Opportunities to Use Hydrogen in Concrete Production

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World demand/year

- Concrete: ~~11 billion ton~~
- Water: ~~1.0 billion ton~~
- Aggregate: ~~9 billion ton~~
- Cement: ~~1.5 billion ton~~

~~Demand for concrete in 2050: 16 billion ton~~

Mehta & Monteiro, third edition, 2006

World demand/year

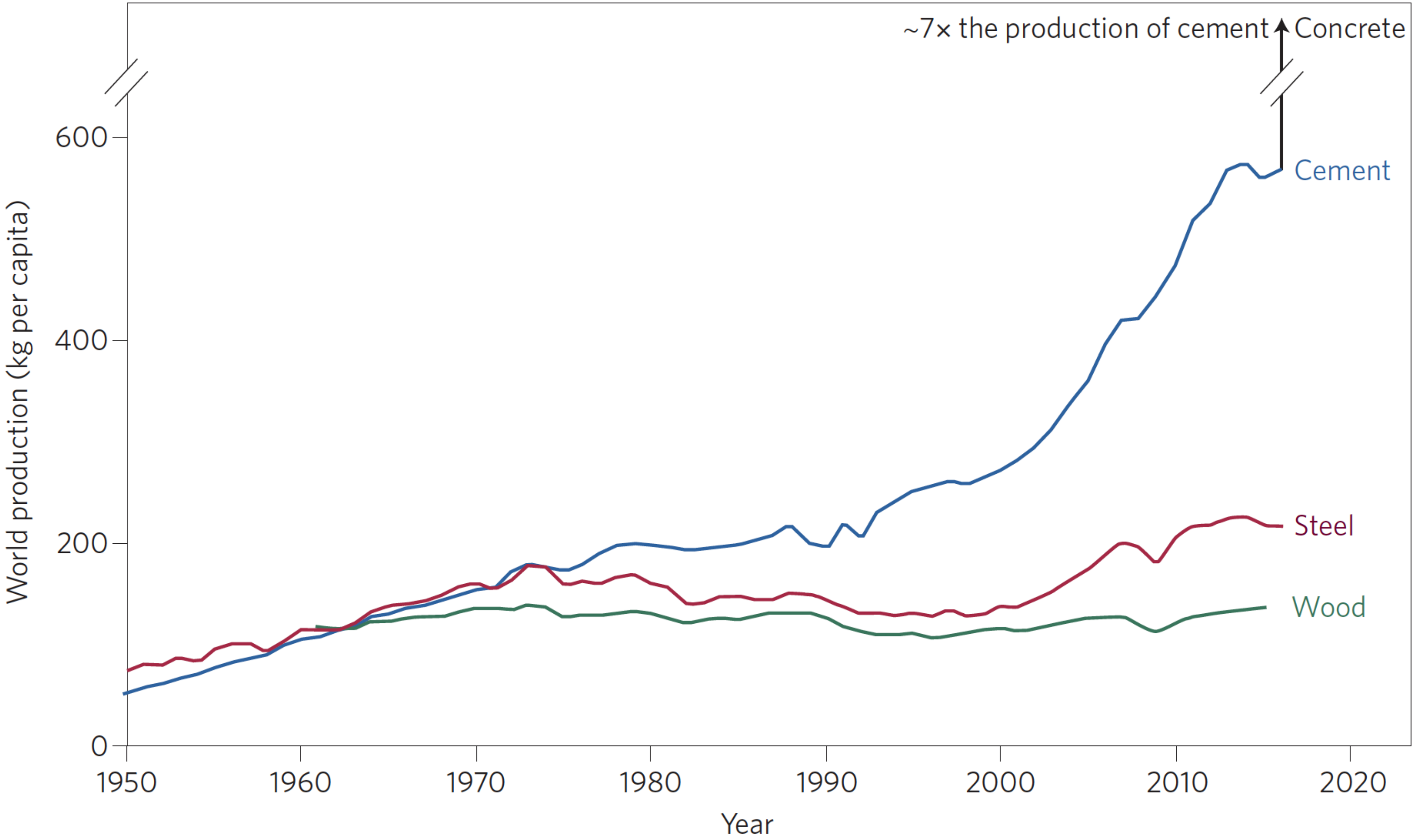
Concrete: 33 billion ton

