CONCRETE MATERIALS

What they do for - and to - Concrete!
“Concrete”
Concrete Composition
Concrete Composition - Detail

- Graded Aggregate
- Workable Mix = No Voids
- Cohesive Mix = No Segregation
- Good Paste Coverage
Concrete Materials

- Cement
- Fly Ash
- Ground Granulated Blast Furnace Slag (GGBFS / ‘Slag’)
- Amorphous Silica(s) / Silica Fume
- Aggregates

- A Brief Review - Geopolymer Concrete and Portland Cement Concrete

- Challenges and Opportunities – materials and geopolymer concrete
(Portland) Cement - Manufacture

- Patented in 1824
- Conversion of a set of ‘natural minerals’ into a set of ‘synthetic minerals’
- Synthetic minerals are anhydrous and (relatively) unstable
- CO₂ from ‘Portland cement’ manufacture ~820kg per tonne
Cement Manufacture cont’d.

Clinker Milling:  Clinker + gypsum + mineral addition => ‘Type GP’ Cement

Gypsum:  Add gypsum (~5%) when milling to manage setting times  
          $\text{C}_3\text{A} \Rightarrow$ Flash Set. Gypsum prevents immediate $\text{C}_3\text{A}$ hydration
Cement Reactivity

Hydration Reaction

All cement minerals react with water – different rates / different heat outputs

Strength performance dominated by Calcium Silicate minerals

\[ \text{CS} + \text{H} \rightarrow \text{CSH} + \text{CH} + \text{Heat} \]

- Calcium silicate + Water
- Calcium silicate hydrate + Lime + Heat

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Heat of Hydration (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_3\text{S} )</td>
<td>502</td>
</tr>
<tr>
<td>( \text{C}_2\text{S} )</td>
<td>260</td>
</tr>
<tr>
<td>( \text{C}_3\text{A} )</td>
<td>867</td>
</tr>
<tr>
<td>( \text{C}_4\text{AF} )</td>
<td>419</td>
</tr>
</tbody>
</table>
Cement Reactivity cont’d.

Reaction Parameters

- Rate of a chemical reaction typically varies with (a) proportion and concentration of reactants, (b) time, and (c) temperature
- With cement - rate also varies with surface area available for reaction
Hydration Products and Cement Paste Structure

<table>
<thead>
<tr>
<th>Phase</th>
<th>Phase name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Initial C-S-H phase</td>
<td>The C-S-H phase is initially formed. C₃A forms a gel fastest.</td>
</tr>
<tr>
<td>(b)</td>
<td>Forming of gels</td>
<td>The volume of cement grain decreases as a gel forms at the surface. Cement grains are still able to move independently, but as hydration grows, weak interlocking begins. Part of the cement is in a thixotropic state; vibration can break the weak bonds.</td>
</tr>
<tr>
<td>(c)</td>
<td>Initial set—development of weak skeleton</td>
<td>The initial set occurs with the development of a weak skeleton in which cement grains are held in place.</td>
</tr>
<tr>
<td>(d)</td>
<td>Final set—development of rigid skeleton</td>
<td>Final set occurs as the skeleton becomes rigid, cement particles are locked in place, and spacing between cement grains increases due to the volume reduction of the grains.</td>
</tr>
<tr>
<td>(e)</td>
<td>Hardening.</td>
<td>Spaces between the cement grains are filled with hydration products as cement paste develops strength and durability.</td>
</tr>
</tbody>
</table>

1. Unhydrated cement
2. C-S-H gel containing gel pores (interlayer water) Gel (or interlayer) pores have a size of 0.5-2.5 nm and occupy about 28 vol. % of C-S-H gel
3. Capillary pores (capillary water) Capillary pores can have sizes from 10 to 1000 nm (1 μm) and even up to 5 μm. Volume and size depend on water/cement ratio and degree of hydration
4. Hexagonal crystals of calcium hydroxide (portlandite)

The chart on the right shows the development of hydration products over time.
## Water : Cement Ratio - Pictorial

<table>
<thead>
<tr>
<th>w:c Ratio</th>
<th>Water (L)</th>
<th>Cement (kg)</th>
<th>Cement (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>180</td>
<td>300</td>
<td>95</td>
</tr>
<tr>
<td>0.5</td>
<td>180</td>
<td>360</td>
<td>114</td>
</tr>
<tr>
<td>0.4</td>
<td>180</td>
<td>450</td>
<td>143</td>
</tr>
<tr>
<td>0.32</td>
<td>180</td>
<td>565</td>
<td>180</td>
</tr>
</tbody>
</table>

