THE "SUSTAINABILITY" OF CEMENT AND CONCRETE

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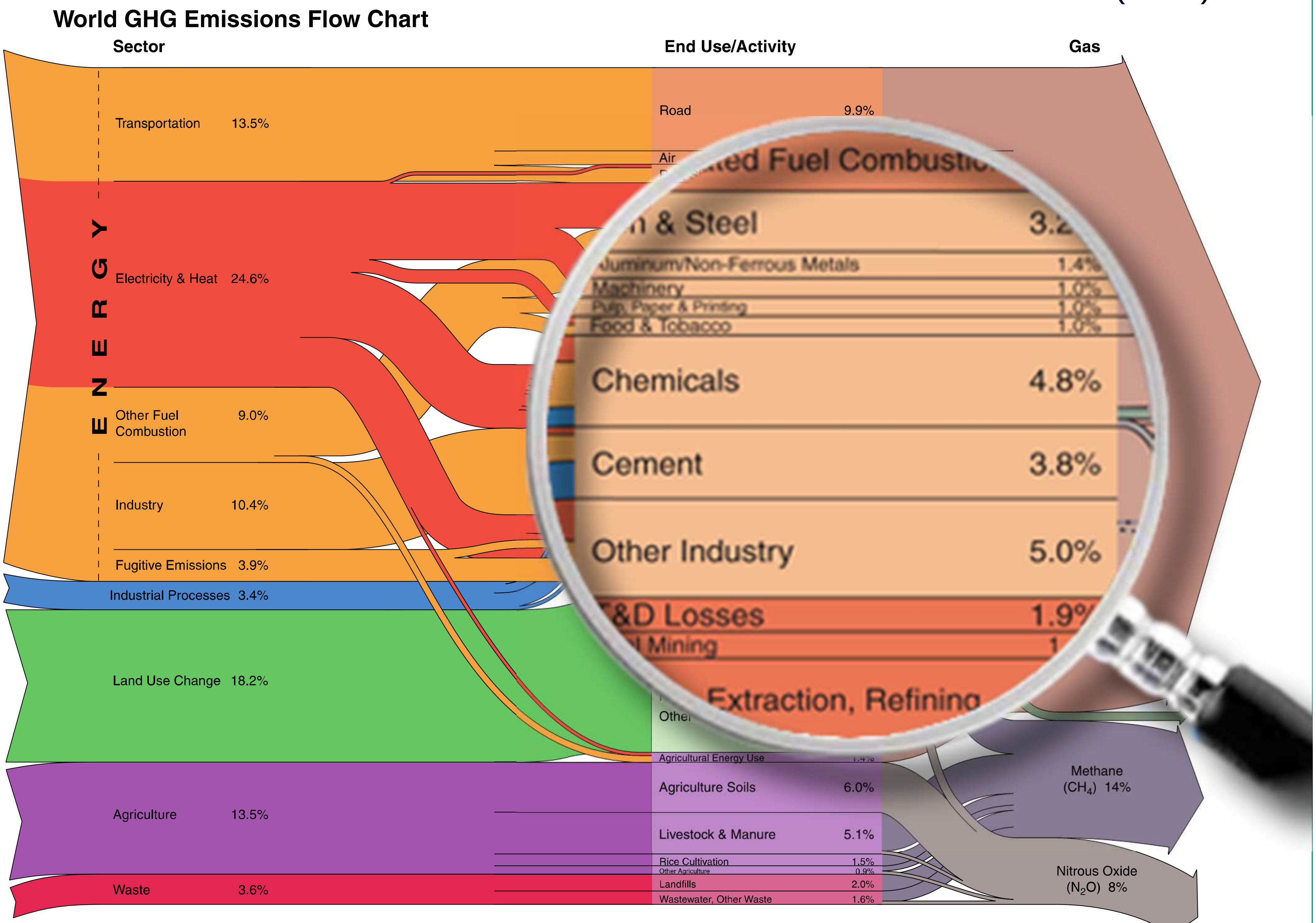
Lafarge Centre de Recherche

1. Cement and CO_2

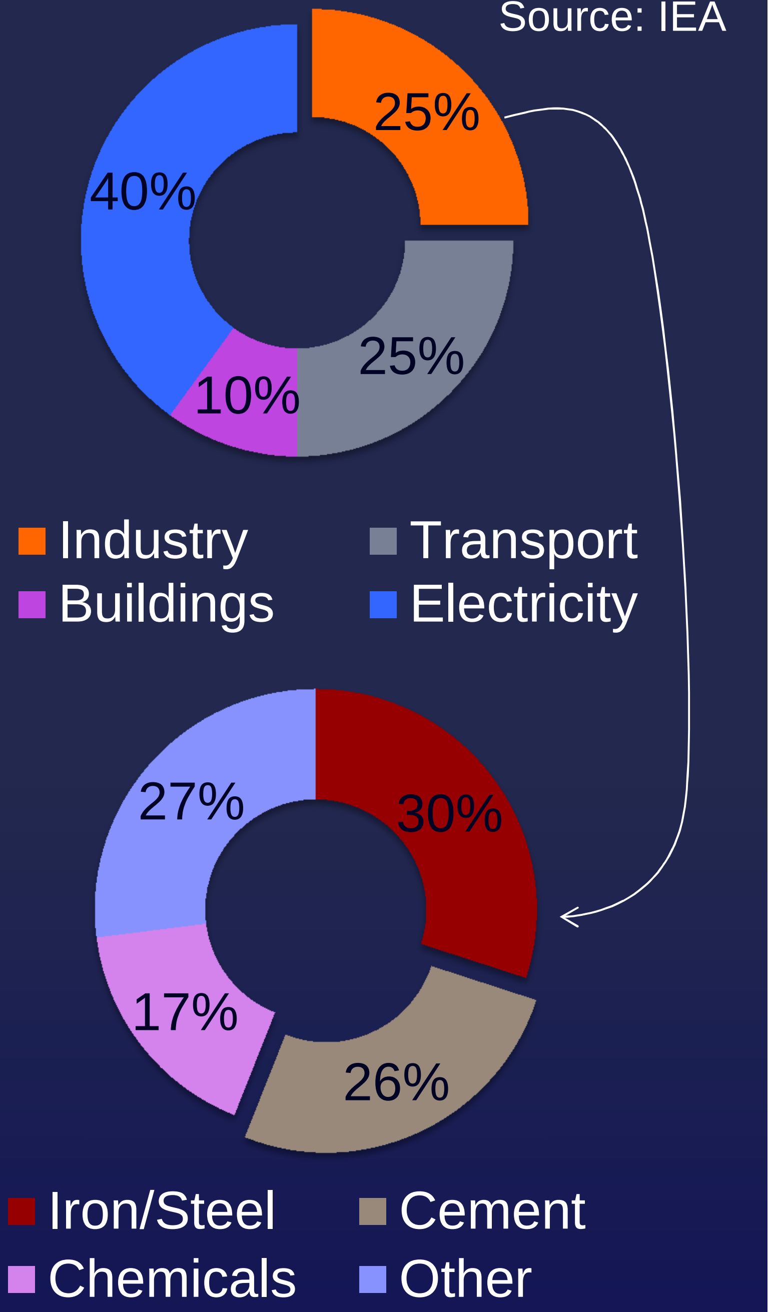
Source: World Resources Institute (2005)



Sources & Notes: All data is for 2000. All calculations are based on CO_2 equivalents, using 100-year global warming potentials from the IPCC (1996), based on a total global estimate of 41,755 $MtCO_2$ equivalent. Land use change includes both emissions and absorptions; see Chapter 16. See Appendix 2 for detailed description of sector and end use/activity definitions, as well as data sources. Dotted lines represent flows of less than 0.1% percent of total GHG emissions.

Cement and CO_2

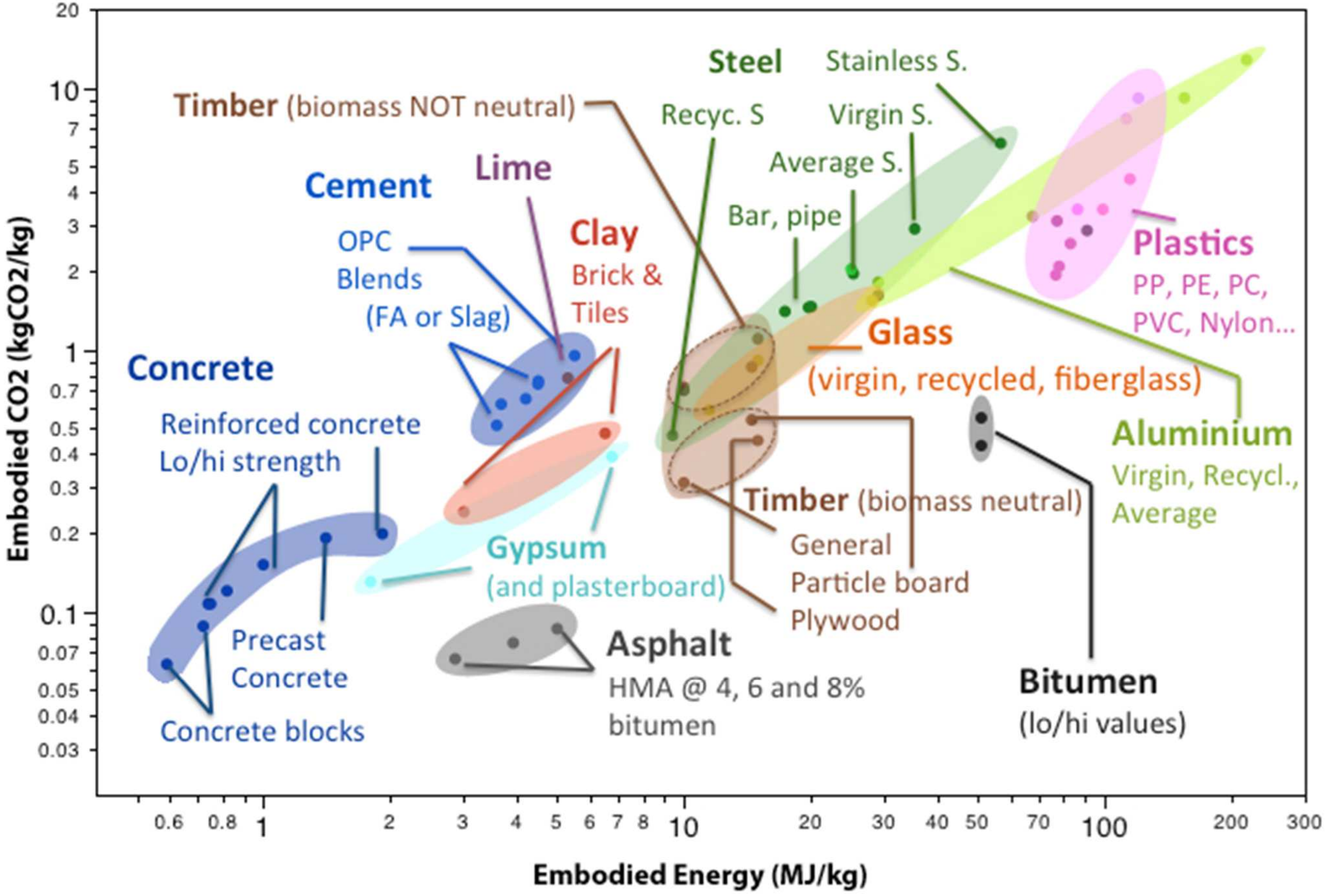
- World Resources Institute
  - 3.8% of worldwide GHG or
  - 5% of worldwide CO_2 emissions
- International Energy Agency
  - 7% of worldwide CO_2 emissions



