Escola Politécnica da USP
Depto. Eng. Construção Civil

# The potential of fillers to mitigate GHG in Cement-based materials

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.....

# Background

- Prospective studies:
  - RoadMap Cement Industry - Brazil
  - UNEP SBCI Working Group

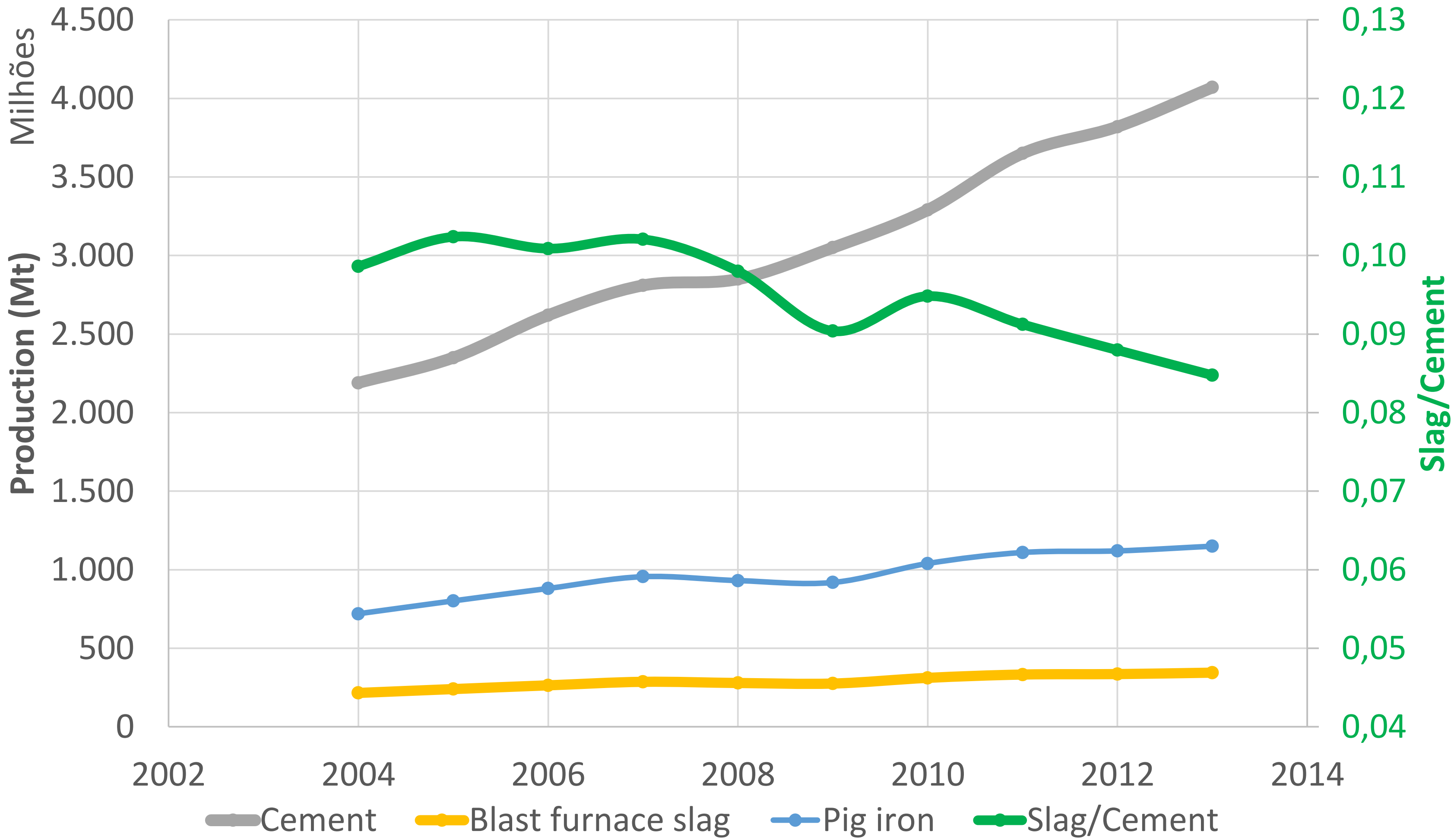
- A candle-light guiding to a desirable the future.
- Our achievements are limited by our ambitions
- “Moore’s Law”

