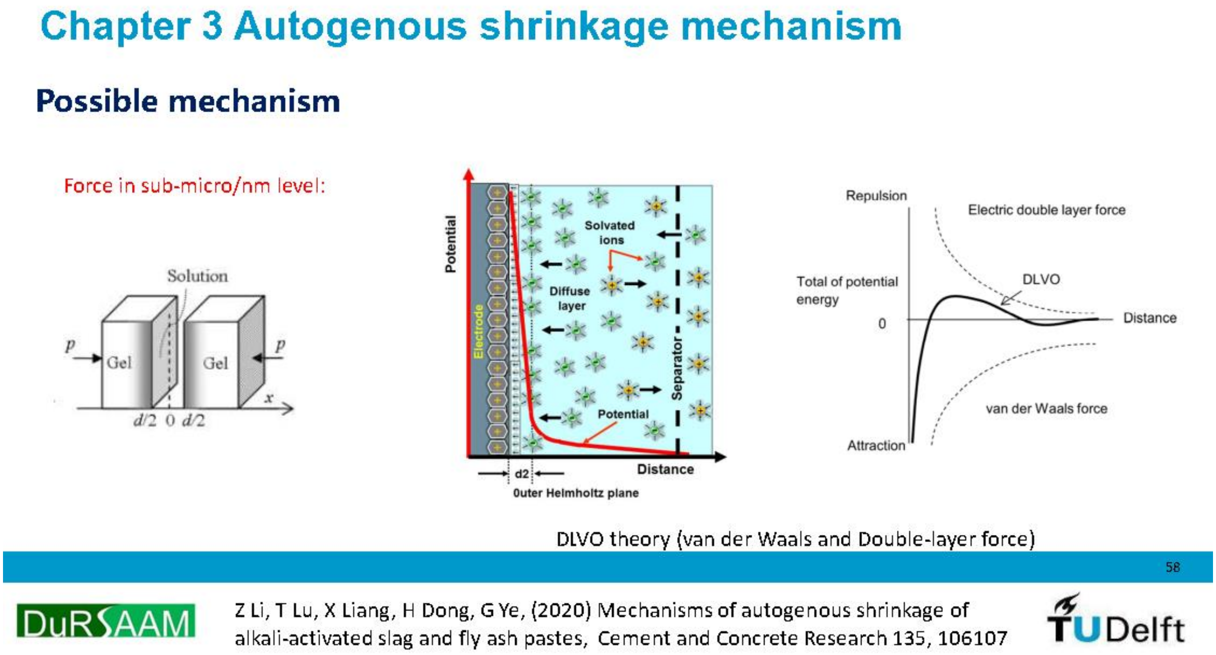
AASF



OPC

- Self-desiccation is not the only mechanism…
- Especially before the deceleration period.

Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107



Chapter 3 Autogenous shrinkage mechanism

Possible mechanism

Force in sub-micro/nm level:

DLVO theory (van der Waals and Double-layer force)

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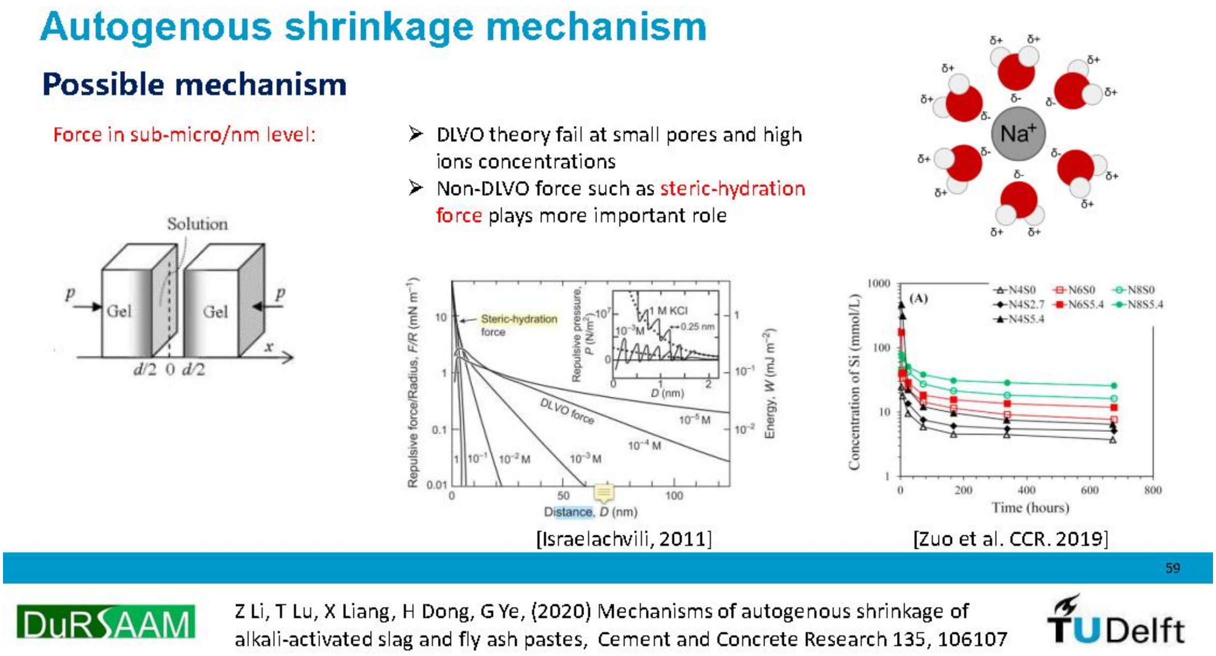
Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107



Autogenous shrinkage mechanism

Possible mechanism

Force in sub-micro/nm level:

- DLVO theory fail at small pores and high ions concentrations
- Non-DLVO force such as steric-hydration force plays more important role

[Israelachvili, 2011]

[Zuo et al. CCR. 2019]

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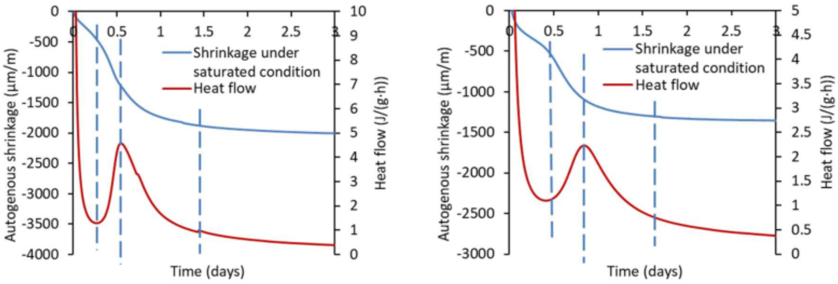
Z Li, T Lu, X Liang, H Dong, G Ye, (2020) Mechanisms of autogenous shrinkage of alkali-activated slag and fly ash pastes, Cement and Concrete Research 135, 106107

Autogenous shrinkage mechanism

Possible mechanism



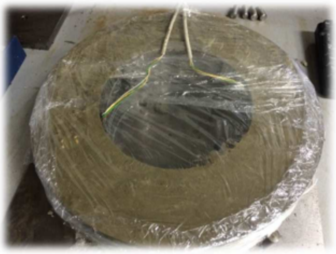
Shrinkage of AAS (left) and AASF (right) under saturated condition, plotted together with the reaction heat

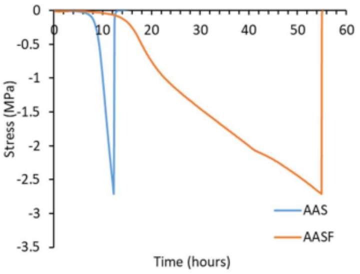
- Ions concentrations ↓
- Repulsive force ↓
- The skeleton shrinks

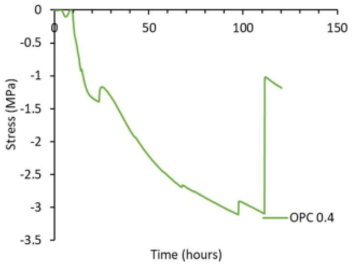
Z Li, S Zhang, X Liang, G Ye (2020) Cracking potential of alkali-activated slag and fly ash concrete subjected to restrained autogenous shrinkage, Cement and Concrete Composites, 103767

Autogenous shrinkage induced stress

Paste, by ring test:







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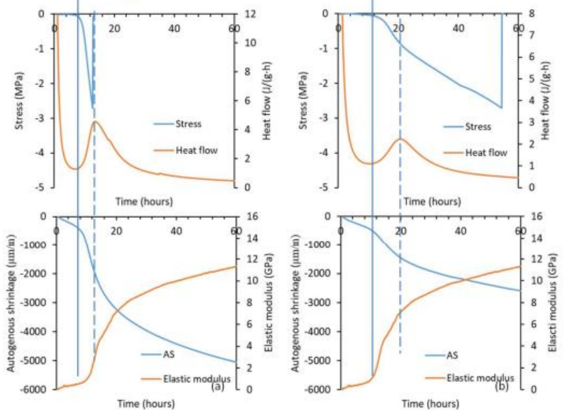
Autogenous shrinkage induced stress



Autogenous shrinkage -induced stress plotted together with reaction heat , autogenous shrinkage (AS) and elastic modulus of (a) AAS and (b) AAS F. 0 h of all the curves represents the moment of adding activator into the precursors. The solid line and the dashed line indicate the start of the acceleration period and the peak ing time of the reaction heat, respectively.

Z Li, S Zhang, X Liang, G Ye (2020) Cracking potential of alkali-activated slag and fly ash concrete subjected to restrained autogenous shrinkage, Cement and Concrete Composites, 103767

Cracking potential of geopolymer concrete

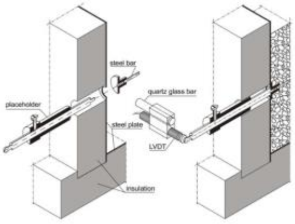
Shrinkage measurement

Shrinkage mechanism

Cracking potential

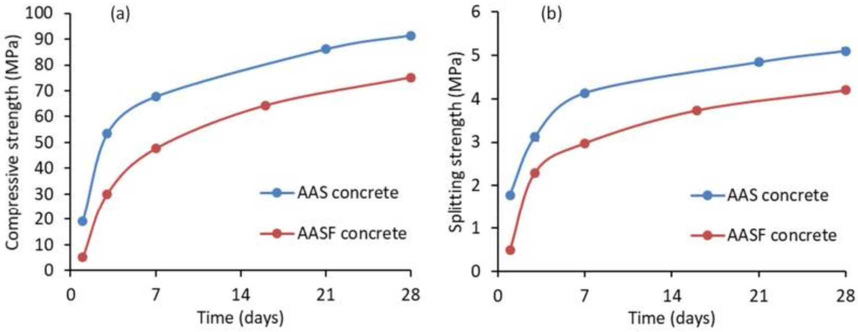
Mitigating strategy

Thermal Stress Testing Machine



Z Li, S Zhang, X Liang, G Ye (2020) Cracking potential of alkali-activated slag and fly ash concrete subjected to restrained autogenous shrinkage, Cement and Concrete Composites, 103767

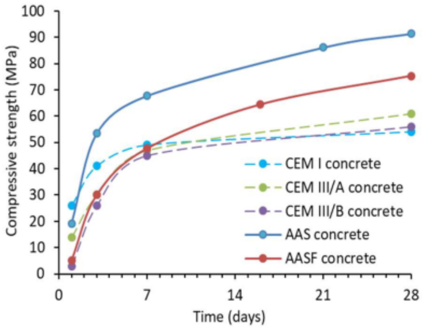
Compressive and splitting strength of geopolymer concrete



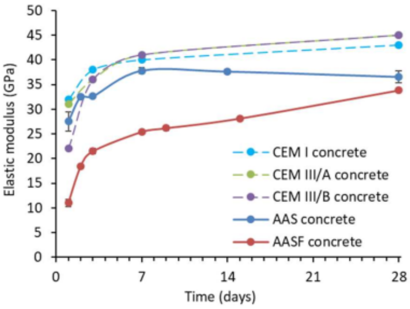
Compressive (a) and splitting strength (b) of AAS and AASF concrete. The strength was tested at 1, 3, 7, 28 days and the day when the beam in TSTM cracked. For splitting strength, the error bar is shown in the diagram, but it is too small to be clearly distinguished from the marker.

Z Li, S Zhang, X Liang, G Ye (2020) Cracking potential of alkali-activated slag and fly ash concrete subjected to restrained autogenous shrinkage, Cement and Concrete Composites, 103767

Compressive and splitting strength of geopolymer concrete



Compressive strength of OPC based concrete (dashed lines), in comparison with AASF concrete (solid line).