Source: IEA

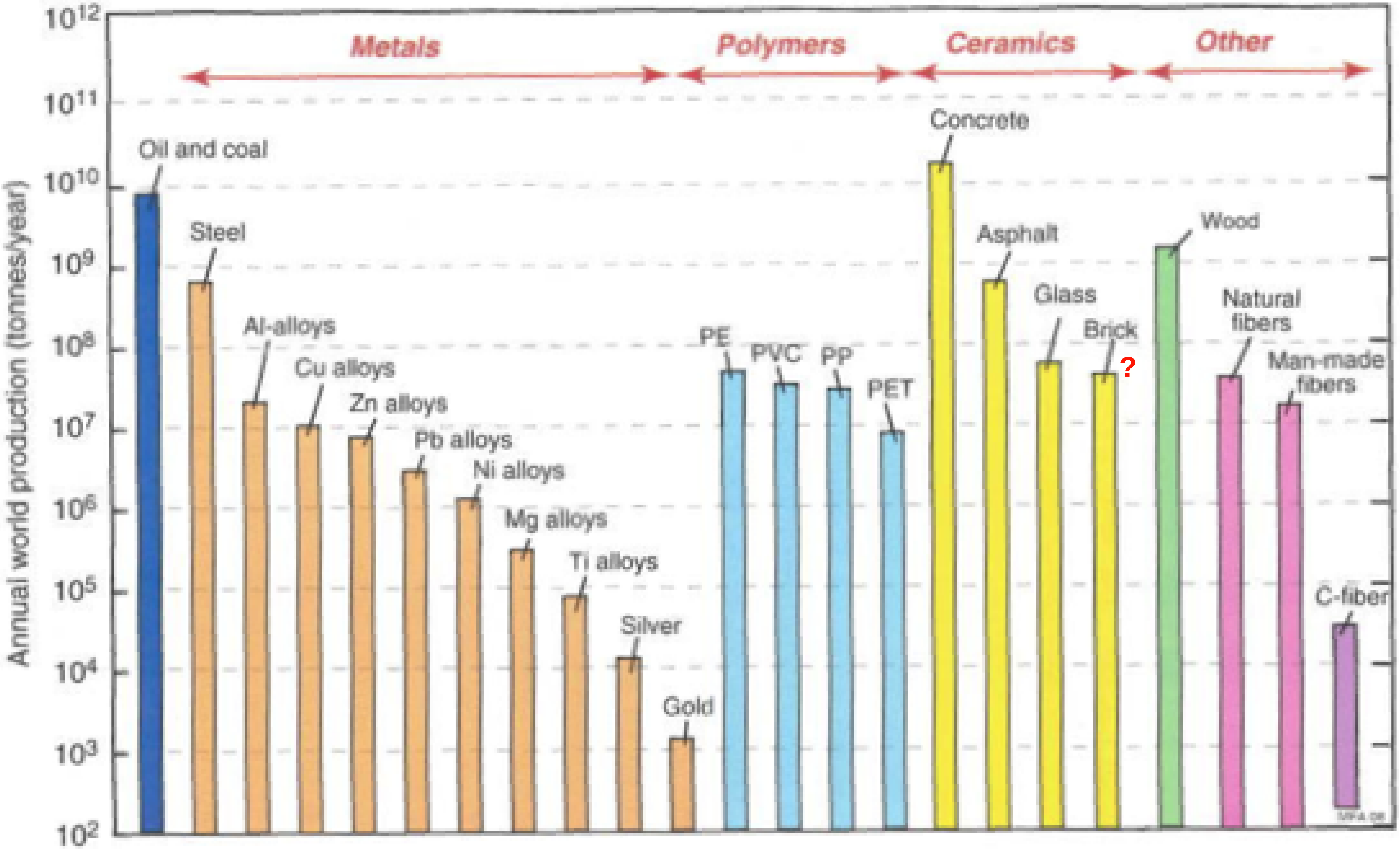
Embodied CO_2 and Energy of Construction Materials

data extracted from Hammond and Jones (2011), University of Bath, UK



Annual production of major materials

from Ashby (2009)



Why such a high CO_2 footprint?

Worldwide annual CO_2 footprint (t CO_2/year)	=	Intrinsic CO_2 footprint (t CO_2/t)	·	Worldwide annual production (t/year)
↑		↓		↑↑

Direct CO_2 emissions in Cement Manufacture

CO_2 from Limestone calcination ⇨ **~535 kg/t clinker**

(fairly constant from plant to plant)

+

CO_2 from fuel combustion ⇨ **~330 kg/t clinker**

(larger variations from plant to plant)

=

Direct CO_2 emissions for clinker ⇨ **~865 kg/t clinker**

x

Average clinker content in cement ⇨ **78%**

(2006 value from CSI)

=

Direct CO_2 emissions for cement ⇨ ~680 kg/t cement

Note: Excludes CO_2 from electricity (about 10% in the case of cement)

The importance of "fossil CO_2" in cement manufacture

(using extremely simplified equations to represent the main processes)

Conventional portland cement clinker manufacture:

$3CaCO_3 + SiO_2 \Rightarrow Ca_3SiO_5 + 3CO_2\uparrow$ ($\approx$3.9 GJ/tonne of CO_2)

300 60 (> 1300° C) 228 132 (mass units)

limestone + silica ⇒ C_3S (cement) + carbon dioxide

The "cement-sulfuric acid" process:

$3CaSO_4 + SiO_2 + 3H_2O \Rightarrow Ca_3SiO_5 + 3H_2SO_4$

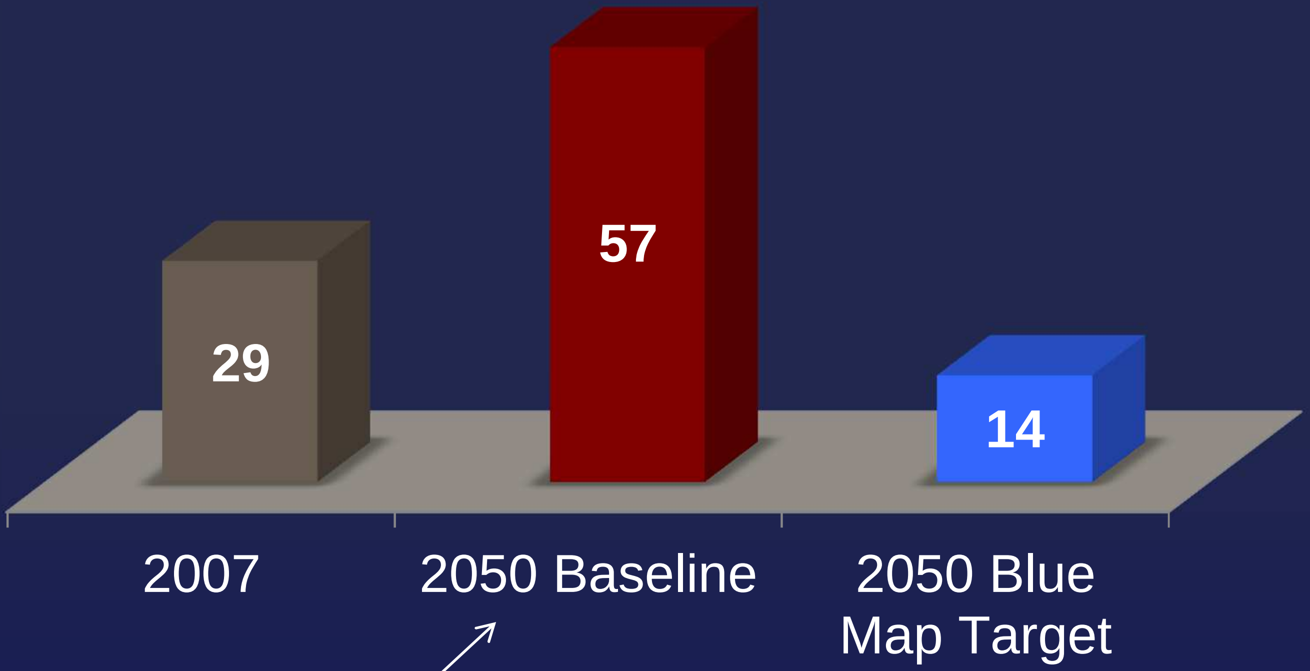
408 60 54 (> 1300° C) 228 294

anhydrite + silica + water ⇒ C_3S(cement) + sulfuric acid

2. Cement Technology Roadmap to Reduce Carbon Emissions

The Blue Map Scenario for Carbon Reduction

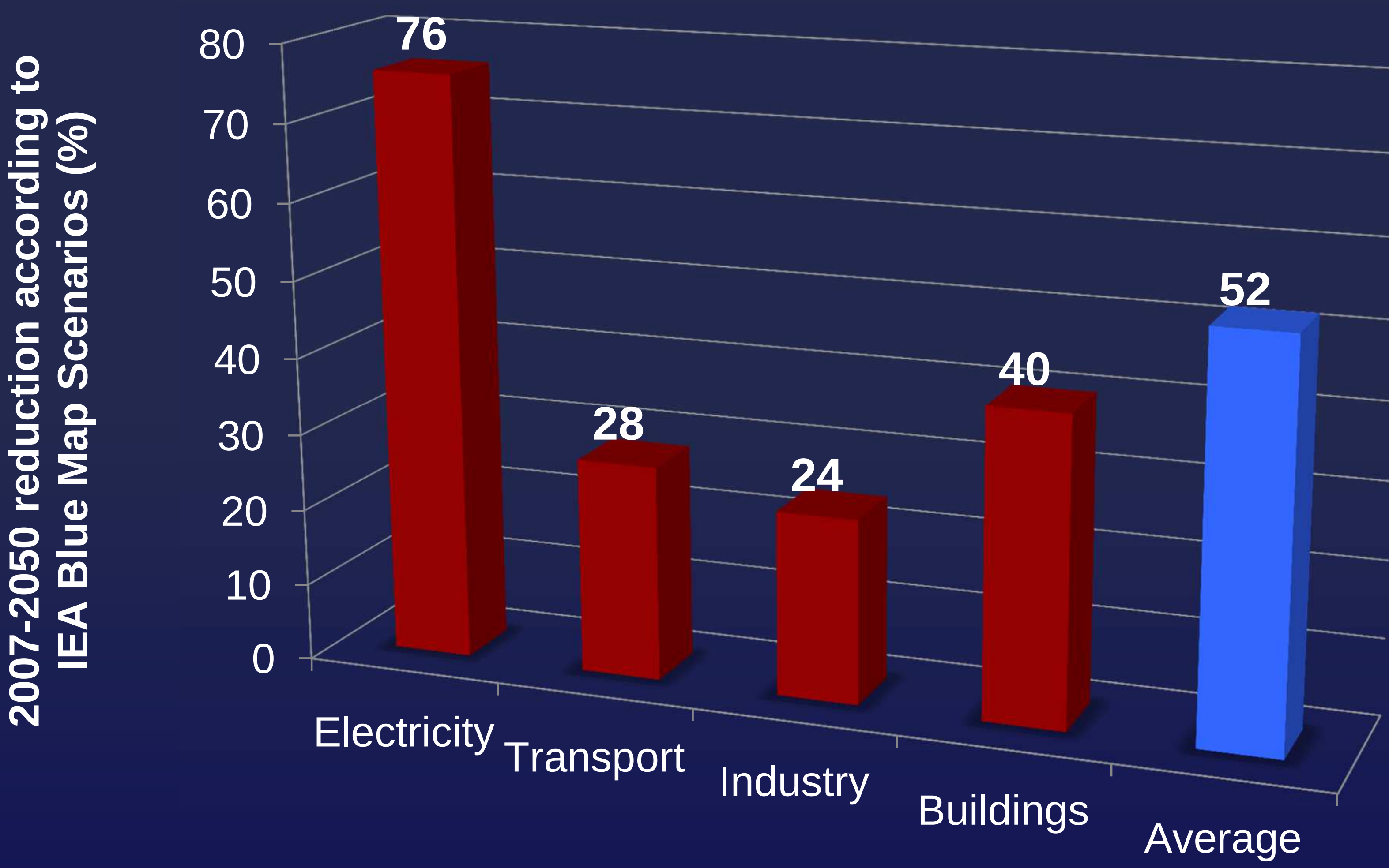
Global CO_2 emissions in Gt/yr (IEA data)