# UNEP SBCI Low-Carbon Cement Working Group – Inaugural meeting

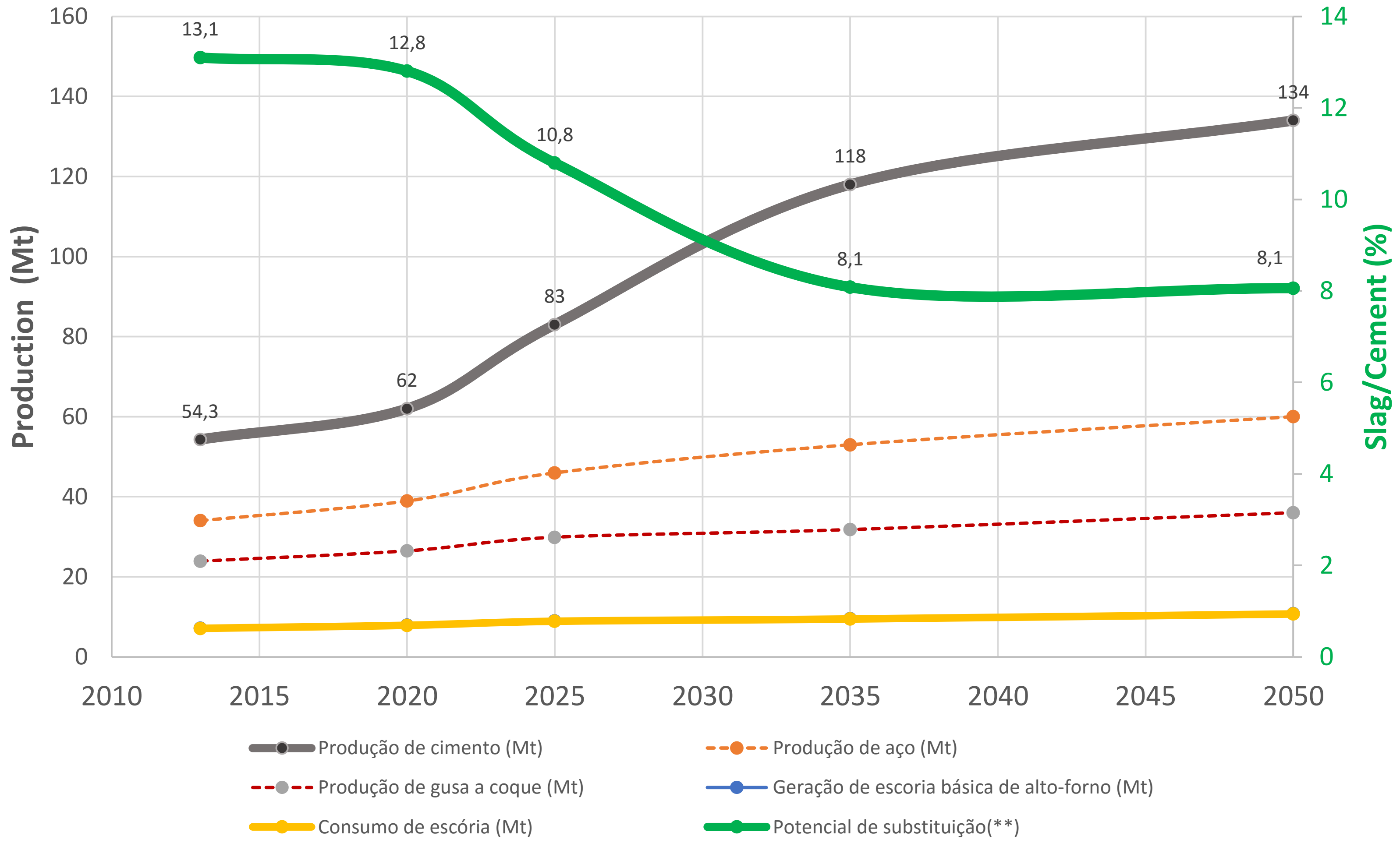
UNEP, Paris, March 18th 2015

# Slag + Fly ash are not enough

# Blast Furnace Slag & Cement

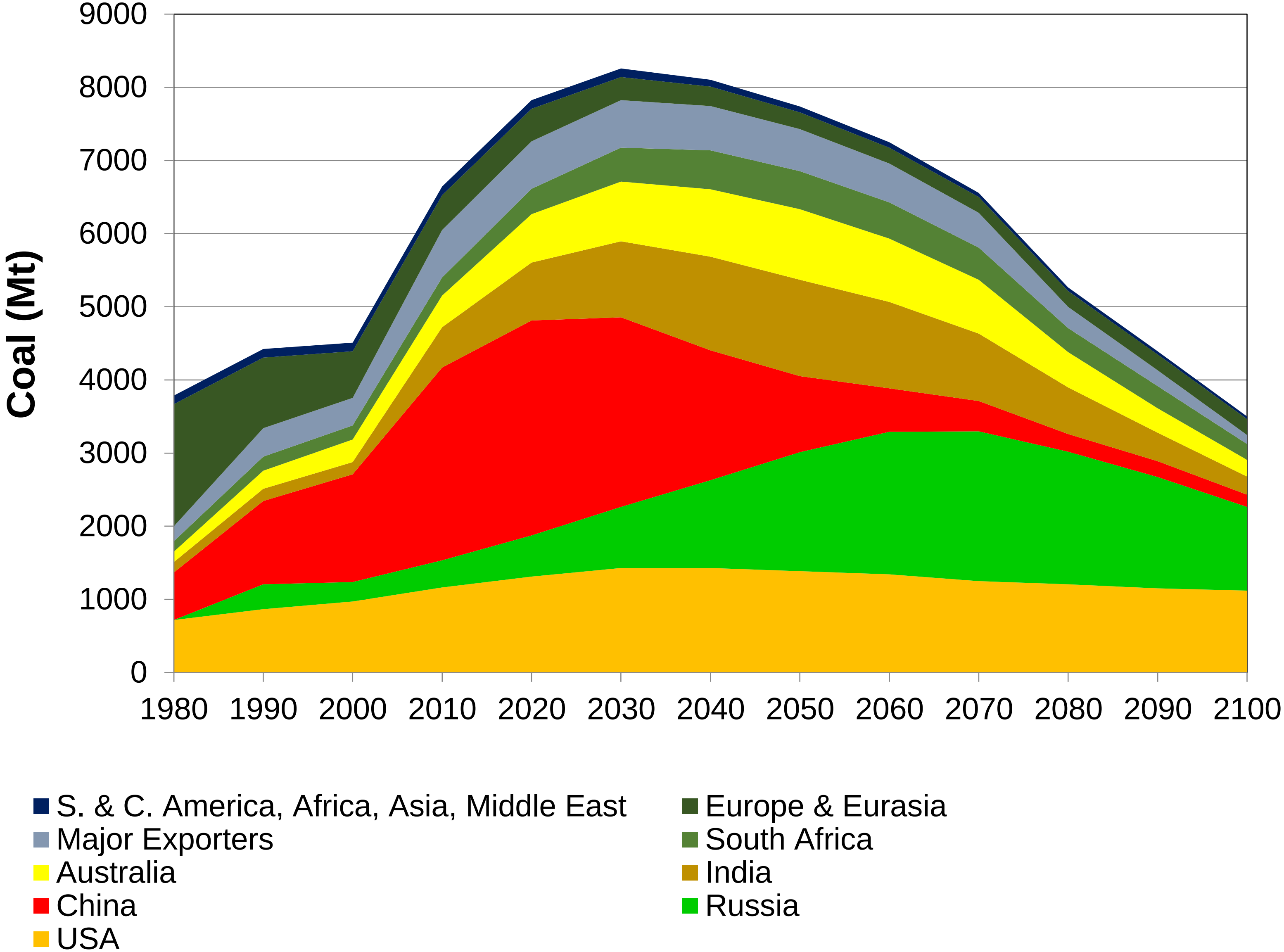


# Basic Blast Furnace Slag in Brazil




Estimativa própria

# Mineral Coal Consumption



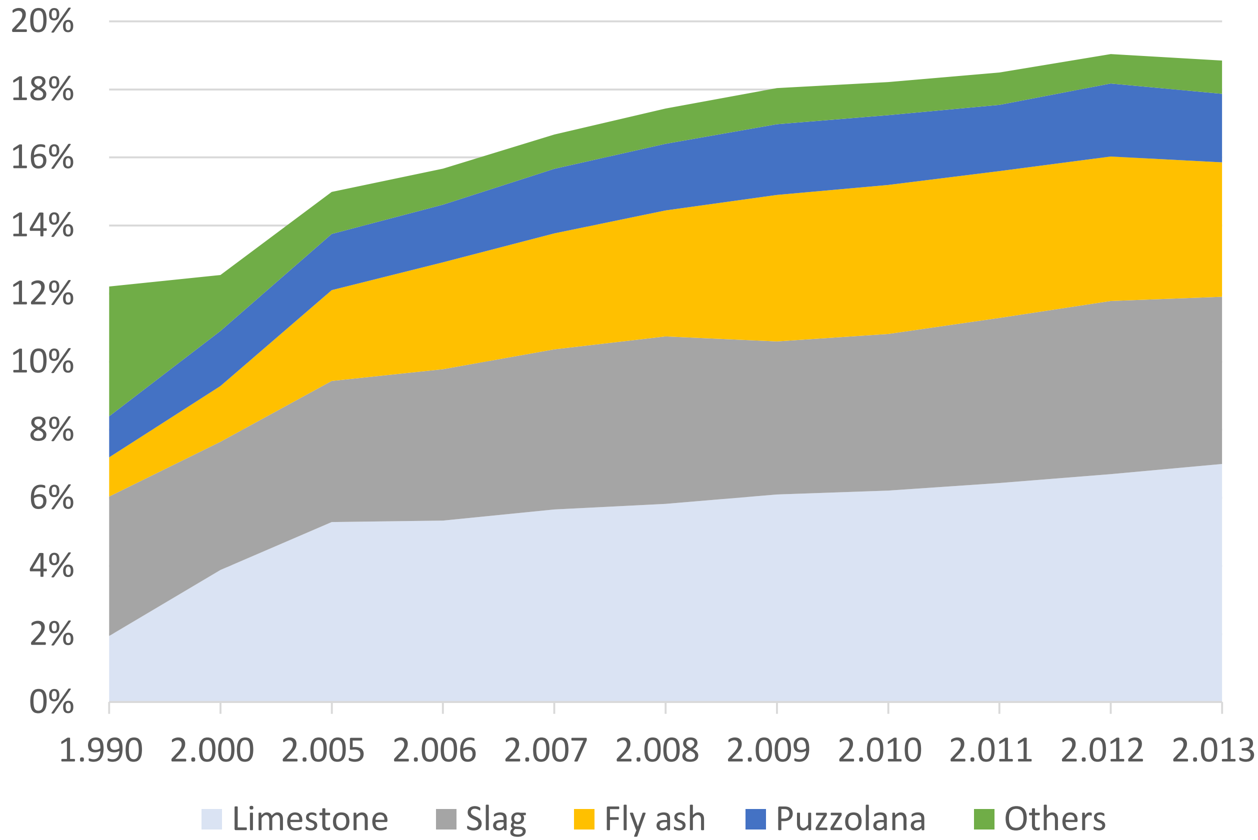
# Coal energy in Brazil

- Historically low
- Gas is a preferred fossil fuel energy source

- 2013:
  - Use 1,6Mt 2,6% of cement (GNR)
  - Availability ~2Mt ~3% of cement
- 2050
  - ? 2-3Mt

- Quality is not the best.

# Actual Clinker Substitution Rates WBCSD CSI companies




2013

**Slag 5%**

**Fly ash 4%**

Limestone Filler 7%

Puzzolana 2%

Gypsum 4%

GNR (2013 data)

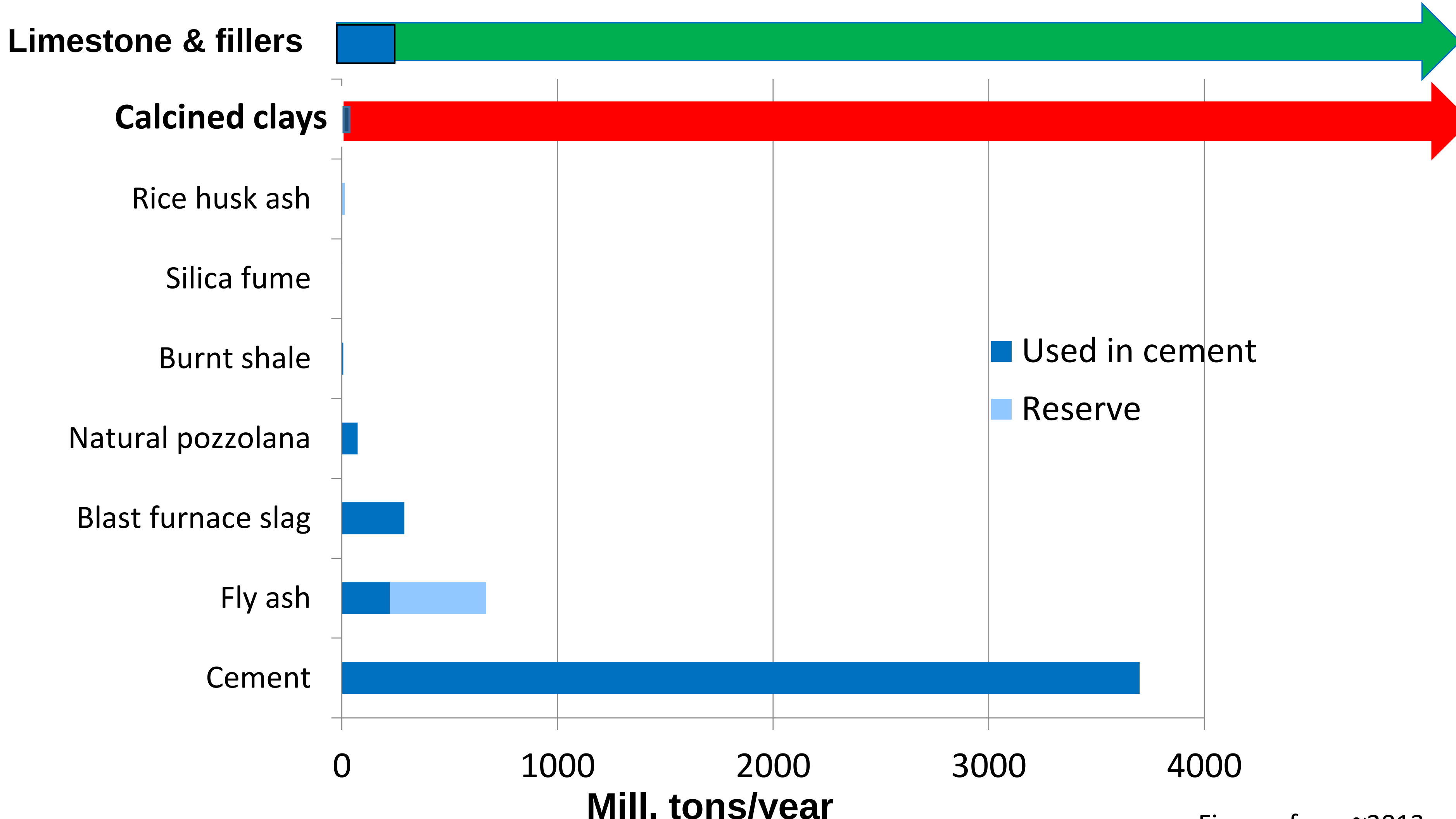
# Fly Ash + Slag

- Global shortage & eventual local abundance
- **<15% of cement**
- Quality, contamination and logistics are crucial.