Elastic modulus of AAM concrete (solid lines), in comparison with OPC based concrete (dashed lines)

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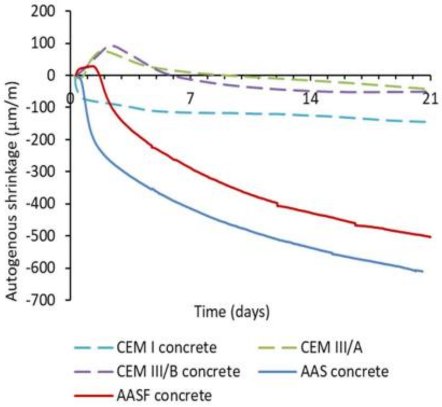
Autogenous shrinkage of geopolymer concrete

Geopolymer concrete



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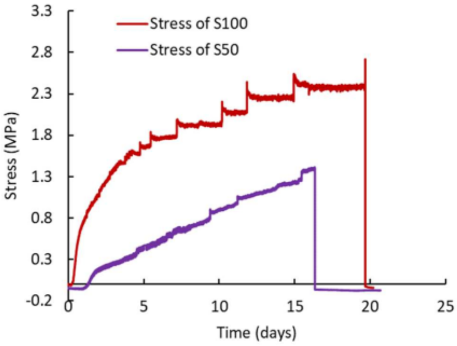
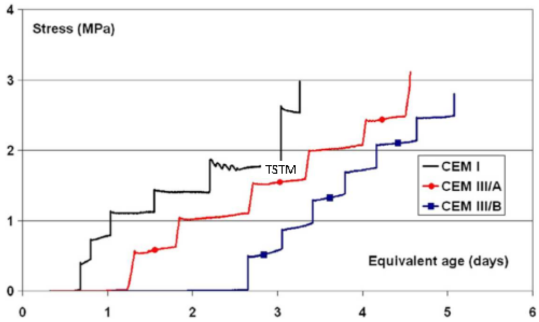
Autogenous shrinkage induced stress – TSTM test



Stress and cracking of geopolymer concrete



Stress and cracking of OPC concrete

Lower stress + Later cracking !

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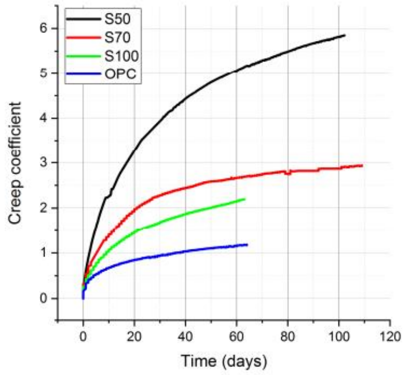
Creep of Geopolymer Concrete



(S0 = 100%FA, S30 = 30%BFS+70%FA……, S100=100%BFS)

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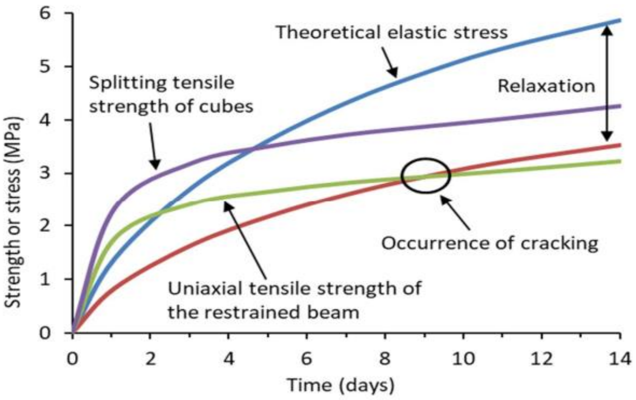
A. Kostiuchenko et al. (15th ICCC and 73th RILEM week, 2019)

TUDelft

Cracking potential of Geopolymer Concrete



Stress development and the resultant cracking of concrete due to restrained shrinkage

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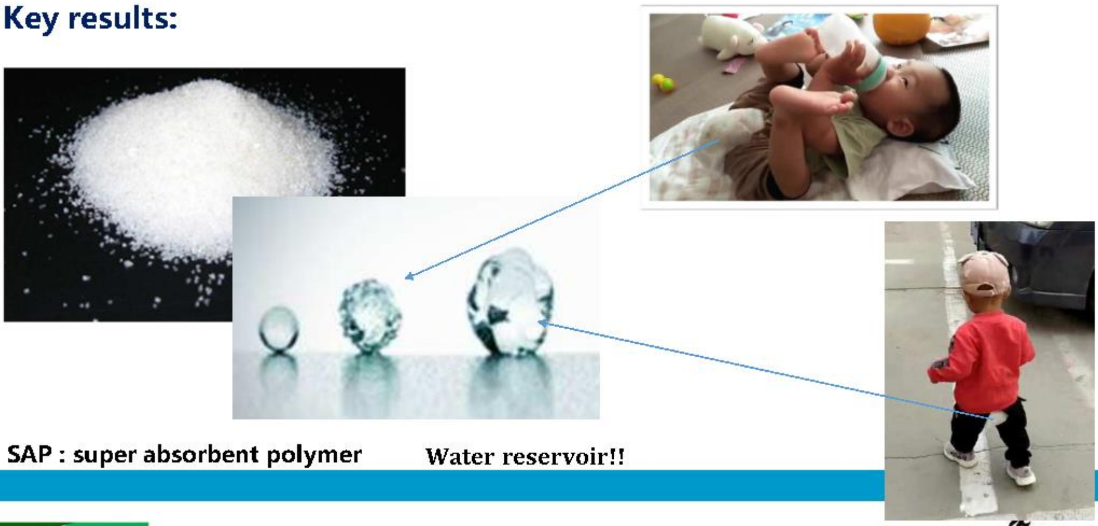
TUDelft

Mitigating strategies. Part 1: Internal curing

Key results:

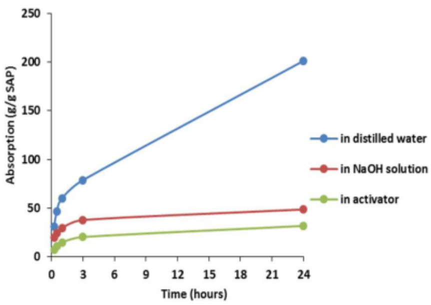


SAP : super absorbent polymer

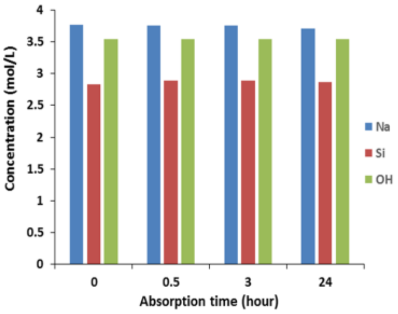
Water reservoir!!

Mitigating strategies. Part 1: Internal curing

Key results:



Absorptions of SAP in distilled water, NaOH solution and activator.

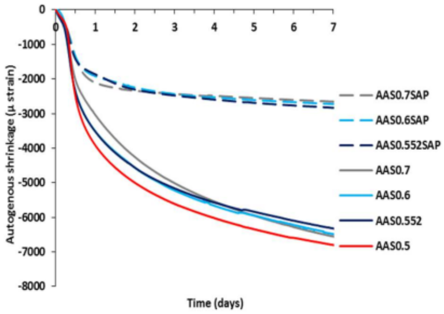


Ions concentrations before and after absorption

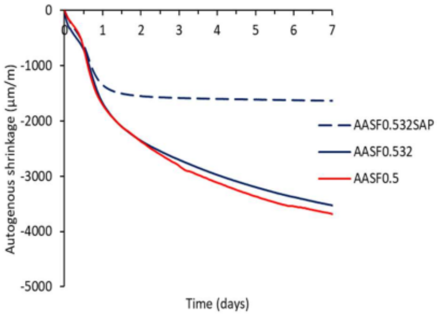
Z Li, M Wyrzykowski, H Dong, J Granja, M Azenha, P Lura, G Ye (2020) Internal curing by superabsorbent polymers in alkali-activated slag, Cement and Concrete Research 135, 106123

Mitigating strategies. Part 1: Internal curing

Key results:



Autogenous shrinkage of AAS paste with and without SAP

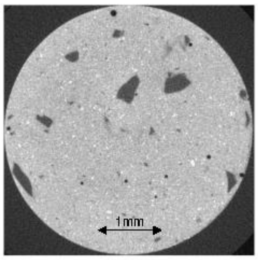


Autogenous shrinkage of AASF paste with and without SAP

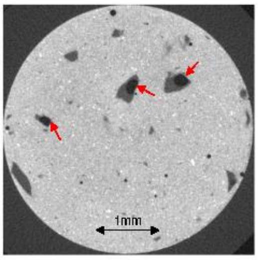
Z Li, M Wyrzykowski, H Dong, J Granja, M Azenha, P Lura, G Ye (2020) Internal curing by superabsorbent polymers in alkali-activated slag, Cement and Concrete Research 135, 106123

Mitigating strategies. Part 1: Internal curing

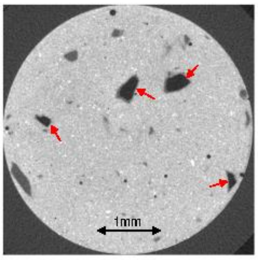
Key results:



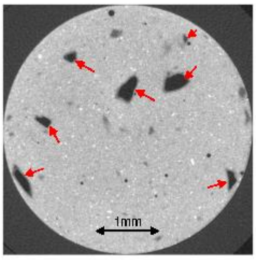
0h



8h



1d



7d

Z Li, M Wyrzykowski, H Dong, J Granja, M Azenha, P Lura, G Ye (2020) Internal curing by superabsorbent polymers in alkali-activated slag, Cement and Concrete Research 135, 106123

Mitigating strategies. Part 2: Adding MK

Key results:

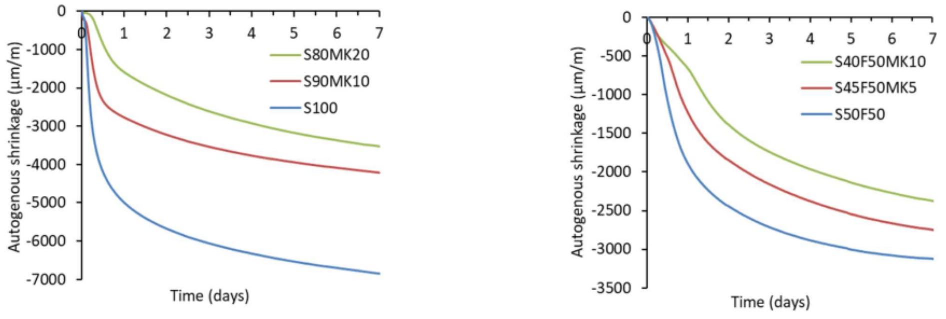
Mixture proportions of AAS and AASF pastes with and without MK.

Mixture	Slag (g)	Fly ash (g)	MK (g)
S100	1000	-	-
S90MK10	900	-	100
S80MK20	800	-	200
S50F50	500	500	-
S45F50MK5	450	500	50
S40F50MK10	400	500	100

Z Li, S Zhang, X Liang, G Ye (2020) Cracking potential of alkali-activated slag and fly ash concrete subjected to restrained autogenous shrinkage, Cement and Concrete Composites, 103767

Mitigating strategies. Part 2: Adding MK

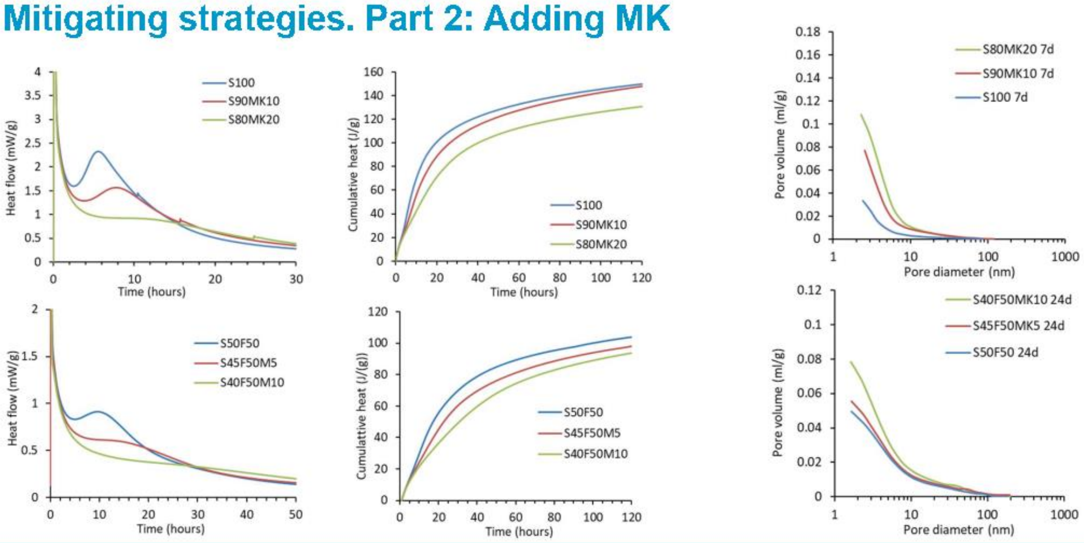
Key results:



Autogenous shrinkage of AAS and AASF pastes with and without MK

Z Li, S Zhang, X Liang, G Ye (2020) Cracking potential of alkali-activated slag and fly ash concrete subjected to restrained autogenous shrinkage, Cement and Concrete Composites, 103767

Mitigating strategies. Part 2: Adding MK



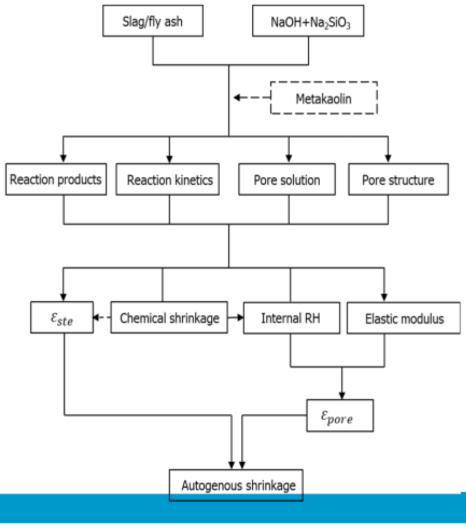
Heat evolution

Pore size distribution

Z Li, S Zhang, X Liang, G Ye (2020) Cracking potential of alkali-activated slag and fly ash concrete subjected to restrained autogenous shrinkage, Cement and Concrete Composites, 103767

Mitigating strategies. Part 2: Adding MK

Mitigating mechanism:



Slag/fly ash

NaOH+Na_2SiO_3

Metakaolin

Reaction products

Reaction kinetics

Pore solution

Pore structure

ε_{ste}

Chemical shrinkage

Internal RH

Elastic modulus

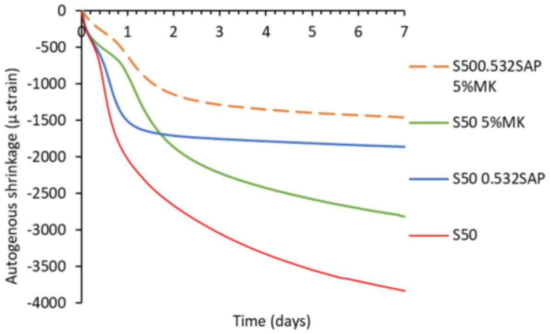
ε_{pore}

Autogenous shrinkage

Z Li, M Wyrzykowski, H Dong, J Granja, M Azenha, P Lura, G Ye (2020) Internal curing by superabsorbent polymers in alkali-activated slag, Cement and Concrete Research 135, 106123

Mitigating strategies. Part 2: Adding MK

Combine SAP + MK:

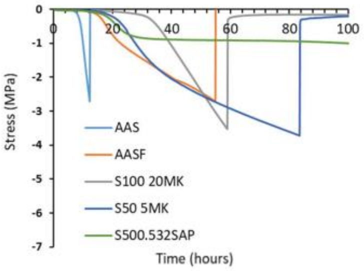


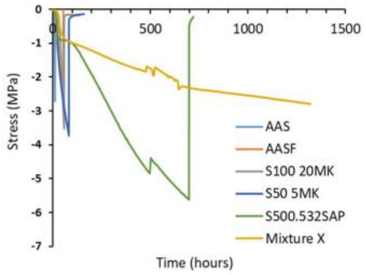
Both the early age the late age autogenous shrinkage is significantly mitigated!

Autogenous shrinakge AAS and AASF pastes with MK and SAP: Mixture X

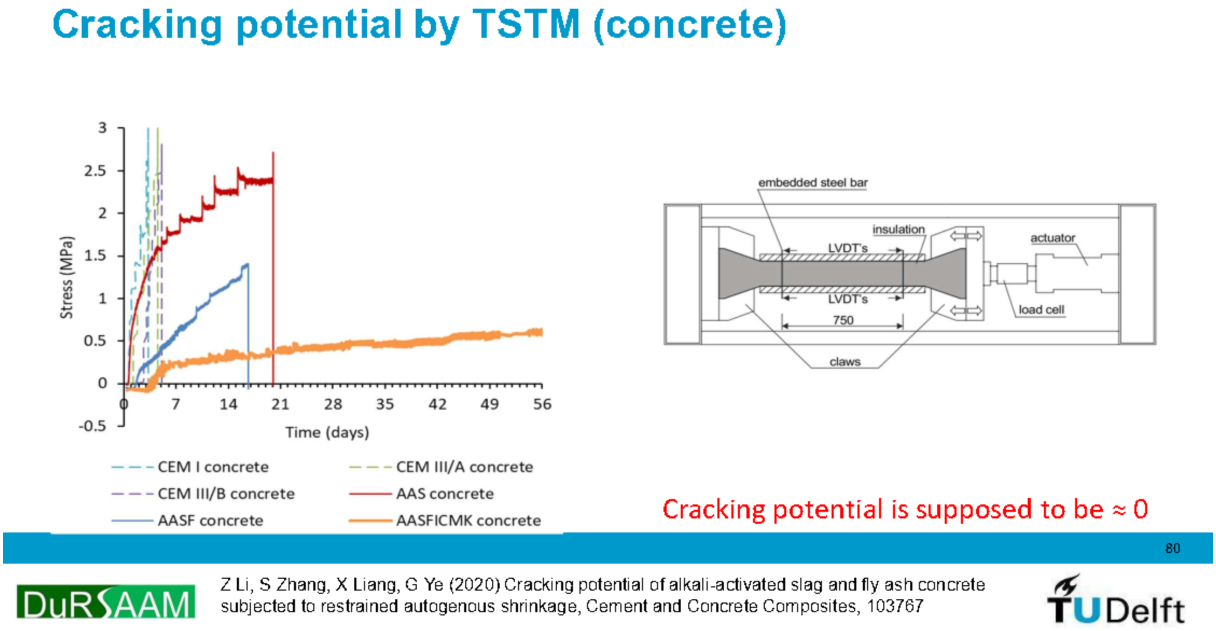
Z Li, S Zhang, X Liang, G Ye (2020) Cracking potential of alkali-activated slag and fly ash concrete subjected to restrained autogenous shrinkage, Cement and Concrete Composites, 103767

Cracking potential by ring test (paste)





Z Li, S Zhang, X Liang, G Ye (2020) Cracking potential of alkali-activated slag and fly ash concrete subjected to restrained autogenous shrinkage, Cement and Concrete Composites, 103767



Cracking potential by TSTM (concrete)

Cracking potential is supposed to be ≈ 0

Z Li, S Zhang, X Liang, G Ye (2020) Cracking potential of alkali-activated slag and fly ash concrete subjected to restrained autogenous shrinkage, Cement and Concrete Composites, 103767

10. Fibre-reinforced AAM concretes

Frank Dehn

Fibre reinforced concretes have become more and more popular of the last decades. This type of concrete is reinforced with short fibres, to improve the post-cracking toughness of the concrete. In this chapter fibre reinforced concrete is discussed both from the perspective of concretes based on ordinary Portland cement and alkali-activated materials.

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Marie Curie
Innovative Training Network

PhD Training Network on **D**urable, **R**eliable and **S**ustainable Structures with **A**lkali-**A**ctivated **M**aterials

Fibre-reinforced concretes

OPC vs AAMs

Prof. Dr.-Ing. Frank Dehn

DuRSAAM – Course on "AAM Technology"

27-29 January 2020

DuRSAAM – H2020-MSCA-ITN-2018-813596

Karlsruhe Institute of Technology

Introduction

Fibre reinforced concrete in ancient times


Aqar Quf (1500 years B.C.) – bricks reinforced with straws or horse hair[1]


Tipu Sultan's palace in Srirangapatna (India) – built with sheep's wool[2]


Roman Colosseum (80 A.C.) – built with horse-hair as secondary reinforcement[3]

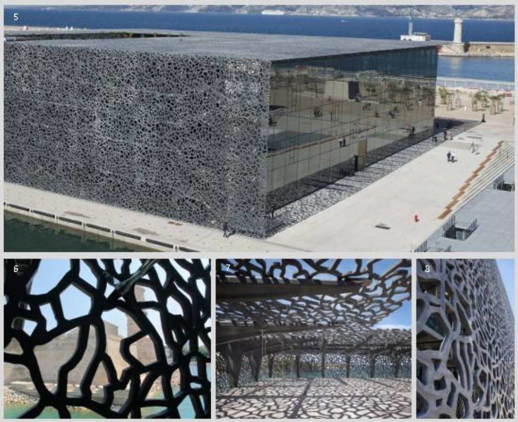

A Pueblo house (1540s) – built with straw reinforcement adobe brick[4]

Images:
1. https://commons.wikimedia.org/wiki/File:%D8%B2%D9%82%D9%88%D8%B1%D8%A9_%D8%B9%D9%83%D8%B1%D9%83%D9%88%D9%81_%D9%81%D9%8A_%D8%A8%D8%BA%D8%AF%D8%A7%D8%AF_2017.jpg
2. https://jooinn.com/img/get
3. https://www.flickr.com/photos/22746515@N02/8082854097
4. https://chambersarchitects.com/blog/pueblo-architecture-taos-new-mexico/

Introduction

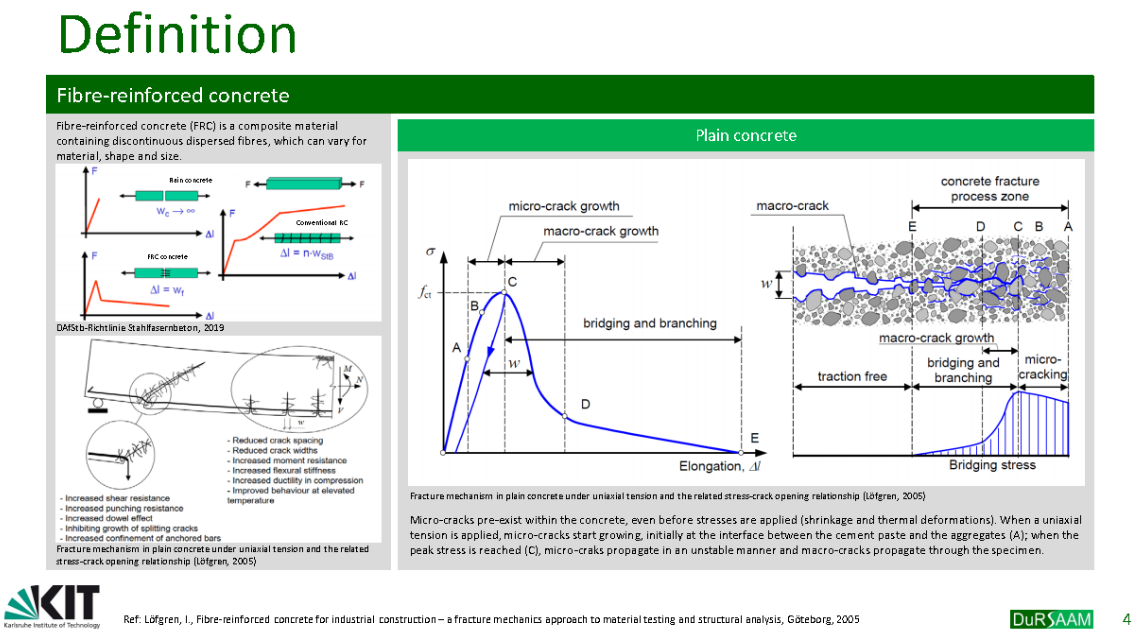
Fibre reinforced concrete today

L'Oceanografic (Valencia) – Access building and restaurant – steel fibre-reinforced concrete shell



Museum of Civilisations from Europe and the Mediterranean (MUCEM), Marseilles – façade built with fibre-reinforced ultra-high performance concrete (UHPC)

Images:
1,2,3. https://structurae.net/en/structures/l-oceanografic-access-building/media
4. https://en.ps-community.com/parks/oceanografic
5. https://www.klm.com/destinations/nq/nq/article/mucem-marseilles-most-beautiful-museum
6. https://upload.wikimedia.org/wikipedia/commons/5/5b/Filtro_%28422510229%29.jpeg
7. https://www.theplan.it/eng/architettura/mucem-museum
8. https://structurae.net/de/bauwerke/museum-der-zivilisationen-europas-und-des-mittelmeers



Definition

Fibre-reinforced concrete

Fibre-reinforced concrete (FRC) is a composite material containing discontinuous dispersed fibres, which can vary for material, shape and size.