Business as usual

Limit global mean temperature increase to <3° C

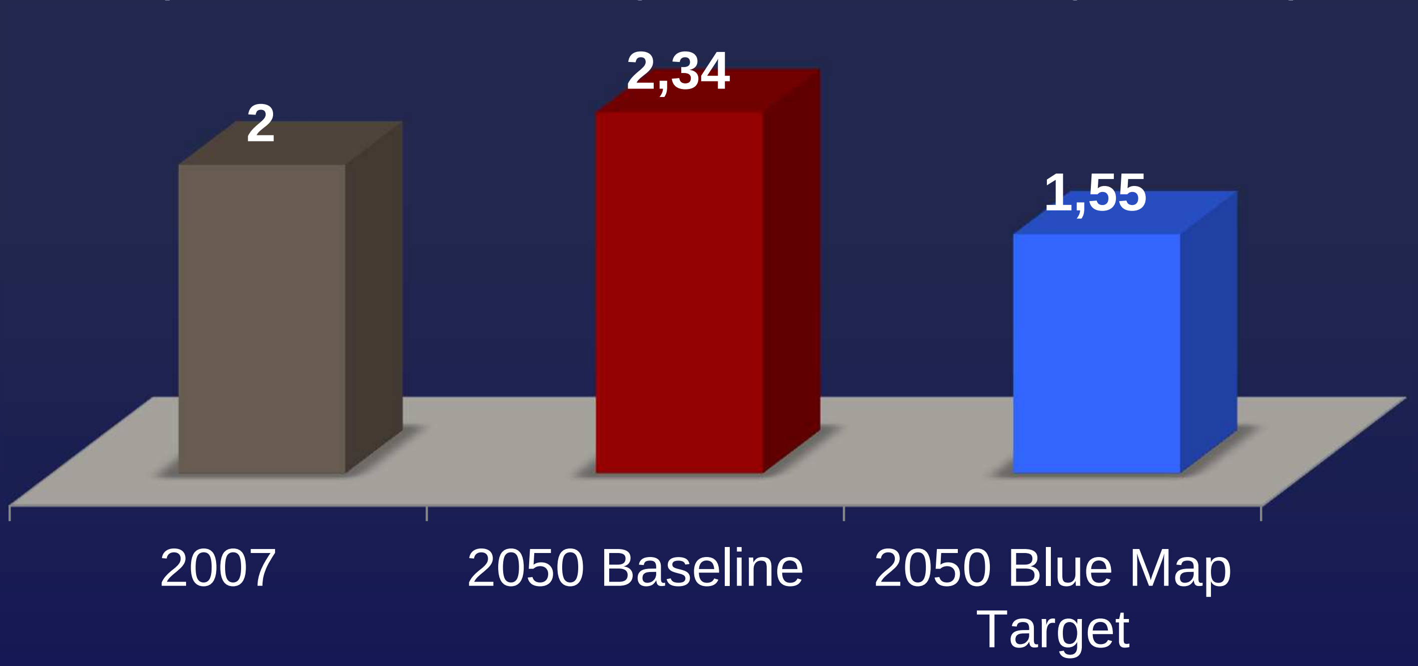
The IEA Sectorial Approach :
the lowest cost way to meet reduction targets



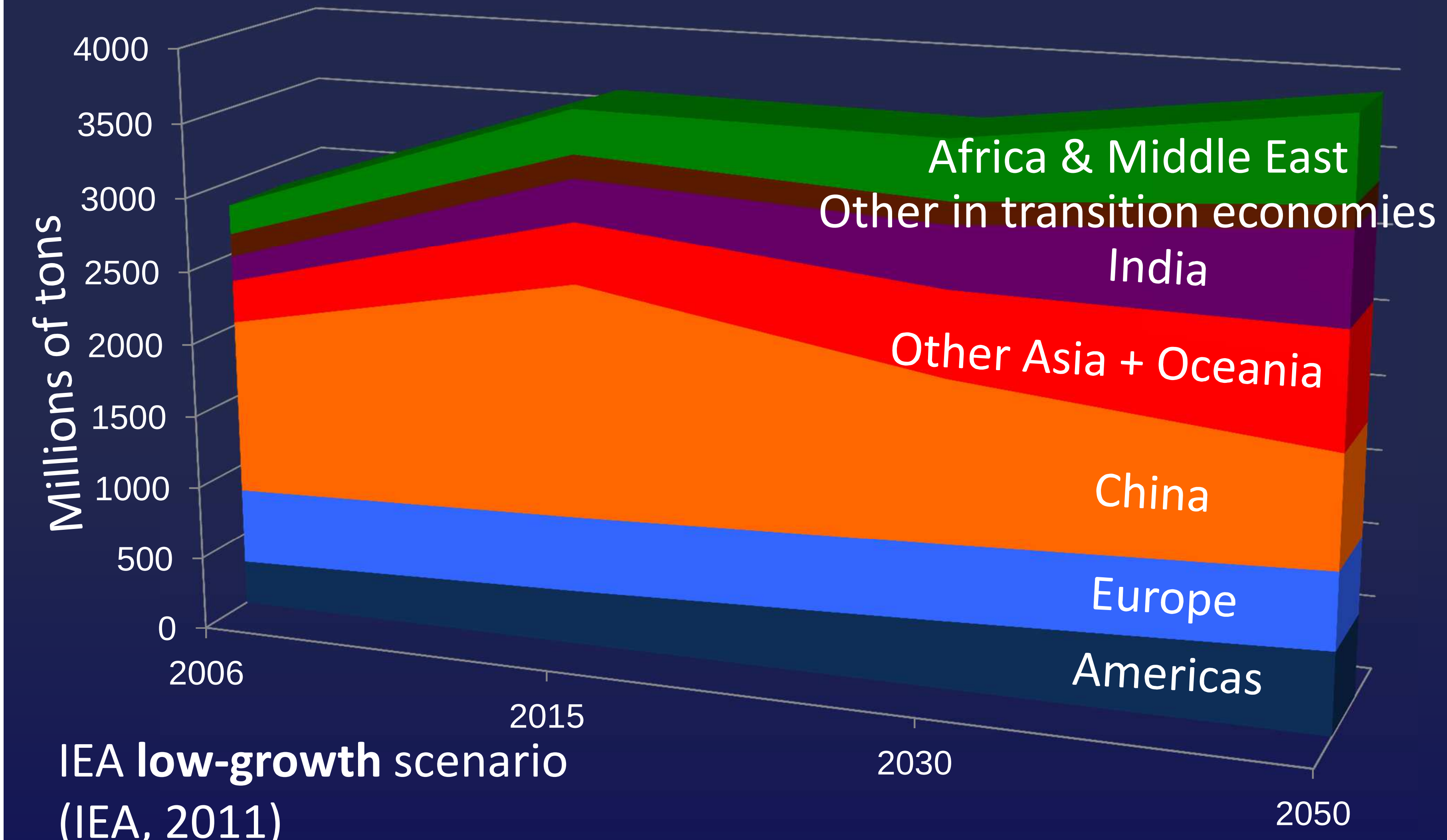
The Cement Industry Technology Roadmap to Reduce Carbon Emissions

The Cement Sustainability Initiative (CSI) and IEA partnered to establish a roadmap for the cement industry:

(total cement industry emissions, in Gt/yr of CO_2)



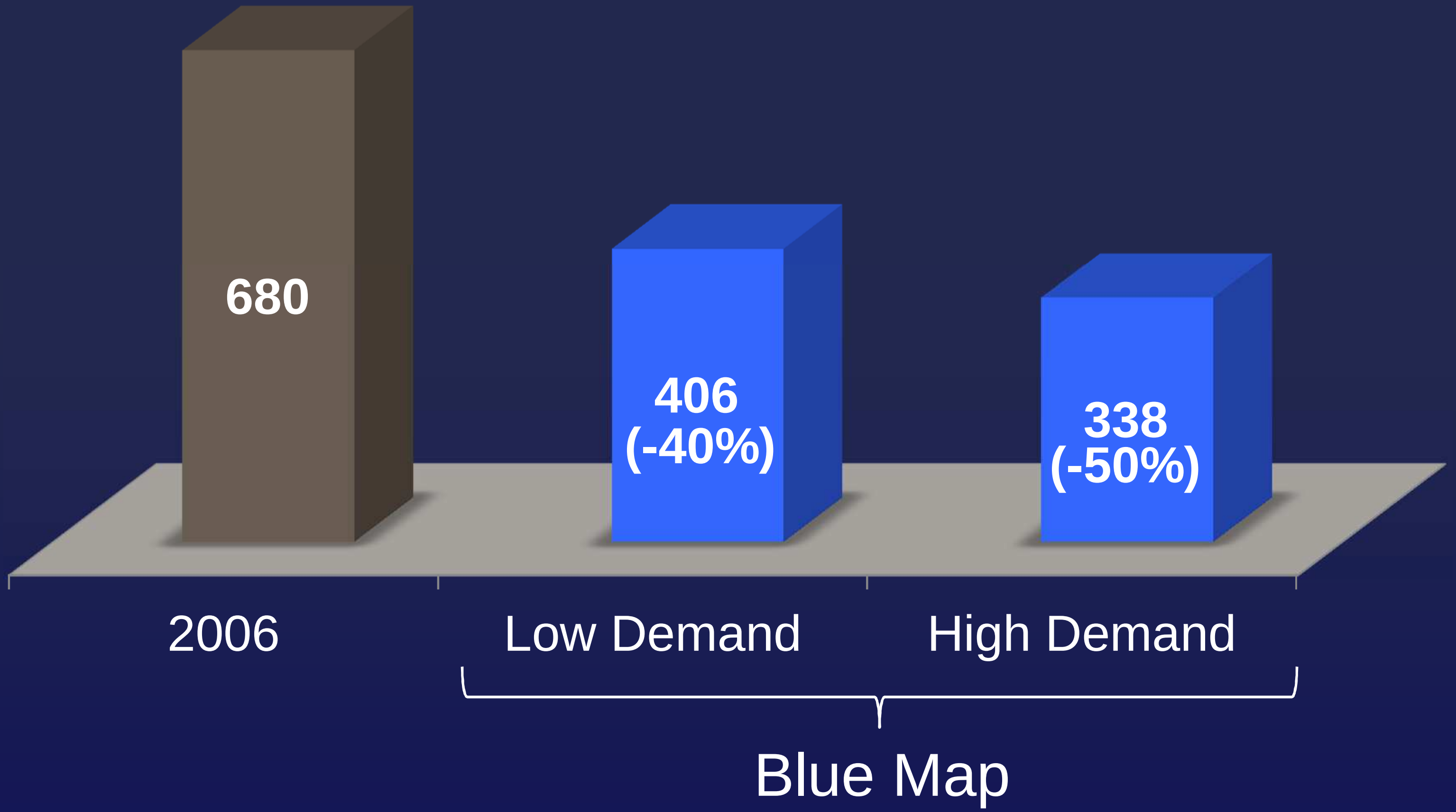
Over the same period, cement production is expected to grow significantly…



