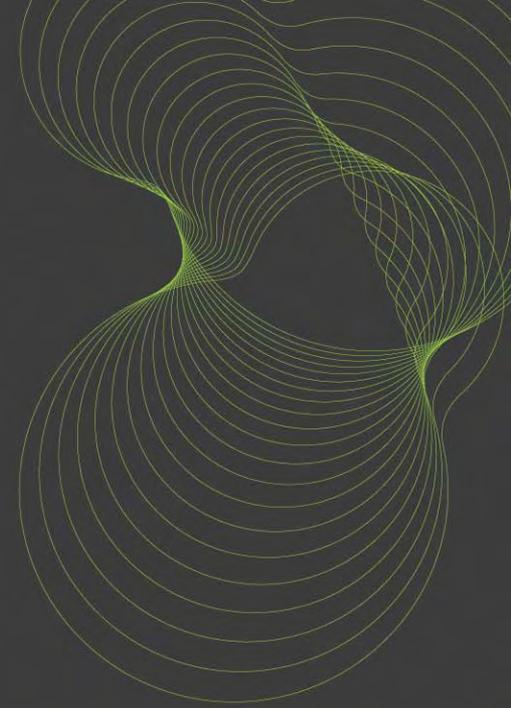


bre

Low-CO₂ Cements based on Calcium Sulfoaluminate

Keith Quillin BRE



About BRE

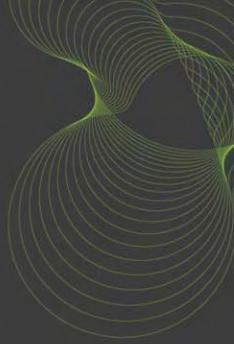
- Over 80 years as a leading authority on the built environment
- Much of work has underpinned UK Government policy, building regulations, codes and standards etc.
- Numerous programmes on cement and concrete
 - Durability and service life
 - Blended Portland cements
 - Alternative cements
 - Structural
- National and international reputation for knowledge and quality
- Privatised in 1997 - Now owned by the BRE Trust
- Have run a number of programmes on low CO₂ cements funded by DETR, DTI, Carbon Trust and Technology Strategy Board with industry support, as well as on a commercial basis

The Impact of Construction



- A big industry
 - *10% GDP in UK*
- major consumer of land and raw materials
 - *90% (260 million tonnes) of non-energy minerals*
- dust, noise and heavy transport
- major user of energy and producer of green house gases
- waste
 - *70 million tonnes in UK*
 - *13 million tonnes wasted on site*

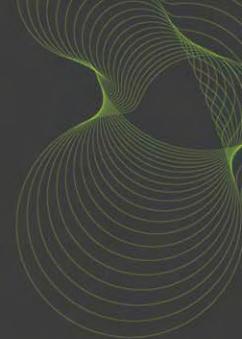
Our need for Concrete



- Most widely used and important construction material
- whole family of materials that can be tailored to almost any use
- made from locally available raw materials

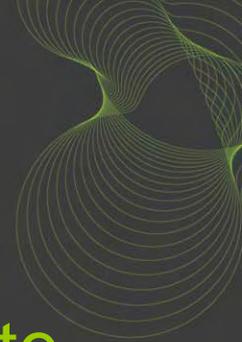
but:

- Largest component of waste stream (53%)
- Aggregate extraction is land-hungry
- Cement is intensive energy user and greenhouse gas producer



Concrete – An economic material

- The quantity of concrete poured in the UK per annum shows that it is a viable economic material. (Currently circa 40 million tonnes p.a.)
- The supply chain is generally considered to be lean and focused on price and delivery. A low margin, bulk supply business.



Factors Influencing the “CO₂-Efficiency” of Concrete.

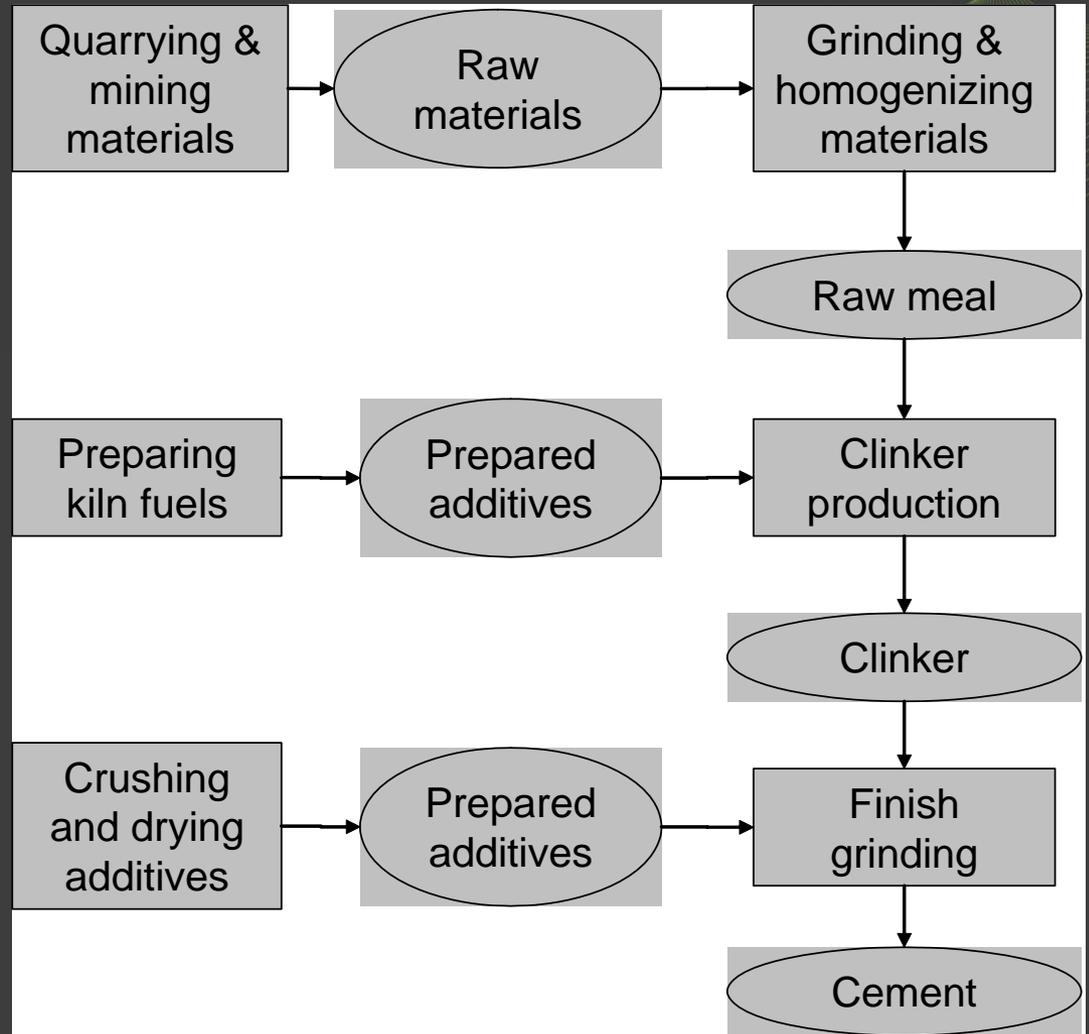
1. The total embodied CO₂ content of the clinker, which is the sum of its raw-materials CO₂ and fuel-derived CO₂ emissions during manufacture.
2. The composition of the cement (binder), considering the total embodied CO₂ content of each of its components.
3. The cement content of the concrete that is ultimately manufactured and must perform to a given specification. (We neglect any embodied CO₂ in aggregates, etc.)

Cement manufacture

- Portland cement clinker manufactured by heating intimate mixture of limestone and clay, generally in rotary kiln.
- Manufacture is intrinsically energy intensive and produces large amounts of CO₂.
- Manufacturing CO₂ emissions are the sum of 2 or 3 contributions:
 - The decarbonation of limestone by the reaction $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$
 - Energy used in heating the kiln to decarbonate limestone and to form components such as alite and belite.
 - Energy used in grinding the clinker

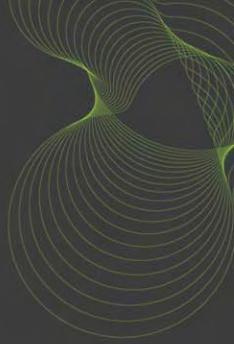
Cement manufacture

Schematic representation of cement manufacturing process^[1]



^[1] M Taylor, Global energy use, CO₂ emissions and the potential for reduction in the cement industry, Cement Energy Efficiency Workshop, Organised by IEA and WBCSD, Paris, September 2006

Energy consumption and CO₂ production in Portland cement manufacture



- Cement manufacture requires a large amount of energy
 - Clinker formation - approx. 1750kJ/Kg
 - Thermal losses
 - Consumption of electricity
 - Total of approx. 3600KJ/Kg
- CO₂ produced in decarbonation of CaCO₃ and in burning fuel
 - ~1.7 billion tonnes cement produced per annum
 - ~1 tonne of CO₂/tonne cement produced
 - 0.08 tonnes CO₂/tonne concrete (based on all concrete produced)
 - Up to 8% global CO₂ production (2% in UK)
- Also need to consider through-life CO₂ emissions from structure

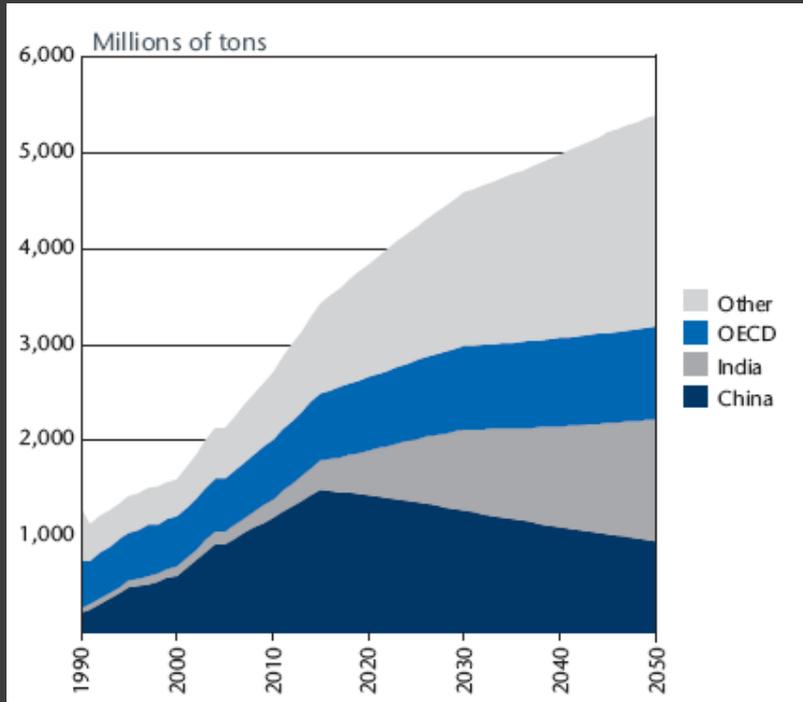


Theoretical Heat Balance for OPC Manufacture

(Assumes dry limestone and clay as kiln feed; analysis based on Lea, 3rd Edn., p126)