DAfStb-Richtlinie Stahlfasernbeton, 2019

- Reduced crack spacing
- Reduced crack widths
- Increased moment resistance
- Increased flexural stiffness
- Increased ductility in compression
- Improved behaviour at elevated temperature

- Increased shear resistance
- Increased punching resistance
- Increased dowel effect
- Inhibiting growth of splitting cracks
- Increased confinement of anchored bars

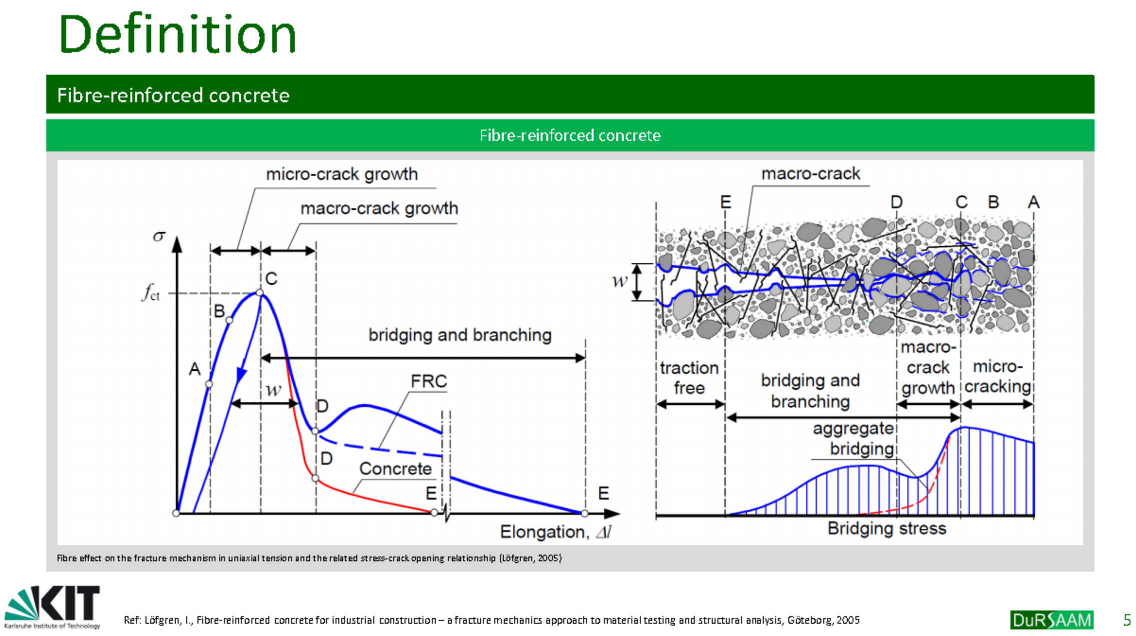
Fracture mechanism in plain concrete under uniaxial tension and the related stress-crack opening relationship (Löfgren, 2005)

Plain concrete

Fracture mechanism in plain concrete under uniaxial tension and the related stress-crack opening relationship (Löfgren, 2005)

Micro-cracks pre-exist within the concrete, even before stresses are applied (shrinkage and thermal deformations). When a uniaxial tension is applied, micro-cracks start growing, initially at the interface between the cement paste and the aggregates (A); when the peak stress is reached (C), micro-craks propagate in an unstable manner and macro-cracks propagate through the specimen.

Ref: Löfgren, I., Fibre-reinforced concrete for industrial construction – a fracture mechanics approach to material testing and structural analysis, Göteborg, 2005



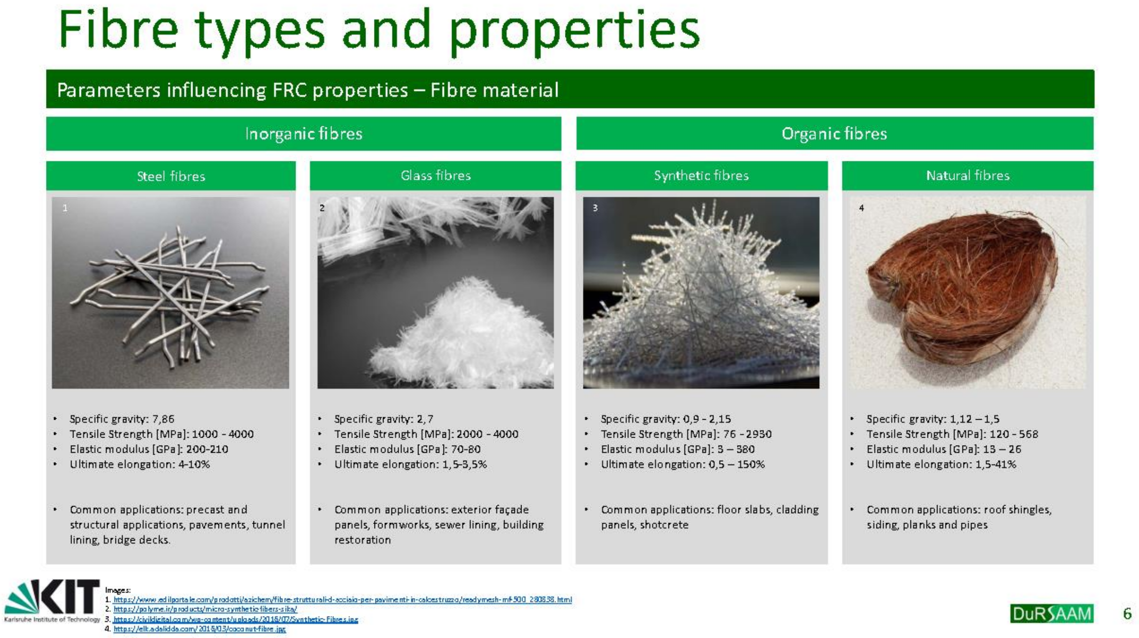
Definition

Fibre-reinforced concrete

Fibre-reinforced concrete

Fibre effect on the fracture mechanism in uniaxial tension and the related stress-crack opening relationship (Löfgren, 2005)

Ref: Löfgren, I., Fibre-reinforced concrete for industrial construction – a fracture mechanics approach to material testing and structural analysis, Göteborg, 2005



Fibre types and properties

Parameters influencing FRC properties – Fibre material

Inorganic fibres

Steel fibres

- Specific gravity: 7,86
- Tensile Strength [MPa]: 1000 - 4000
- Elastic modulus [GPa]: 200-210
- Ultimate elongation: 4-10%

- Common applications: precast and structural applications, pavements, tunnel lining, bridge decks.

Glass fibres

- Specific gravity: 2,7
- Tensile Strength [MPa]: 2000 - 4000
- Elastic modulus [GPa]: 70-80
- Ultimate elongation: 1,5-3,5%

- Common applications: exterior façade panels, formworks, sewer lining, building restoration

Organic fibres

Synthetic fibres

- Specific gravity: 0,9 - 2,15
- Tensile Strength [MPa]: 76 - 2930
- Elastic modulus [GPa]: 3 – 380
- Ultimate elongation: 0,5 – 150%

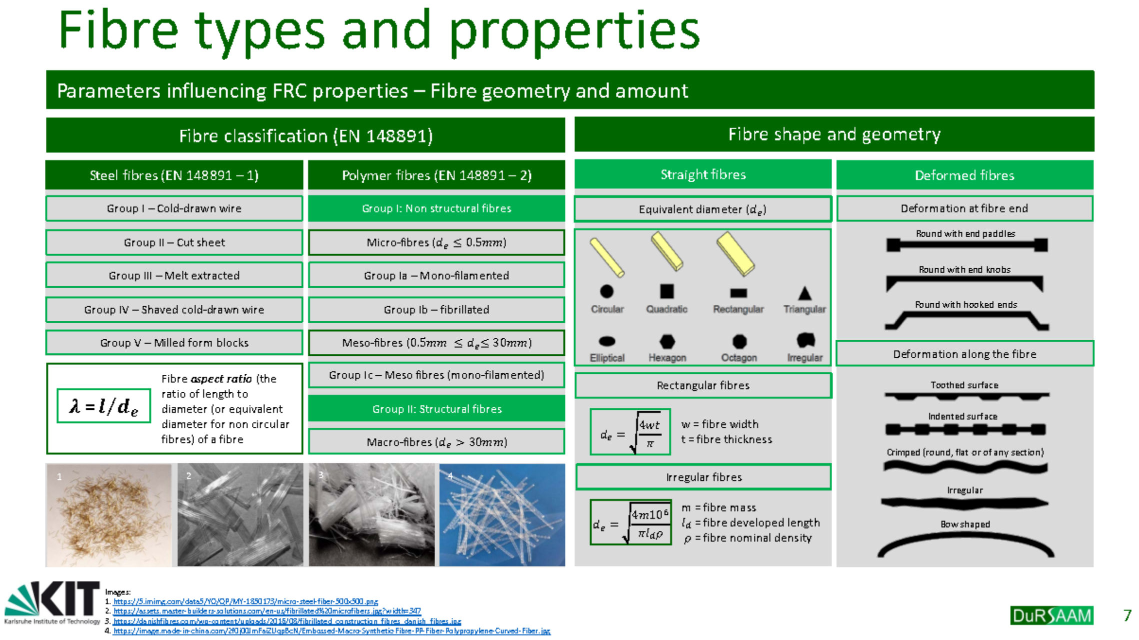
- Common applications: floor slabs, cladding panels, shotcrete

Natural fibres

- Specific gravity: 1,12 – 1,5
- Tensile Strength [MPa]: 120 - 568
- Elastic modulus [GPa]: 13 – 26
- Ultimate elongation: 1,5-41%

- Common applications: roof shingles, siding, planks and pipes

Images:
1. https://www.edilportale.com/prodotti/azichem/fibre-strutturali-d-acciaio-per-pavimenti-in-calcestruzzo/readymesh-mf-500_280836.html
2. https://polyme.ir/products/micro-synthetic-fibers-sika/
3. https://civildigital.com/wp-content/uploads/2016/07/Synthetic-Fibres.jpg
4. https://elk.adalidda.com/2016/03/coconut-fibre.jpg



Fibre types and properties

Parameters influencing FRC properties – Fibre geometry and amount

Fibre classification (EN 148891)

Steel fibres (EN 148891 – 1)

- Group I – Cold-drawn wire
- Group II – Cut sheet
- Group III – Melt extracted
- Group IV – Shaved cold-drawn wire
- Group V – Milled form blocks

$\lambda = l/d_e$ Fibre *aspect ratio* (the ratio of length to diameter (or equivalent diameter for non circular fibres) of a fibre

Polymer fibres (EN 148891 – 2)

- Group I: Non structural fibres
- Micro-fibres ($d_e \leq 0.5mm$)
- Group Ia – Mono-filamented
- Group Ib – fibrillated
- Meso-fibres ($0.5mm \leq d_e \leq 30mm$)
- Group Ic – Meso fibres (mono-filamented)
- Group II: Structural fibres
- Macro-fibres ($d_e > 30mm$)

Fibre shape and geometry

Straight fibres

Equivalent diameter (d_e)

Rectangular fibres

$$d_e = \sqrt{\frac{4wt}{\pi}}$$

w = fibre width
t = fibre thickness

Irregular fibres

$$d_e = \sqrt{\frac{4m10^6}{\pi l_d \rho}}$$

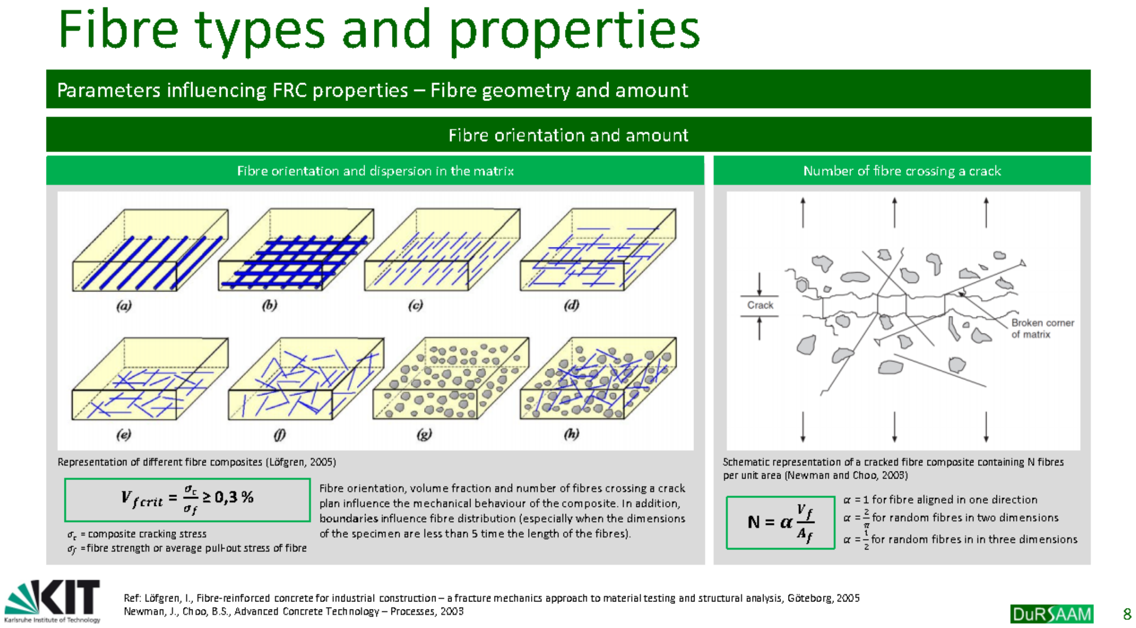
m = fibre mass
l_d = fibre developed length
ρ = fibre nominal density

Deformed fibres

Deformation at fibre end

Deformation along the fibre

Images:
1. https://5.imimg.com/data5/YO/QP/MY-1850173/micro-steel-fiber-500x500.png
2. https://assets.master-builders-solutions.com/en-us/fibrillated%20microfibers.jpg?width=347
3. https://danishfibres.com/wp-content/uploads/2015/08/fibrillated_construction_fibres_danish_fibres.jpg
4. https://image.made-in-china.com/2f0j00JmFaiZUqpBcN/Embossed-Macro-Synthetic-Fibre-PP-Fiber-Polypropylene-Curved-Fiber.jpg



Fibre types and properties

Parameters influencing FRC properties – Fibre geometry and amount

Fibre orientation and amount

Fibre orientation and dispersion in the matrix

Representation of different fibre composites (Löfgren, 2005)

$$V_{f\,crit} = \frac{\sigma_c}{\sigma_f} \geq 0{,}3\,\%$$

σ_c = composite cracking stress
σ_f = fibre strength or average pull-out stress of fibre

Fibre orientation, volume fraction and number of fibres crossing a crack plan influence the mechanical behaviour of the composite. In addition, boundaries influence fibre distribution (especially when the dimensions of the specimen are less than 5 time the length of the fibres).