Water: 2.7 billion ton

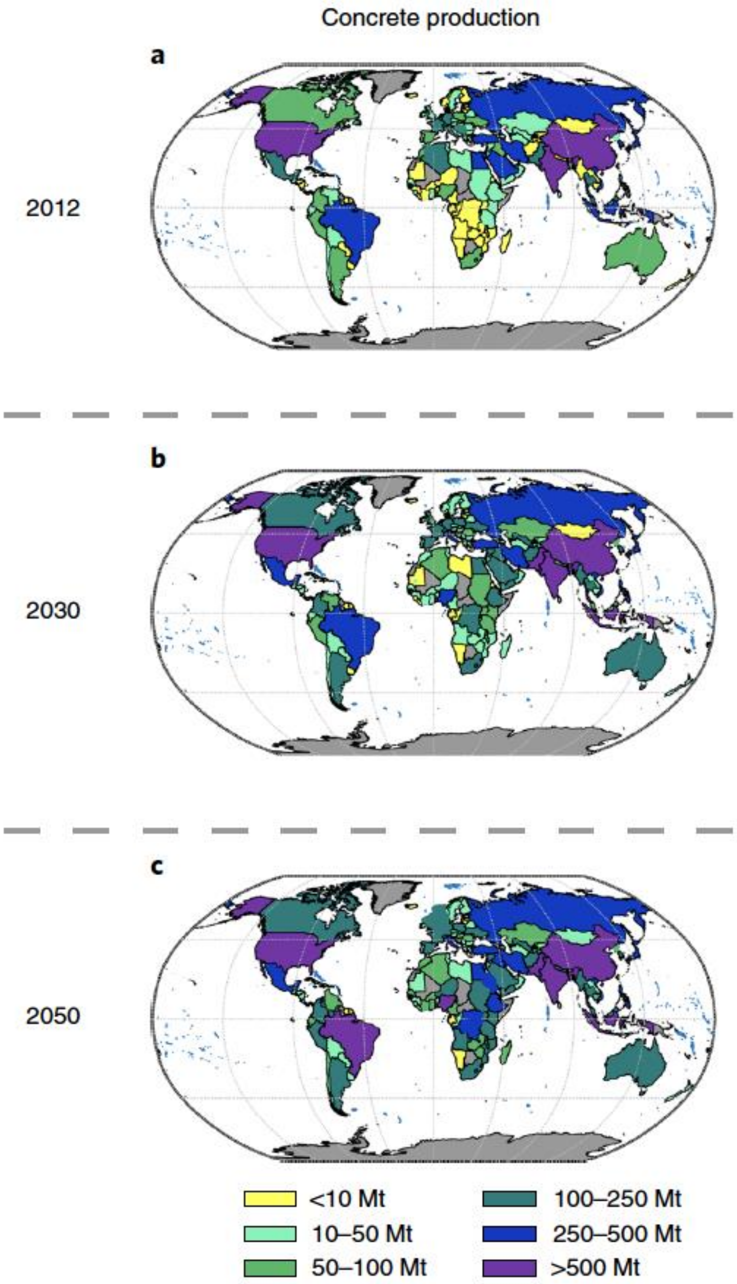
Aggregate: 27 billion ton

Cement: 3.7 billion ton

Mehta & Monteiro, fourth edition, 2014

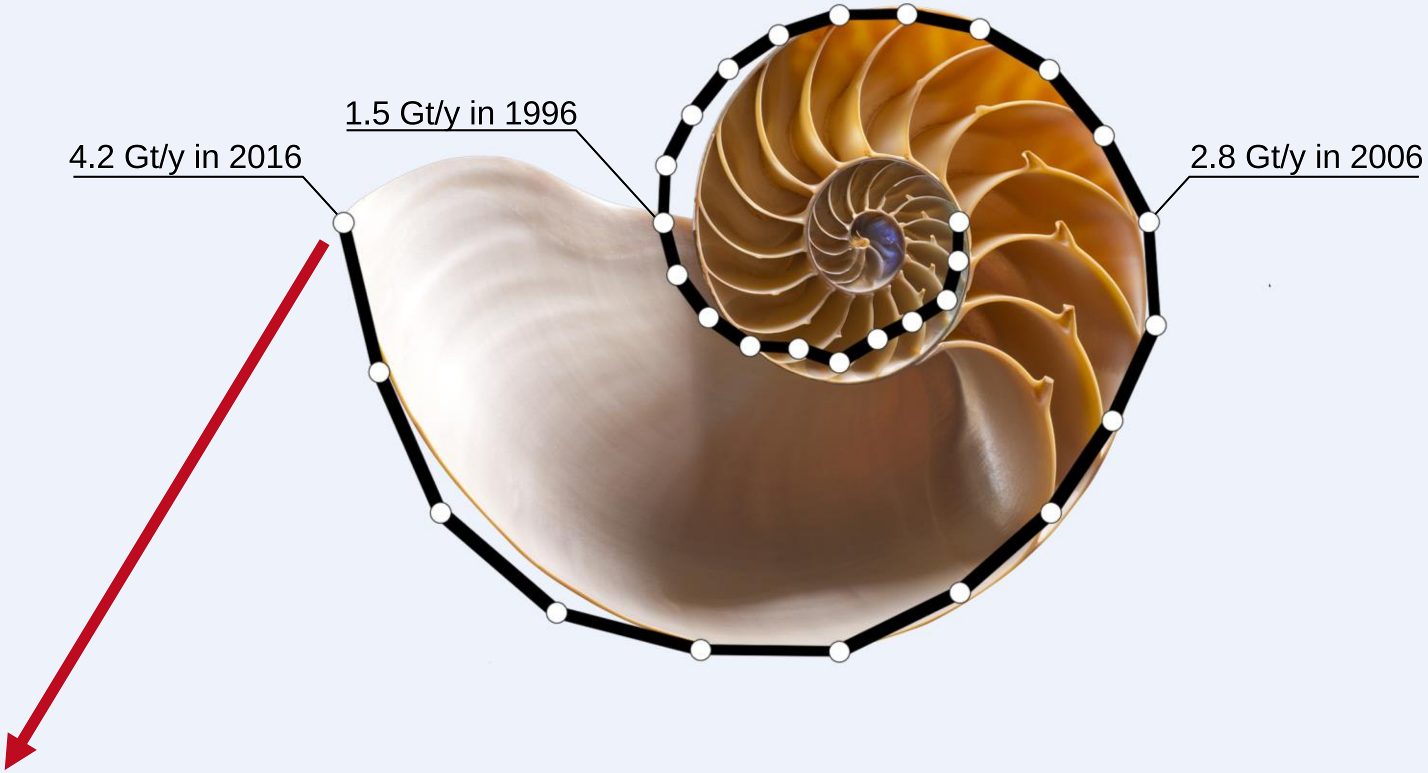


Monteiro et al. *Nature Materials*, 2017



Miller, Horvath and Monteiro, *Nature Sustainability*, 2018

Growth of the World Cement Production
1986-2016



Major business opportunity: $400B/y just with cement
$ 921B/y if concrete is included

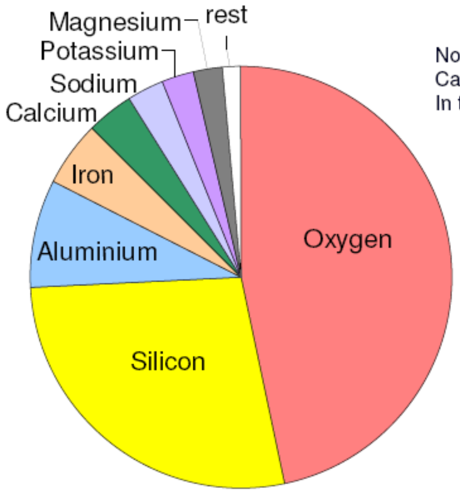
Environmental Impact

Production 1 ton of cement generates 0.87 ton of CO_2

Cement industry generates ~3.3 billion ton of CO_2

Constraints for the new cement

- Raw materials easily available all over the world



Proportions of the principal elements in the Earth's crust

Note: Portland Clinker contains
Ca, O, Si, Al and Fe
In that order of concentration