- Brazil:
  - **shortage** of slag and fly ash
  - **~ 10%**

## Looking for other options

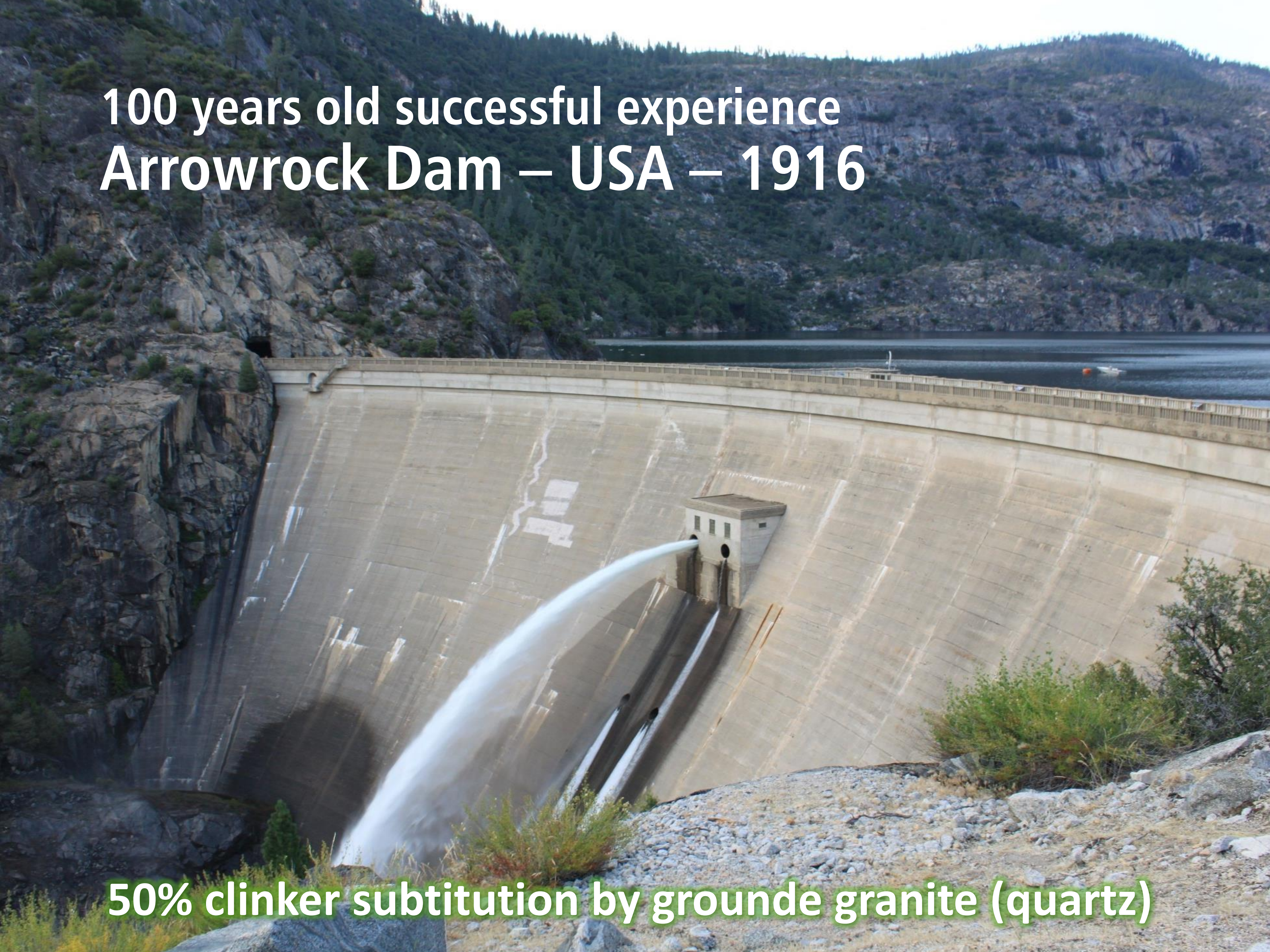
# Availability of SCMs




Figures from ~2013

(adapted from Prof. Karin Scrivener EPFL)

# Why fillers?


100 years old successful experience
Arrowrock Dam – USA – 1916
50% clinker subtitution by grounde granite (quartz)

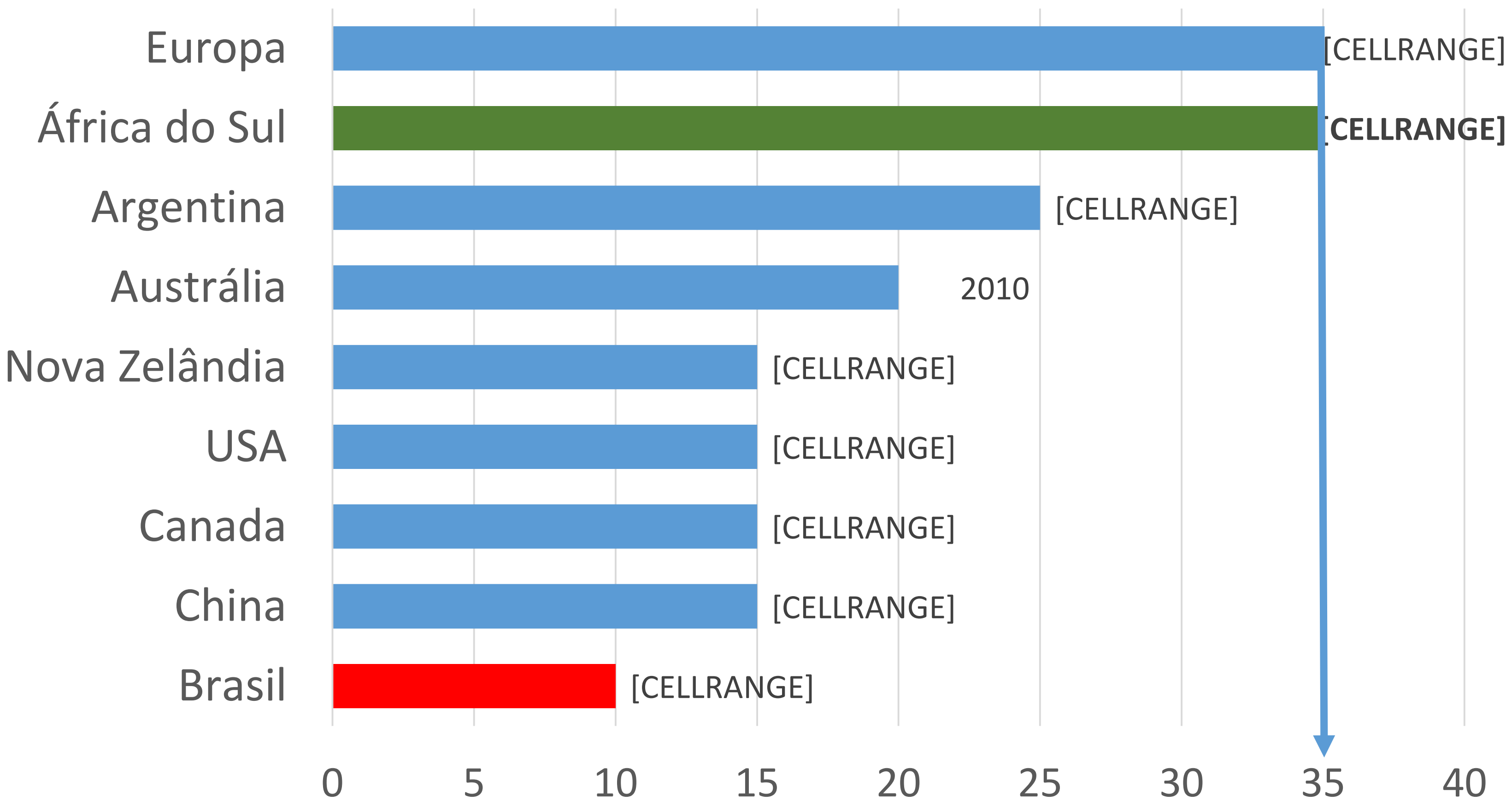
# History filler cement
# USA SAND - CEMENT

- USA 1912 to 1916
  - "**sand-cement**" Bureau of Reclamation
  - Arrowrock Dam on the Boise River
  - Elephant Butte Dam, Rio Grande River in New Mexico
- 45% Granite ground to pass #20
- 55% coarse Cement
- Mixture interground 90% #200
- Cost: 30% reduction (1.63 x 2.36)