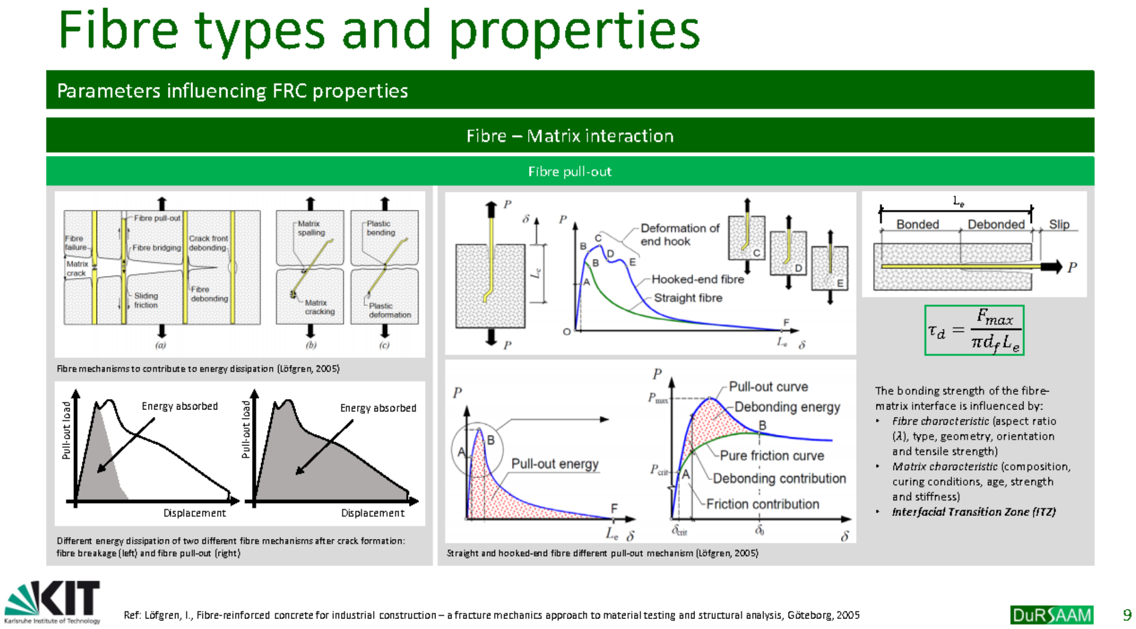
Number of fibre crossing a crack

Schematic representation of a cracked fibre composite containing N fibres per unit area (Newman and Choo, 2003)

$$N = \alpha \frac{V_f}{A_f}$$

α = 1 for fibre aligned in one direction
$\alpha = \frac{2}{\pi}$ for random fibres in two dimensions
$\alpha = \frac{1}{2}$ for random fibres in in three dimensions

Ref: Löfgren, I., Fibre-reinforced concrete for industrial construction – a fracture mechanics approach to material testing and structural analysis, Göteborg, 2005
Newman, J., Choo, B.S., Advanced Concrete Technology – Processes, 2003



Fibre types and properties

Parameters influencing FRC properties

Fibre – Matrix interaction

Fibre pull-out

Fibre mechanisms to contribute to energy dissipation (Löfgren, 2005)

Different energy dissipation of two different fibre mechanisms after crack formation: fibre breakage (left) and fibre pull-out (right)

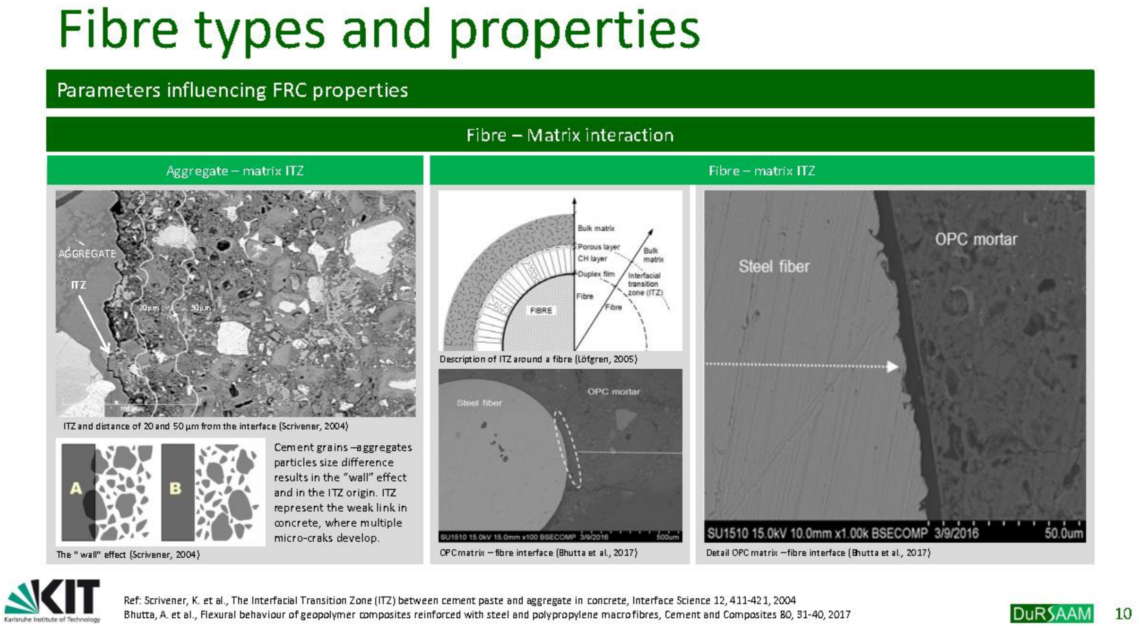
Straight and hooked-end fibre different pull-out mechanism (Löfgren, 2005)

$$\tau_d = \frac{F_{max}}{\pi d_f L_e}$$

The bonding strength of the fibre-matrix interface is influenced by:

- *Fibre characteristic* (aspect ratio (λ), type, geometry, orientation and tensile strength)
- *Matrix characteristic* (composition, curing conditions, age, strength and stiffness)
- ***Interfacial Transition Zone (ITZ)***

Ref: Löfgren, I., Fibre-reinforced concrete for industrial construction – a fracture mechanics approach to material testing and structural analysis, Göteborg, 2005



Fibre types and properties

Parameters influencing FRC properties

Fibre – Matrix interaction

Aggregate – matrix ITZ

ITZ and distance of 20 and 50 µm from the interface (Scrivener, 2004)

Cement grains –aggregates particles size difference results in the "wall" effect and in the ITZ origin. ITZ represent the weak link in concrete, where multiple micro-craks develop.

The " wall" effect (Scrivener, 2004)

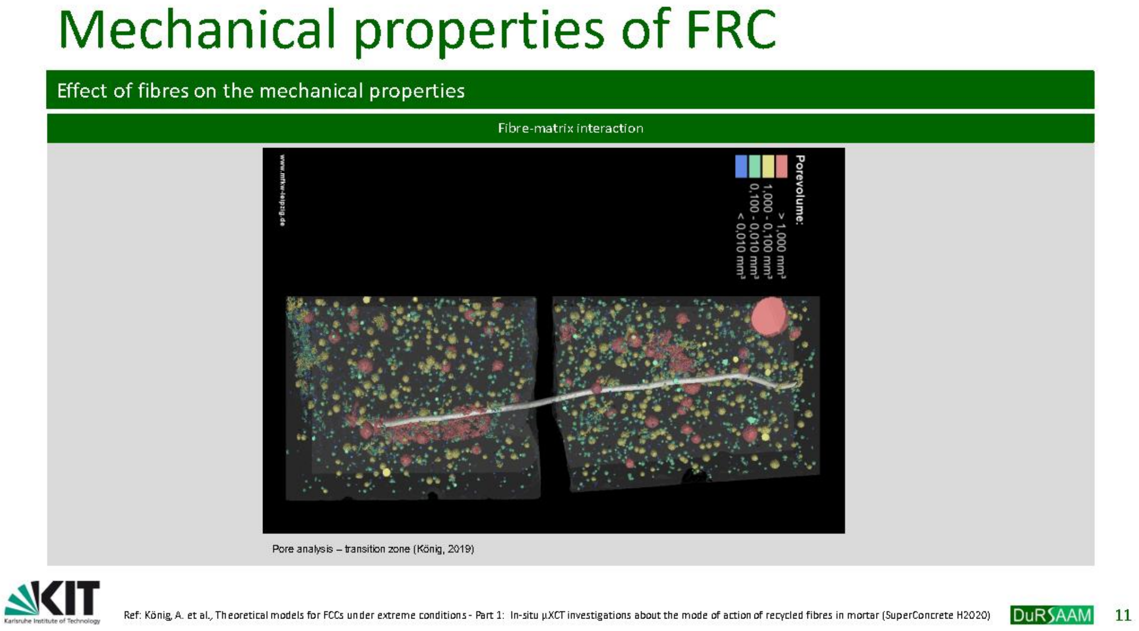
Fibre – matrix ITZ

Description of ITZ around a fibre (Löfgren, 2005)

OPC matrix – fibre interface (Bhutta et al., 2017)

Detail OPC matrix – fibre interface (Bhutta et al., 2017)

Ref: Scrivener, K. et al., The Interfacial Transition Zone (ITZ) between cement paste and aggregate in concrete, Interface Science 12, 411-421, 2004
Bhutta, A. et al., Flexural behaviour of geopolymer composites reinforced with steel and polypropylene macrofibres, Cement and Composites 80, 31-40, 2017



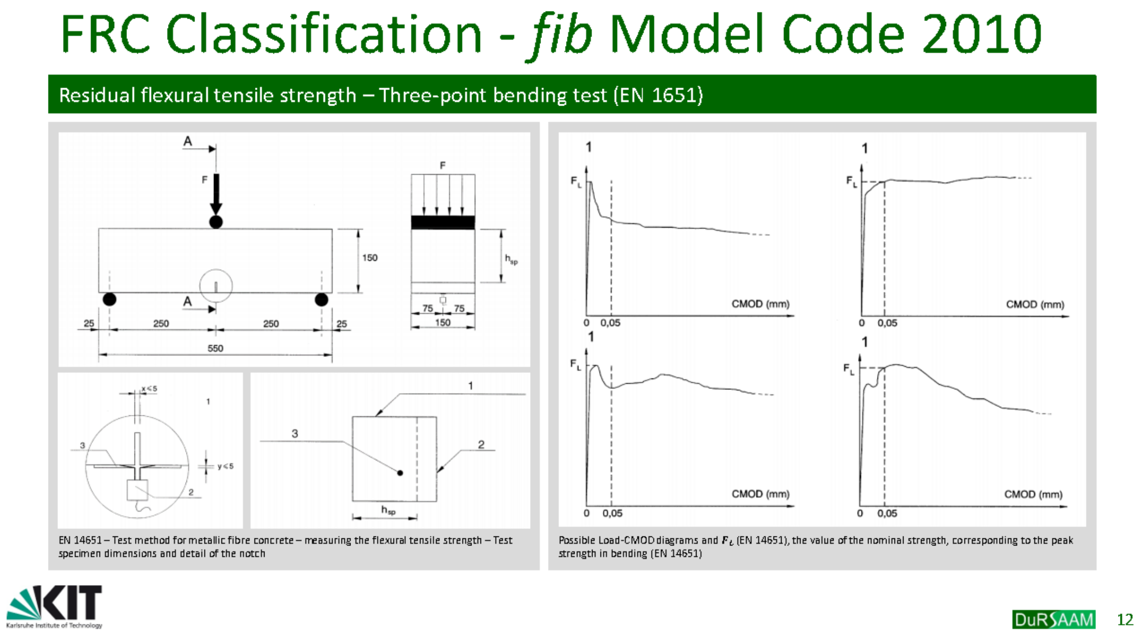
Mechanical properties of FRC

Effect of fibres on the mechanical properties

Fibre-matrix interaction

Pore analysis – transition zone (König, 2019)