IEA **low-growth** scenario
(IEA, 2011)

The Cement Industry's Technology Roadmap to reduce Carbon Emissions

In terms of specific emissions (kg of CO_2 per ton of cement):

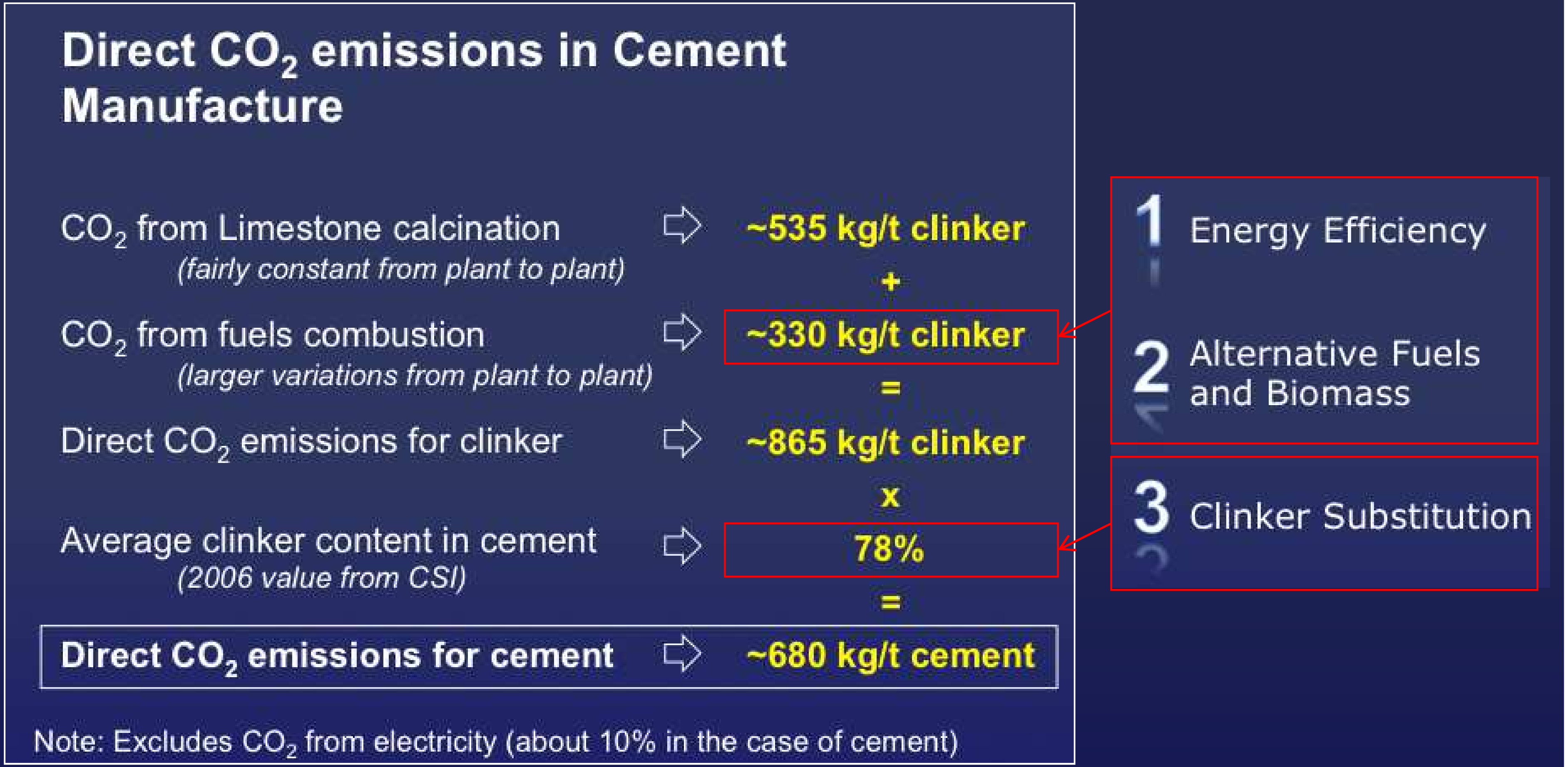


3. Conventional technical approaches for reducing Cement and Concrete CO_2 emissions

Standard approaches to reducing cement and concrete CO_2 emissions:

1. Energy Efficiency
2. Alternative Fuels and Biomass
3. Clinker Substitution
(either in cement or concrete)

Standard approaches to reducing CO_2 emissions



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Note: Excludes CO_2 from electricity (about 10% in the case of cement)

1 Energy Efficiency

2 Alternative Fuels and Biomass

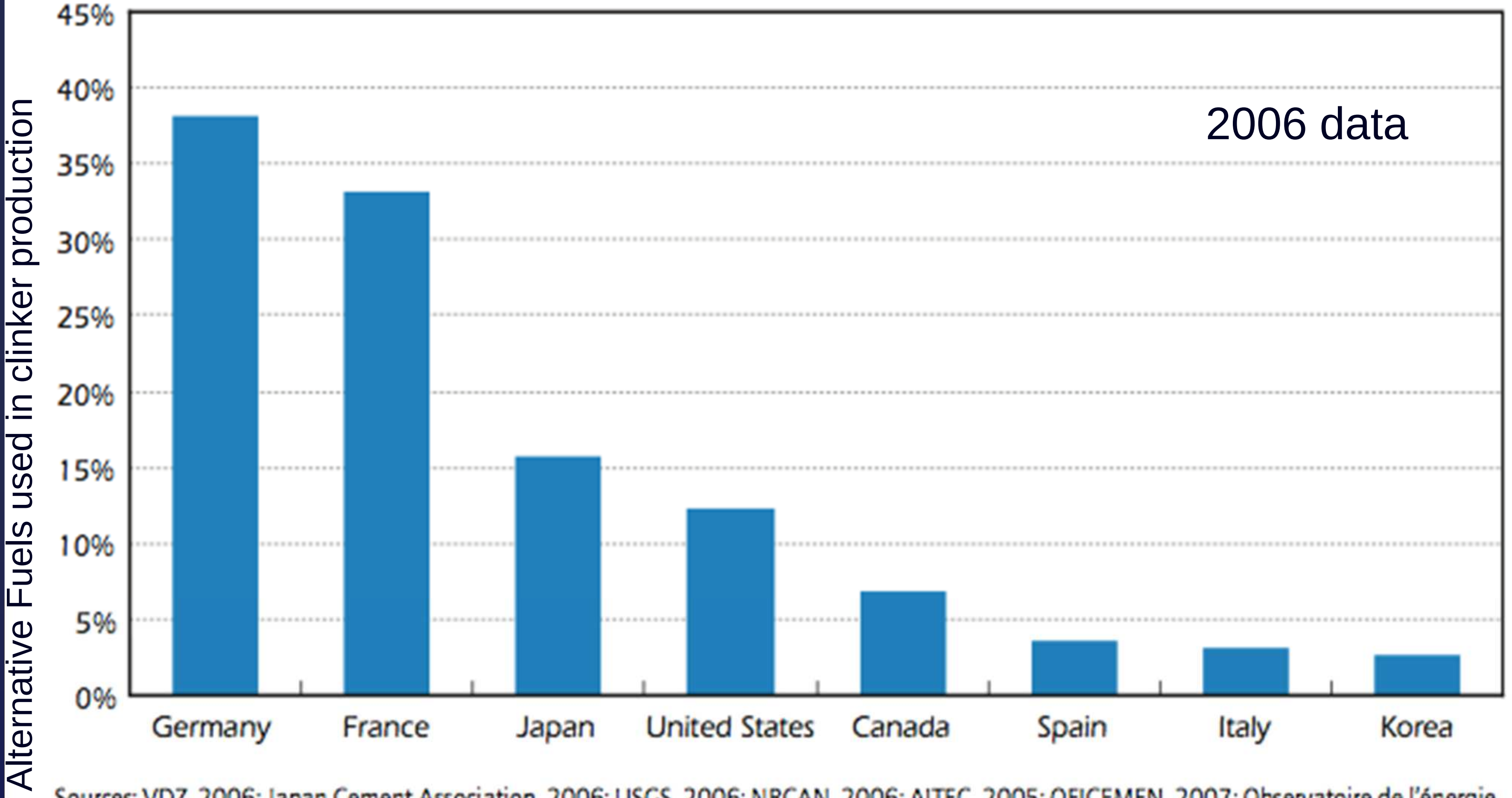
3 Clinker Substitution

1. Energy Efficiency of Cement Kilns

Process	**Typical Fuel Consumtion (GJ/t)**	***Efficiency (%)***
Theoretical consumption	***1.75***	
Vertical Shaft Kilns	~5	*35%*
Wet Kilns	5.9 - 6.7	*25-30%*
Dry Kilns		
Long Dry Kilns	4.6	*38%*
2 Stages Pre-Heater (PH)	3.8	*46%*
4 Stages PH	3.3	*53%*
4 Stages PH + Pre-Calciner (PC)	3.1	*56%*
5 Stages PH+PC (BAT)*	**3**	***58%***