- **w:c ratio = 0.6**
- **w:c ratio = 0.32**
- **w:c ratio = 0.32 (No water reducer)**
# Hydration Products and Cement Paste Structure

<table>
<thead>
<tr>
<th>Phase</th>
<th>Phase name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Initial C-S-H phase</td>
<td>The C-S-H phase is initially formed. C₃A forms a gel fastest.</td>
</tr>
<tr>
<td>(b)</td>
<td>Forming of gels</td>
<td>The volume of cement grain decreases as a gel forms at the surface. Cement grains are still able to move independently, but as hydration grows, weak interlocking begins. Part of the cement is in a thixotropic state; vibration can break the weak bonds.</td>
</tr>
<tr>
<td>(c)</td>
<td>Initial set—development of weak skeleton</td>
<td>The initial set occurs with the development of a weak skeleton in which cement grains are held in place.</td>
</tr>
<tr>
<td>(d)</td>
<td>Final set—development of rigid skeleton</td>
<td>Final set occurs as the skeleton becomes rigid, cement particles are locked in place, and spacing between cement grains increases due to the volume reduction of the grains.</td>
</tr>
<tr>
<td>(e)</td>
<td>Hardening</td>
<td>Spaces between the cement grains are filled with hydration products as cement paste develops strength and durability.</td>
</tr>
</tbody>
</table>

**Diagram:**

1. **Unhydrated cement**
2. **C-S-H gel containing gel pores (interlayer water)**
   - Gel (or interlayer) pores have a size of 0.5-2.5 nm and occupy about 28 vol. % of C-S-H gel
3. **Capillary pores (capillary water)**
   - Capillary pores can have sizes from 10 to 1000 nm (1 μm) and even up to 5 μm. Volume and size depend on water/cement ratio and degree of hydration
4. **Hexagonal crystals of calcium hydroxide (portlandite)**

**Graph:**

A graph showing the amount of hydration products over time, including C-S-H, Ca(OH)₂, C₃A, F-H₃, Monosulfate, and Ettringite, indicating the hydration process over minutes, hours, and days.
Hydration Products

Paste – showing CSH gel; Portlandite; Ettringite; pores

Ettringite – hydration product of C₃A in presence of calcium sulfate – calcium aluminate sulfate hydrate (C-A-S-H)
Cement Paste - Porosity & Permeability

- Cement paste – a porous system
- Permeability – the ease with which a fluid can move through a porous medium
- Reduce porosity & permeability by (a) using lower w:c ratio, and (b) curing - and using SCM’s
Hydrated Cement - Pores & Pore Water

- Mechanical properties of hardened cement and concrete depend on physical structure (not chemical composition) of hydration products.
- Hardened cement paste = poorly crystallised hydrates of several compounds (gel) + crystals of lime + unhydrated cement particles + residue of water-filled spaces (from fresh paste) i.e. capillary pores (diameter about 0.1 – 1.3µm).
- Gel - High porosity (~28%) / interstitial voids (~3nm diameter) / water filled.
- Hydration products are colloidal / have high surface area / large amount of adsorbed free water on surface.
- If no water movement to/from cement paste, ongoing hydration uses up water => lower RH => ‘self desiccation’ => lower levels of hydration (cf. moist-curing).
- If w:c ratio >0.5 then hydration proceeds; if <0.42 then incomplete hydration.
- Ratio of CSH : Lime is about 7:2 (by mass).
Shrinkage

Volume changes in cement paste and concrete induce stresses that may result in cracking. Most significant volume change is due to paste shrinkage, including:

**Plastic shrinkage** – a volume contraction that occurs in the plastic state through the loss of water by evaporation or by suction (into the ‘ground’)

**Autogenous shrinkage** – due to loss of water used in ongoing hydration reaction

**Drying shrinkage** – loss of water from hardened concrete (paste) to unsaturated atmospheres. A slow process. Restrained to a degree by aggregate (volume and top size)

**Effects of Cement on Shrinkage** (AS2350.13)
1. High C₃A and fine grind => increased shrinkage
2. Type SL cement

**Drying Shrinkage at 50% R.H.**
Capillary Porosity and Plastic Shrinkage Cracking (PSC)

- Plastic shrinkage cracking occurs when surface of plastic concrete dries out
- Drying because bleed rate < evaporation rate
- Drying causes pore water to evaporate => increase in tensile capillary pressure
- Tensile strain capacity of fresh concrete >> hardened concrete
- Strain capacity lowest at ‘initial setting time’
- Need restraint for PSC to occur
Cement Paste at Aggregate Interface (Transition Zone)