Ref: König, A. et al., Theoretical models for FCCs under extreme conditions - Part 1: In-situ µXCT investigations about the mode of action of recycled fibres in mortar (SuperConcrete H2020)

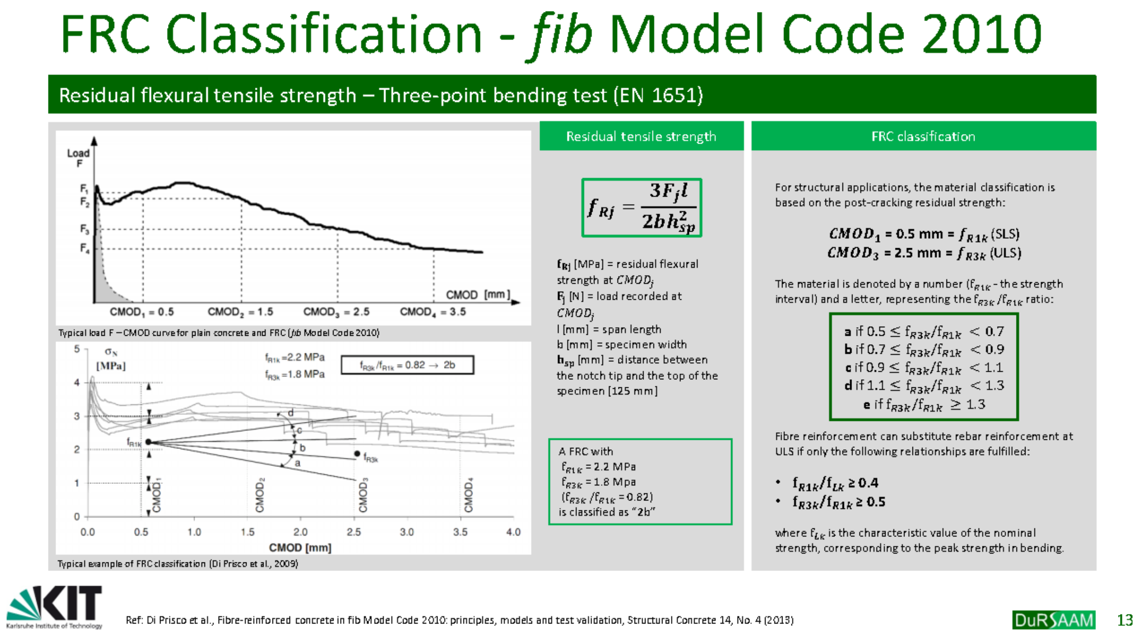


FRC Classification - *fib* Model Code 2010

Residual flexural tensile strength – Three-point bending test (EN 1651)

EN 14651 – Test method for metallic fibre concrete – measuring the flexural tensile strength – Test specimen dimensions and detail of the notch

Possible Load-CMOD diagrams and F_L (EN 14651), the value of the nominal strength, corresponding to the peak strength in bending (EN 14651)



FRC Classification - *fib* Model Code 2010

Residual flexural tensile strength – Three-point bending test (EN 1651)

Typical load F – CMOD curve for plain concrete and FRC (*fib* Model Code 2010)

Typical example of FRC classification (Di Prisco et al., 2009)

Residual tensile strength

$$\boxed{f_{Rj} = \frac{3F_j l}{2bh_{sp}^2}}$$

f_{Rj} [MPa] = residual flexural strength at $CMOD_j$
F_j [N] = load recorded at $CMOD_j$
l [mm] = span length
b [mm] = specimen width
h_{sp} [mm] = distance between the notch tip and the top of the specimen [125 mm]

A FRC with
f_{R1k} = 2.2 MPa
f_{R3k} = 1.8 Mpa
(f_{R3k} / f_{R1k} = 0.82)
is classified as "2b"

FRC classification

For structural applications, the material classification is based on the post-cracking residual strength:

$CMOD_1$ **= 0.5 mm =** f_{R1k} (SLS)
$CMOD_3$ **= 2.5 mm =** f_{R3k} (ULS)

The material is denoted by a number (f_{R1k} - the strength interval) and a letter, representing the f_{R3k} /f_{R1k} ratio:

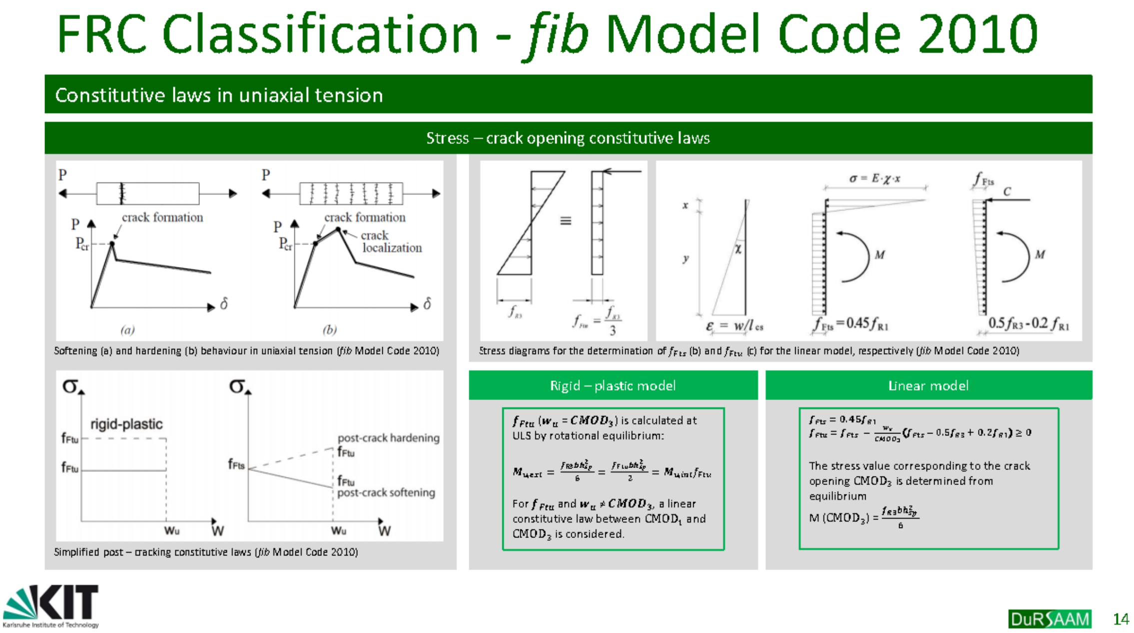
a if $0.5 \leq f_{R3k}/f_{R1k} < 0.7$
b if $0.7 \leq f_{R3k}/f_{R1k} < 0.9$
c if $0.9 \leq f_{R3k}/f_{R1k} < 1.1$
d if $1.1 \leq f_{R3k}/f_{R1k} < 1.3$
e if $f_{R3k}/f_{R1k} \geq 1.3$

Fibre reinforcement can substitute rebar reinforcement at ULS if only the following relationships are fulfilled:

- $f_{R1k}/f_{Lk} \geq 0.4$
- $f_{R3k}/f_{R1k} \geq 0.5$

where f_{Lk} is the characteristic value of the nominal strength, corresponding to the peak strength in bending.

Ref: Di Prisco et al., Fibre-reinforced concrete in fib Model Code 2010: principles, models and test validation, Structural Concrete 14, No. 4 (2013)



FRC Classification - *fib* Model Code 2010

Constitutive laws in uniaxial tension

Stress – crack opening constitutive laws

Softening (a) and hardening (b) behaviour in uniaxial tension (*fib* Model Code 2010)

Simplified post – cracking constitutive laws (*fib* Model Code 2010)

Stress diagrams for the determination of f_{Fts} (b) and f_{Ftu} (c) for the linear model, respectively (*fib* Model Code 2010)

Rigid – plastic model

f_{Ftu} ($w_u = CMOD_3$) is calculated at ULS by rotational equilibrium:

$$M_{u,ext} = \frac{f_{R3} b h_{sp}^2}{6} = \frac{f_{Ftu} b h_{sp}^2}{2} = M_{u,int} f_{Ftu}$$

For f_{Ftu} and $w_u \neq CMOD_3$, a linear constitutive law between $CMOD_1$ and $CMOD_3$ is considered.

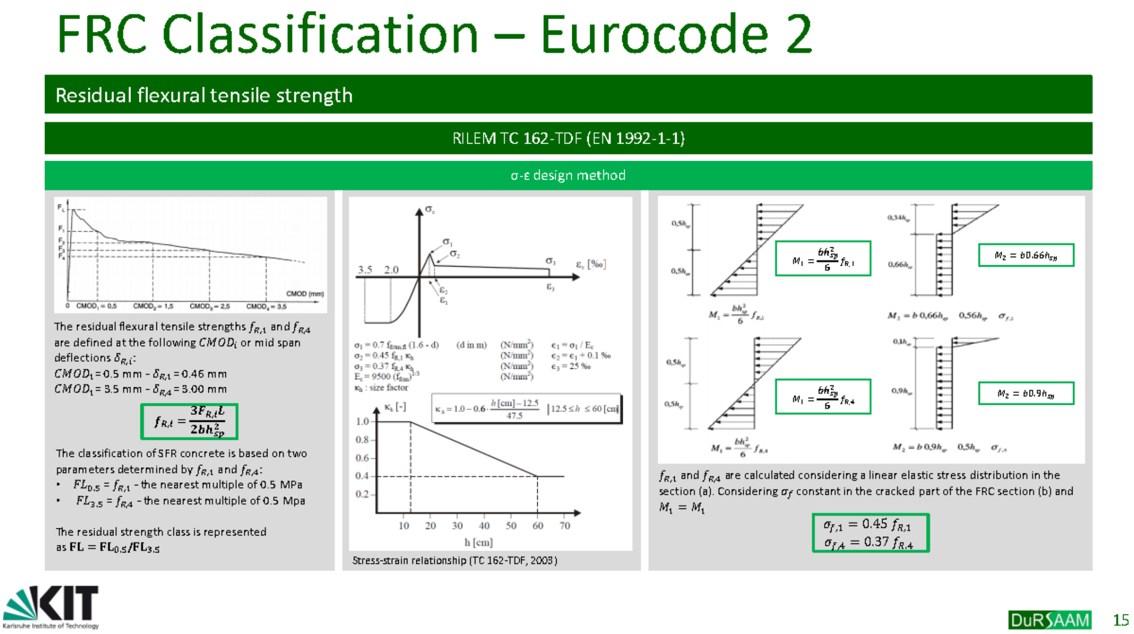
Linear model

$f_{Fts} = 0.45 f_{R1}$

$f_{Ftu} = f_{Fts} - \frac{w_u}{CMOD_3}(f_{Fts} - 0.5 f_{R3} + 0.2 f_{R1}) \geq 0$

The stress value corresponding to the crack opening $CMOD_3$ is determined from equilibrium

M ($CMOD_3$) = $\frac{f_{R3} b h_{sp}^2}{6}$



FRC Classification – Eurocode 2

Residual flexural tensile strength

RILEM TC 162-TDF (EN 1992-1-1)

σ-ε design method

The residual flexural tensile strengths $f_{R,1}$ and $f_{R,4}$ are defined at the following $CMOD_i$ or mid span deflections $\delta_{R,i}$:

$CMOD_1$ = 0.5 mm - $\delta_{R,1}$ = 0.46 mm

$CMOD_1$ = 3.5 mm - $\delta_{R,4}$ = 3.00 mm

$$f_{R,i} = \frac{3F_{R,i}L}{2bh_{sp}^2}$$

The classification of SFR concrete is based on two parameters determined by $f_{R,1}$ and $f_{R,4}$:

- $FL_{0.5} = f_{R,1}$ – the nearest multiple of 0.5 MPa
- $FL_{3.5} = f_{R,4}$ – the nearest multiple of 0.5 Mpa

The residual strength class is represented as $\mathbf{FL = FL_{0.5}/FL_{3.5}}$

$\sigma_1 = 0.7\, f_{fctm,fl}\, (1.6 - d)$ (d in m) (N/mm²) $\epsilon_1 = \sigma_1 / E_c$

$\sigma_2 = 0.45\, f_{R,1}\, \kappa_h$ (N/mm²) $\epsilon_2 = \epsilon_1 + 0.1$ ‰

$\sigma_3 = 0.37\, f_{R,4}\, \kappa_h$ (N/mm²) $\epsilon_3 = 25$ ‰

$E_c = 9500\, (f_{fcm})^{1/3}$ (N/mm²)