Other elements abundant
enough to be considered
include H, C, S, N, Cl & P

- Cheap: $100/ton

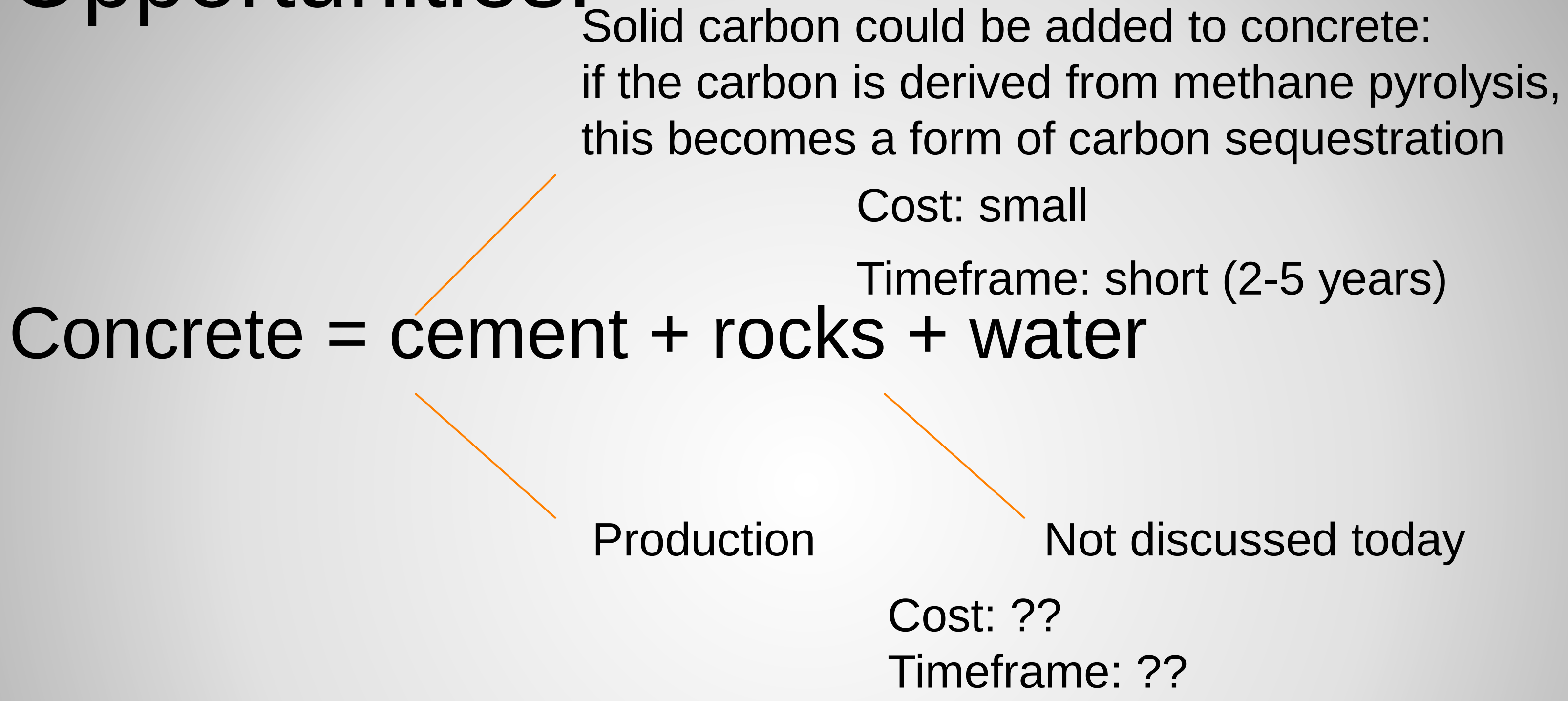
- Field construction done by workers with different qualifications

- Interesting?
  - Maybe…
    - What is the relevance to H_2?

The takeaways of this presentation:

- Large production of cement and concrete
- Concrete can host a large amount of waste products.
- H_2 can be used in the production of Portland cement

Opportunities:



Solid carbon could be added to concrete:
if the carbon is derived from methane pyrolysis,
this becomes a form of carbon sequestration

Cost: small

Timeframe: short (2-5 years)

Concrete = cement + rocks + water

Production

Not discussed today

Cost: ??
Timeframe: ??

Question:

How much can carbon particles replace Porland cement?

Materials

- Carbon
  - Graphite disk
    - GD1 44 µm (Sigma Aldrich)
    - GD2 3-5 µm (Asbury Carbons)
    - GD3 0.1 – 0.2 µm, 180 m^2/g (Asbury Carbons)
  - Carbon fiber
    - CF1 diameter 6-7 µm, length 50-80 µm (Alibaba)
    - CF3 diameter 6-7 µm, length 1-2 mm (Alibaba)
  - Carbon black
    - CB1 254 m^2/g (Asbury Carbons)
- White Portland cement (wPC)
- Superplasticizer
  - Polycarboxylate-ether (PCE)
- Standard quartz sand

- Same hydration reaction as in ordinary Portland cement
- Low Fe content for white color
- Clear vision of carbon distribution (PC is grey)

- For workability adjustment
- Expensive
- Low dosage is desired

Materials

Graphite disk: GD1 44 µm; GD2 3-5 µm; GD3 0.1-0.2 µm
Carbon fiber: CF1 diameter 6-7 µm length 50-80 µm;
CF3 diameter 6-7 µm length 1-2 mm
Carbon black: CB1 254 m^2/g

- Paste
  - Replacement level 2%, 5%, 10% weight of cement
  - Water/solid ratio (w/s) 0.485, 0.4, 0.3
  - "Dry mix"[1] for CF1, CF3, GD1, GD2; "Wet mix"[2] for GD3