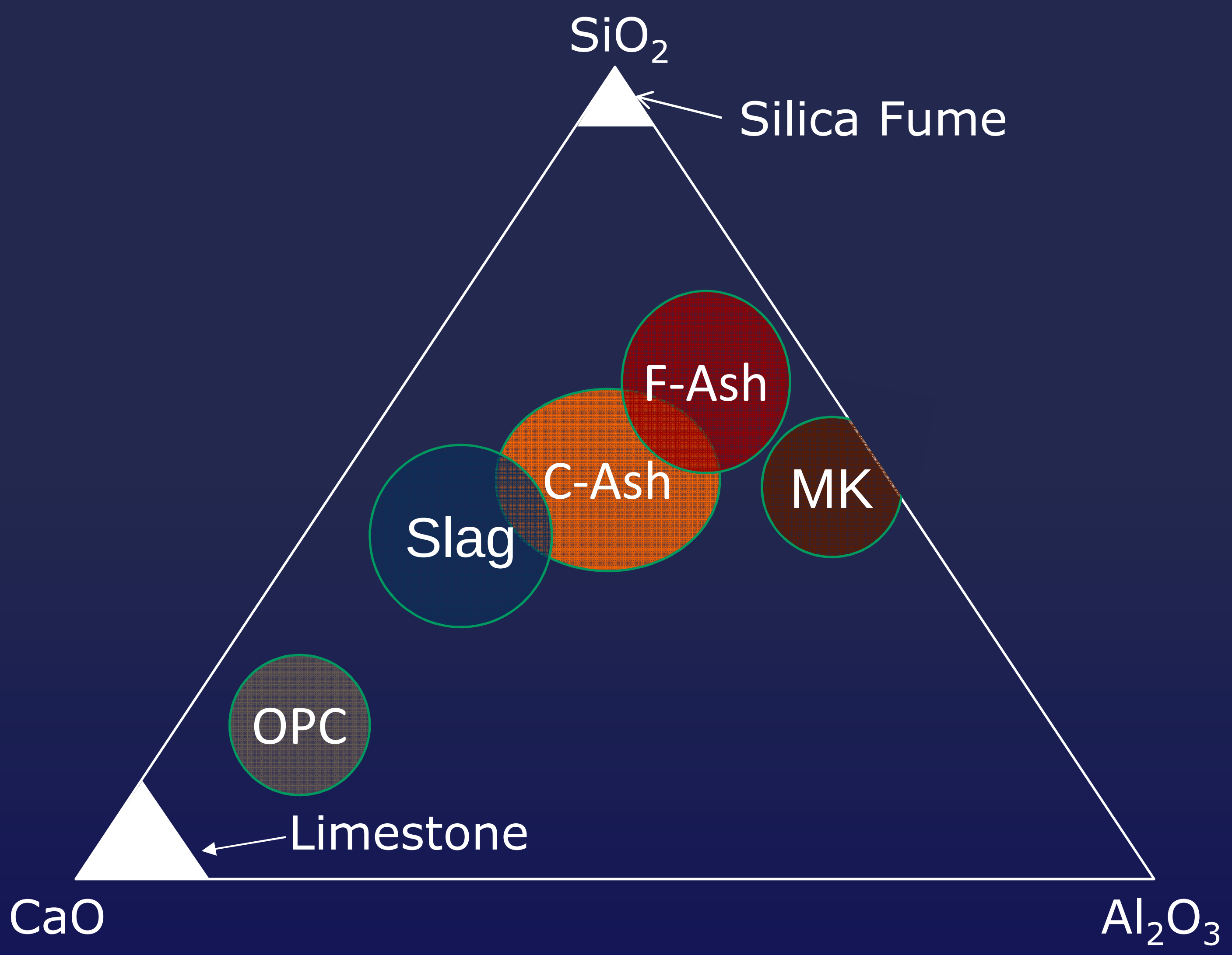
* Industry's Best Available Technology

2. Alternative Fuels and Biomass use

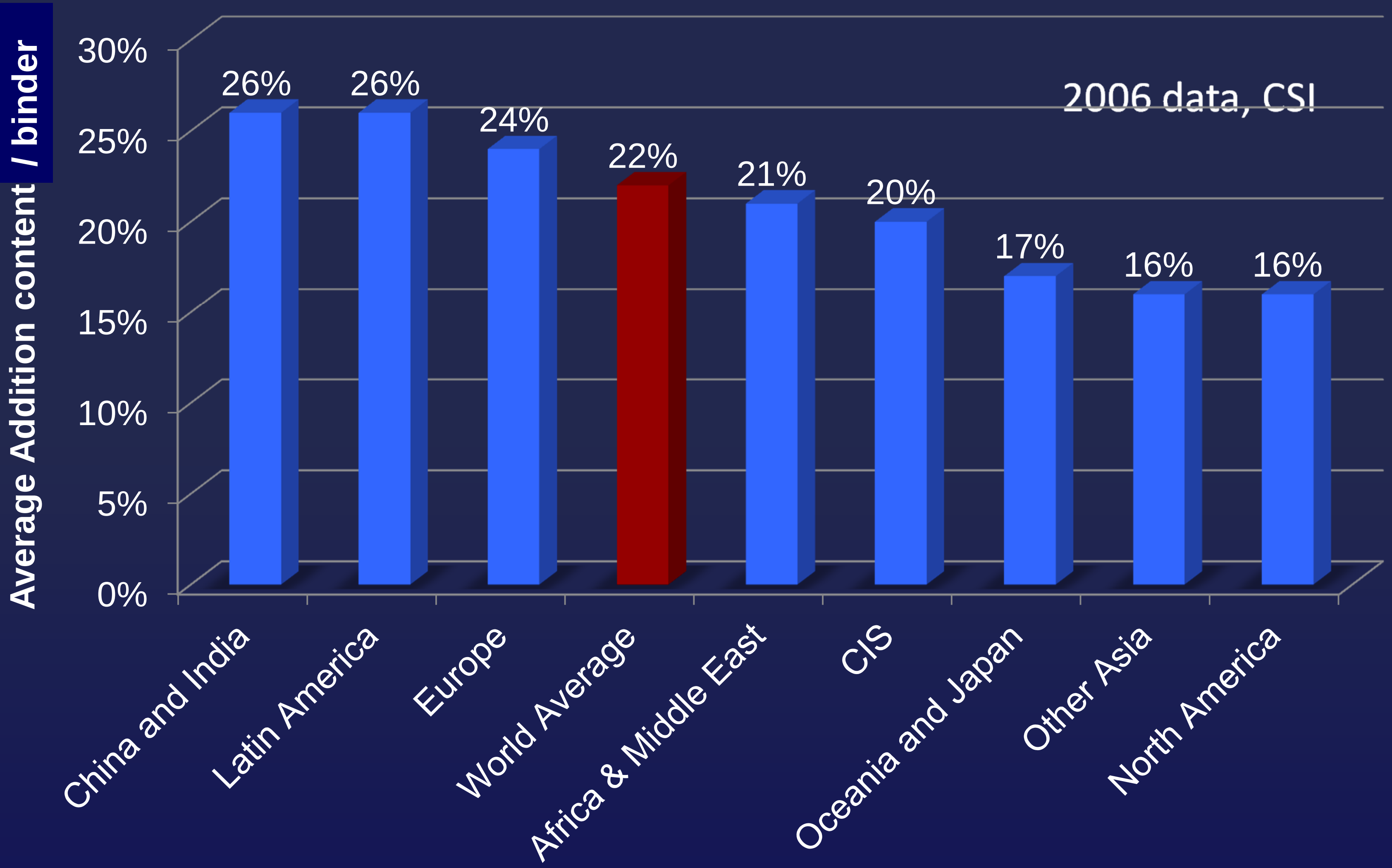


Sources: VDZ, 2006; Japan Cement Association, 2006; USGS, 2006; NRCAN, 2006; AITEC, 2005; OFICEMEN, 2007; Observatoire de l'énergie, 2003; and Dong-Woon, 2006.