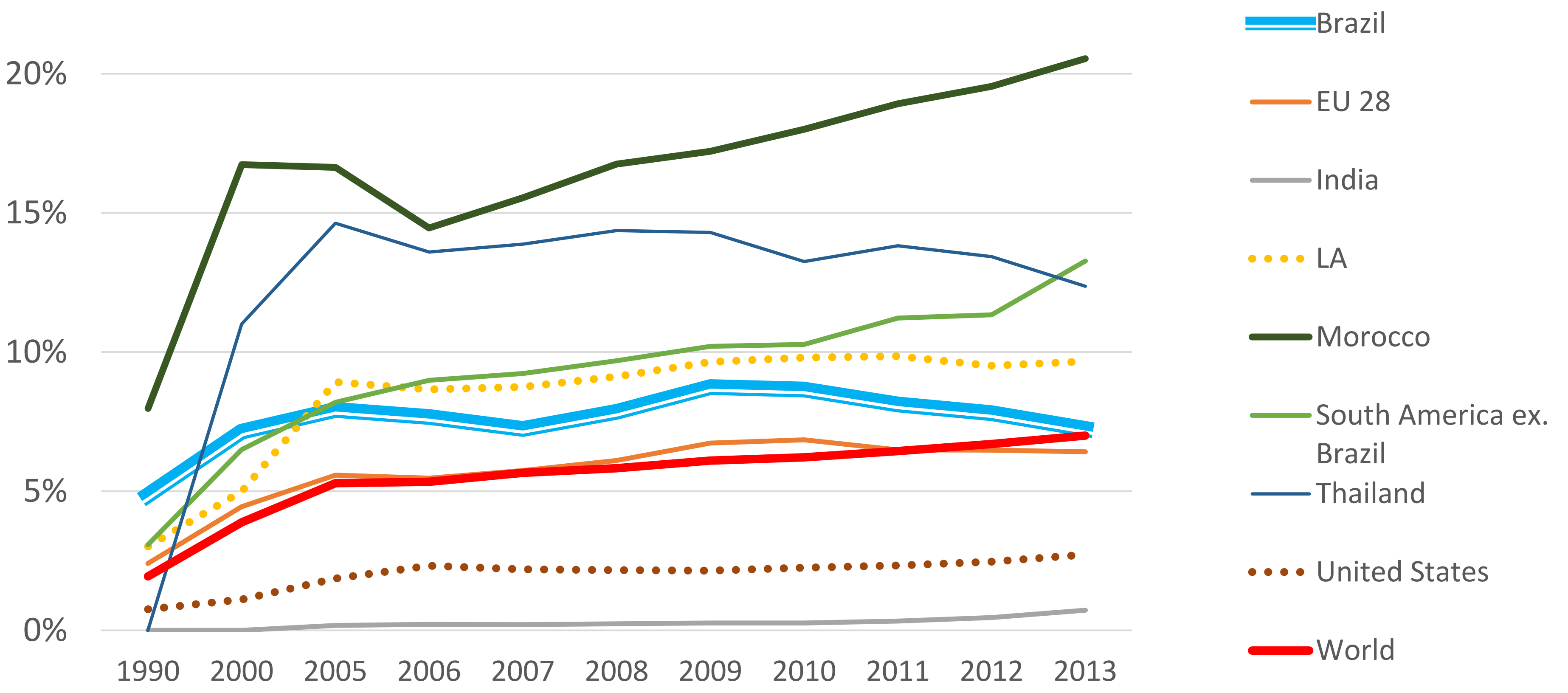
Meissner (1949)

# +30 years standardized practice

## Max Limestone Filler in standards



# Average Limestone Filler in Cement (GNR WBCSD CSI 2013)




Why average values are << maximum?

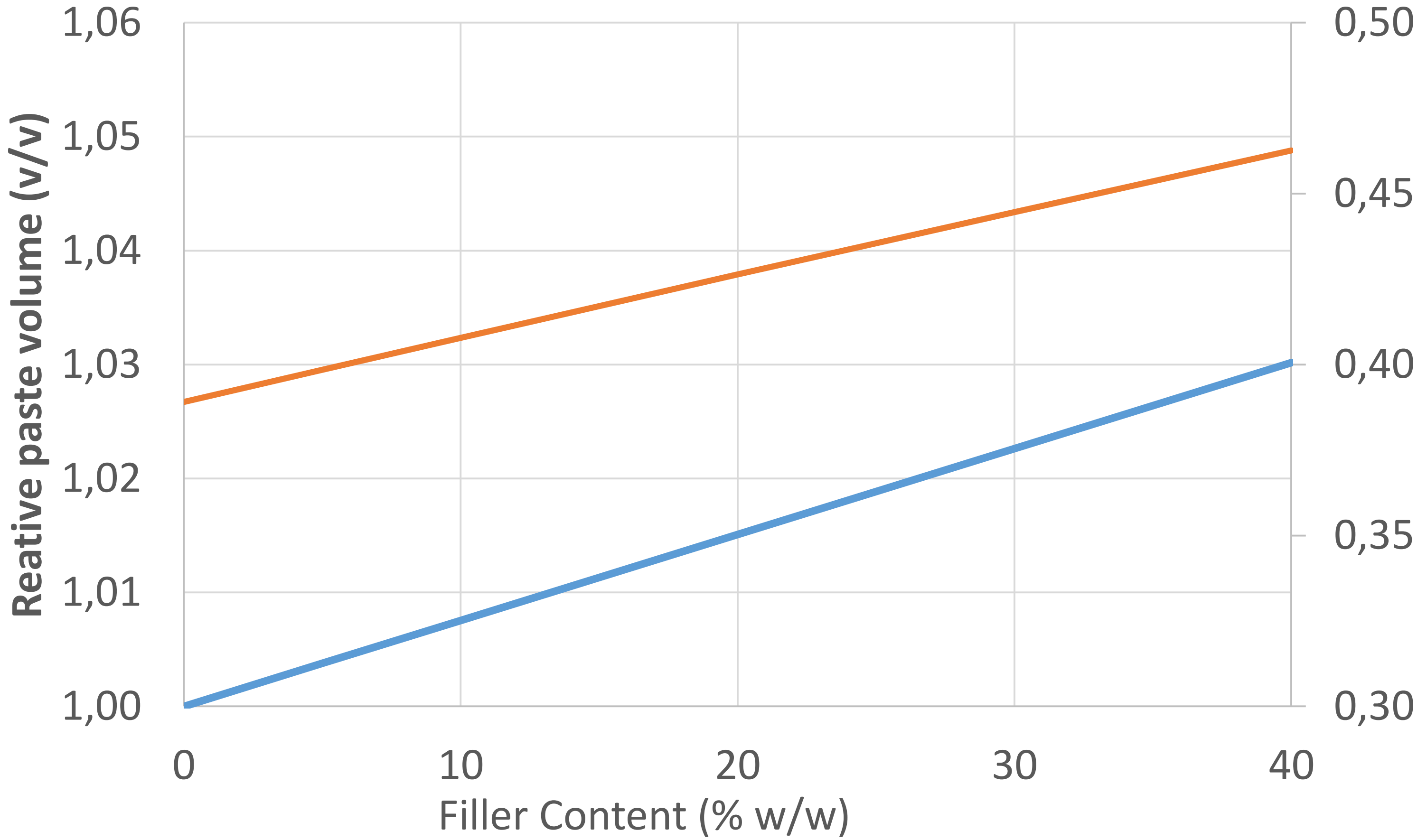
## Current filler technology:
# Why average values are low?

- Interground limestone with clinker
- Limestone are smaller than binder fraction
- **No PSD engineering is possible**

# It is a simple dilution!

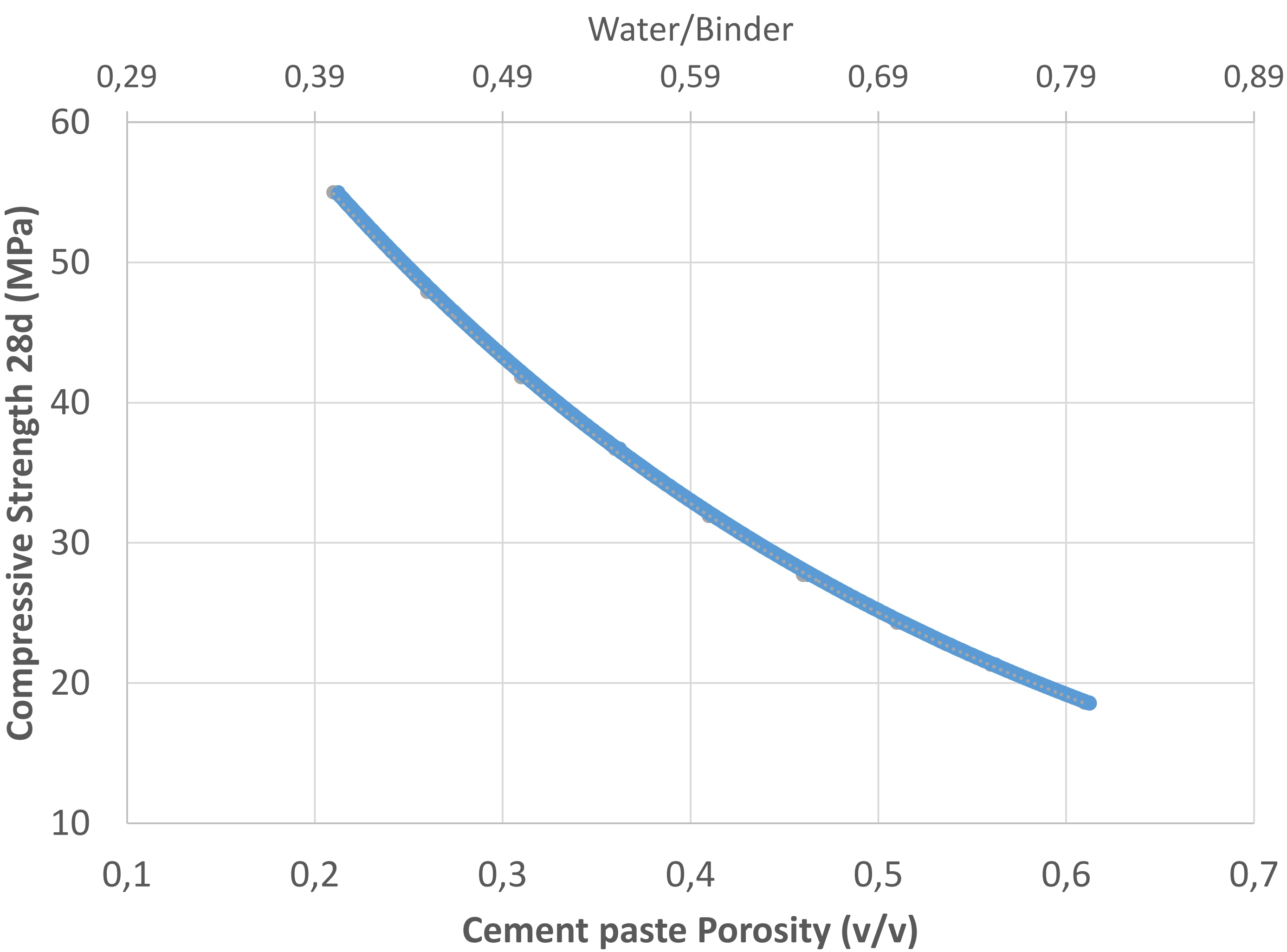
Little engineering on it.