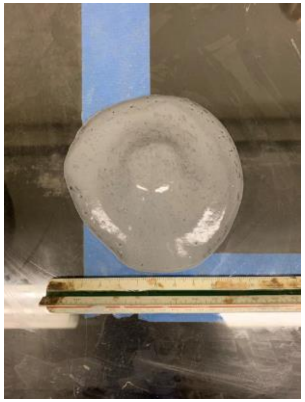
- Mortar
  - Replacement level 0%, 5%, 10%
  - Water/solid ratio (w/s) 0.485, 0.4, 0.3
  - Paste/sand volume ratio ~ 0.79*
  - "Dry mix" for CF1, CF3, GD1, GD2; "Wet mix" for GD3 and CB1
  - 50-mm cube
  - Demold at 24hr; then store in fog room until test

50-mm mortar cubes
Replacement with GD1 (44 µm), at w/s = 0.485

Methods

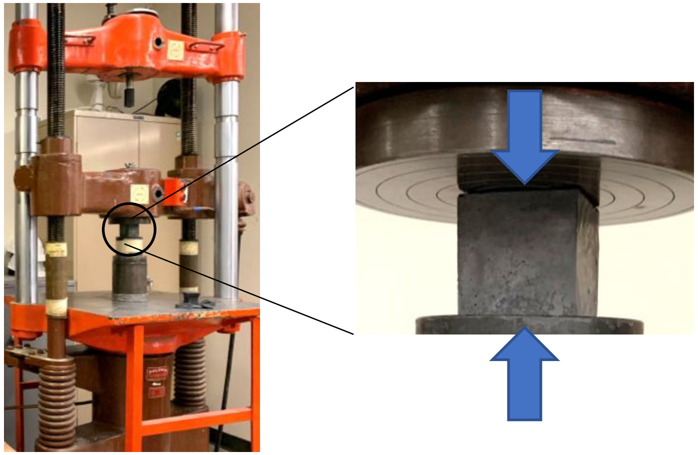

Hobart mixer

paste

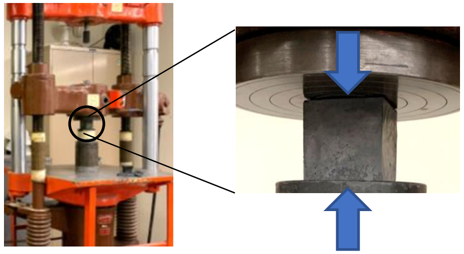

Mini-slump test


Setting time measurement

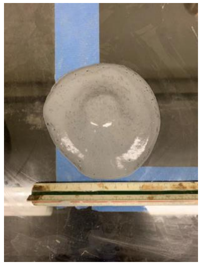
mortar


Uniaxial compression test

Objectives, Progress, and Plans



- Protocol for the incorporation of carbon
  - ✓ Protocols for “dry mix” and “wet mix” have been determined.
  - Carbon incorporation by ultra-sonication will be examined for 10s-nm carbon products.
- Compressive strength of mortar and concrete at carbon% = 0, 2, 5, 10% and w/s = 0.3-0.6
  - ✓ Reference mortar mixes (carbon% = 0) have been examined at w/s = 0.3, 0.4, 0.485, and 0.58.
  - ✓ Mortar mixes at w/s = 0.485 and carbon% = 5, 10% have been examined for three graphite disks, two carbon fibers, and one carbon black. The promising carbon products are determined.
  - ✓ Mortar mixes with GD1 and CF1 are being examined at w/s = 0.3, 0.4, and 0.58 for the influence of w/s.
  - Concrete mixes of the references and most promising mix designs will be examined.

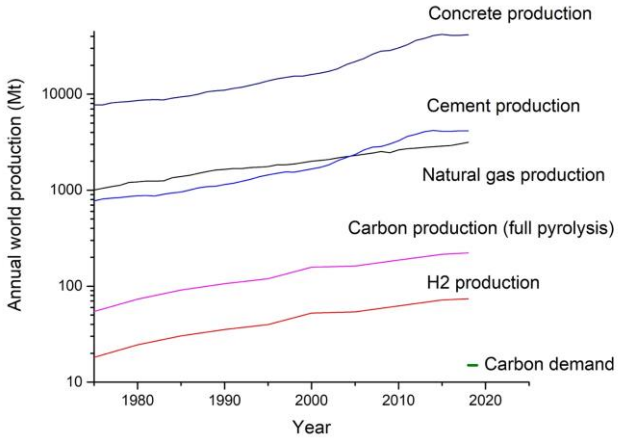


- Setting time, flow, slump, and consistency of the promising groups
  - ✓ Setting time and mini-slump have been examined for the influence of
    - ✓ w/s (0.3-0.485) with graphite disk
    - ✓ carbon particle size with graphite disk
    - ✓ carbon% with graphite disk and carbon fiber
    - ✓ carbon shape (disk vs. fiber)
  - ✓ Consistency of paste, flow of mortar, and slump of concrete are being measured for the references and most promising mix designs.
- Microstructure analysis
  - Microstructural characterization of the best and worst samples will be conducted to understand the experimental findings.