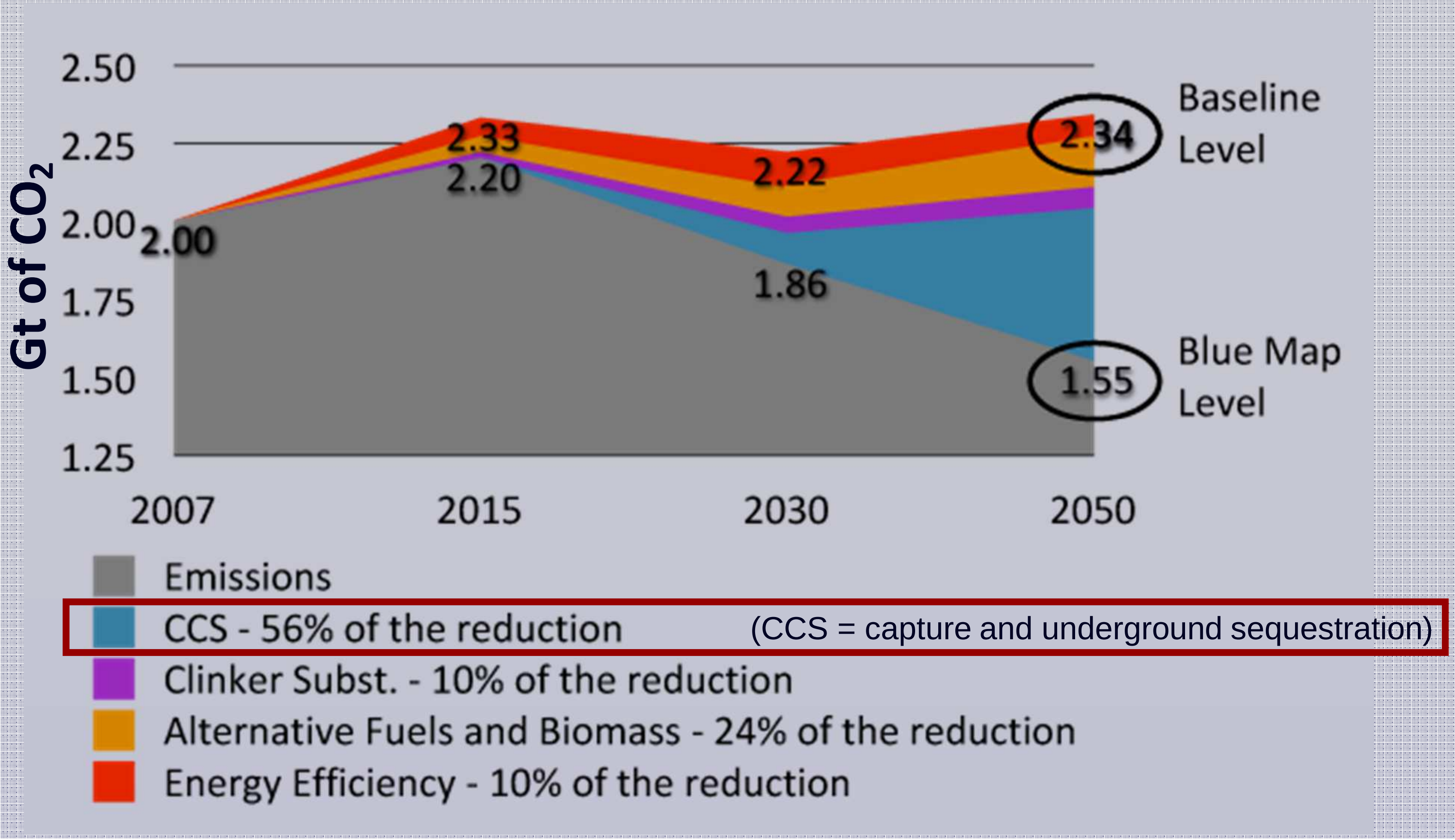
3. Supplementary cementitious materials



Clinker Substitution in Concrete



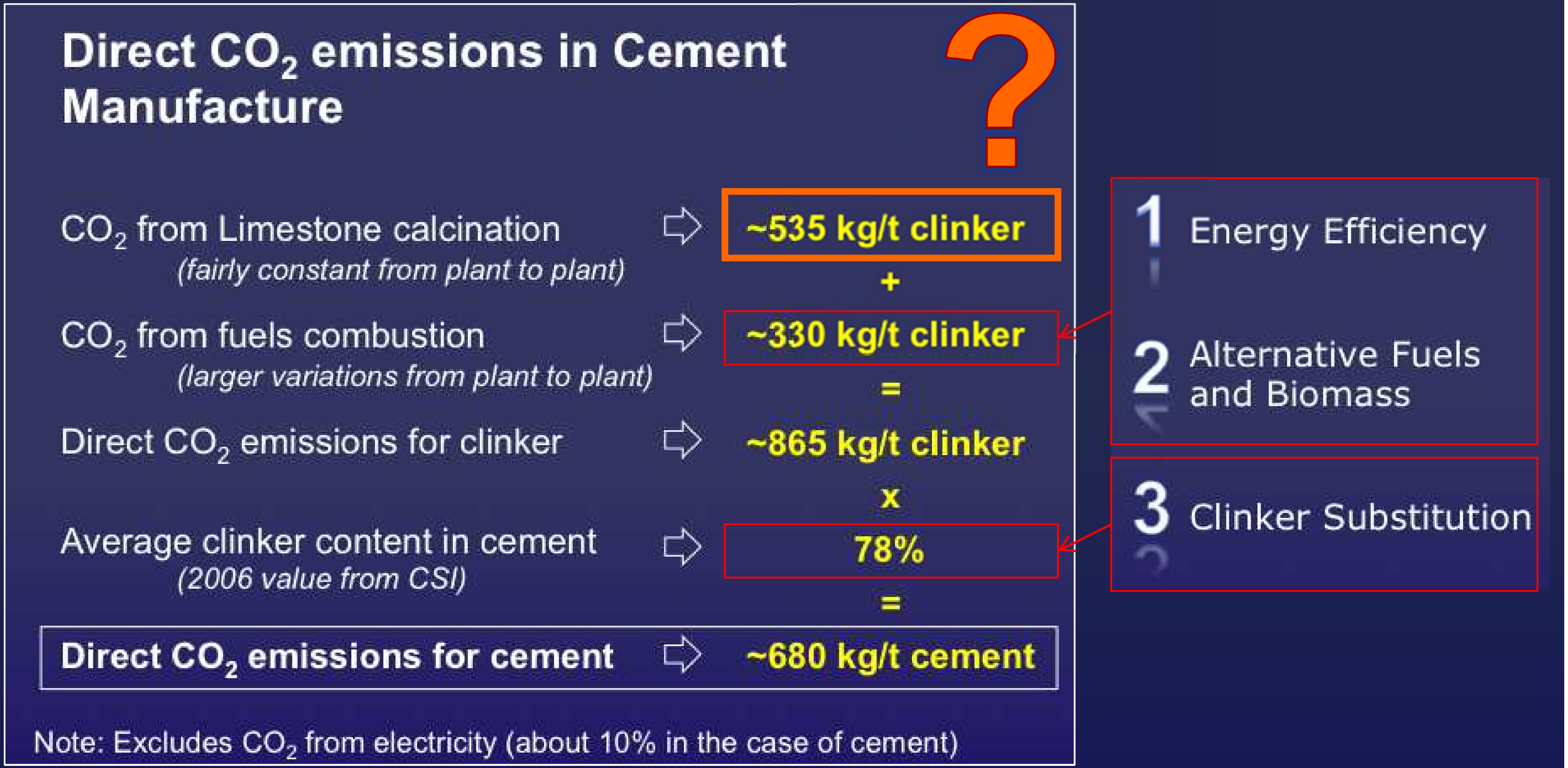
The cement technology roadmap implies that more than half of the reduction in 2050 must come from alternative approaches like CCS:



(CCS = capture and underground sequestration)

4. Beyond the industry roadmap: reformulating “clinker” chemistry (novel approaches to avoid CCS)

A 4th approach to reducing CO_2 emissions: change clinker chemistry



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1 Energy Efficiency

2 Alternative Fuels and Biomass

3 Clinker Substitution

Pertinent Mineral Resources for Alternative Cements

- *Based on their terrestrial abundance, we can consider the following:*
    - **Limestones and dolomites (abundant and widespread)**
    - **Quartz (abundant and widespread)**
    - **Hydrous aluminosilicates (e.g. clays) - (abundant and widespread)**
    - **Basic aluminosilicate rocks (e.g. feldspars) - (abundant and widespread)**
    - **Peridotites (e.g. olivines & serpentines) - (abundant but localized)**
    - **Amorphous volcanic rocks (e.g. tuffs, pumices) (abundant but localized)**
    - **Iron ores (abundant but localized)**
    - **Coal (containing sulfur and aluminosilicates) (abundant but localized)**

- *Pure calcium sulfates, sodium salts (carbonates, chlorides), bauxites, magnesites and phosphate ores are not sufficiently abundant or widespread to serve as the <u>major</u> ingredient in cement manufacture.*

Currently proposed alternatives to PC-based binders

The following are currently being investigated by various groups:

1. Reactive aluminosilicates (pozzolans) activated by lime and/or alkalis
    - **e.g. HVFAC (high-volume fly ash cements), and “Geopolymers”**
2. Reactive calcium silicates produced by “non-Portland” processes
    - **e.g. “Celitement” (KIT/Schwenk, Germany)**
3. Systems based on MgO hydration and carbonation
    - **e.g. systems proposed by Tec-Eco (AU) and Novacem (UK)**
4. Systems based on precipitation of calcium carbonates
    - **e.g. systems proposed by Calera Corp. (USA)**
5. Systems based on calcium aluminates + silicates with higher A/S than PC
    - **e.g. belite/calcium sulfoaluminate/ferrite cements (Lafarge’s “Aether”)**

In all of the above systems the raw materials are sufficiently abundant to be of global interest, but the practical performance and manufacturing costs are not yet known in detail.

Activated aluminosilicate binders

- This category extends all the way from fairly standard portland-pozzolan blended cements to pure alkali-activated aluminosilicates.

- The attraction is the ability to use readily-available resources of either man-made by-products (especially fly ashes) or natural pozzolans

- Insofar as these materials are available locally in a dry state, they can be considered to have low associated energy and CO_2 costs.

- Alkaline activators (R_2O) can help reduce overall CO_2 emissions if:
    1. **One mole of R_2O replaces >> 1 mole of CaO in the products**
    2. **The R_2O can be obtained at a reasonably low energy and CO_2 cost**

- The calcium source does not have to be PC clinker or lime.
    - **It can be slag – but unused blast-furnace slag resources are very limited.**
    - **It can be gypsum, but then the alkali source must provide all the alkalinity.**

What is a “Geopolymer?”

- The term “geopolymer” was first registered as a trademark by Joseph Davidovits, who made it freely available for public use. It is widely accepted to refer to binders based on the reaction between certain aluminosilicates (AS_x) and concentrated alkali* solutions.

- The general reaction, often called “geopolymerization,” is as follows:

$$AS_x + \overbrace{NS_y + nH}^{\text{liquid “activator”*}} \Rightarrow \overbrace{NAS_{(x+y)}H_\delta}^{\text{solid “gel”}} + \overbrace{(n-\delta)H}^{\text{excess water}} \qquad (1)$$

** (N is usually Na_2O but can be K_2O)*

- The “activator” can range from a pure alkali* hydroxide (e.g. NaOH) solution (y=0) to a high-silica water glass solution (y>3). It must be very concentrated (typically > 6 molar) in order to get a rapid reaction.

- In general, the aluminosilicates that can be activated in this way are also classed as “pozzolans” for use with lime or Portland cement. Examples are metakaolin (AS_2), fly ashes and many natural pozzolans.

Are alkali-activated cements a practical alternative?

- Alkali activators are usually either NaOH (manufactured via the electrolysis of NaCl solutions in the “chlor-alkali” process), or sodium silicates (usually made by melting soda + silica in a glass furnaces).
- Both of these process are capital- and energy-intensive, and the CO_2 emissions per mole of R_2O are greater than for CaO in PC or lime.
- If significant global volumes of alkali-activated binders are to be used, major activator manufacturing capacity increases will be needed.
- The bulk of the binder (>80%) is typically a mixture of pozzolans and calcium sources (slags, clinker, gypsum, etc.). The reactions are complex and raw materials quality control will be a major issue.
- It is not yet proven that sufficient volumes of pozzolan will be cheaply available. Manufacture of artificial pozzolans specifically for cement uses may be fairly energy-intensive (e.g. calcination of clays, etc.)

Karlsruhe Institute of Technology’s “Celitement™”

Celitement is a C-S-H-based binder with an inherently high filler content.

It is produced from limestone and quartz by a two-step thermal process:

1. Calcine (at ≈1000° C) a relatively pure crushed limestone to give lime:
   - **$CaCO_3 \Rightarrow CaO + CO_2\uparrow$**
   - **Enthalpy of calcination = 3.9 GJ/t.CO_2 = 3.1 GJ/t.CaO produced**
2. Grind lime together with quartz in a 2:1 molar ratio and hydrate in an autoclave at ≈200° C
   - **$2CaO + SiO_2 + H_2O \Rightarrow Ca_2(HSiO_4)(OH) = \alpha\text{-}C_2SH$**
   - **The reaction requires a pressure of about 10-15 atm.**
3. Grind resulting product (α-C_2SH) at about 1:1 with a hard filler (e.g. quartz) to make the final binder, (which also usually needs a superplasticizer).
4. During hydration of the binder, the α-C_2SH reacts with water to produce “normal” C-S-H, binding together the quartz filler particles.

MgO-based binders: general background

- MgO-based binders have been used for many years in the form of “Sorel Cements,” based on the formation of hydrated basic magnesium chlorides or sulfates. But these binders have limited applications due to high raw materials costs and poor water-resistance in use.
  - **They behave like stronger but more expensive gypsum plasters!**
- More recently it was found *(J. Harrison, Tec-Eco)* that very reactive MgO (produced by low-temperature calcination) can act as an hydraulic binder on its own, and can be strengthened further by carbonation:
  - **$MgO + H_2O \Rightarrow Mg(OH)_2$; $Mg(OH)_2 + CO_2 \Rightarrow MgCO_3.nH_2O$, etc.**
  - **Atmospheric carbonation of $Mg(OH)_2$ is normally slow due to formation of protective carbonates; but it might be accelerated.**
- However, conventional methods for producing MgO (decarbonation of magnesite rock or treatment of seawater or Mg-rich brines with lime followed by calcination) are expensive and emit too much fossil CO_2.