- Cement paste structure adjacent to aggregate differs from bulk of paste
- Interface region – width of ~30-50µm
- Higher porosity - water film
  - less dense cement
  - lime / ettringite enrichment

- Can modify ‘interface / transition’ region
- >5% silica fume => more dense zone

- Potentially some reaction with aggregate
  Limestone + $C_3A$ => calcium carbo-aluminate
Cement Properties – Recent Changes

Two significant changes in cement properties over last 50 years

1. Increase in Fineness
2. Increase in $C_3S = \text{decrease in } C_2S$

**Fineness Index** typically increased from $\sim300\text{m}^2/\text{kg}$ to $\sim400\text{m}^2/\text{kg}$

$C_3S$ typically increased from $\sim50-55\%$ to $\sim65\%$

**Results:** (1) Cement hydrates quickly; strength gain is faster; MPa/kg is considerably higher, (2) Required strengths achieved with higher w:c ratio = lower cement contents $\Rightarrow$ higher levels of porosity, (3) higher heat & more lime produced.

**General belief:** Modern concrete less durable than earlier concrete

**Counter-point:** High(er) levels of SCM use $\Rightarrow$ improved durability performance
AS 3972 (2010)

- First Australian cement Standard (AS A2) – published in 1925
- AS 3972 (2010) featured (most prominently) an increase in the allowable level of ‘mineral addition’ from 5% to 7.5% - though initial proposal was to increase the allowable upper limit to 10%.
- ‘Mineral addition’ – typically limestone, fly ash or slag – usually inter-ground
- AS 3972 is primarily a ‘performance-based’ Standard
- Seven cement ‘types’ are described:

<table>
<thead>
<tr>
<th>General Purpose Cements</th>
<th>Special Purpose Cements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type GP</td>
<td>Type HE (High Early)</td>
</tr>
<tr>
<td>Type GB</td>
<td>Type LH (Low Heat)</td>
</tr>
<tr>
<td>Type GL</td>
<td>Type SL (Shrinkage Limited)</td>
</tr>
<tr>
<td></td>
<td>Type SR (Sulfate Resisting)</td>
</tr>
</tbody>
</table>

Notes:
- Type GB – no upper limit for fly ash and/or slag. Max. 10% silica fume
- Type GL – upper limit of 20% limestone (inter-ground)
- Special Purpose cements - no compositional limits
- performance limits nominated for tests specific to each cement type
Cement - Key Points

• (Portland) cement is a universal material (some different raw materials)
• The technology is proven and well understood
• The hydration reaction is of critical importance
• Mechanical properties of hardened cement / concrete depend on the physical structure of hydration products
• Reduced paste porosity and permeability are obtained fundamentally with (a) low w:b ratio, and (b) good curing
• The complex paste pore structure affects most concrete properties
• The transition / interface zone between the cement paste and aggregate surfaces is complex and important and its performance can be modified
• Changes to the physical nature and mineralogy of modern cements have had (arguably) positive and negative effects – ‘negative’ can be mitigated
• The high level of embodied CO$_2$ of Portland cement will continue to present challenges with its ongoing use
Supplementary Cementitious Materials (SCM’s)

- **Fly ash**: Ground granulated blast furnace slag (GGBFS); Amorphous silica (including Silica fume)
- Mostly ‘waste’ materials - derived from large industrial processes – amorphous structure
- Typically process the ‘waste’ to yield a ‘Concrete Grade’ product
- Material properties specified in **Australian Standard 3582** series (revised in 2016)
  - Part 1: Fly ash; Part 2: Slag – Ground granulated blast furnace; Part 3: Amorphous silica

Not ‘cementitious’ alone – require Portland cement and water

Contribute to reducing embodied CO₂ levels in concrete:

OPC ~ 820kg CO₂ / t  Australian Cementitious ~ 590kg CO₂ / t
The Materials

- OPC
- GGBFS
- FLY ASH (1)
- FLY ASH (2)
- SILICA FUME
The Pozzolanic Reaction

1. Cement Hydration Reaction

\[
\text{CS} + \text{H} \rightarrow \text{CSH} + \text{CH}
\]