Kiln section	Temperature range	Process	Heat required, kJ/g (GJ/t) of clinker
Preheater	20 – 900° C	heating raw feed to 900° C	+1.53
“	about 450° C	dehydration of clays	+0.17
“	20 – 900° C	cooling CO₂ and H₂O	- 0.59
Calciner	about 900° C	dissociation of calcite	+1.99
“	about 900° C	reactions of dehydrated clays	- 0.04
Rotary Kiln	900 –1400° C	heating feed from 900 to 1400° C	+0.52
“	900 –1400° C	formation of clinker phases	- 0.31
Clinker cooler	1400 – 20° C	cooling of clinker to 20° C	- 1.51
		Net heat required:	+1.76

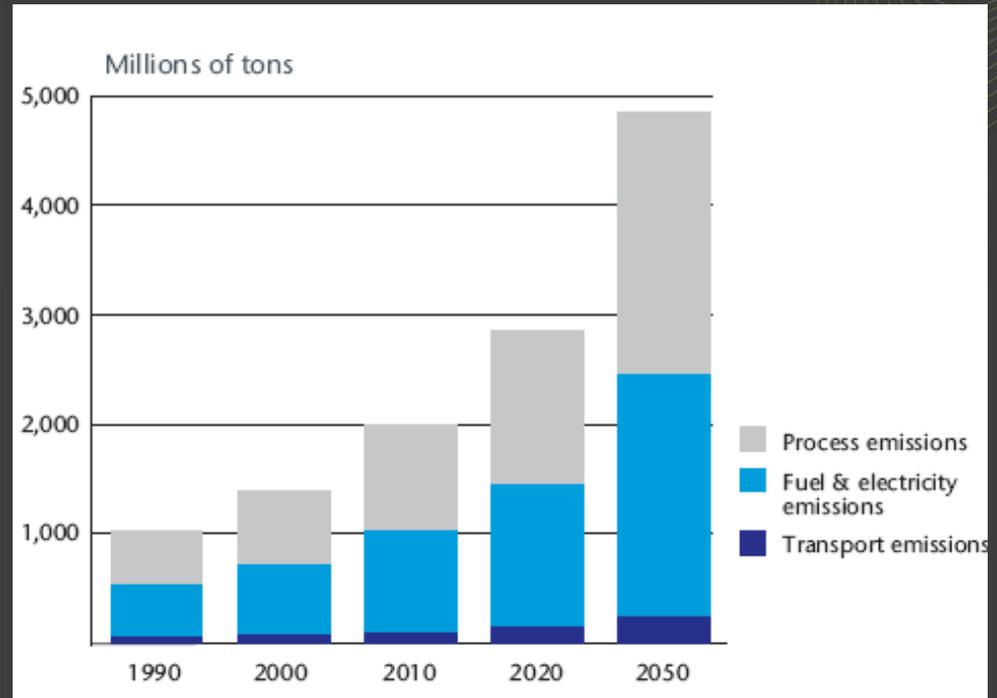
Projections for global cement manufacture and CO₂ emissions to 2050 (industry data)



Predicted growth in global cement demand (million tonnes p.a)

Currently ~2 billion tonnes pa

Rising to over 5 billion tonnes pa by 2050



Cement-related CO₂ emissions (no change in current practices)

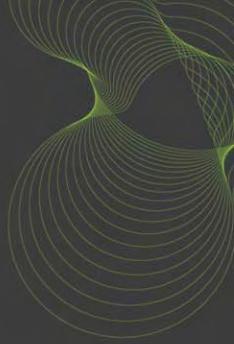
If best practice implemented globally CO₂ emissions would rise to 2.4–2.7 billion tonnes pa.

~5 billion tonnes pa if current practices remain

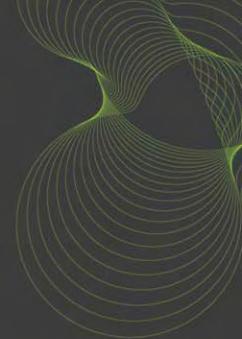
Cement Production and Associated CO₂ Emissions

	Production (%)	CO₂ emissions (%)
Africa	2.4	2.0
Latin America	5.9	4.7
North America	5.1	5.5
Middle East	7.1	6.7
OECD Pacific	6.3	4.3
Eastern Europe and Former Soviet Union	4.7	4.1
Europe	9.4	6.9
Other Asia	8.6	8.2
India	5.9	5.9
China	44.7	51.8
Total	100	100.0

Approaches to energy conservation and reduced CO₂ emissions



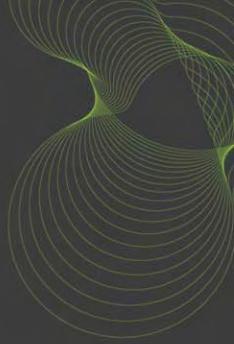
- Ongoing process improvements
- Use of wastes as fuels
- Use of waste materials as raw feed
- Fluxes and mineralisers to reduce clinkering temperatures
- More efficient use of cement
- Use of additions (e.g. pfa and ggbs)
- Alternative cements
- Capture of CO₂ emissions
- Recarbonation



Cement Manufacture

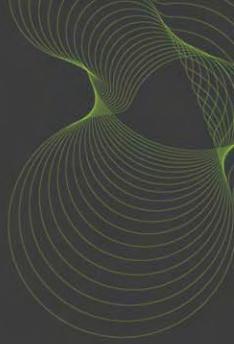
- 1 tonne CO₂/tonne cement often quoted
 - Industry data indicate 0.83 tonnes of CO₂/tonne Portland cement
 - 0.51 tonnes CO₂/tonne for decarbonation of limestone for PC
- Fuel-derived CO₂ emissions will diminish slowly for purely economic reasons.
- Cannot address decarbonation without changing composition of the cement

Cementing Systems of Potential Interest for General and Widespread Application



- Limestone-based cements:
 - Calcium silicate cements (portland cements; belite & alinite cements)
 - Lime-pozzolan cements (includes portland-pozzolan cements & hydraulic limes)
 - Calcium aluminosilicate cements (based on CAS glasses or blast furnace slags)
 - Calcium aluminate cements (based principally on CA)
 - Calcium sulfoaluminate cements (based principally on C_4A_3S)
 - Various combinations of the above systems
- Non limestone-based cements:
 - Alkali activated pozzolans (e.g. “Geopolymers”)
 - Calcium sulfate cements (“plasters”, etc.)
 - Mg-based cements

What is a low CO₂ cement?



- A low CO₂ cement can be defined as one which:
 - Releases less CO₂ from decarbonation of raw materials during manufacture than PC
- And/or
- Releases less CO₂ from energy use in manufacture than PC
 - It could also be one which reabsorbs significantly more CO₂ during use in a concrete or mortar than PC
 - *It may be possible to design concrete made using Portland cement to facilitate carbonation.*



Requirements for low carbon cements

In addition to low net CO₂ emissions:

- Economic to produce
- Readily available raw materials
- Ease of use in concrete
 - Properties of wet concrete
 - Strength development
- Suitable physical properties
- Durability and chemical resistance
- No problems with by-products, emissions, leachates etc
- Others?

Comparable or better than PC?

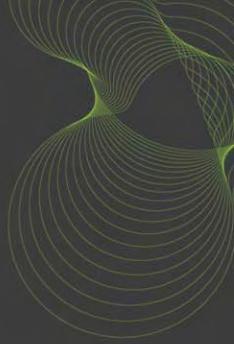


Apart from strength, what other performance-related parameters should we compare?

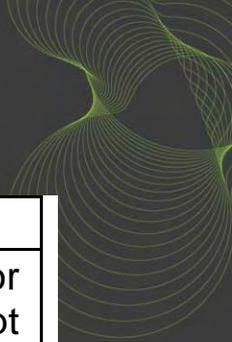
- Robustness with respect to:
 - Impurities in the cement-manufacturing process
 - Temperature and water-content variations in the fresh concrete
 - Admixtures or impurities in the concrete
 - Curing of the concrete
 - Surface finishing
- Durability with respect to:
 - Dissolution in pure water, or in dilute acids or bases, salt solutions, etc.
 - Attack by atmospheric gases (especially CO_2)
 - Protection of embedded reinforcement (steel, glass, etc.)
 - Time, humidity and temperature-dependent phase changes that can cause strength loss.
 - Paste volume changes that can cause cracking (e.g. due to changes in T or RH)
 - Reactions between the cement paste and the aggregates that can cause cracking
 - Excessive creep (generally a function of RH).

Such data are far from complete for most systems other than OPCs

Data on Portland cement concrete



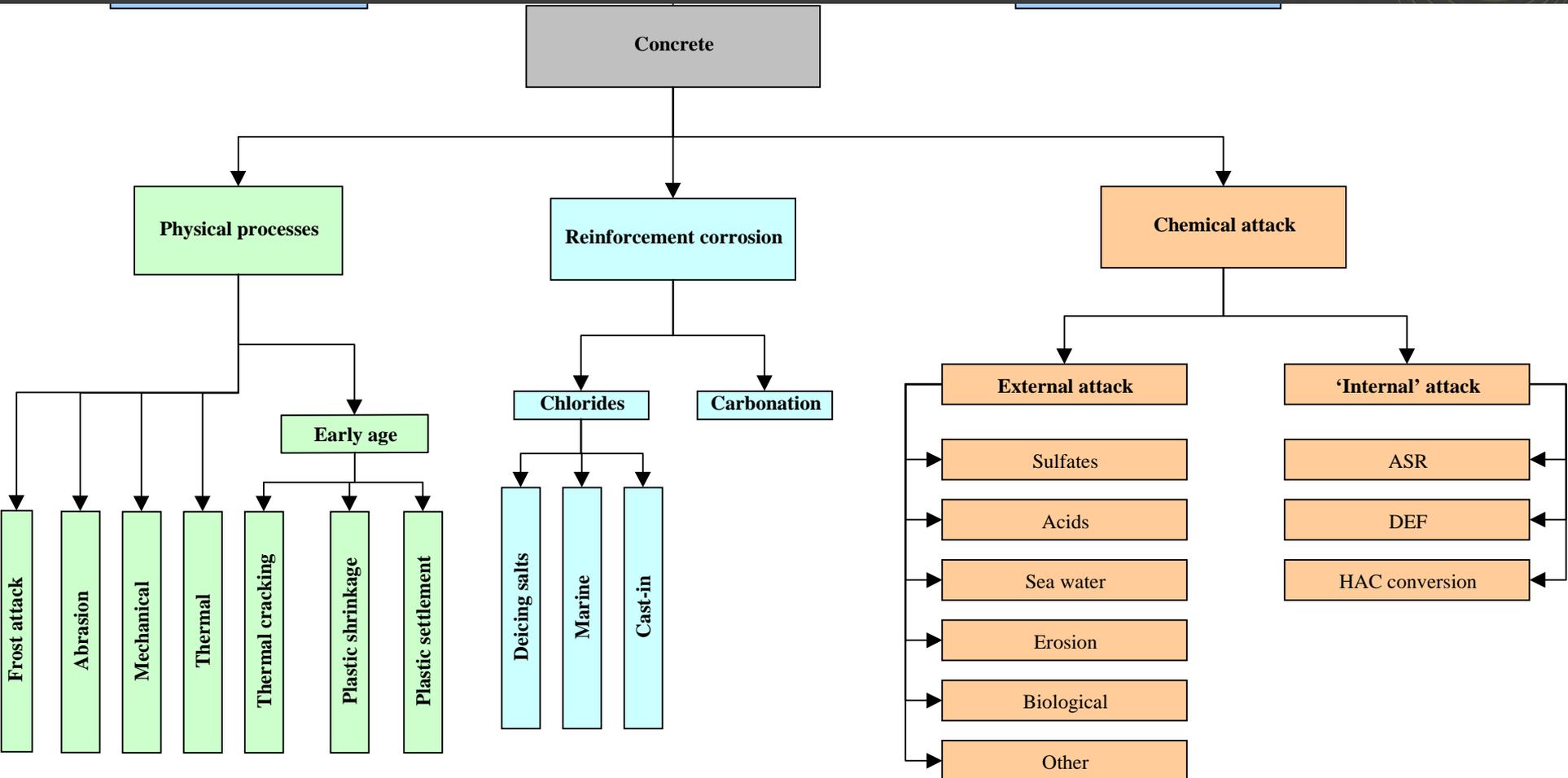
- There is a huge database of performance information on PC concrete:
 - Decades of use backed by research
 - Relationships between composition (cement content, water: cement ratio, aggregate type etc) and performance
 - Long term durability
- Provides strong foundation for codes and standards, guidance etc.
- This information is NOT applicable to new cements
- Similar data and guidance is essential if alternative cements are to be used by inherently cautious industry
- Major barrier to uptake