Major point

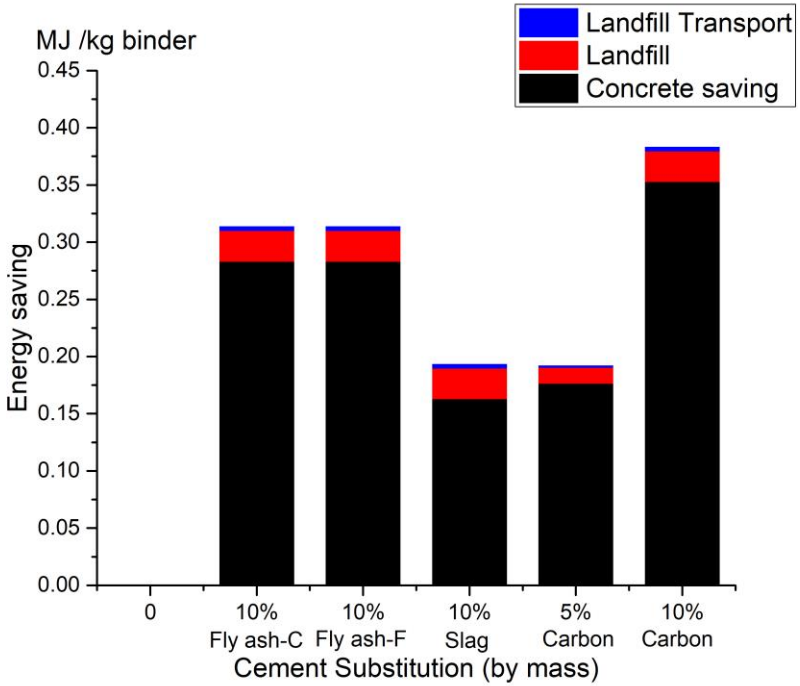
- Up to 10% of cement can be replaced by carbon particles without side effects

- Current world H2 demand:74 Mt/yr; US demand: 10 Mt/yr
- If full pyrolysis: global C production: 210 Mt/yr; US production: **30 Mt/yr**
- Global demand of carbon products: **15-20 Mt/yr**
- Current global cement production: 4.1 Bt/yr; US consumption: **100 Mt/yr**
- **Oversupply** of carbon products for **US** concrete industry (C/cement ratio 10%)
- **NOT** oversupply of carbon products for concrete worldwide



Total energy saving

- Substitution level governs the saving
- 10% C group saves more energy
- Negligible contribution from landfill transportation (50 km)