(Calcium Silicates) (Water)  \hspace{50pt} \text{(Calcium Silicate Hydrate)} \hspace{50pt} \text{(Lime)}

2. Pozzolanic Reaction

\[
\text{CH} + \text{Si} \rightarrow \text{CSH}
\]

(Lime) (Silica)  \hspace{50pt} \text{(Calcium Silicate Hydrate)}

(in the presence of water)
Fly Ash

- Derived from minerals associated with **hard** coal (clays, quartz, siderite etc.) - heated to \( \sim 1800^\circ\text{C} \) in furnace - melted & then quenched
- Mainly spherical, **amorphous** glass particles - typically 60-70% glass - mineral components may include quartz, mullite and magnetite
- Size range typically 0.1 - 100\( \mu \)m. ‘Concrete Grade’ mmd = 10 - 15\( \mu \)m

**Key quality parameters** [AS 3582.1 (2016)]
- Fineness = % passing 45\( \mu \)m sieve (typically 75 – 85%)
- Loss on Ignition (unburned coal char) = <4% (typically 1 – 2%)

- Test in concrete - assess effect on plastic & hardened properties
- General use - 25% cement replacement
  - HVFA – 40% (+?) replacement
- Two States in Australia produce fly ash (Qld & NSW)
- Some importation of fly ash from India

*Inter-bedding of coal and minerals*
Coal-fired Power Station

- Coal Stockpile
- Coal Mill
- Ash Collection
- Furnace
Fly Ash

• Derived from minerals associated with hard coal (clays, quartz, siderite etc.) - heated to ~1800°C in furnace - melted & then quenched
• Mainly spherical, amorphous glass particles - typically 60-70% glass - mineral components may include quartz, mullite and magnetite
• Size range typically 0.1 - 100µm. ‘Concrete Grade’ mmd = 10 - 15µm

Key quality parameters [AS 3582.1 (2016)]

Fineness = % passing 45µm sieve (typically 75 – 85%)
Loss on Ignition (unburned coal char) = <4% (typically 1 – 2%)

• Test in concrete - assess effect on plastic & hardened properties
• General use - 25% cement replacement
  - HVFA – 40% (+?) replacement
• Two States in Australia produce fly ash (Qld & NSW)
• Some importation of fly ash from India

Inter-bedding of coal and minerals
Fly Ash(es)

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>72.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>23.5%</td>
</tr>
<tr>
<td></td>
<td>Fe₂O₃</td>
<td>1.0%</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>49.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>26.0%</td>
</tr>
<tr>
<td></td>
<td>Fe₂O₃</td>
<td>14.5%</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>4.5%</td>
</tr>
</tbody>
</table>
Fly Ash in Concrete – Plastic State

- High (or ultra-fine) fly ash LOI => reduced air entrainment
- Fly ash can lower water demand (relative to 100% OPC)
  - typically 5 – 12L.m\(^{-3}\)
- Workability improved - ‘Ball bearing’ effect or ‘paste volume’ effect?
  (Fly ash SG ~ 2.1 – 2.3)
  - replace 100kg OPC with 100kg fly ash => extra ~15L paste volume
- More fines => more cohesive mix => improved pumping characteristics
- Less water + more cohesive + more fines => less concrete bleed
- Less OPC = slower stiffening/setting => delayed finishing (~30 minutes)
- Less bleed + slower set => higher propensity for plastic shrinkage cracking
- Less bleed + slower set => increased risk of finishing too early
- More paste => easier finishing
Fly Ash in Concrete – Hardened State

• OPC replacement level – typically (25%) & HVFA concrete (40%)
• Slower strength gain, but higher later age strengths
• Durability improved – chloride ion penetration / sulfate resistance
• ASR mitigation - minimum 20-25% cement replacement

Rapid Chloride Permeability (to AASHTO T277-83)

Sulfate Expansion (to AS 2350.14)
Ground Granulated (Iron) Blast Furnace Slag (GGBFS)

- Known generally as ‘Slag’
- Waste from iron blast furnace operations
- Mineral impurities (from ore) + limestone + heat => molten slag
- Quench slag – rapid cooling => glassy, sand-like product (Granulated Slag)
- Mill granulated slag in ‘cement’ mill to Fineness > cement (+gypsum?)
  mmd = 10-15 microns
- Replacement proportions: General use ~ 30% OPC replacement
  LH & high durability ~ 65% OPC replacement
- One domestic slag granulate source (Port Kembla); balance imported