Exposure categories for concrete from EN206 and BS8500

Group	Class	Description
No risk of corrosion	X0	<ul style="list-style-type: none"> Concrete without reinforcement or embedded metal: All exposures except freeze/thaw, abrasion or chemical attack. Concrete with reinforcement or embedded metal: Very dry
Carbonation-induced corrosion	XC1	Dry or permanently wet
	XC2	Wet, rarely dry
	XC3/XC4	Moderate humidity or cyclic wet and dry
Chloride-induced corrosion resulting primarily from de-icing salts	XD1	Moderate humidity
	XD2	Wet, rarely dry
	XD3	Cyclic wet and dry
Corrosion induced by chlorides from sea water	XS1	Exposed to airborne salt but not in direct contact with sea water
	XS2	Permanently submerged
	XS3	Tidal, splash and spray zones
Freeze-thaw attack	XF1	Moderate water saturation without de-icing agent
	XF2	Moderate water saturation with de-icing agent
	XF3	High water saturation, without de-icing agent
	XF4	High water saturation, with de-icing agent or sea water
Chemical attack	XA1	Slightly aggressive chemical environments
	XA2	Moderately aggressive chemical environments
	XA3	Highly aggressive chemical environments

Deterioration processes affecting concrete



Sometimes steel corrodes.....



Carbonation induced corrosion





Background to the BRE-Carbon Trust project (2004-6)

- Managed by Building Research Establishment.
- Funded partly by the UK Carbon Trust and partly by and Industrial Consortium:
 - Lafarge
 - Cemex
 - Castle Cement
 - Marshalls
 - CRH
 - Fosroc



Background to the BRE-Carbon Trust project (2004-7)

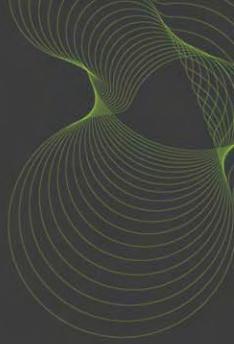
- Technical Objective:

“To facilitate a step change reduction in CO₂ emissions from cement manufacture within the UK and Europe by encouraging the development and implementation of low CO₂-producing cements based on calcium sulfoaluminate and belite”

Focusing on concrete technology:

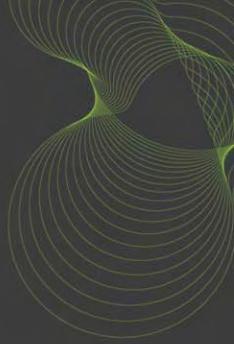
- Investigating effects of composition on properties
- Properties of wet concrete
- Strength development with time
- Robustness and durability

Belite-calcium sulfoaluminate cements



- C_2S , lower CaO than C_3S and produced at lower T
- But slower hydration than C_3S
- Activate C_2S or add reactive component – e.g. C_4A_3s (also low CO_2)
- Benefits:
 - Up to 50% reduced CO_2 from calcination - More if activation of pfa and ggbs considered
 - (Rapid) early age strength development mainly due to C_4A_3s hydration (to form ettringite)
 - Long-term strength development due to C_2S hydration
 - Good chemical resistance and durability
 - Reduced NO_x emissions

Belite-calcium sulfoaluminate cements

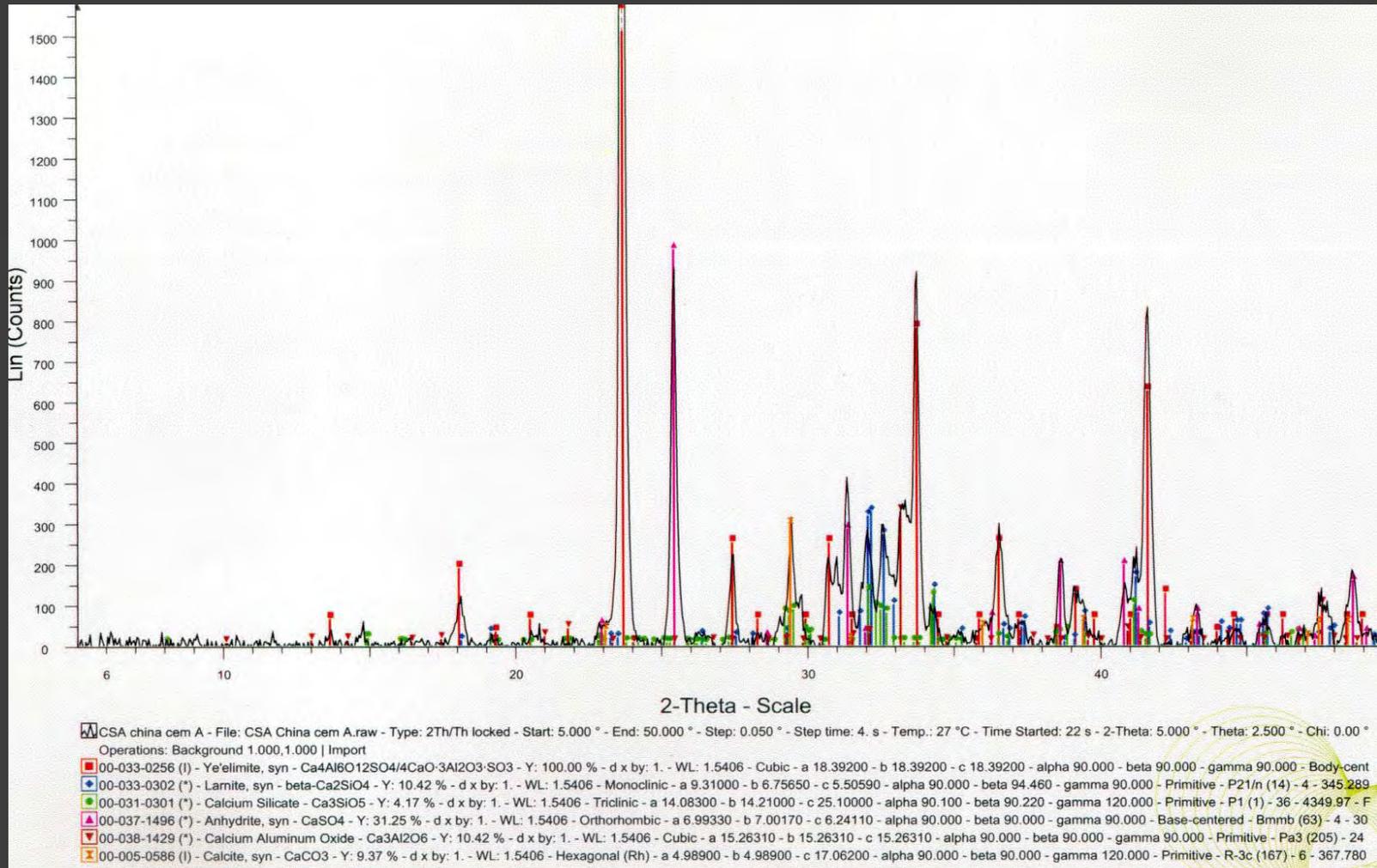


- Manufactured on commercial scale in China since 1970's
 - NOT produced as low carbon cements
 - Production >1 million tonnes per annum
 - Considerable experience in China of using these cements in structural and non-structural concrete
 - UK use as special cement
- Manufacturing process similar to that of Portland cement
 - Mixture of limestone, bauxite and CaSO_4
 - Heated to 1300 - 1350°C