# Binder Dilution increases Porosity

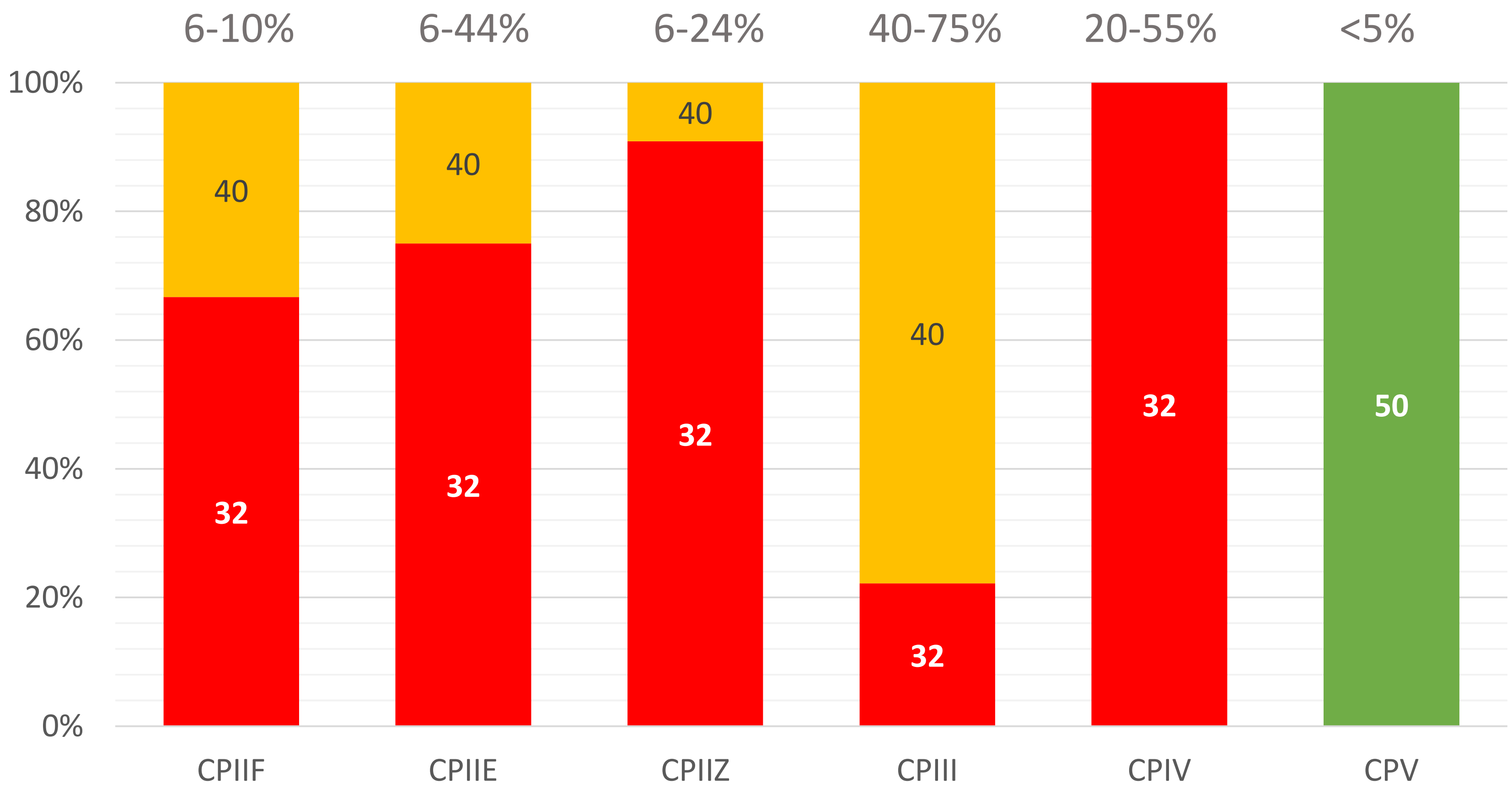



*Density: Cement 3.1 g/cm³; Filler 2,6 g/cm;*
*Combined Water : 0,24g/g binder, w/solids constant*

# Porosity controls strength

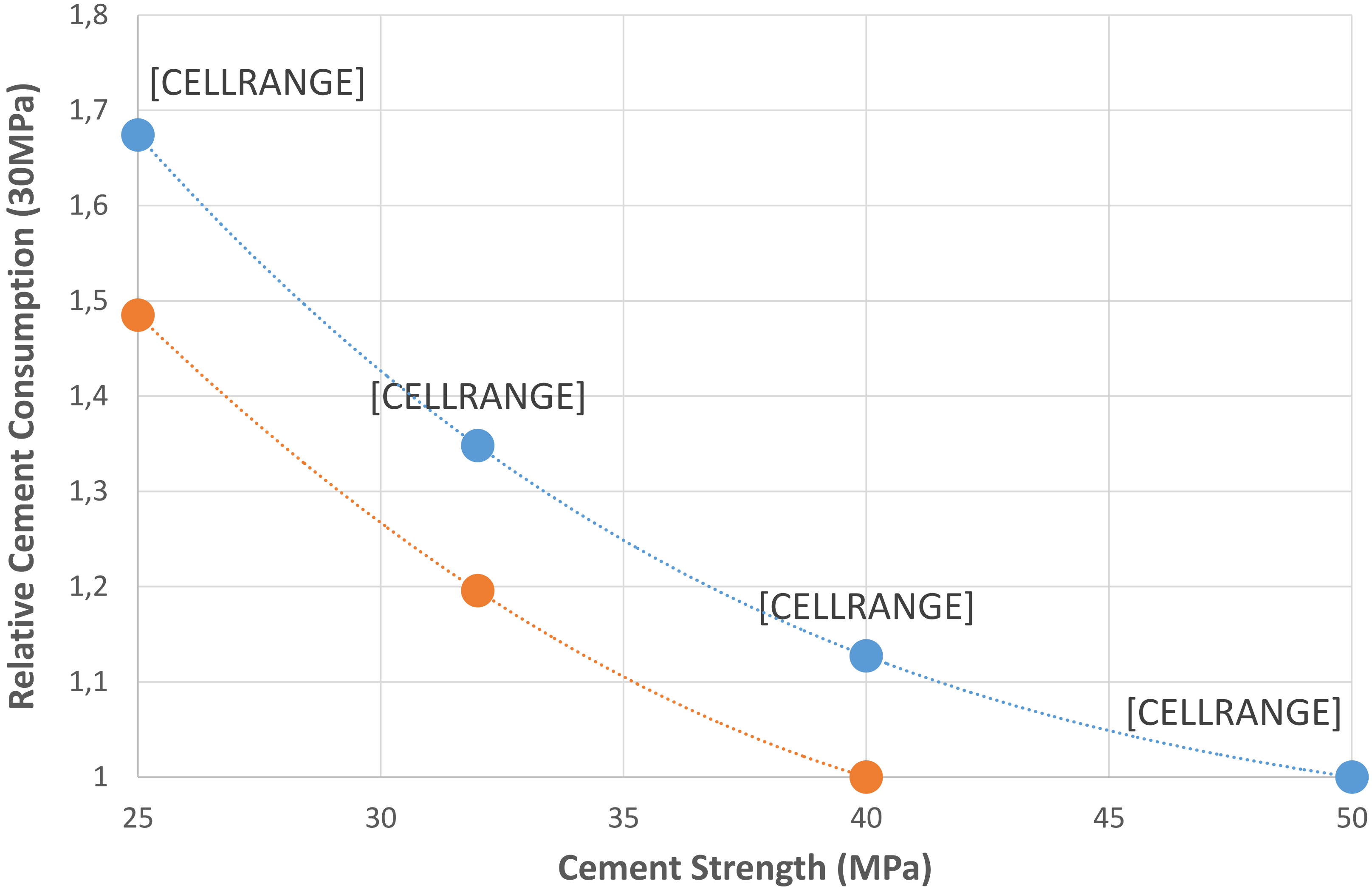


# Dilution effect:
# Blended cements = lower strength




Class strength frequency of Brazilian Cements – A Google Search
Daniel Reis, Pedro Abrão, VM John. June 2016. ©VM John