κ_h : size factor

$\kappa_h = 1.0 - 0.6 \cdot \frac{h\,[cm] - 12.5}{47.5}$ $\quad | 12.5 \leq h \leq 60$ [cm]

Stress-strain relationship (TC 162-TDF, 2003)

$M_1 = \frac{bh_{sp}^2}{6} f_{R,1}$

$M_2 = b0.66h_{sp}$

$M_1 = \frac{bh_{sp}^2}{6} f_{R,4}$

$M_2 = b0.9h_{sp}$

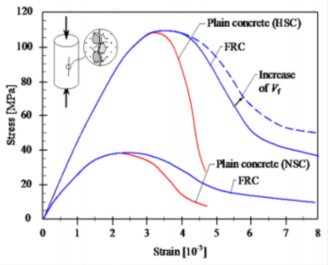
$f_{R,1}$ and $f_{R,4}$ are calculated considering a linear elastic stress distribution in the section (a). Considering σ_f constant in the cracked part of the FRC section (b) and $M_1 = M_1$

$$\sigma_{f,1} = 0.45\, f_{R,1}$$
$$\sigma_{f,4} = 0.37\, f_{R,4}$$

Mechanical properties of FRC

Effect of fibres on the mechanical properties

Compressive strength

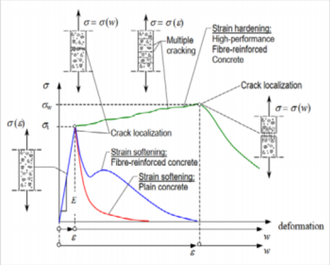


Plain and fibre-reinforced concrete (FRC) having both normal and high strength under uniaxial compression (Löfgren, 2005)

Fibres slightly influence the compressive strength, offering resistance against longitudinal crack growth.
The effect of fibres is highly dependent on:

- Type, size and properties of fibre used
- Volume fraction (Vf)

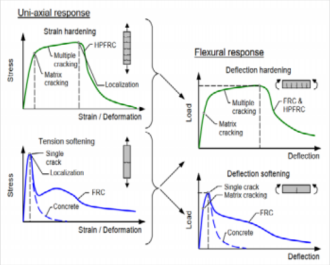
Tensile strength



The tensile behaviour based on uniaxial response and classified as strain-softening or pseudo strain-hardening (Löfgren, 2005).

Plain concrete and fibre-reinforced concrete with low or moderate volume fractions of fibre can be considered as **strain-softening** materials. However, fibres have a considerable impact on the tensile fracture behaviour.

Flexural behaviour



Characterisation of the tensile and flexural behaviour (Jansson, 2008).

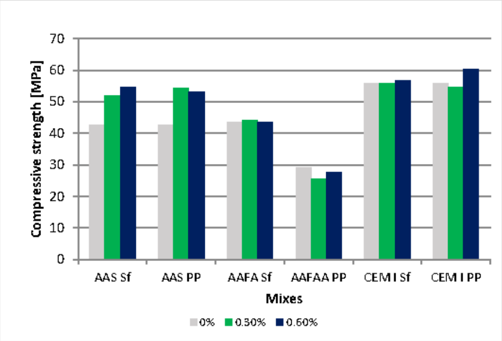
A material showing a tension-softening behaviour when loaded under uniaxial stress can show either deflection hardening or softening behaviour. This behaviour depends on the toughness of the material as well as the dimension of the specimen. In fact, fibre distribution and orientation are influenced by the specimen geometry.

Ref: Löfgren, I., Fibre-reinforced concrete for industrial construction – a fracture mechanics approach to material testing and structural analysis, Göteborg, 2005
Jansson, A., et al., Design methods for fibre-reinforced concrete: a state-of-the-art review, Nordic Concrete Research 38, 21-36 (2008)

Mechanical properties of FRC

Effect of fibres on the mechanical properties – OPC vs AAMs

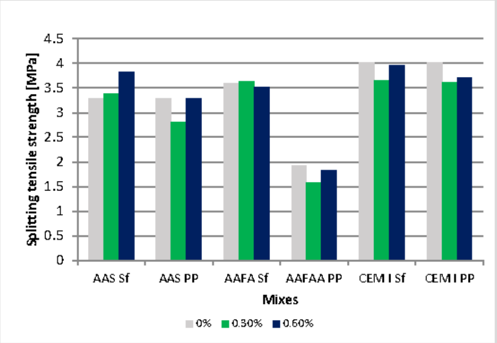
Compressive strength



Compressive strength of different matrix (OPC, fly ash and slag) and different fibre type and vol.%

Compressive strength is not significantly affected by fibre type and volume fraction

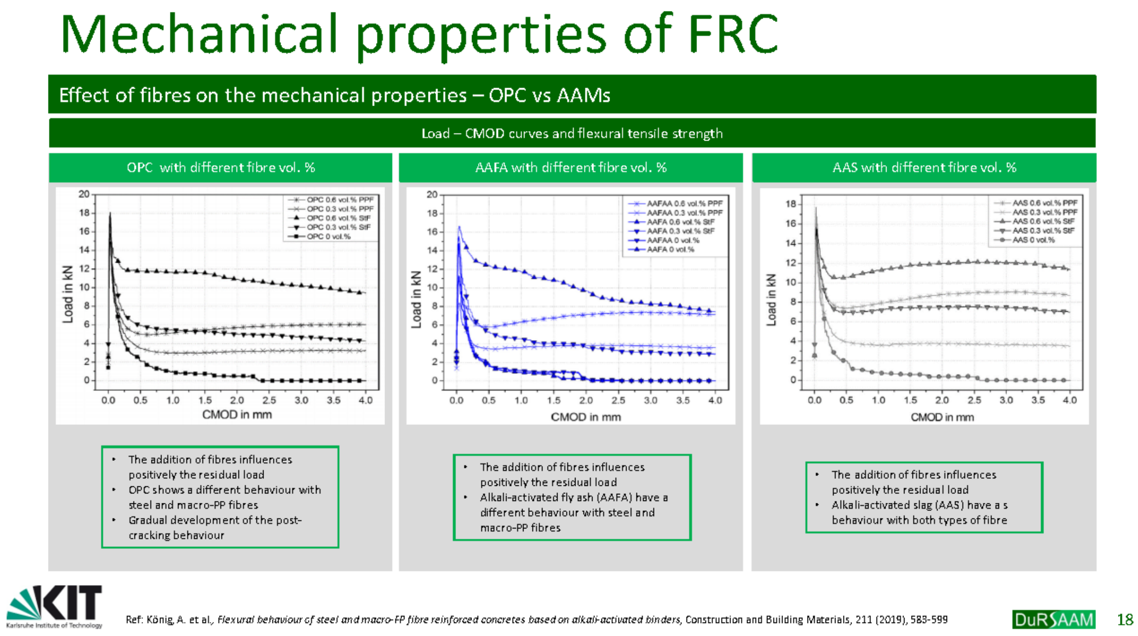
Splitting tensile strength



Splitting tensile strength of different matrix (OPC, fly ash and slag) and different fibre type and vol.%

Splitting tensile strength is not significantly affected by fibre type and volume fraction. Fibres influence the residual strength.

Ref: König, A. et al., *Flexural behaviour of steel and macro-FP fibre reinforced concretes based on alkali-activated binders*, Construction and Building Materials, 211 (2019), 583-599



Mechanical properties of FRC

Effect of fibres on the mechanical properties – OPC vs AAMs

Load – CMOD curves and flexural tensile strength

OPC with different fibre vol. %	AAFA with different fibre vol. %	AAS with different fibre vol. %

- The addition of fibres influences positively the residual load
- OPC shows a different behaviour with steel and macro-PP fibres
- Gradual development of the post-cracking behaviour

- The addition of fibres influences positively the residual load
- Alkali-activated fly ash (AAFA) have a different behaviour with steel and macro-PP fibres

- The addition of fibres influences positively the residual load
- Alkali-activated slag (AAS) have a s behaviour with both types of fibre

Ref: König, A. et al., *Flexural behaviour of steel and macro-PP fibre reinforced concretes based on alkali-activated binders*, Construction and Building Materials, 211 (2019), 583-599

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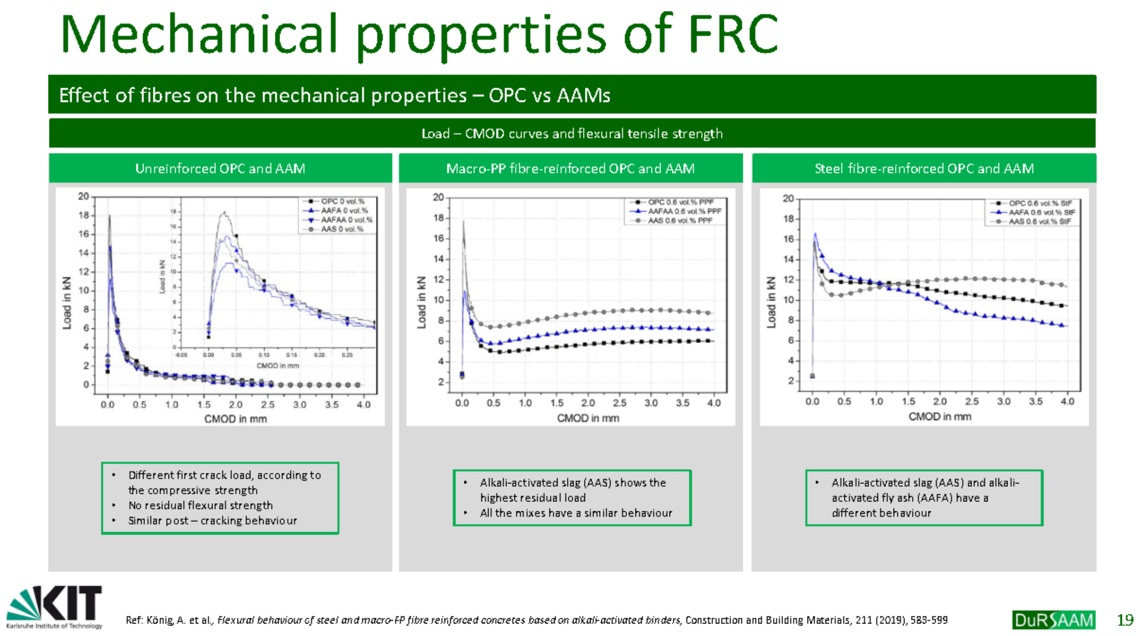

Mechanical properties of FRC

Effect of fibres on the mechanical properties – OPC vs AAMs

Load – CMOD curves and flexural tensile strength

Unreinforced OPC and AAM	Macro-PP fibre-reinforced OPC and AAM	Steel fibre-reinforced OPC and AAM

- Different first crack load, according to the compressive strength
- No residual flexural strength
- Similar post – cracking behaviour

- Alkali-activated slag (AAS) shows the highest residual load
- All the mixes have a similar behaviour

- Alkali-activated slag (AAS) and alkali-activated fly ash (AAFA) have a different behaviour

Ref: König, A. et al., *Flexural behaviour of steel and macro-PP fibre reinforced concretes based on alkali-activated binders*, Construction and Building Materials, 211 (2019), 583-599

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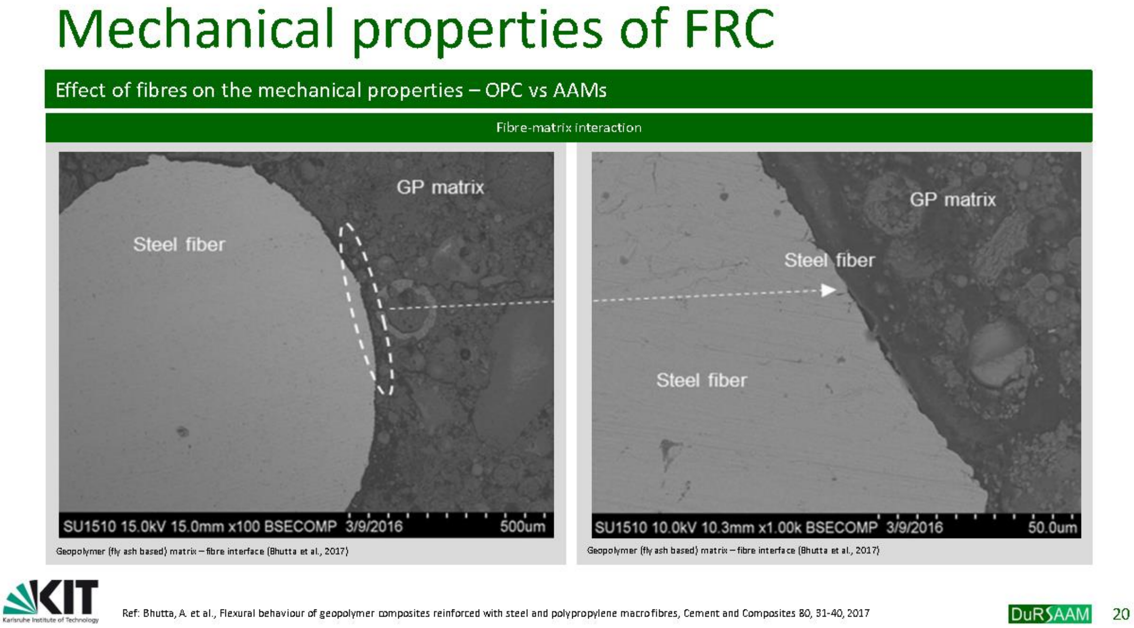