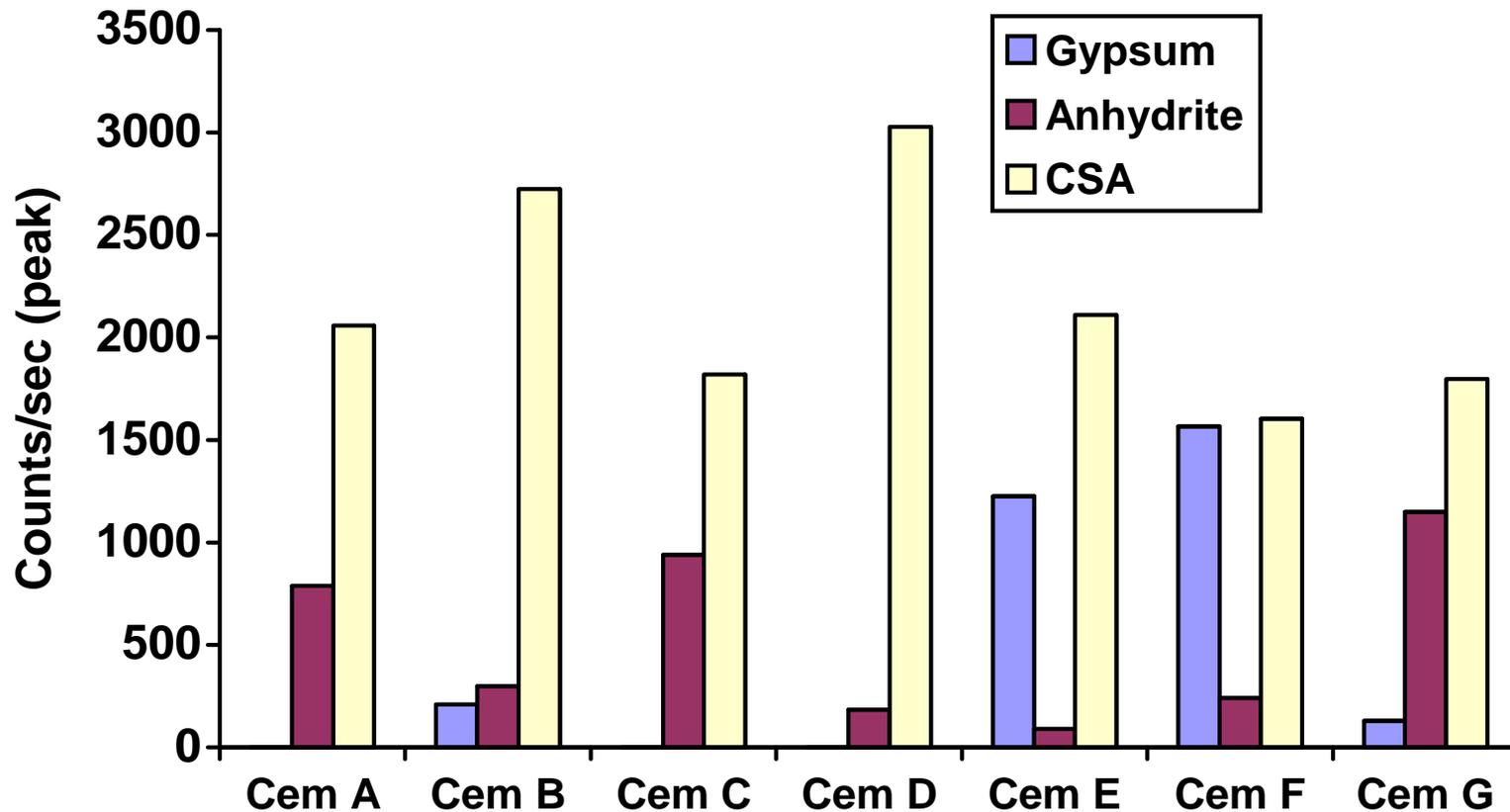
Estimated cement phase compositions

	Amount in clinker						
Oxide/ compound	525 ^a (China)	SAC ^a (China)	Barnstone (B2) ^b	CSA ^c (Mehta - 3)	CSA ^c (Mehta - 5)	50PC:50 ggbs	PC
CaO	42	40.92	47	48.3	51.8		
SiO ₂	8.35	11.16	9.9	8.7	15.7		
Al ₂ O ₃	25.6	24.41	33.2	18.4	13.1		
Fe ₂ O ₃	2.84	2.29	1	13.2	5		
SO ₃	13.8	14.66	7.9	11.4	14.4		
MgO	2.01	2.89					
Cs	12.9	14.7	0.1	15	20	0.75	1.5
C ₄ A ₃ S	47.5	45.8	59.9	20	20		
C ₂ S	23.9	32.0	22.2	25	45	8.25	16.5
C ₃ S			8.2			32	64
C ₃ A						1.75	3.5
C ₁₂ A ₇			4.9				
Cc						1.25	2.5
C ₄ AF	8.64	7.0	3	40	15	4.75	9.5
CO ₂ from decarb*	51.5	54.1	60.8	59.0	61.2	50	100

Estimated cement phase compositions – cements from China



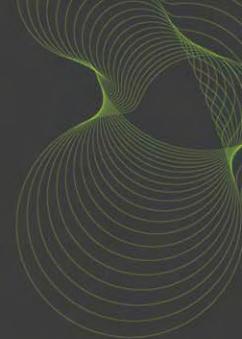
Estimated cement phase compositions – cements from China





Two different approaches based on CSA

- CSA-rich clinkers blended with ggbs, pfa, calcium sulfate and other non-clinker ingredients:
- Belite-CSA-ferrite clinkers which can be made in conventional OPC kilns (*Lafarge BCSAF cements*)
- Strength development associated with formation of a calcium sulfoaluminate hydrate known as ettringite ($6\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SO}_3\cdot 32\text{H}_2\text{O}$)
- CO₂ savings 25% - 80% relative to neat PC but depends on:
 - *composition*
 - *raw materials availability*
 - *use of cement replacements*



Blended CSA cements

- Lafarge Barnstone CSA (B2) mainly used
- Cements sourced from China used in other programmes
- Blended with different proportions of
 - Ggbs
 - Anhydrite
 - Lime
 - Pfa
 - Limestone
- Studies have included compressive strength development and durability to 2 years for concretes
- ~70-80% reduction in CO₂ emissions from decarbonation compared to neat PC

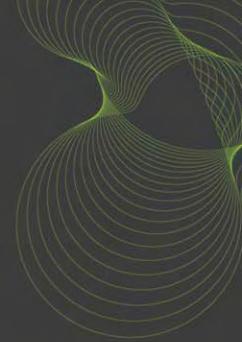
Binder compositions used in concrete tests

BINDER COMPOSITIONS (kg/m ³)							% CO ₂ (decarb)	Binder Remark
	Total kg/m ³	PC	B2	Slag	Anhydrite	Lime		
x 1	300	0	300	0	0	0	60%	B2 only
x 2	300	0	150	150	0	0	30%	50% B2; 50% ggbs
x 3	300	300	0	0	0	0	100%	PC only
x 4	300	150	0	150	0	0	50%	50 % PC; 50% ggbs
x 5	300	0	120	150	30	0	24%	40% B2; 10% Anhydrite; 50% ggbs
x 6	300	0	90	150	60	0	18%	30% B2; 20% Anhydrite; 50% ggbs
x 7	300	0	114	150	30	6	23%	38% B2; 10% Anhydrite; 2% Lime; 50% ggbs
x 8	300	0	144	150	0	6	29%	48% B2; 2% lime; 50% ggbs
x 9	300	0	84	150	60	6	17%	28% B2; 20% Anhydrite; 2% lime; 50% ggbs

The OPC used for comparison was a CEM I - 42.5R.

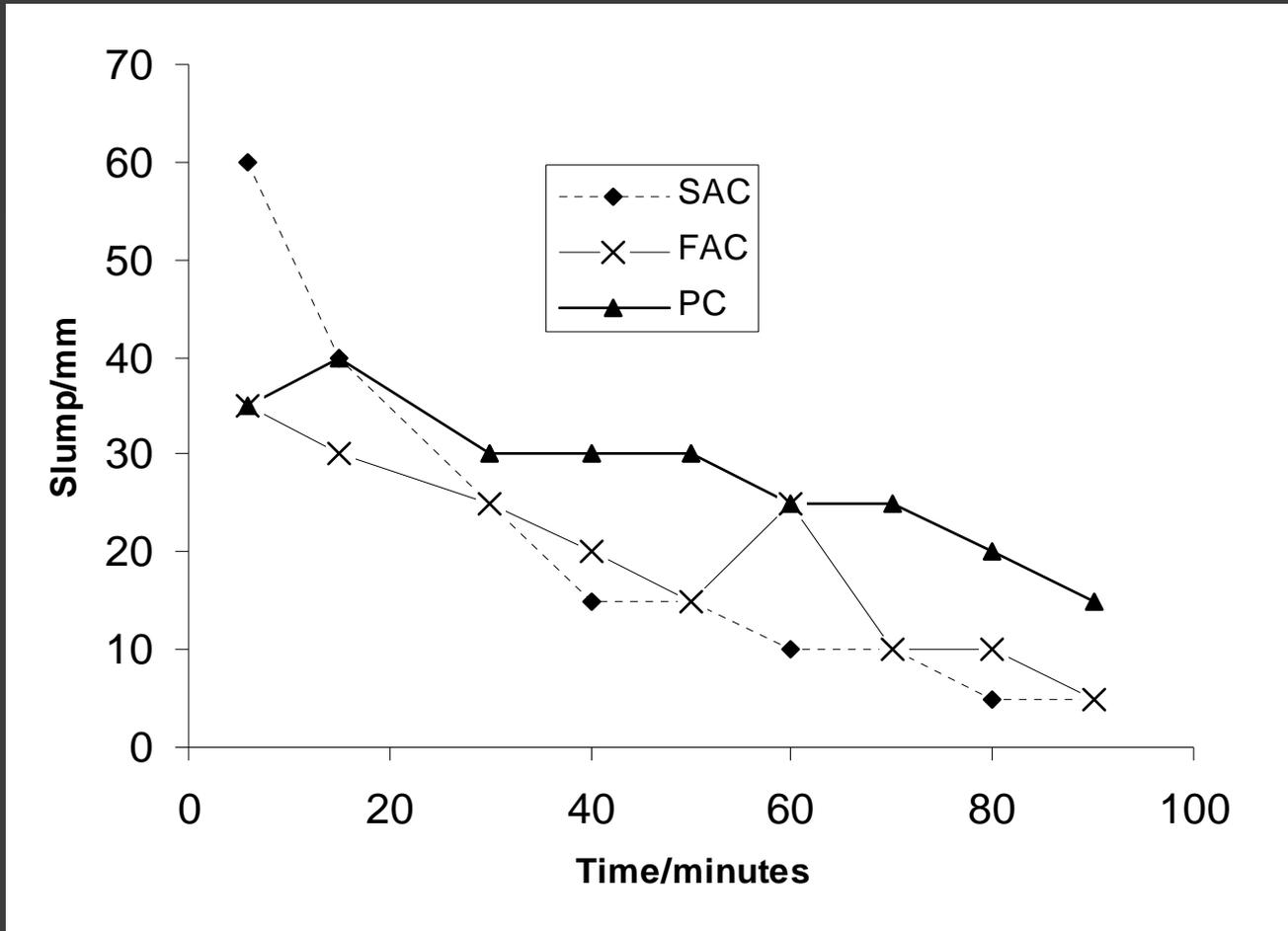
“%CO₂ decarb” represents RM-CO₂ as a percentage of that of the OPC

Concrete – observations on fresh properties



- Premature stiffening (5 -1 0 minutes).
- Rework of concrete produced small periods of workability.