# Lower cement strength, higher cement content in concrete




*Daniel Reis, Pedro Abrão, VM John. June 2016. ©VM John*

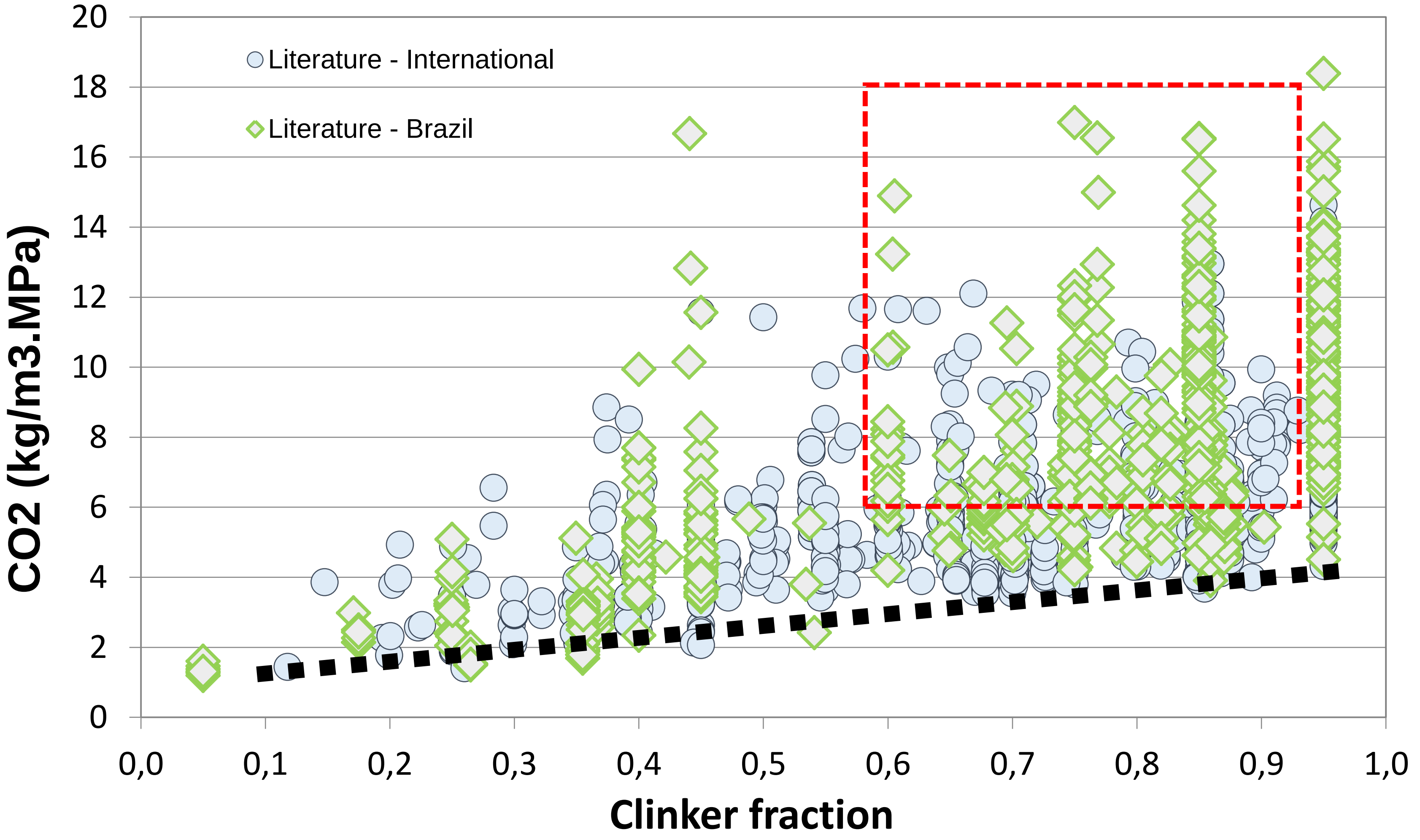
## Simple clinker dilution may

# Increase $CO_2$ footprint of concrete

| | $CO_2$ ($kgCO_2.m^{-3}.MPa^{-1}$) | | |
|---|---|---|---|
| **Clinker** | **Mín** | **Med** | **Máx** |
| CPII F 32 | 10,7 | 10,9 | 11,2 |
| CPII F 40 | 8,9 | 9,1 | 9,3 |
| CPII E 32 | 6,4 | 8,8 | 11,2 |
| CPII E 40 | 5,4 | 7,4 | 9,3 |
| CPII Z 32 | 8,9 | 10,0 | 11,2 |
| CPII Z 40 | 7,5 | 8,4 | 9,3 |
| CPIII 32 | 2,6 | 5,1 | 7,6 |
| CPIII 40 | 2,2 | 4,3 | 6,3 |
| CPV 40 | 9,4 | 9,7 | 10,0 |
| CPIV 32 | 5,1 | 7,6 | 10,0 |
| CPV 50 | 8,4 | 8,6 | 8,8 |

Model is conservative. Neglects differences in water demand for workability and SCMs. SCMs are carbon neutral. Cement demand for a 30MPa. Abrams curves from ABCP.

# $CO_2$ Intensity increase is confirmed by other studies



## Dilution compensation

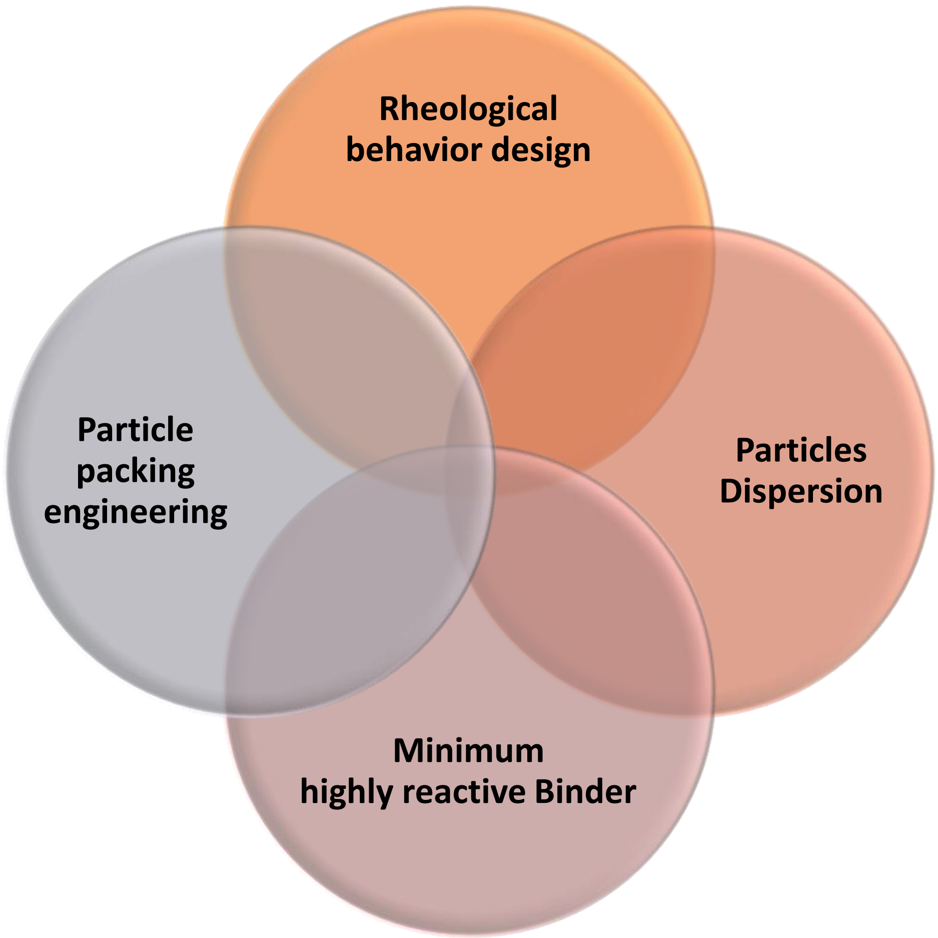
# LEAP cements concept

Low Emission, Advanced Performance

# Terminology

- **Binder**: reactive, high-temperature, scarce material.
- **Filler**: grinded mineral, no thermal treatment, little or no hydration.
- **Cement**: combination of binders, fillers and dispersants admixtures.

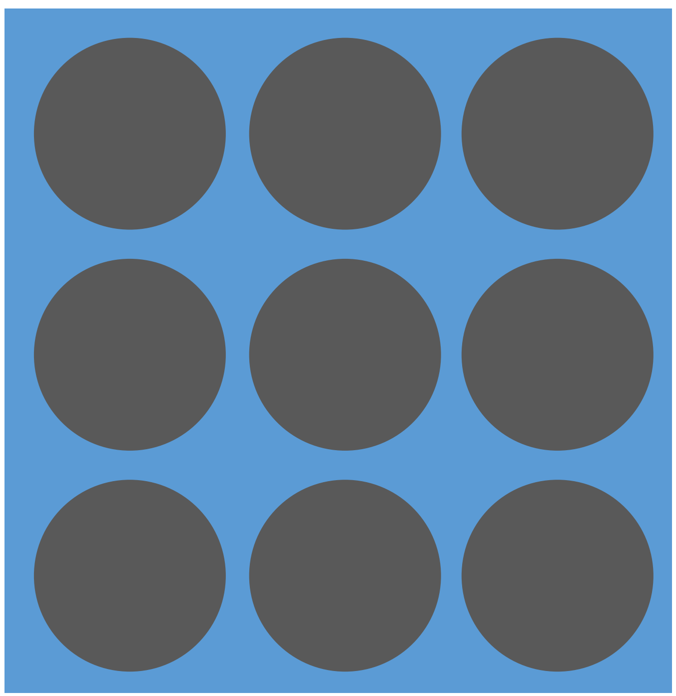
# LEAP fundamentals:
# A water minimization technology



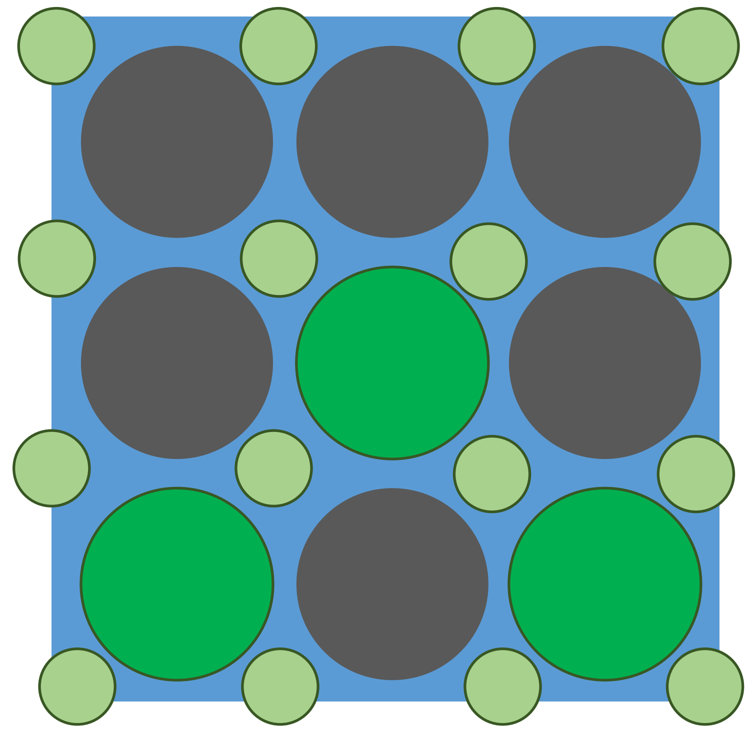
# LEAP at the cement industry

- Separate grinding (multi-modal PSD)
  - Minimum Binder (clinker, slag, fly-ash)
  - Maximization of inert fillers
- Disperser Admixture added during powder mixing
- Market segmentation
  - Cement mix-design accordingly to clients needs