MgO-based binders: new approach from Novacem

- Novacem (UK) claims to be able to make reactive MgO at a low cost (both in energy and CO_2) from common basic magnesium silicate rocks (peridotites). If this can be demonstrated, it will be a significant breakthrough in accelerating the natural weathering processes by which such basic rocks slowly absorb atmospheric CO_2, e.g.:

$$\mathbf{Mg_2SiO_4 + 4CO_2 \Rightarrow 2Mg^{++} + 4HCO_3^- + SiO_2\downarrow \Rightarrow 2MgCO_3\downarrow + 2CO_2\uparrow}$$

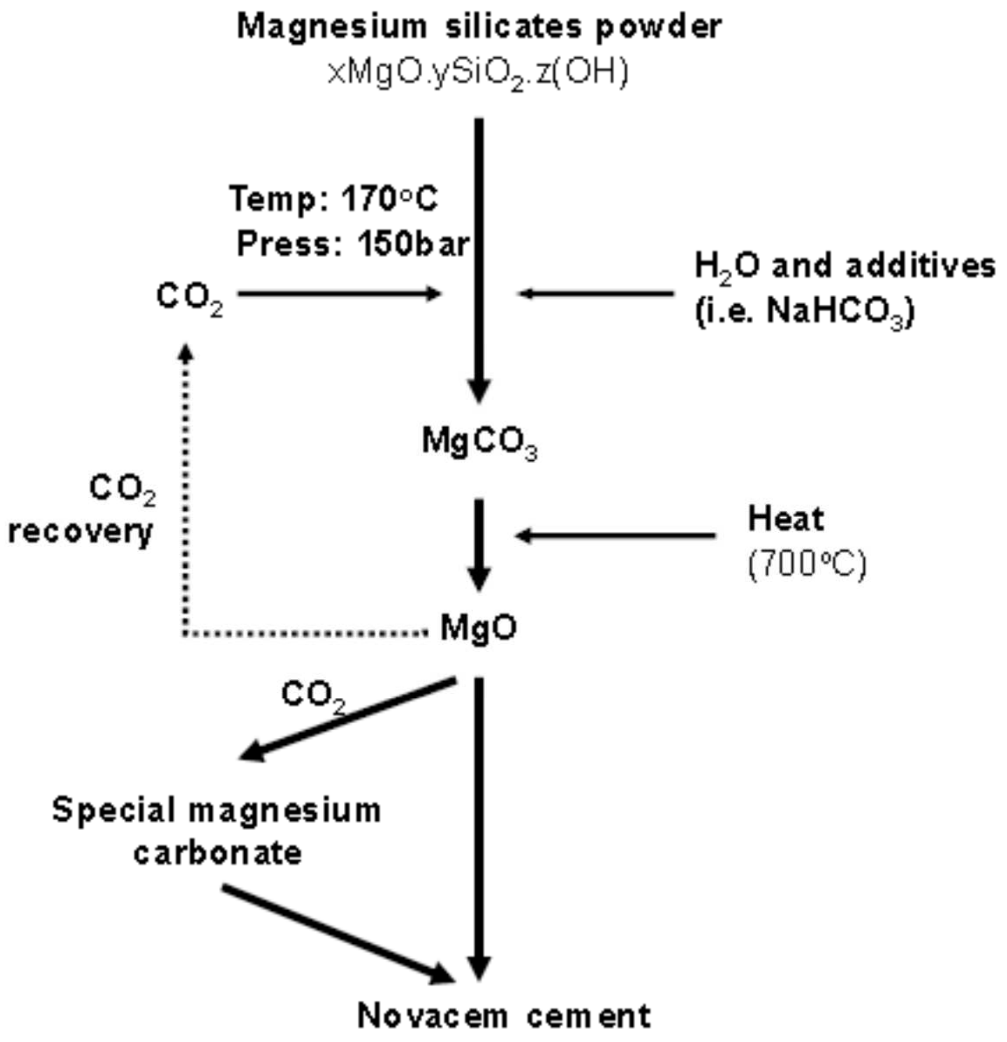
rainwater ⇒ rivers ⇒ lakes, seas

- The MgO is combined with certain magnesium carbonates to form Novacem's patented "magnesium hydroxy-carbonate" binders.*

- Even if the overall CO_2 balance of the Novacem process is negative in the long term (as claimed), there is as yet no indication that the resulting MgO-based binders will give suitable performance for all construction applications in which Portland-based cements are used.

* ***N. Vlasopoulos & C. R. Cheeseman, World Patent Application WO2009156740, (2009).***

The Novacem Process *(N. Vlasopoulos, SCI mtg., London, 25/11/2010)*



Initial advantages

- No CO_2 emissions from the raw materials
- Low temperature allows full use of fuels with low energy content

Initial disadvantages

- High pressure/high cost system
- Corrosion/reliability of system components
- High energy requirement for raw materials milling

Calcium carbonate-based binders

- It is known that amorphous calcium carbonates can be precipitated from highly supersaturated solutions and stabilized by certain cations (e.g. Mg^{++}). More recently, it has been shown that these amorphous phases can be used as hydraulic cements *(see Combes et al, Biomaterials, 2006):*

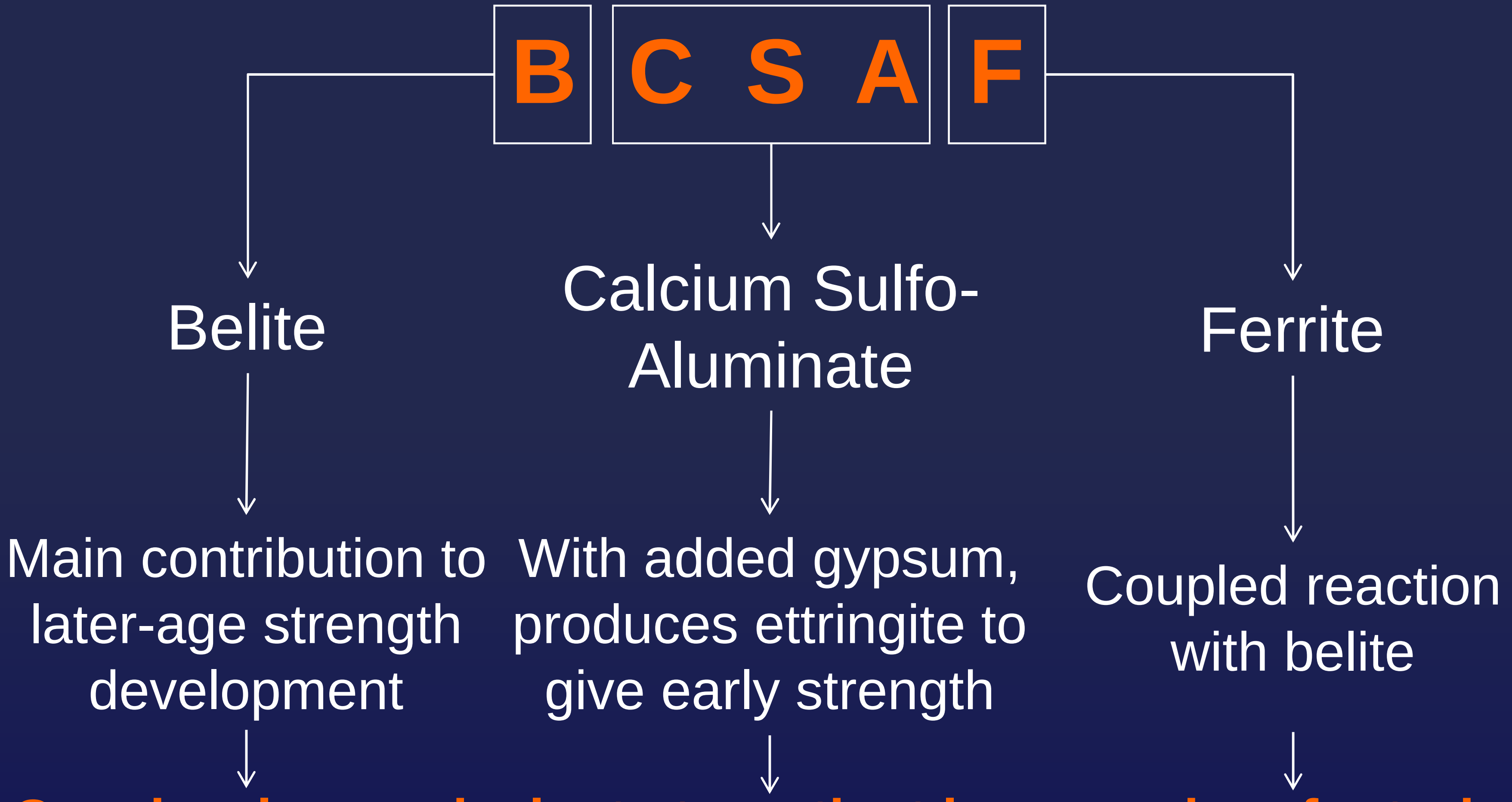
$$\mathbf{CaCO_3\ (amorph)\ \Rightarrow (aq.\ soln + nuclei)\ \Rightarrow CaCO_3\ (calcite\ or\ aragonite)}$$

Note: these appear to be hydraulic cements without hydration!

- Calera Corp. (USA) has reportedly been developing such binders, using CO_2 + various calcium sources including brines, plus an electrochemical process to provide alkalinity. The main interest is in the capture of CO_2.

- However, such binders are essentially pH-neutral and would not be expected to protect reinforcing steel, so they would probably be restricted in their applications (although this may also be true for many of the other alternative binders discussed here).

BCSAF Clinker (Lafarge's Aether^{TM})



B C S A F

Belite

Calcium Sulfo-Aluminate

Ferrite

Main contribution to later-age strength development

With added gypsum, produces ettringite to give early strength

Coupled reaction with belite

Can develop equivalent strength at lower carbon footprint

BCSAF on C-A-S triangle:

How much lower is the carbon footprint?

CO2 per ton of clinker	PCC	BCSAF Clinker (Aether^{TM})	difference
Limestone decarbonation	~535 kg/t	~375 kg/t	-30%
Fuel consumption	~330 kg/t	~240 kg/t	-27%
Total Direct CO_2	**~865 kg/t**	**~615 kg/t**	**-29%**

Key benefits of BCSAF clinkers (Aether^{TM})

- Reduction of up to 30% of the CO_2 footprint of clinker manufacturing
- Potential additional saving on indirect CO_2 from electricity, as clinker is easier to grind than PC clinker
- Gives high level of early reactivity, allowing us to maintain clinker substitution at the same levels as with OPC
- Later-age strength development similar to OPC
- Can be manufactured in existing cement plants: no need for large capital expenditures, and possibility of production rate increases
- Manufacture already demonstrated on an industrial scale

Challenges

- Some additional raw materials must be brought to the cement plant, increasing raw materials costs (depending on location). The cost differential must be acceptable.
  - Additional cost compared to PCC is nevertheless significantly lower than CCS in relation to CO_2 emissions avoided.
- Cement and Concrete science has 100+ years of R&D and still many aspects are not fully mastered. We have just scratched the surface with BCSAF technology.
  - Durability testing is likely to be the slowest step in gaining acceptance. Theory is insufficient for large extrapolations.
- Specifications, acceptance, etc..