Concrete – observations on fresh properties



Slump against time for CSA and PC concrete

Concrete – observations on hardened concrete

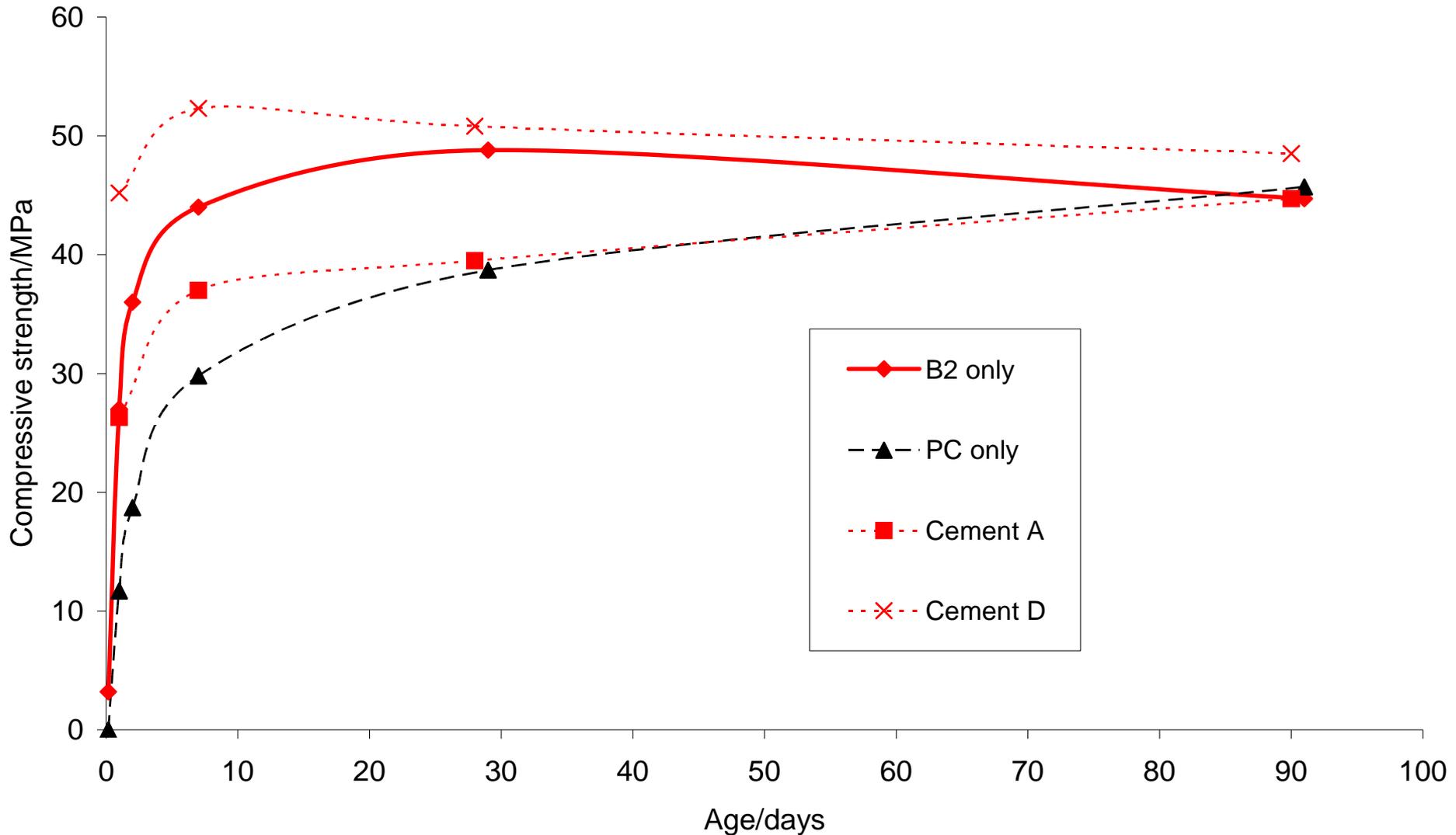


- Standard curing regime – 24 hours under damped hessian. Thereafter in standard water immersion curing.

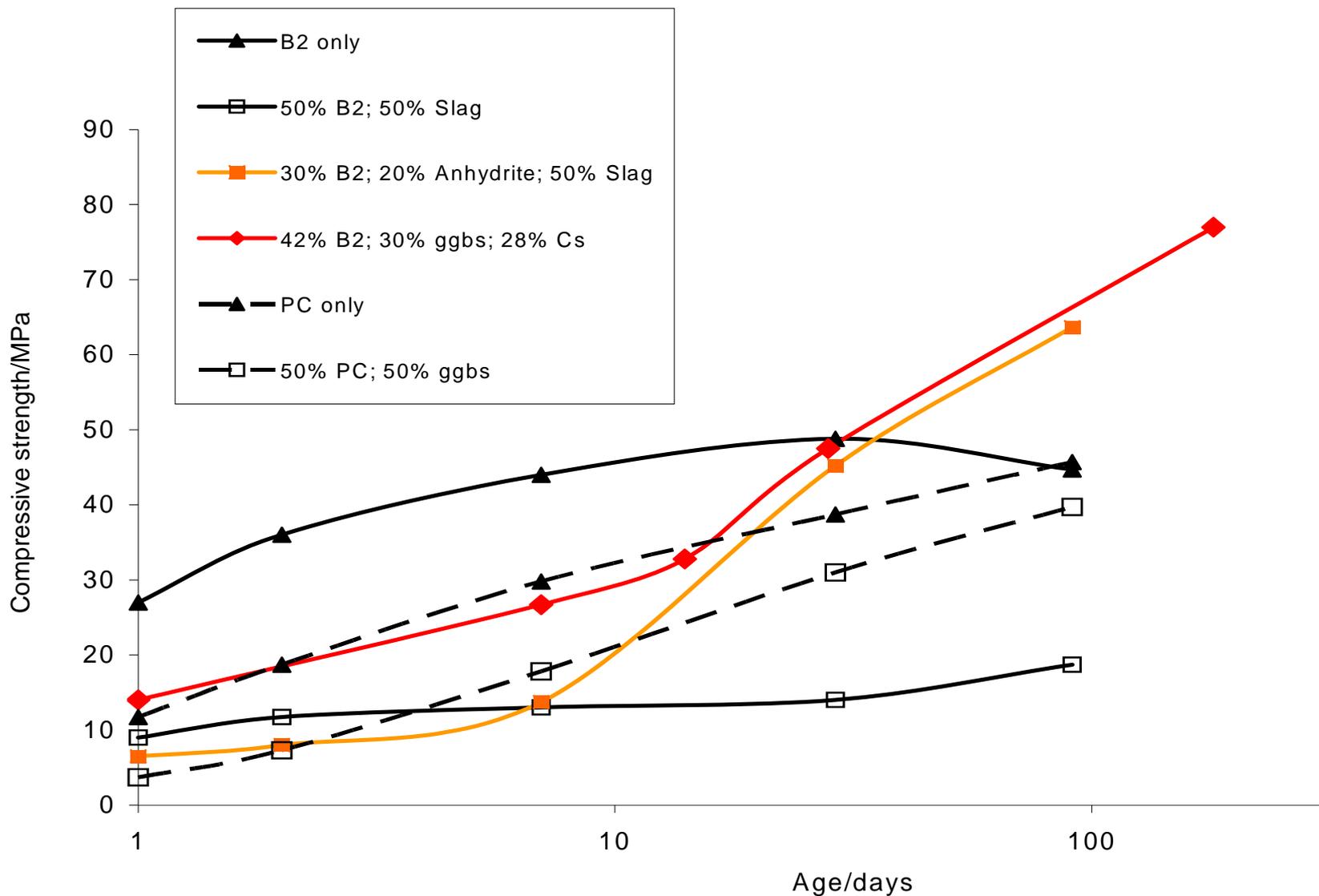
Cubes left in the dedicated water tank developed a sticky white slimy deposit on their surfaces, which could be scraped off easily.

The deposit was analysed and found to be ettringite.
- Hardened concrete failed in compression tests conventionally.

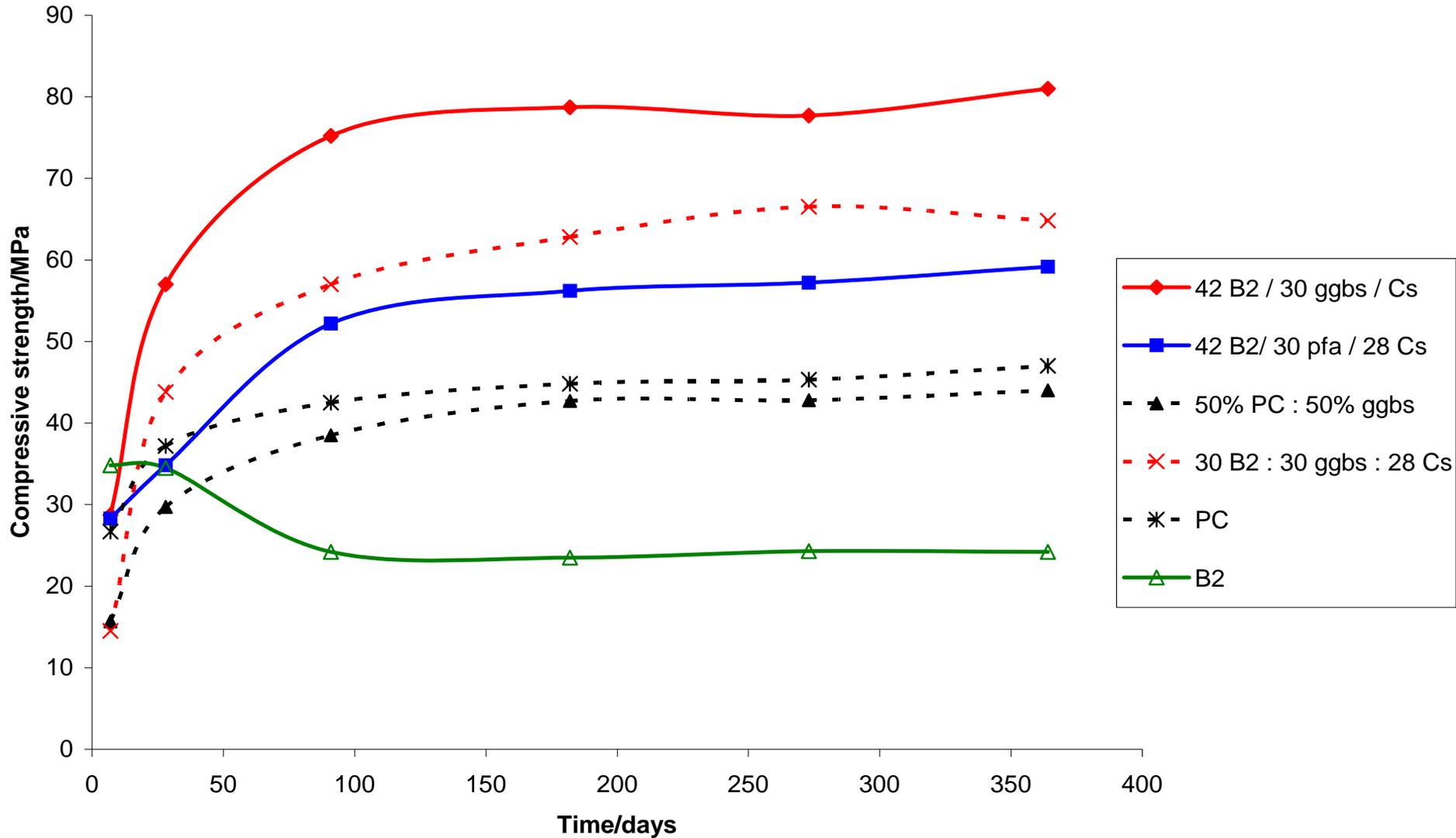
Compressive strength development in neat CSA concrete (cement content = 300kg/m³; w/c = 0.55)