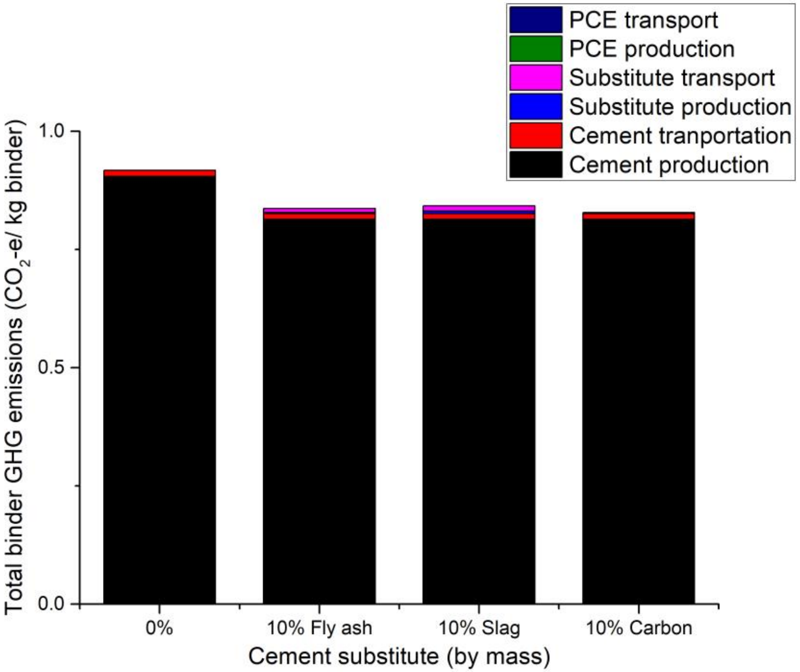


numbers generated by the team in Berkeley and under review by the team at Shell

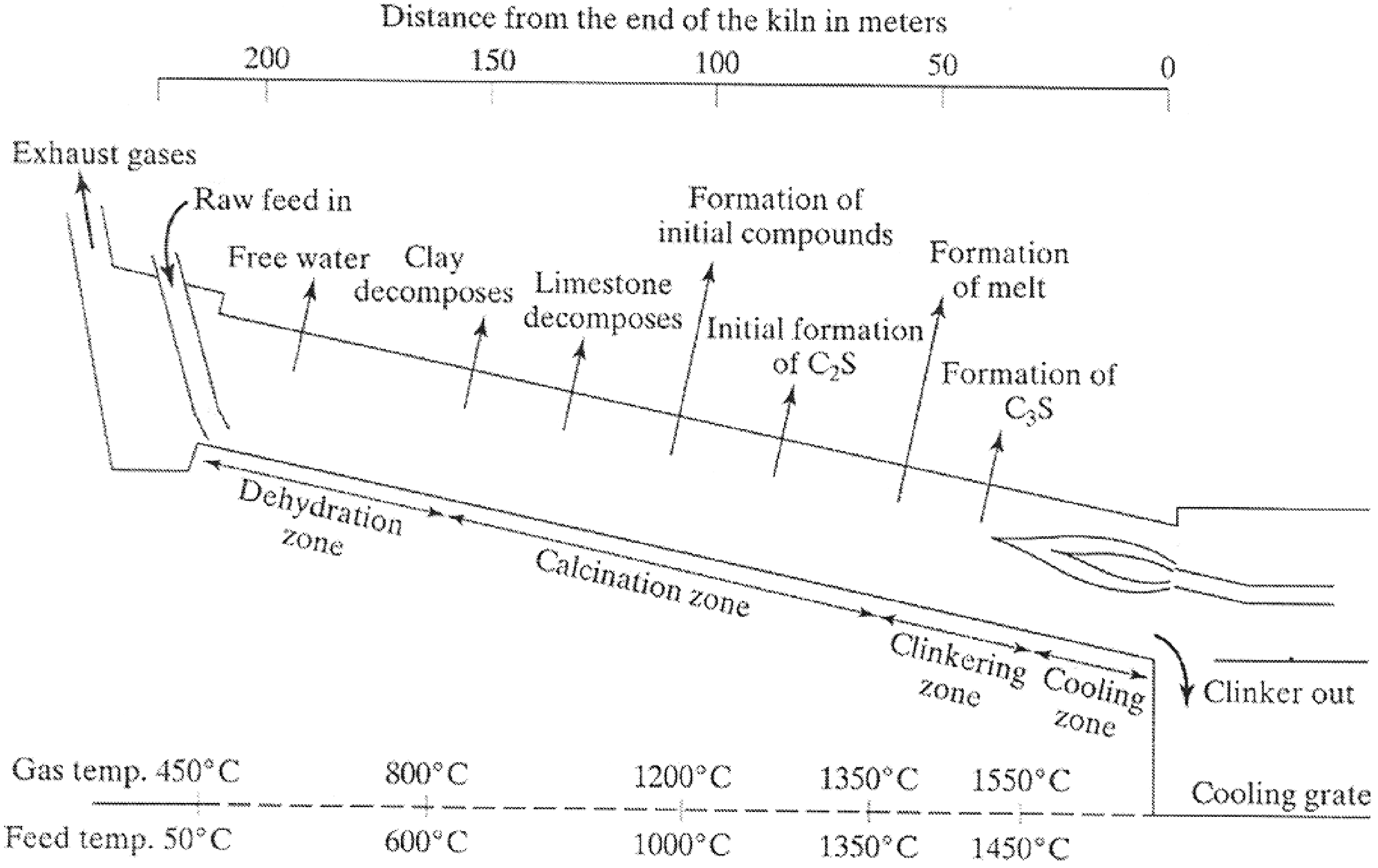
Breakdown: GHG emission saving

- Substitution level governs the saving
- 10% C saves 9.7% GHG emission
- Byproduct's processing and transportation are the minor contributors
- Binder saving: 7 Mt CO2 in US

~300-400 Mt CO2 worldwide



Decarbonization of the cement industry from H2 industry



Source: Mindess, Young, Darwin

Clinkering: Reactions

Breakdown clinker manufacture

Clinker manufacture GHG emissions (867 kg CO2 /t clinker):