Key Quality Parameters [AS 3582.2 (2016)]
- Fineness = % passing 45 micron sieve (No limit in Standard)
- Alumina (Al$_2$O$_3$) = 18.0% maximum

NOTE: GGBFS glass content typically >95%
GGBFS Production

Iron Ore + Coke + Limestone (flux)

Quench (Air or Water Spray)

Fineness Index (Approx. 450-500m²/kg)

Granulated Slag
Ground Granulated (Iron) Blast Furnace Slag (GGBFS)

- Known generally as ‘Slag’
- Waste from iron blast furnace operations
- Mineral impurities (from ore) + limestone + heat => molten slag
- Quench slag – rapid cooling => glassy, sand-like product (Granulated Slag)
- Mill granulated slag in ‘cement’ mill to Fineness > cement (+gypsum?)
  \[ \text{mmd} = 10-15 \text{ microns} \]
- Replacement proportions: General use ~ 30% OPC replacement
  LH & high durability ~ 65% OPC replacement
- One domestic slag granulate source (Port Kembla); balance imported

Key Quality Parameters [AS 3582.2 (2016)]
- Fineness = % passing 45 micron sieve (No limit in Standard)
- Alumina (\(\text{Al}_2\text{O}_3\)) = 18.0% maximum

NOTE: GGBFS glass content typically >95%
GGBFS Activation and Hydration

- GGBFS can be activated by alkalis or sulfates
- GGBFS – a latent hydraulic material – some reaction from first water contact
- In blends with OPC – (a) initial activation due to high pH; (b) gradual reaction in layers to form CSH-type products driven primarily by lime (CH)
- With sulfate activation – ‘super-sulfated cements’ – contain about 10% OPC plus about 10% CaSO₄ => good concrete performance, particularly sulfate resistance
- Boral - Envisia® - a low-carbon, high-performance concrete – uses an activated slag binder
- Minefill – slag-based binders work very well in low-grade backfill materials used to fill mine-voids in metalliferous mines where sulfur-containing ores are present. Sulfates present activate the slag to give very high early and later-age strengths (able to use lower binder contents to achieve the strengths required.)
GGBFS in Concrete – Plastic State

- Concrete mix handling not dis-similar to OPC concrete
- Only slight paste volume increase (slag SG ~ 2.9)
- Slag mixes can show higher bleed levels (bleed rate and total bleed)
- Slowing of stiffening / setting time due to OPC reduction
- Finishing characteristic similar to OPC concrete
GGBFS in Concrete – Hardened State

- Slower strength gain, but good later age strengths
- Sometimes purple / blue / green colouration - after forms removed
- Concrete otherwise whiter - less ‘grey’
- Durability significantly improved – particularly resistance to chloride ion penetration and sulfate attack – with GGBFS substitution 60%+
- Australian research (1980’s) – use of 60% slag concrete in submerged tube structures in Sydney Harbour Tunnel – high durability (chloride ion and sulfate resistance and low-heat of hydration) =>100 year design life
- ASR resistance improved – minimum 50% cement replacement
- Concrete drying shrinkage - increased (?)

Source: Concrete Construction – 31 August, 2013
Canadian Chancery, Washington D.C., USA
Amorphous Silica(s)

- Diverse group of materials – natural and synthetic sources, including:
  - Waste from silicon / ferro-silicon processes (since 1970’s)
  - Volcanic / geothermal deposits (e.g. NZ)
  - Rice Husk Ash
  - Meta-kaolin (anhydrous calcined kaolin – calcined at about 650 - 700°C)
  - Natural sources – e.g. Pitchstone (Nth. Qld.)
- Most common – Silica Fume (imports / WA and Tasmanian sources)
- In NZ - ‘Microsilica’ – mined from geothermal deposits near Rotorua

Key Quality Parameters [AS 3582.3 (2016)]
- Total silica content = 85% SiO₂ minimum
- Loss on Ignition = 6.0% maximum
Amorphous Silica(s)

Xibei Ferroalloys, China

Spring 2001

Spring 2002

Meta-kaolin

Rice Husk Ash

NZ Microsilica
Silica Fume in Concrete – Plastic State

- When used at 10% OPC replacement concrete is very cohesive / ‘sticky’.
- Use SP’s for workability management. Target 25-50mm higher slump to assist with placement and compaction.
- Concrete highly cohesive => very low bleed rates – high risk of ‘plastic shrinkage cracking’.
- Cohesive nature and low bleed impact ability to finish.
- Very useful in shotcrete.