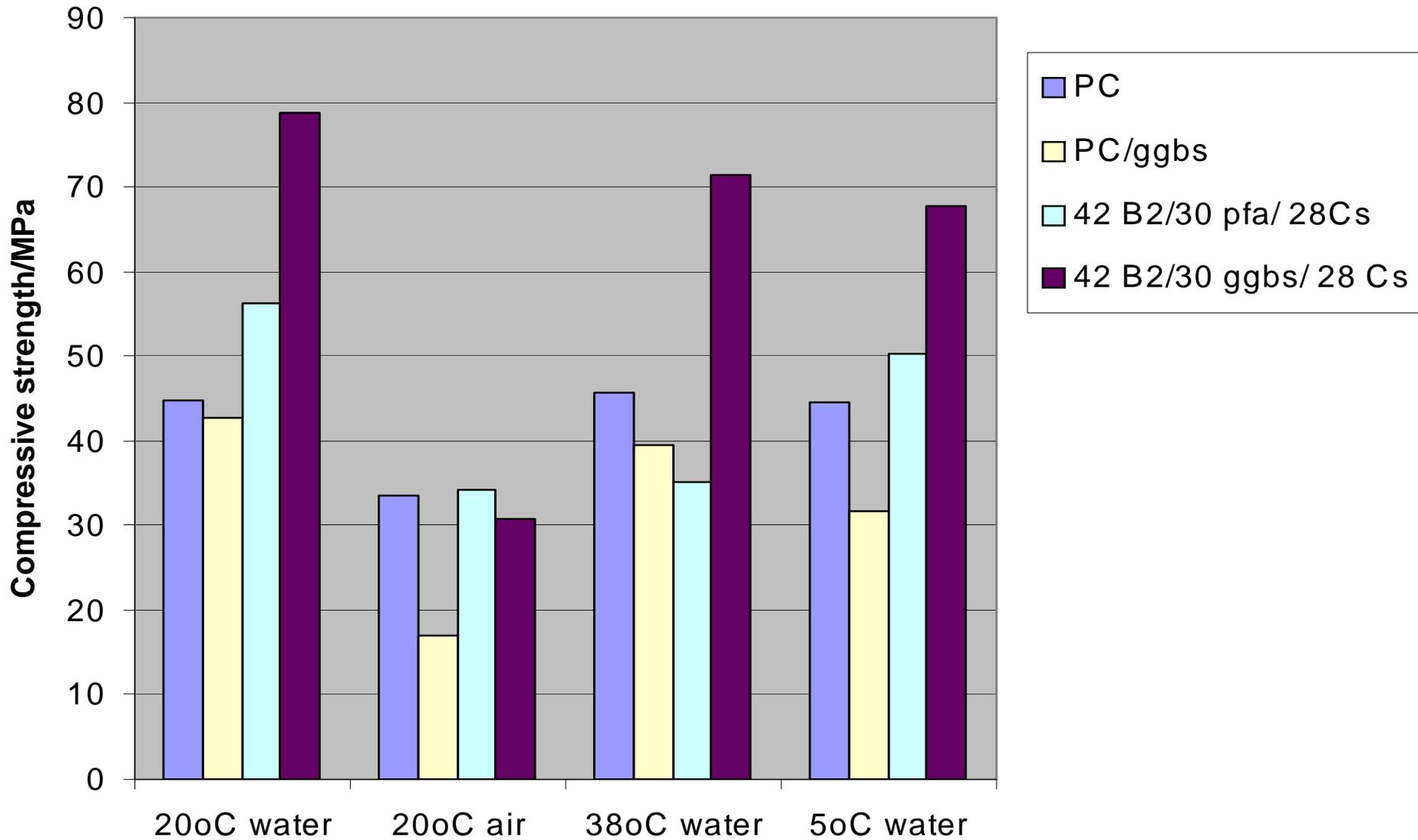
Compressive strength development in blended CSA concrete (cement content = 300kg/m³; w/c = 0.55)

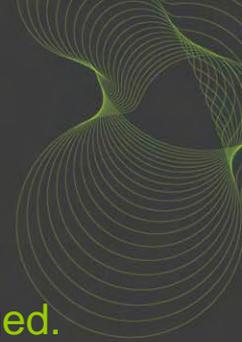


Compressive strength development in concretes made using B2/ggbs/Cs and B2/pfa/Cs blends (cement content = 300kg/m³; w/c = 0.55)



Compressive strength at 180 days



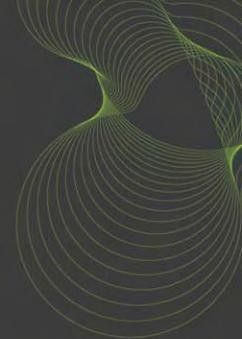


Effect of temperature and curing on strengths:

The mix design used was the same for all tests, with only the cement composition changed. The total binder content was 300kg/m³ throughout. The free water: binder ratio was 0.55. No additives were used.

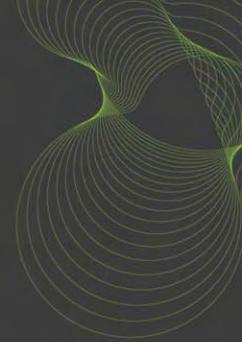
Neat PC (A05/5135)					42 B2: 30 ggbs: 28 Cs (A05/5140-5142)				
Mix number	5135	5135	5135	5135	Mix number	5140	5141	5141	5142
Age/days	20°C water	20°C air	38°C water	5°C water	Age/days	20°C water	20°C air	38°C water	5°C water
7	26.7				7	28.7			
28	37.2	30.2	36.5	30.0	28	57.0	31.8	47.8	38.5
91	42.5				91	75.2			
182	44.8	33.5	45.7	44.5	182	78.7	30.7	71.5	67.8

50PC: 50 ggbs (A05/5136)					42 B2: 30 pfa: 28 Cs (A05/5143-5145)				
Mix number	5136	5136	5136	5136	Mix number	5143	5144	5144	5145
Age/days	20°C water	20°C air	38°C water	5°C water	Age/days	20°C water	20°C air	38°C water	5°C water
7	15.67				7	28.3			
28	29.67	16.17	33.17	17.33	28	34.8	33.2	31.0	30.2
91	38.50				91	52.2			
182	42.67	17.00	39.50	31.67	182	56.2	34.3	35.2	50.3



Carbonation depth by phenolphthalein test

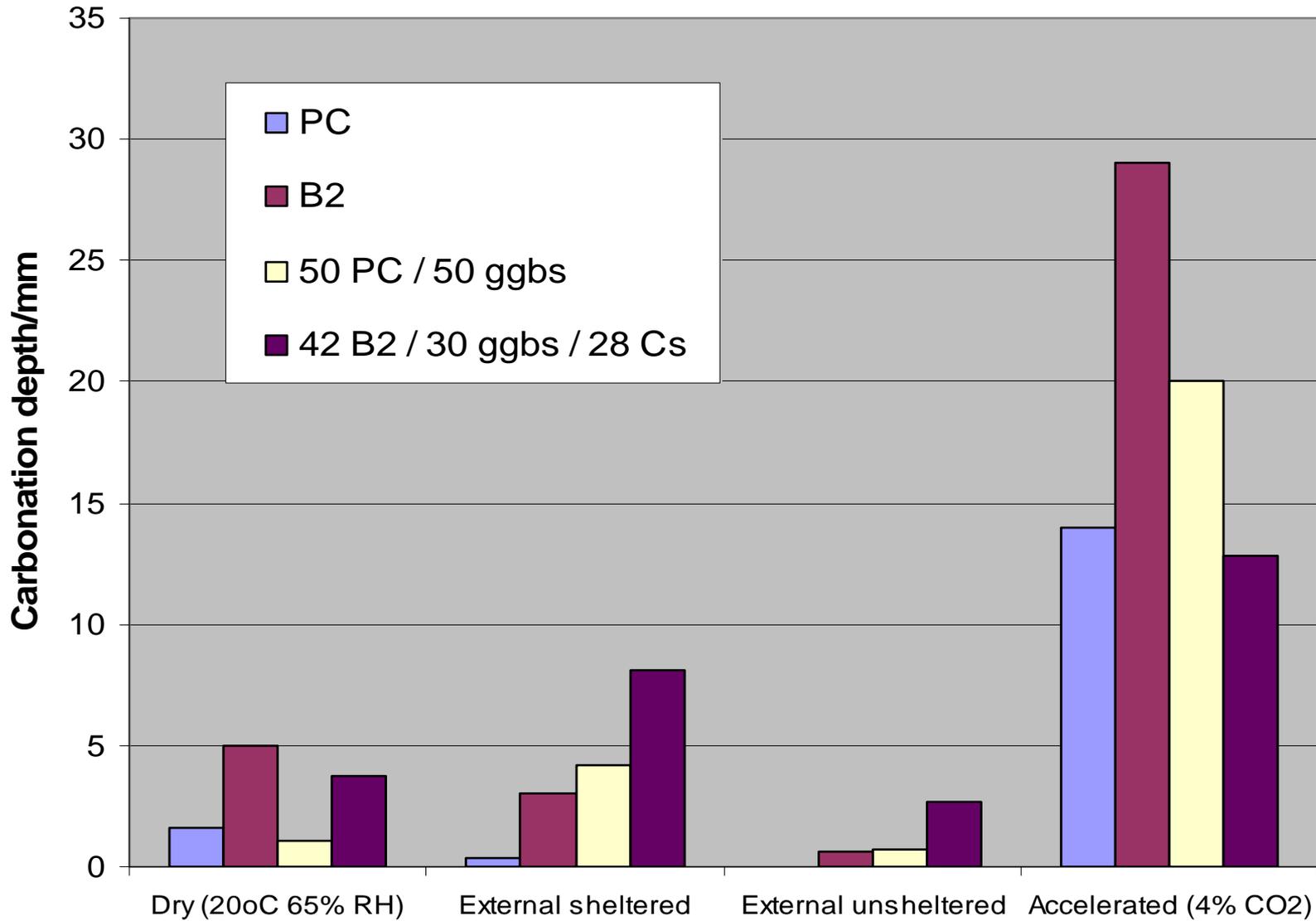
- Depth in mm as measured on 75x75x200mm concrete prisms
- Accelerated carbonation
 - Specimens stored in water to 28 days followed by 28 days conditioning at 20° C and 65%RH prior to testing.
- Natural carbonation
 - Specimens not cured prior to exposure – carbonation rates for blends are therefore higher (especially unsheltered) than predicted from accelerated tests.



Carbonation depth by phenolphthalein test



Carbonation depth at 90 days



Concrete expansion under water



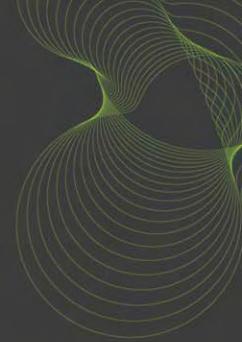
Expansion on storage in water has been monitored for periods of up to **365** days using 75x75x200mm prisms which were cast with inserts to facilitate measurement. Mix designs are as with compressive strength and carbonation. Specimens were demoulded at 24 hours (initial measurement) and stored in water at 20°C.

Mix	Expansion at 182 days (%)	Expansion at 273 days (%)	Expansion at 365 days (%)
Neat B2 (A05/5134)	0.041	0.046	0.058
Neat PC (A05/5135)	0.008	0.020	0.025
50% PC: 50% ggbs (A05/5136)	0.017	0.023	0.023
30% B2: 50% ggbs: 20% anhydrite (A05/5139)	0.048	0.065	0.079
42% B2: 30% ggbs: 28% anhydrite (A05/5142)	0.014	0.021	0.12
42% B2: 30% pfa: 28% anhydrite (A05/5142)	0.024	0.029	0.032



Principal results of concrete test

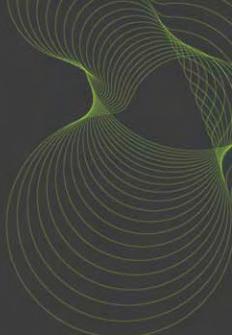
- On its own, CSA-rich clinker is not a good activator for conventional SCMs
- However, combinations of CSA with calcium sulfate (but not with lime) show good strength development properties when combined with GGBS.
- Concrete tests of this type of blend show no significant expansion in water over 9 months and a rate of carbonation higher than OPC but not extreme.
- Theoretical CO₂ savings can be > 70% vs. pure OPC.