- Operation 0.52GJ/t (62.1 CO2 kg/t) → Low contribution
- Process-based CO2 $CaCO_3 = CaO + CO_2$ (513 kg/t) → Hard to reduce
- Intrinsic heat for calcination + inefficiency → Already optimized

Nature

3 GJ/t from Fuel
(current highest efficiency) → Fuel dependent

Typical fuel composition in the US

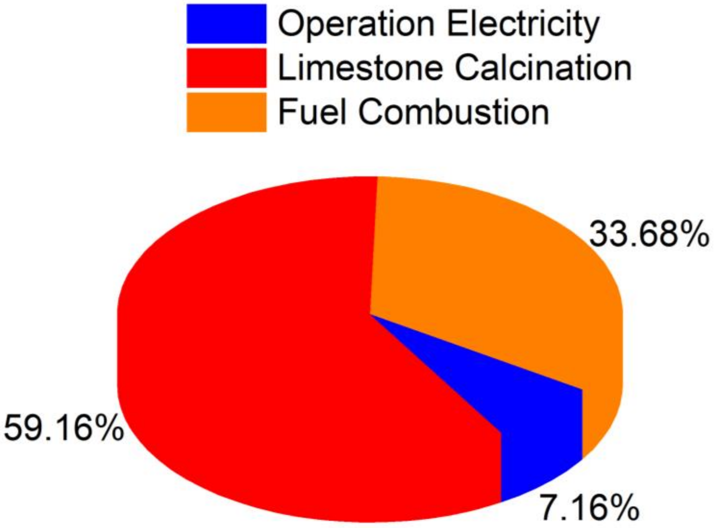
Coal and coke (85%)
Natural gas (4%)
Waste (10%)

→ 292 CO2 kg/t

Decarbonize clinker

- Clinker composition: almost invariable
  - **Worldwide resources availability**
  - Performance
  - Cost

Emission of CO2



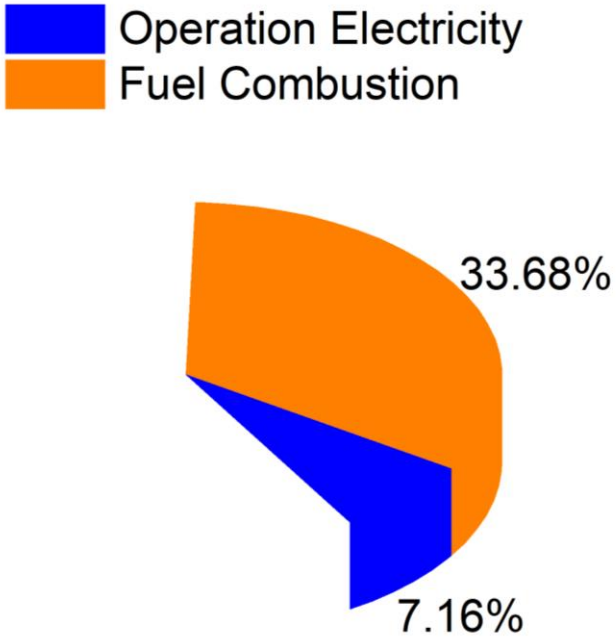
Decarbonize clinker manufacture: switch from coal to NG

- Decarbonize e-grid
- **Decarbonize fuel**

○ Possible to feed H2

○ Pricy

○ Cement in US $113/t



Fuel scenarios (3 GJ/t fuel input)

CO2 kg/t clinker

Coal and coke (85%)
Natural gas (4%)
Waste (10%)

292 US average fuel

Natural gas (90%)
Waste (10%)

189
Otherwise, landfill

H_2 (90%)
Waste (10%)

CO2 kg/kg H2

256 SMR (12.4)
92 Pyrolysis (3.72)
47 Electrolysis wind (1.34)
Mean value

Note: Emission factor is critical for all causes and it will determine its feasibility.
Early analysis indicates the critical emission factor is ~ 9.1

Innovative scenarios

Pure O2 vent, not air = Higher fuel efficiency
From 3GJ/t (air) to 2.4GJ/t (O2) thermal requirement*)
O2= possibly from water electrolysis
O2 is cheaper than H2

Coal and coke (85%)
Natural gas (4%)
Waste (10%)

Natural gas (90%)
Waste (10%)

292 if still air

Compare with (0.87t/t clinker)

233 US average **6.8%**

If O2

152 **16%**

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* Habert. 2010 Cement & Concrete Research