Mechanical properties of FRC

Effect of fibres on the mechanical properties – OPC vs AAMs

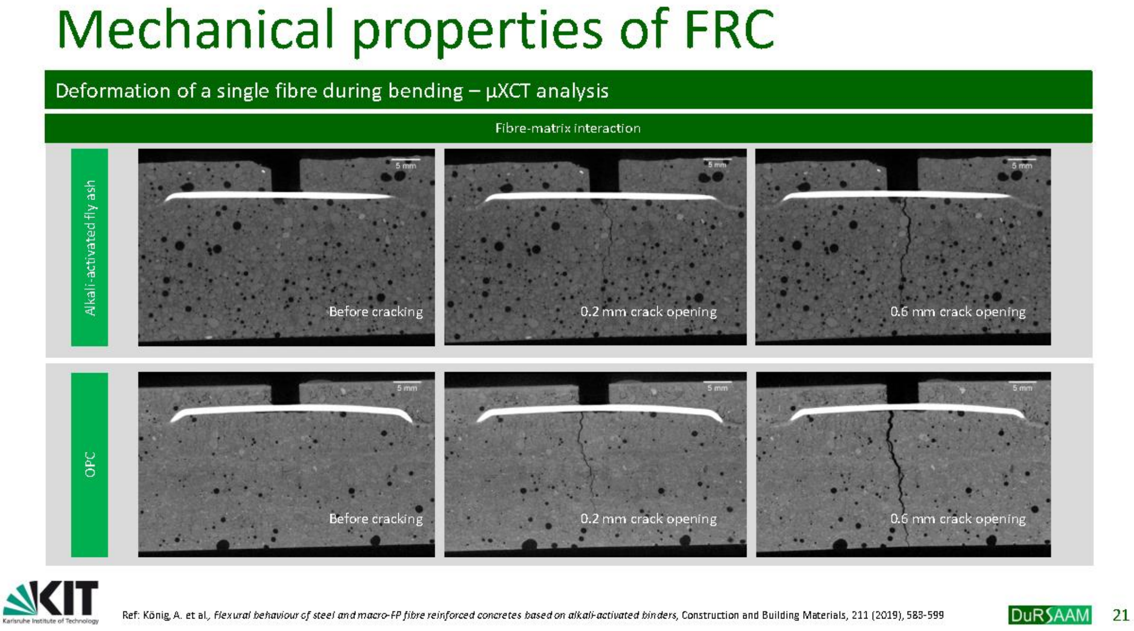
Fibre-matrix interaction

Geopolymer (fly ash based) matrix – fibre interface (Bhutta et al., 2017)

Geopolymer (fly ash based) matrix – fibre interface (Bhutta et al., 2017)

Ref: Bhutta, A. et al., Flexural behaviour of geopolymer composites reinforced with steel and polypropylene macro fibres, Cement and Composites 80, 31-40, 2017

DuRSAAM 20



Mechanical properties of FRC

Deformation of a single fibre during bending – µXCT analysis

Fibre-matrix interaction

Ref: König, A. et al., *Flexural behaviour of steel and macro-PP fibre reinforced concretes based on alkali-activated binders*, Construction and Building Materials, 211 (2019), 583-599

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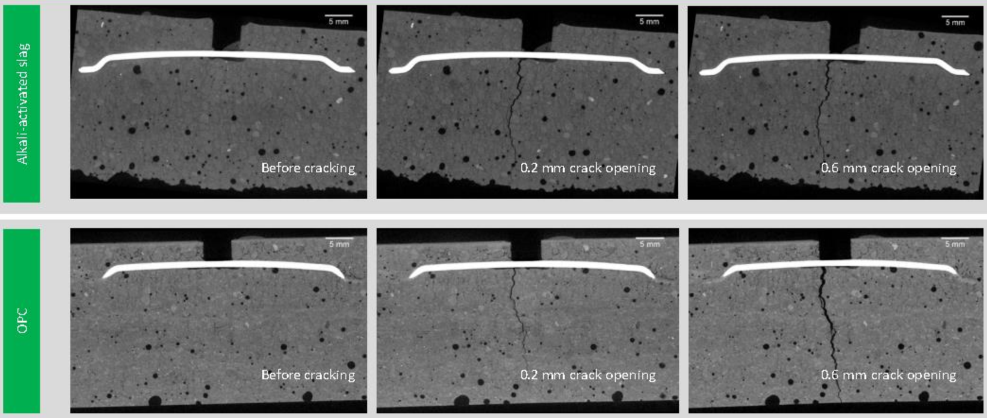
Mechanical properties of FRC

Deformation of a single fibre during bending – µXCT analysis

Fibre-matrix interaction

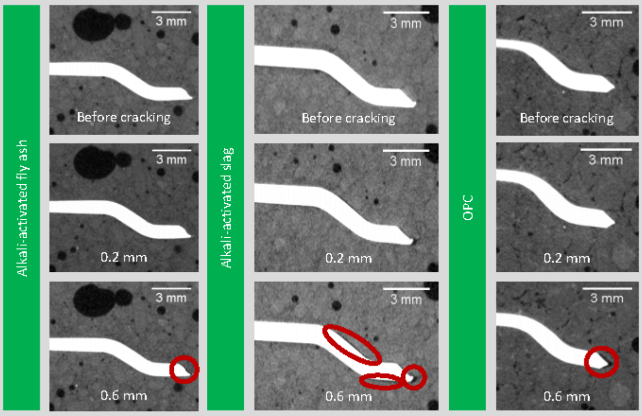


Ref: König, A. et al., *Flexural behaviour of steel and macro-PP fibre reinforced concretes based on alkali-activated binders*, Construction and Building Materials, 211 (2019), 583-599

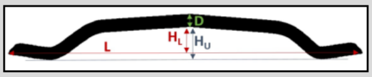
Mechanical properties of FRC

Deformation of a single fibre during bending – µXCT analysis

Fibre-matrix interaction



Fibre length variation



Parameters chosen to measure the length variation of the fibre

Parameter	Length variation					
Sample	AAFA [mm]		AAS [mm]		CEM I [mm]	
	0.2 mm	0.6 mm	0.2 mm	0.6 mm	0.2 mm	0.6 mm
H_U	0.00	0.08	0.09	0.08	0.06	0.17
H_L	0.06	0.21	0.06	0.08	0.13	0.20
L	0.03	-0.09	0.00	-0.21	0.00	-0.18
D	-0.03	-0.01	-0.03	-0.01	0.00	-0.01

The fibre thickness is not measurable once affected by deformation, which is not satisfactory explained by the values chosen.

Ref: König, A. et al., *Flexural behaviour of steel and macro-PP fibre reinforced concretes based on alkali-activated binders*, Construction and Building Materials, 211 (2019), 583-599

11. AAM lab work

Frank Dehn

Having gained theoretical insights with respect to alkali-activated concrete, it might be good to experience the manufacturing of AAM concrete. This can be easily achieved in a concrete lab or similar workshop, provided that you can get hold on the constituent materials. In this chapter, two exemplary mix designs (one concrete and one mortar) are provided for those who want to get first experience with making AAM concrete.

Part 1: Fly ash concrete

Material and Proportions

Product	Mass (kg)
Fly Ash (class F)	15.032
NaOH solution (50% solid, 50% water)	2.270
Waterglass (35% solid, 65% water)	4.026
Extra water	1.187
Aggregate (0-2 mm)	16.681
Aggregate (2-8 mm)	16.681
Aggregate (8-16 mm)	22.242
Superplasticizer : BB334-BASF	0.075

Moulds of (15cm*15cm*15cm)

Corresponding parameters

water:binder = 0.33 (kg:kg)
SiO_2:Na_2O = 0.91 (mol:mol, in the solution)
SiO_2:H_2O = 0.065 (mol:mol, in the solution)

Protocol

Mix aggregates and binder	60s
Add waterglass, then sodium hydroxide, then water and let mix	60s
Add progressively superplasticizer, if needed	
Fill cubes (15cm*15cm*15cm)	

Curing

-2 cubes at ambient conditions (T=20°C, RH=65%)
-2 cubes cured at 70°C during 48 hours then ambient temperature

Compressive strength after 7 days

Compressive strength (MPa)

Curing conditions	Sample 1	Sample 2	Average
Ambient conditions			
Curing 70°C 48 hours			

Part 2: Metakaolin mortars

Material and Proportions

Product		Mass (g) for Specimen 1	Mass (g) for Specimen 2
Metakaolin	(MetaMax)	300	300
NaOH solution	(50% solid, 50% water)	180	180
Waterglass	(35% solid, 65% water)	320	320
Extra water		-	50
Sand	(0-2 mm)	1350	1350

Moulds of 4cm*4cm*16cm

Corresponding parameters

water:binder = 1.00 (kg:kg)
SiO_2:Na_2O = 0.92 (mol:mol, in the solution)
SiO_2:H_2O = 0.085 (mol:mol, in the solution)

Protocol

1. Sand + metakaolin mixed for 30s.
2. After 30s, add activators.
3. Let all mix during 60s at low speed.
4. Stop the mix for 30s during which one should remove the material from the paddle.
5. Mix again at high speed during 60s.

Workability

	Specimen 1	Specimen 2
Workability		

Compressive strength after 7 days (storage: T=20°C, RH=65%)

Compressive strength (MPa)

Sample	Specimen 1	Specimen 2
1		
2		
3		

About the teachers

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Chair of Building Materials and Concrete Construction at the Institute of Concrete Structures and Building Materials (IMB), Director of the Materials Testing and Reasearch Laboratory (MPA), Member of the Presidium and Co-Chair of Techical Council of the International Federation for Strcutural Concrete (*fib*), Co-Chair of RILEM TC MPA - Mechanical Properties of Alkali-activated Materials, Member of National and International Standardization Commitees and Expert Boards related to Concrete, Editor-in-Chief “Structural Concrete”

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Associate professor in the Section of Materials and Environment of TUDelft, chair of the research group of Concrete Modelling and Materials Behavior, author/co-author of 300 journal/conference papers, editor/co-editor of 8 conference proceedings and Chapter contribution of 6 books, member of several RILEM Technical Committees like TC-ICC, TC-ATC, TC-SHC and TC-SAP, TC-DTA and *fib* committee of 8.10 and 8.12.

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Stijn Matthys is full professor on renovation of civil structures at Ghent University, Magnel Laboratory for Concrete Research. He is manager of the Ghent University "DuraBUILDmaterials" knowledge cluster. His expertise relates to structural renovation of civil structures, fibre reinforced polymer (FRP) reinforcement, structural behaviour of concrete structures, damage diagnostics and monitoring, and technologies for durable building materials and techniques.

About DuRSAAM

DuRSAAM is a collaborative PhD framework creating a critical mass of experts skilled in innovative alkali-activated material (AAM) concrete, as a key enabling technology for a sustainable and resilient built environment. AAM technology presents a new generation of materials, ideally conceived to respond to the need for more efficient, durable, eco-friendly and reliable construction, and utilizing by-product resources as raw materials. Modern concrete will be produced with low carbon footprint (CO2 emissions reduced by 80%), lower energy consumption and reduced use of primary resources (>1.5 t raw materials are quarried per t Portland cement clinker; this will be reduced by >60%), and with an addressable market for AAM binders of 5 B€/yr. DuRSAAM answers unmet industry demands, to facilitate emerging AAM technology for continued market entry and to unlock its potential in society.

The consortium brings together 7 academic and 15 non-academic partners, to excel in the scientific development and exploitation of AAM concrete, advancing design, modelling and practice beyond the state-of-the-art. It holds a unique focus on: (1) today's concerns of users and engineers that the durability and sustainability of AAM concrete is yet insufficiently quantified; and (2) provision of an AAM technology for rehabilitation of structures to meet the growing demand for renovation, to be developed in parallel with AAM for new concrete structures.

DuRSAAM runs from 2018 till 2023 and delivers world-leading training in this multidisciplinary field through 13 PhDs in interrelated aspects of AAM concrete, fibre reinforced high-performance concrete, and textile-reinforced mortar, as well as sustainability assessment. The outcomes will be instrumental in delivering a sustainable future in Europe's construction industry, which is increasingly driven by the growing demand for durable yet cost-effective solutions, driving a greater focus on reliable and comprehensive eco-efficient material technologies such as AAM.

The PhD Training Network on Durable, Reliable and
Sustainable Structures with Alkali-Activated Materials

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