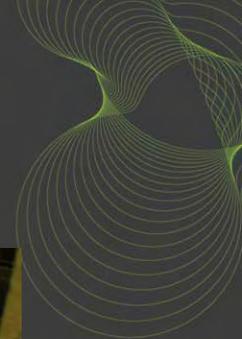
Precast trial – paver manufacture

- 30% B2 / 50% ggbs / 20% Cs used
- Preliminary laboratory work identified suitable admixture to control setting
- Produce Concrete Block Paving in a standard production environment
 - Produce concrete in production sized forced action pan mixer
 - Hold concrete in holding hopper
 - Convey concrete to block plant via belt-feed
 - Vibro-compact concrete in a block machine to form Concrete Block Paving
 - Cure the produced CBP in standard curing chambers at 27°C & 85% humidity)

Paving Blocks made from the CSA/slag/anhydrite blend (courtesy of Ian Ferguson, Marshalls, UK)



Paving Blocks made from the CSA/slag/anhydrite blend (courtesy of Ian Ferguson, Marshalls, UK)

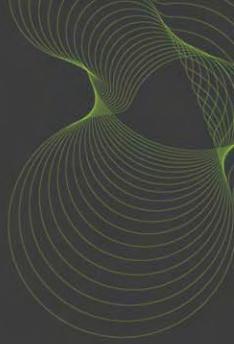




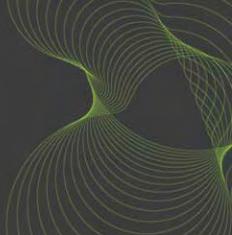
Precast trial – paver manufacture

- Finished product subjected to conformance testing to BS EN 1338:
 - Strength
 - Water Absorption
 - Polishing (Polished Paver Value)
 - Skid Resistance (Unpolished Skid Resistance Value)
 - Abrasion (Wide Wheel Abrasion)
 - Durability (Freeze / Thaw)
- Trial went very well
 - Wear, freeze/thaw, slip risk and wear resistance were all excellent
 - Nice buff colour!

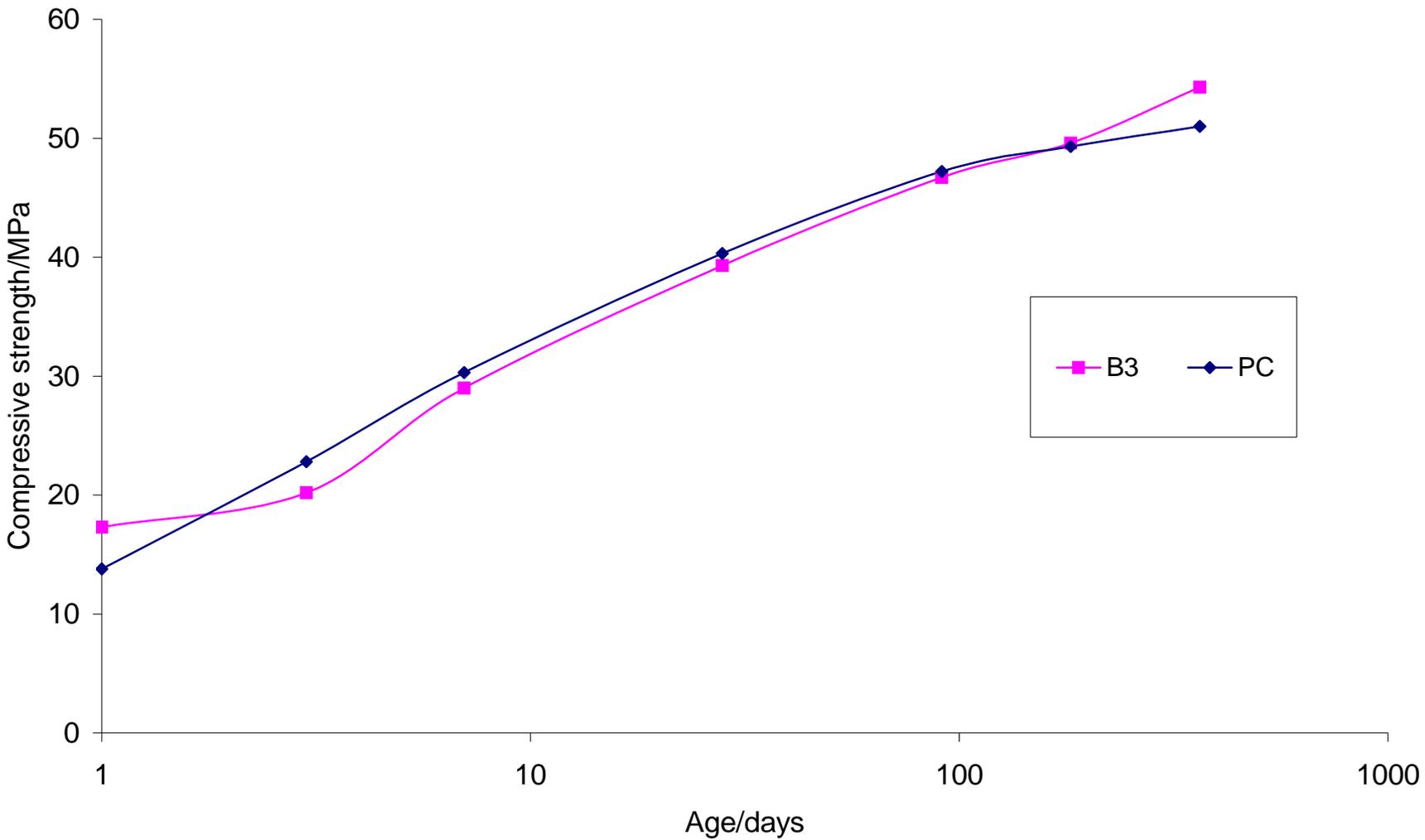
Lafarge Central Research novel Belite-CSA-Ferrite (BCSAF) cements



- LCR approach was to attempt to produce clinkers that would perform at least as well as those claimed in the Mehta patent but based on realistic raw materials.
- Certain combinations of minor elements allowed significant activation of the belite phase.
- The ferrite phase also appears to be somewhat reactive, as was previously reported by Mehta.



BRE concrete data at $w/c = 0.55$, 300kg/m^3 for pilot batch of BC SAF (B3) compared to OPC (CEM I 42.5)





BRE concrete data at w/c = 0.55, 300kg/m³ for pilot batch of BCSAF (B3) compared to OPC (CEM I 42.5)

Initial durability tests:

- Freeze/thaw comparable to PC/pfa blends
- Reinforcement corrosion
- Sulfate attack
- Carbonation
- Dimensional stability

XRD shows that the following hydrates are present in carbonated concrete:

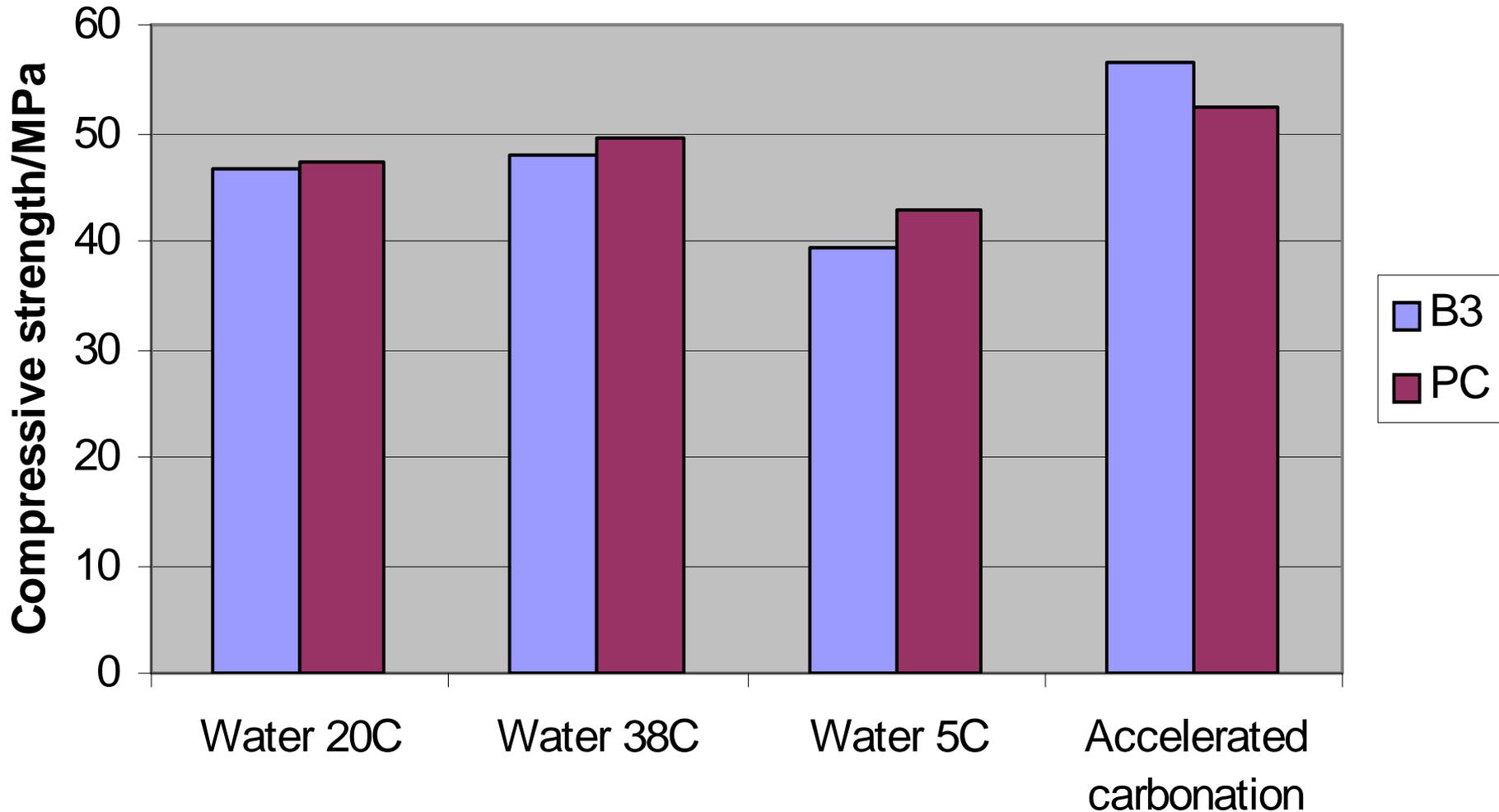
Ettringite



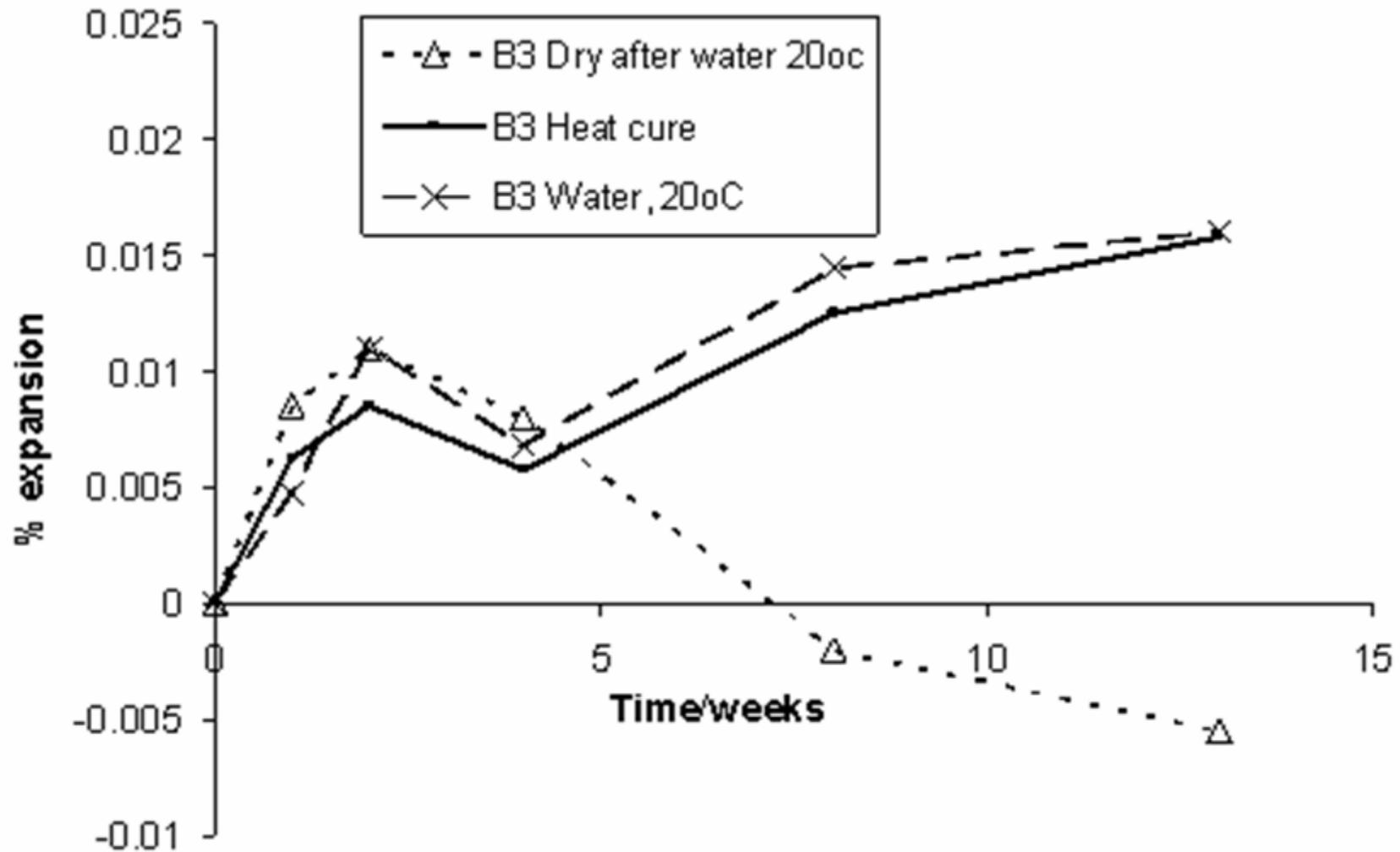
C_4AcH_{11} or gypsum

Calcite and quartz are also present

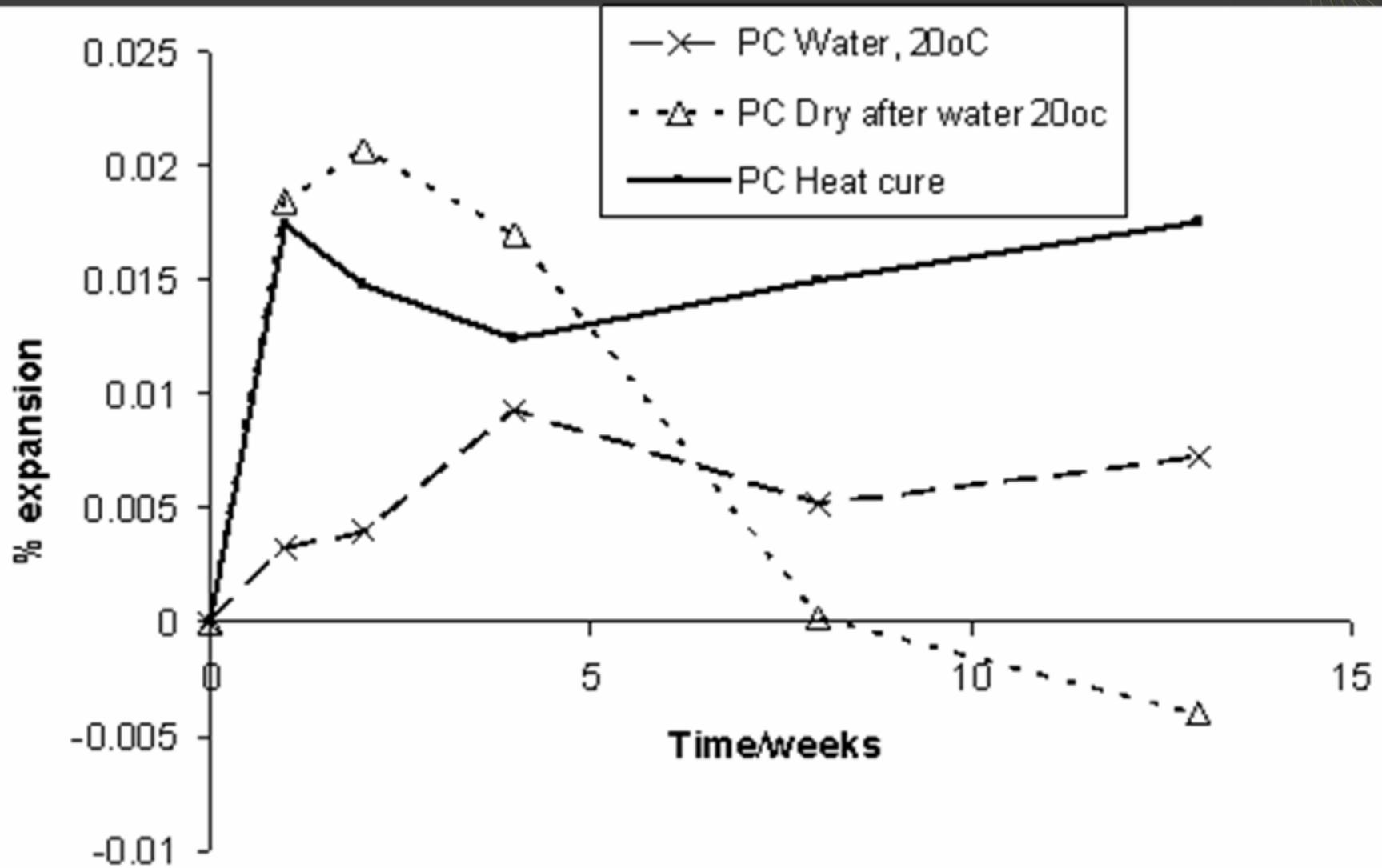
Effect of curing/storage conditions on B3 concrete (after 91 days)



Dimensional stability in B3 concrete



Dimensional stability in PC concrete



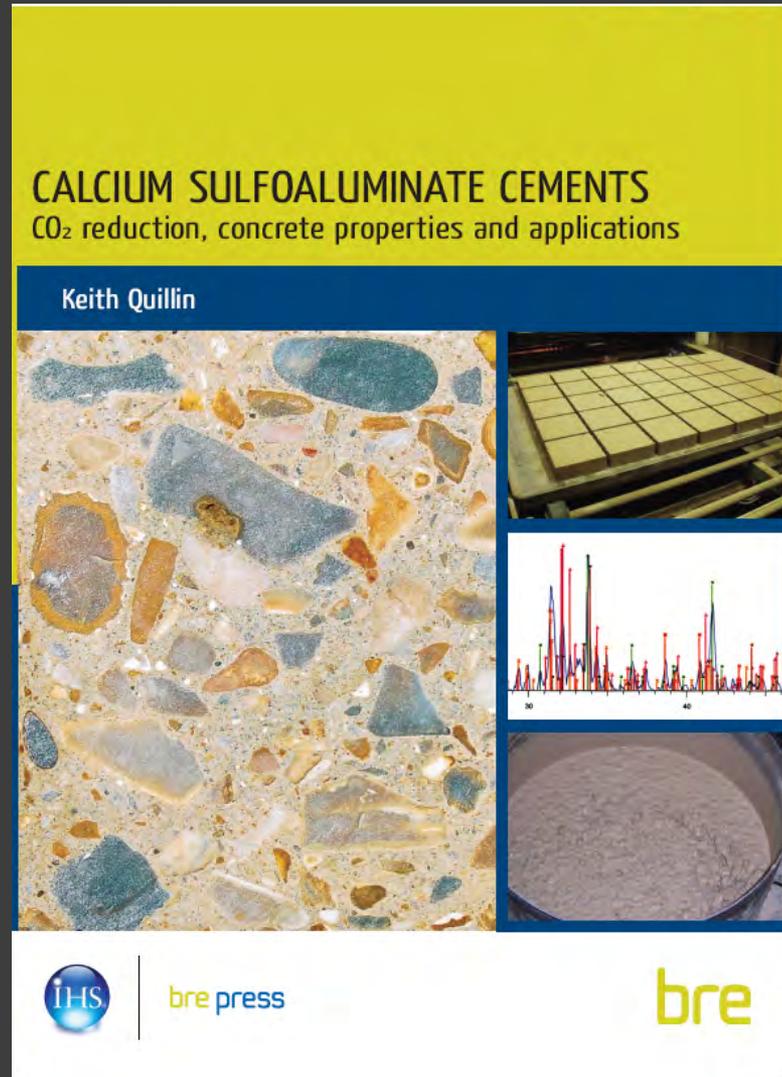


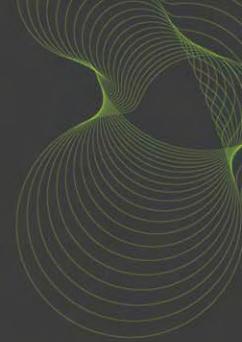
CONCLUSIONS

- To have the potential to significantly reduce global CO₂ emissions from cement manufacture 'Low carbon' cements must:
 - Be able to produce concrete with appropriate physical and durability properties
 - Be based on widely available raw materials (even if the materials are available, transportation costs can be high).
- Cements based on C₄A₃S̄ plus ferrites, calcium sulfates and either GBFS or activated belite are a promising option. They can tolerate high sulfate contents and hydrate to form mainly ettringite, C-S-H & AFm phases.
- Significant reductions in CO₂ emissions relative to Portland cement
- Preliminary concrete tests of two alternative approaches to this have shown promising strength and durability results
- Much more work is needed to establish data for Codes and Standards etc.

'Calcium sulfoaluminate cements', BR496

- Includes work on UK Carbon Trust-funded programme on belite-calcium sulfoaluminate cements
- Also includes earlier BRE work on CSA cements





Acknowledgements

- Carbon Trust
- Steering Group
- Ellis Gartner *Lafarge Central Research*
- John Fifield *CRH*
- Ian Ferguson *Marshalls*
- Roy Lewis *Marshalls*
- Steve Angel *Cemex*
- Mary Condon *Lafarge Roofing*
- Paul Livesey *Castle Cement*
- Bob Viles *Fosroc International*
- Steve Odell *Lafarge UK*

- BRE
- Philip Nixon
- Andrew Dunster
- Clive Tipple