Graphics from “The History of Silica Fume in Concrete” by Elkem Materials

OPC = 400m²/kg; Silica Fume = 20,000m²/kg
Silica Fume in Concrete – Hardened State

- Silica fume used for high strengths and high durability. Cementitious efficiency >> OPC.
- Effectiveness in concrete > mortar / grout
- Excellent for high-strength columns – not ideal for flat-work.
- Strength growth limited after 28-days.
- To achieve optimum strength and durability need >5% replacement levels.
- Refined pore structure => low permeability => excellent resistance to chloride ion penetration and sulfate attack
- ASR resistance due to alkali ‘binding’ and reduced water ingress
- Carbonation low for high-strength concrete

In Iceland, where aggregates derive from volcanic sources with high (alkali) reactivity, silica fume at 7% replacement level has been successfully used for ASR control since 1979.
# Compressive Strength Performance of SCM’s

<table>
<thead>
<tr>
<th>Age</th>
<th>OPC</th>
<th>25% FA</th>
<th>40% FA</th>
<th>30% GGBFS*</th>
<th>65% GGBFS*</th>
<th>10% SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-days</td>
<td>65</td>
<td>50</td>
<td>45</td>
<td>60</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>7-days</td>
<td>80</td>
<td>65</td>
<td>60</td>
<td>75</td>
<td>75</td>
<td>85</td>
</tr>
<tr>
<td>28-days</td>
<td>100</td>
<td>95</td>
<td>85</td>
<td>100</td>
<td>105</td>
<td>120</td>
</tr>
<tr>
<td>90-days</td>
<td>115</td>
<td>125</td>
<td>125</td>
<td>120</td>
<td>115</td>
<td>125</td>
</tr>
</tbody>
</table>

Notes: Values for 28-day results relative to one another. Values for 3, 7 and 90-day results relative to 100% for the 28-day result for that material. Performance of GGBFS materials dependent on Fineness and use (or not) of gypsum additive. All mixes nominal 400kg.m⁻³ binder content.

Typical ‘cement equivalence’ values – Fly ash = ~70-110% at 25% substitution; less at 40% substitution. GGBFS = ~100%. Silica Fume = ~200-400% (depending on substitution rate and binder content).
SCM’s and Concrete Durability

• Primarily through the modification of paste pore structure as a result of (a) increased paste volume, (b) production of additional CSH, and (c) dilution of Portland cement - SCM’s improve all aspects of durability performance.

• Modifying cement chemistry or mineralogy (e.g. ASTM Types I – V) is a much less effective way of improving durability performance – as exampled by using low-C₃A cements for SR => lower resistance to Cl⁻ penetration.

<table>
<thead>
<tr>
<th>Type of cement</th>
<th>D x 10⁹ cm²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC/65% BFS</td>
<td>4.1</td>
</tr>
<tr>
<td>OPC/30% PFA</td>
<td>14.7</td>
</tr>
<tr>
<td>OPC</td>
<td>44.7</td>
</tr>
<tr>
<td>SRPC</td>
<td>100.0</td>
</tr>
</tbody>
</table>

**Chloride Ion Diffusivity**

Cement paste (25°C) – w:c 0.5
(from CIA – Durable Concrete Structures)

**Sulfate Expansion** (to AS 2350.14)

**Reduction in ASR Expansion with SiF**

Effects of dose rate and SiO₂ Content
Aggregates - General

• About 75% of concrete volume
• Affect economic and physical performance
• Plastic state - Workability
  - Finishing
  - Bleed
  - Pumping
• Hardened state - Compressive strength
  - Drying shrinkage
  - Durability
  - Abrasion
  - Appearance

Key Quality Parameters [AS 2758.1 (2009)]
Density (Bulk & Particle) and Absorption
Grading (Each material and combined)
Durability
Key Plastic State Effects

Workability – the ability to place and finish concrete is critical to its performance. Compaction of slumped concrete is vital in achieving strength and durability performance. Flowing concrete allows placement in large / congested elements. Good workability relies on proper combined aggregate grading.

Segregation – concrete must be cohesive enough to resist segregation and still allow proper placing. Proportion and grading of fines are critical.

Pumping – delivery of concrete by pumps is now a standard practice and ‘pump mixes’ are a thing of the past – (almost) all mixes must be able to be pumped. Combined grading and fines at 300µm and 150µm are critical.