Comparison of OPC and Aether™ hydration:

(note: “reactions” shown here are not fundamental steps)

OPC:

Alite: $C_3S + 5.3H \Rightarrow C_{1.7}SH_4 + 1.3CH$

Belite: $C_2S + 4.3H \Rightarrow C_{1.7}SH_4 + 0.3CH$

C_3A+gypsum: $C_3A + 3C\hat{S}H_2 + 26H \Rightarrow C_6A\hat{S}_3H_{32}$

C_3A+limestone: $C_3A + C\hat{C} + 11H \Rightarrow C_4A\hat{C}H_{11}$

ferrite+limestone: $C_4AF + C\hat{C} + 15H \Rightarrow C_4A\hat{C}H_{11} + CH + FH_3$

Aether:

CSA + anhydrite: $C_4A_3\hat{S} + 2C\hat{S} + 38H \Rightarrow C_6A\hat{S}_3H_{32} + 2AH_3$

CSA alone: $C_4A_3\hat{S} + 18H \Rightarrow C_4A\hat{S}H_{12} + 2AH_3$

Belite + AH_3: $C_2S + AH_3 + 5H \Rightarrow C_2ASH_8$

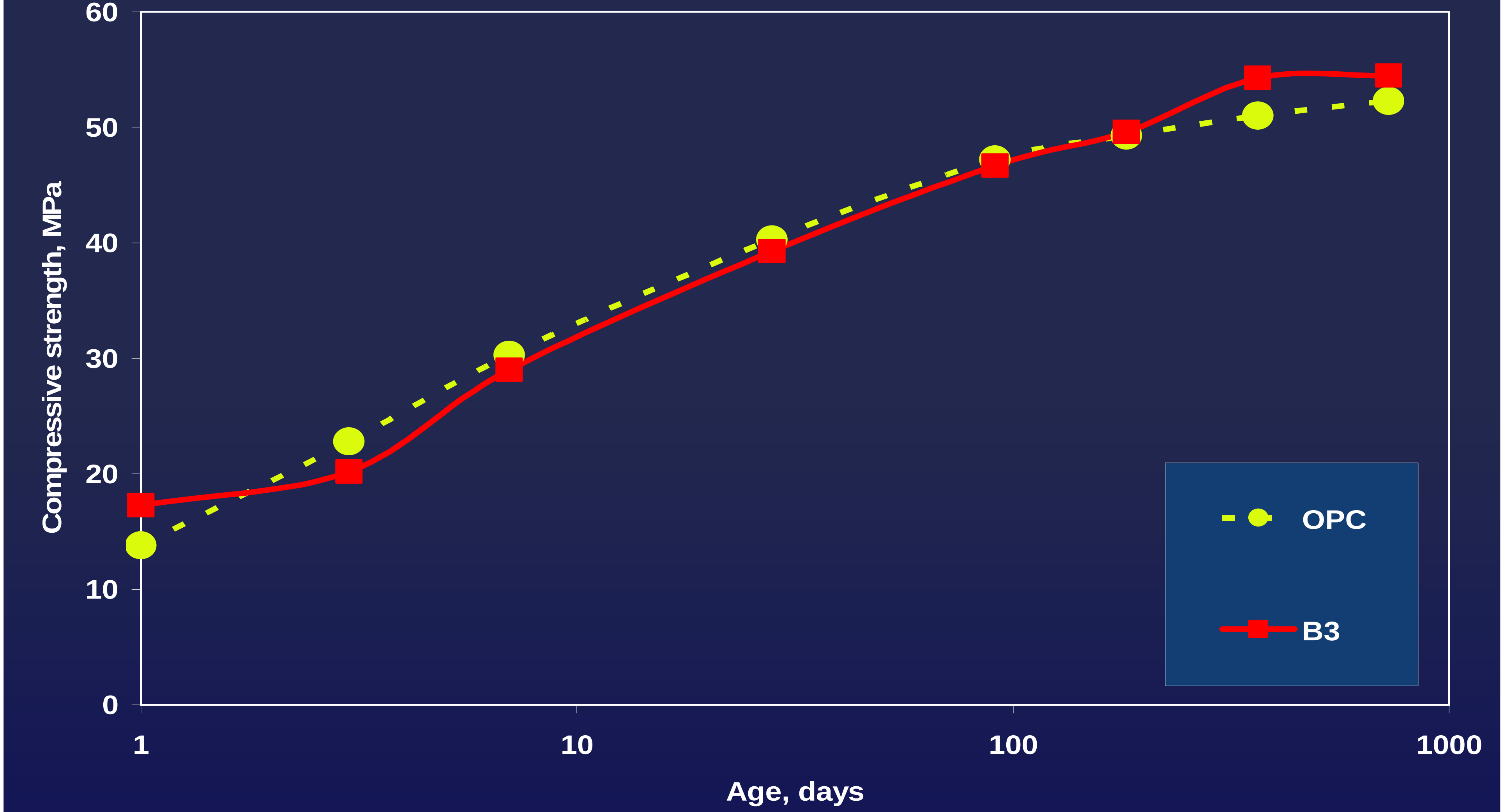
Belite + ferrite: $C_2S + C_2(A,F) + 5H \Rightarrow C_3(A,F)SH_4 + CH$

CH + strätlingite: $C_2ASH_8 + CH \Rightarrow C_3ASH_4 + 5H$

Belite alone: $C_2S + 4.3H \Rightarrow C_{1.7}SH_4 + 0.3CH$

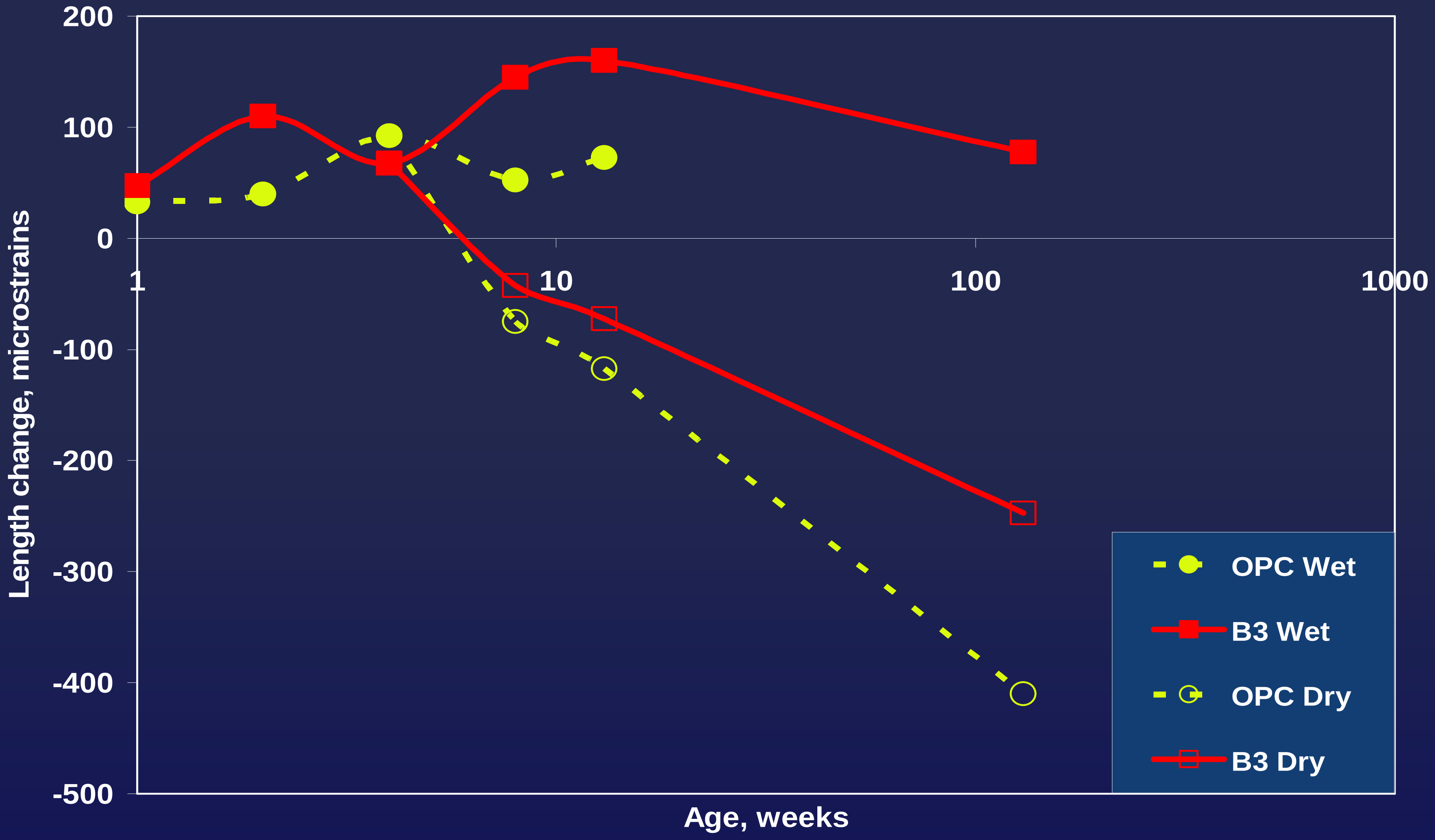
BRE concrete data at w/c = 0.55, 300kg/m^3 for pilot batch of Aether (B3) compared to OPC (CEM I 42.5) (at 20° C).

(K. Quillin, Calcium Sulfoaluminate Cements – CO$_2$ reduction, concrete properties and applications, BRE Report (Garston, UK), BR 496 (2007).)



Dimensional stability of B3 concrete

(vs. OPC concrete, at 20° C, either in water or at 65% RH)



WRAP-UP

The IEA estimates that CO_2 emissions must be **cut in half** to keep temperature rise below 3° C

IEA proposes a **sectorial approach** as the **least cost way** to reduce emissions

The cement industry is a **large contributor** to global man-made CO_2 emissions, mainly because of very large production **volumes**

The cement industry and IEA partnered to build a technology roadmap for CO_2 reduction

The roadmap calls for **23%** reduction of **absolute** CO_2 emissions and **40 to 50%** of **specific** emissions.

Existing levers (energy eff., clinker subst.) should lead us **half-way**. **High costs** forecast for CCS

Lafarge is proposing **one novel approach** to help reduce carbon emissions through **clinker reformulation**. **BCSAF clinkers** (Aether^{TM}) have the opportunity to **reduce by up to 30%** the CO_2 footprint of clinker manufacturing

THANK YOU FOR INVITING ME!