# Filler + Dispersion:
# Low water demand for given rheology

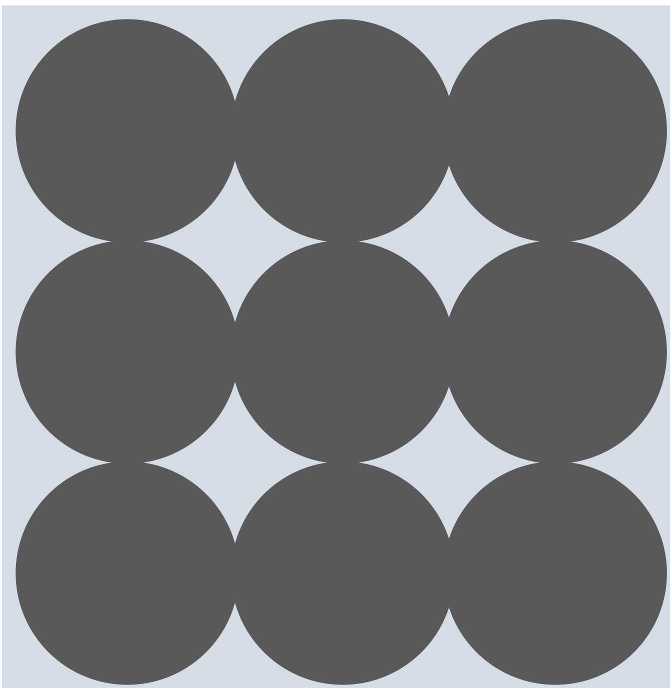


Typical cement

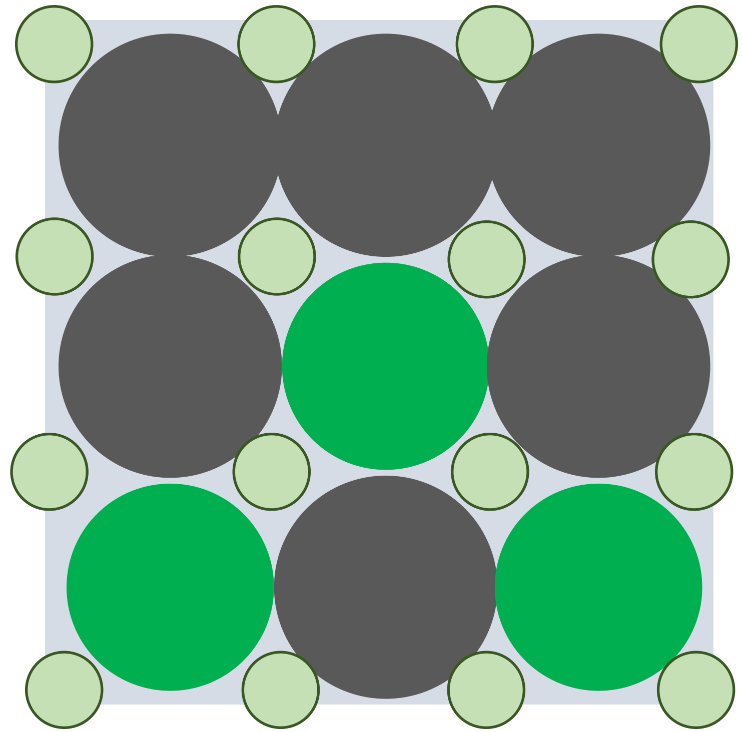


LEAP cement + filler

# Filler + Dispersion:
# Low water, low porosity, higher strength

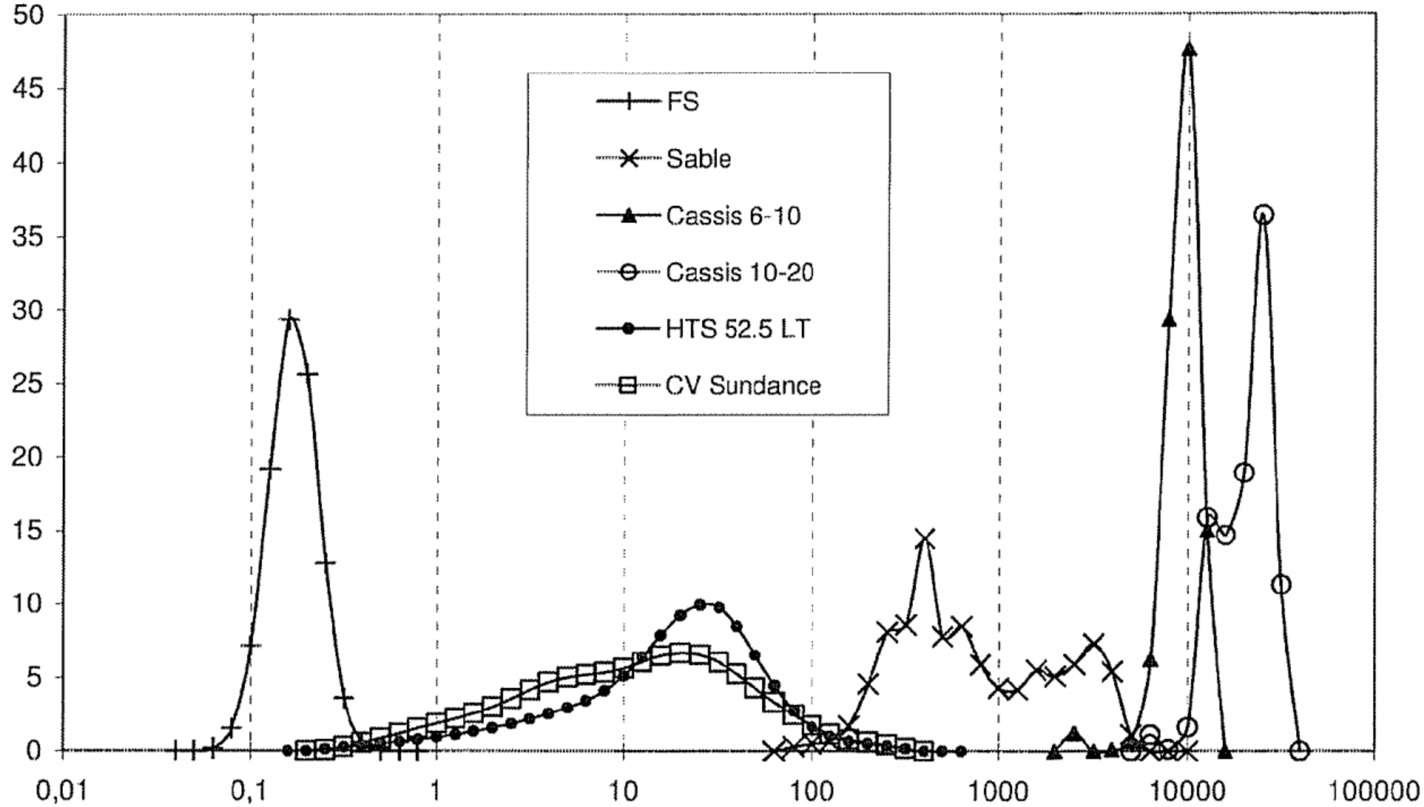


Typical cement



LEAP cement + filler

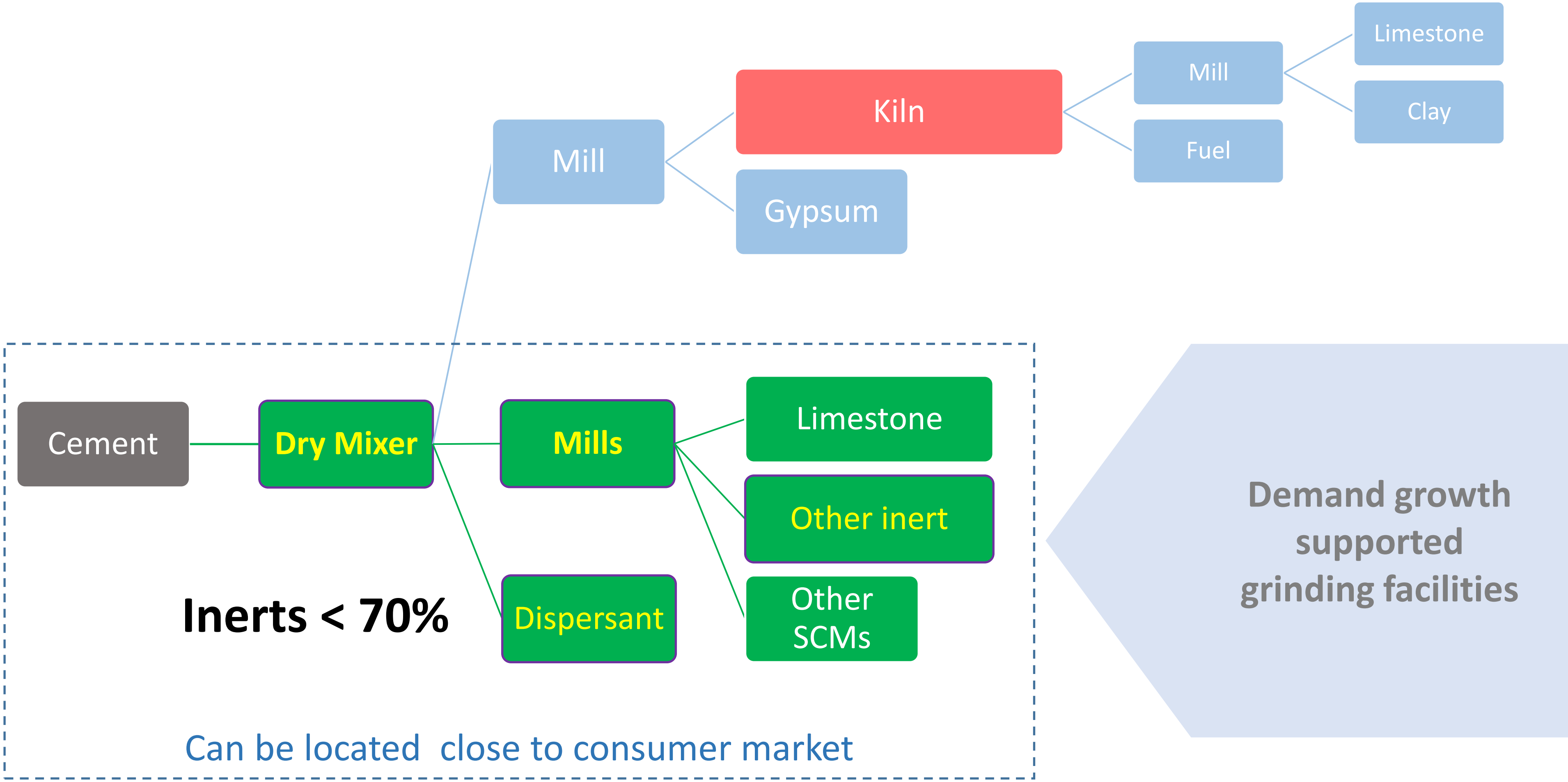
# Lafarge
# low-binder concrete and pre-mix