Bleed – one of the most common issues in domestic concrete is Plastic Shrinkage Cracking – as previously described. In industrial floors, management of bleed is critical to the prevention of delamination.
Key Hardened State Effects

- **Compressive strength** – **optimise** compressive strength performance by using max. aggregate size and a combined grading that provides the required workability and allows use of the lowest possible water:binder ratio and cement content.

- **Drying shrinkage** – while it is the cement paste that ‘shrinks’, larger aggregate and higher aggregate proportions can assist by (a) reducing the cement (paste) requirement, and (b) helping to restrain drying shrinkage.

- **ASR** – an expansive reaction that can occur over time between highly alkaline cement paste and reactive minerals found in some aggregates.

**ASR Mitigation** (non-aggregate methods):
1. Use low-alkali cement
   
   [Total alkali $<$0.6% (as Na$_2$O equivalent)]

2. Reduce concrete permeability

   Water helps limit ASR gel expansion

3. Use SCM’s

---

**Drying shrinkage and aggregate volume**
Alkali Silica Reaction (ASR) – Aggregate Factors

- **Reactive aggregate** – aggregate containing ‘reactive’ silica minerals – often ‘altered’ by geological activity
- **Reactive minerals** – includes chalcedony, tridymite and opal – and these may occur in a variety of rock types
- **Alkali-aggregate reactivity** – may be determined from (a) petrographic examination, (b) mortar / concrete testing (c) history of use

ASR - requires the presence of (a) reactive mineral, (b) high levels of alkali (sodium and potassium – generally from cement), and (c) water.

Reactive silica + water => alkali-silicate gel

Alkali- silicate gel + water => ‘unlimited’ swelling

Swelling of hard aggregate particles => cracking
Aggregate Testing for Alkali Reactivity

- Two new Australian Standards (2014):
  AS 1141.60.1  Accelerated mortar bar test (AMBT)
  AS 1141.60.2  Concrete prism test (CPT)
- **AMBT**
  Aggregate + cement => mortar prisms – expose to NaOH at 80°C for 21-days – measure expansion and compare with limits – aggregate may be either Non-Reactive; Slowly-Reactive; Reactive
- **CPT**
  Concrete produced with aggregate and cement containing elevated alkali content – stored in water-bath at 38°C – measure expansion and compare with limit at 52 weeks. Can extend to 2 years.

Current Research – industry bodies/companies/universities - testing the AMBT with SCM’s – possible rapid method to assess SCM effectiveness in mitigating ASR
ASR Mitigation

- Simplest means of mitigating ASR is by using SCM’s to replace some cement

- SCM replacement levels:
  - Fly Ash: 20-25%
  - GGBFS: >50%
  - Silica Fume: 7-10%

Why do SCM’s work?

- (a) Very fine particles react with alkali; (b) High silica content exceeds ‘pessimum’ value; (c) Innocuous calcium alkali silicate formed; (d) Reduce permeability and limit water ingress.

- SCM differences: - Each have different proportions & reactivity of silica species
  - Fly ash – 50-70% SiO$_2$; GGBFS – 35% SiO$_2$; Silica Fume – 90%+ SiO$_2$ (ULTRA-FINE)

- Crushed glass as an aggregate replacement – susceptible to ASR
- Mitigate by either (a) SCM substitution, or (b) reduce top size to <300µm

Manufactured Sands

- **Manufactured Sand** – a purpose-made crushed fine aggregate produced from a suitable source material and designed for use in concrete …………..
- Need for manufactured sands driven by (a) reduced availability of natural sands, and (b) need to better utilise quarry materials
- Significant early resistance from specifiers due to lack of standardisation. Industry project created to assess (a) suitable tests, (b) how they should be used, and (c) acceptance criteria.

**Findings**

- Grading – not a specified test – general grading requirements nominated
- Deleterious Fines – a quality/quantity determinant: (% -75µm x MBV) < 150
- Shape / Texture – Flow Cone not suitable for ‘MS’ alone, but useful for blends
- Durability – use Degradation Factor or Sodium Sulfate Soundness tests
- Particle Density – acceptable range is 2.1 – 3.2 tonnes.m⁻³ (at SSD)

**Result:** AS 2758.1 (2009) amended to include Manufactured Sand requirements

A great example of the ‘industry’ overcoming a problem with a sustainable solution!
Concrete Performance Overview

Graded Aggregate

Workable Mix = No Voids

Cohesive Mix = No Segregation

Good Paste Coverage
Comparison – Geopolymer / Portland Cement Concrete

Portland Cement (patented by Aspdin - 1824)
- Widely used since about 1850
- Vast amount of research and experience
- Entrenched in construction and materials Standards
- Cement industry emits 5-7% of anthropogenic CO₂

Geopolymers (Professor Joseph Davidovits - 1979)
- Relatively new binder option
- Very considerable international research
  - Australia is a leading proponent
- Generally not included in Standards
  - work underway (e.g. RILEM)
- Some limited usage in construction
  - Australia is a leader
- Significantly lower embodied CO₂
Geopolymers – The Great Debate!

- Is it - the comparison with OPC concrete? No!
- It is - are Geopolymers and Alkali Activated Materials (AAM’s) the same?
- Yes! – University of Sheffield / RILEM; No! – Professor Davidovits

**Cement** hydration – CS + H => CSH  
A hydration reaction – combines water

**Activated slag** (after Glukhovsky) – forms CSH; CASH; NASH – combines water

**Geopolymers** (after Davidovits) – form cross-linked, inorganic polymers – a condensation reaction – ‘expels’ water as a by-product

**Davidovits view:**
- No water contained in molecular ‘geopolymer’ structure (IR Spectroscopy), and
- Evidence of cross-linked structure (NMR)

**RILEM view:** that hydration products and polymeric products co-exist, and they define them as AAM’s.
## Comparison – Geopolymer / Portland Cement Concrete

<table>
<thead>
<tr>
<th>Property</th>
<th>OPC Concrete</th>
<th>Geopolymer Concrete</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nature of Binder</td>
<td>CSH structure + Lime</td>
<td>Inorganic polymer (+CSH?)</td>
</tr>
<tr>
<td>Universality</td>
<td>Common mineral set</td>
<td>Variable – define by performance</td>
</tr>
<tr>
<td>Processing</td>
<td>High capital/heavy industry</td>
<td>Blending process</td>
</tr>
<tr>
<td>Technology</td>
<td>Common worldwide</td>
<td>Proprietary mixes</td>
</tr>
<tr>
<td>CO₂</td>
<td>Known – relatively high</td>
<td>Lower – no agreed calc’s.</td>
</tr>
<tr>
<td>Binder Standards</td>
<td>Well entrenched</td>
<td>Nil</td>
</tr>
<tr>
<td>Concrete Standards</td>
<td>Well entrenched</td>
<td>OPC-concrete Stds. applied</td>
</tr>
<tr>
<td>Binder Materials</td>
<td>Standardised</td>
<td>Various possible</td>
</tr>
<tr>
<td>Cost</td>
<td>Well understood</td>
<td>Higher than OPC-based</td>
</tr>
<tr>
<td>Workability</td>
<td>Easy to compact / finish</td>
<td>Readily compact / finish?</td>
</tr>
<tr>
<td>w:b Cohesive Range</td>
<td>About 0.3 – 1.0</td>
<td>Much narrower</td>
</tr>
<tr>
<td>Strength/Durability</td>
<td>Well understood</td>
<td>Low HoH; Good Comp. &amp; Tensile Strength; Low Shrink.</td>
</tr>
</tbody>
</table>
Materials - Challenges and Opportunities

**Cement**
No. 1 - CO$_2$: Persisting with rational investigation of mitigation strategies

**Fly Ash**
No. 1 - Sourcing: Knowing and understanding domestic and international options
No. 2 - Quality: Creating a commercially-sound understanding of product quality

**Slag**
No. 1 - Sourcing: Canvassing international options
No. 2 - Quality: Ensuring a commercially-sound understanding of product quality

**Amorphous Silica(s)**
No. 1 - Sources: Understand and evaluate ‘natural’ AS materials

**Aggregates**
No. 1 - Sourcing: Developing well-located quarries with a ‘licence to operate’
No. 2 - Quality: Ensuring technically sound understanding of key quality parameters

**Geopolymers**
No. 1 - Develop an improved understanding of binder cost and embodied CO$_2$
No. 2 - Develop application-specific understanding of geopolymer technology
Acknowledgements

Documentation published by the Concrete Institute of Australia (CIA) and Cement Concrete & Aggregates Australia (CCAA) has been used in the preparation of this talk. The use of the information is acknowledged and appreciated.

Thank you for attending!