(19) **United States**
(12) **Patent Application Publication** (10) **Pub. No.: US 2007/0266906 A1**
**Garcia** (43) **Pub. Date: Nov. 22, 2007**

(54) **CONCRETE WITH A LOW CEMENT CONTENT** (52) **U.S. Cl.** ......... **106/817**; 106/638; 106/705; 106/737

# LEAP and cement plants of the future



# Filler & $CO_2$

- Filler reduces thermal energy
- Do not affect electricity consumption
  - Clinker require 2 grinding steps.
  - Filler one, more sophisticated grading

- Filler ~0,02 $tCO_2/t$
- Clínquer ~0,85 $tCO_2/t$
- **For every 10% filler, 8,3% less CO2, same or higher strength**

# Filler & CAPEX

- IEA GHG Cost Model
- Filler (% pure cement cost)
  - CAPEX <37%
  - Operational <33%
- Dispersant: 1-2% of the cost?

- **Every 10% of filler → 6,5% cost reduction**

IEA GHG R&D Programme. *CO2 capture in the Cement Industry*. (International Energy Agency(IEA), 2008). at <http://ieaghg.org/docs/General_Docs/Reports/2008-3.pdf>

# LEAP Approach
# HOW MUCH FILLER?

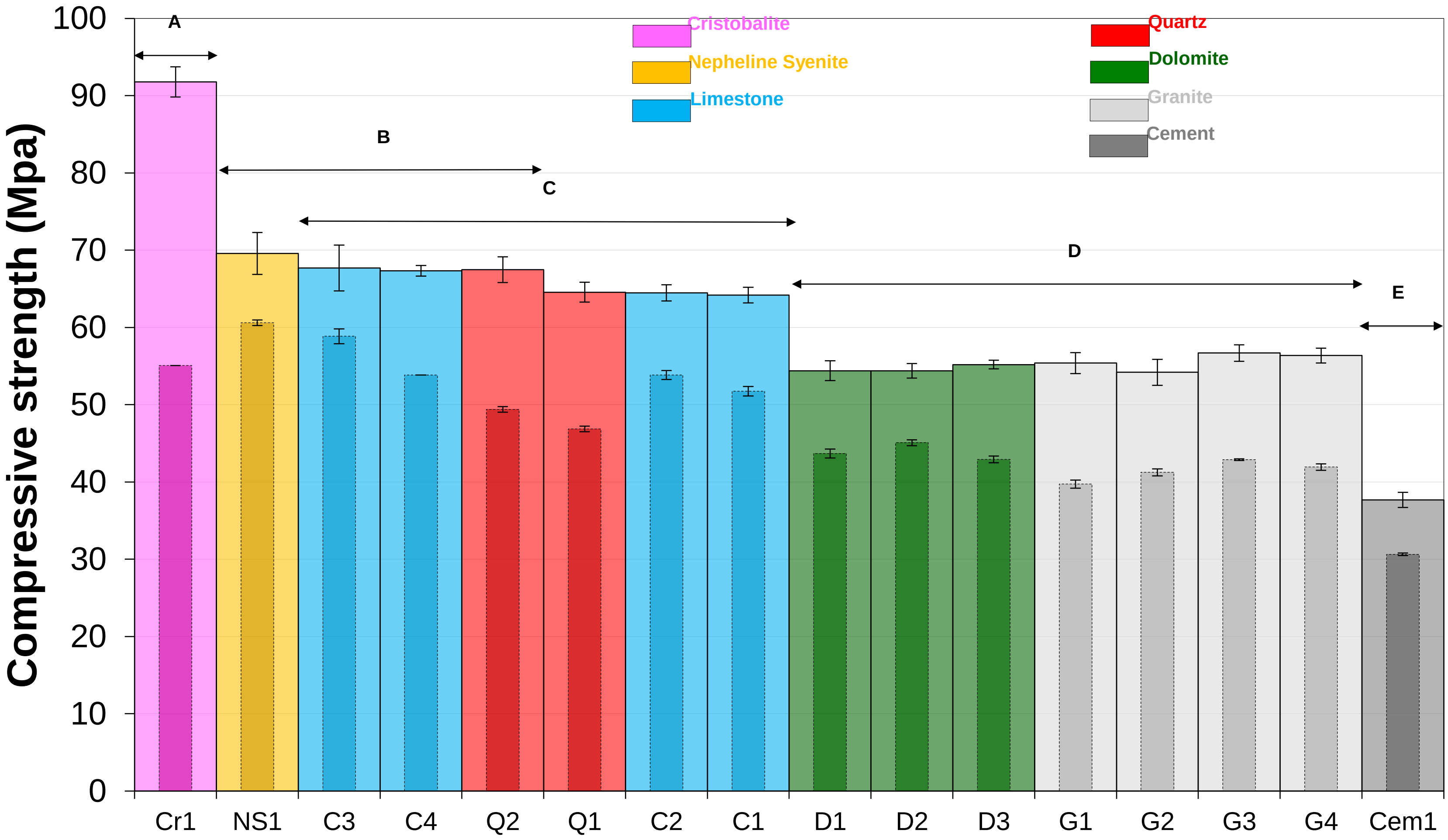
# Exploratory test:
# Fillers Mineralogy

| Mineral | D90 | Density | BET ($m^2/g$) |
|---|---|---|---|
| Dolomite (3) | 10 - 85 | 2,82 | 0.5-4.42 |
| Limestone (4) | 7-15 | 2,7 | 1.3-10 |
| Nepheline (1) | 7 | 2,62 | 3,7 |
| Quartz (2) | 1,9-3,6 | 2,65 | 1-4.1 |
| Cristobalite | 7,6 | 2.35 | 3.9 |
| Granite (4) | 41-56 | 2.67 | 1.7-2.8 |
| Cements (2) | 34-42 | 3,1 | 0.8-1.8 |

50% mass substitution
w/b = 0.5 and lower
Dispersant (superplasticizer)
Paste

Damineli, B. L. Concepts for formulation of low-binder concretes. PhD Thesis, USP 2013)

# Efffect of 50% filler on Strength
## water/binder=0.5




Damineli, B. L. Concepts for formulation of low-binder concretes. PhD Thesis, USP 2013)

# Water reduction can compensate dilution

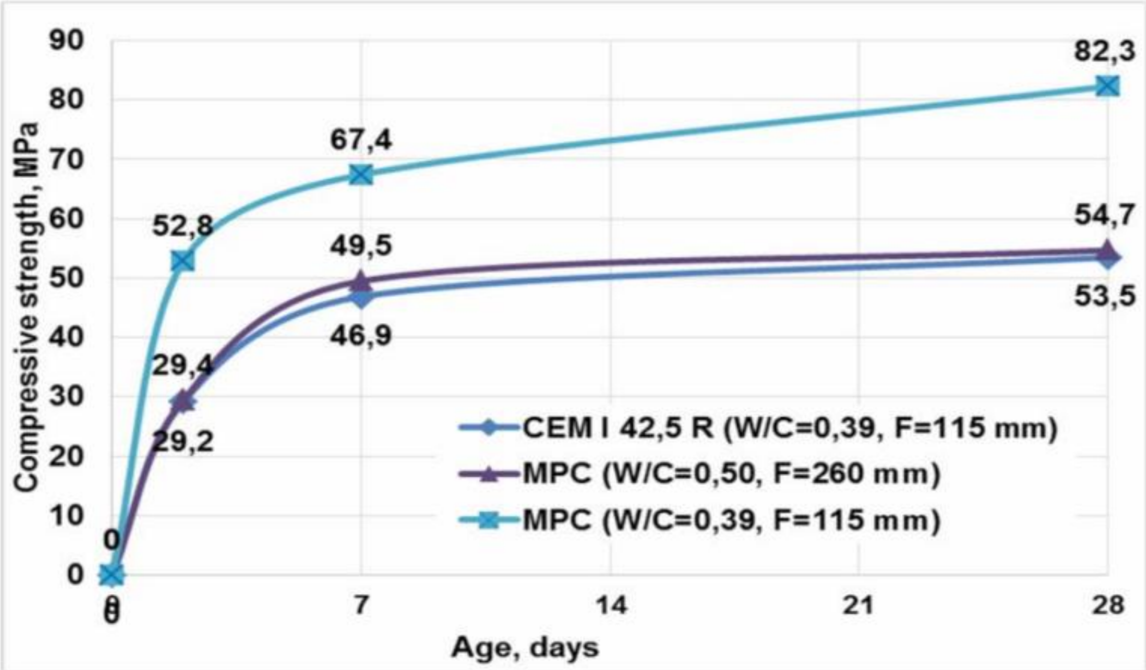
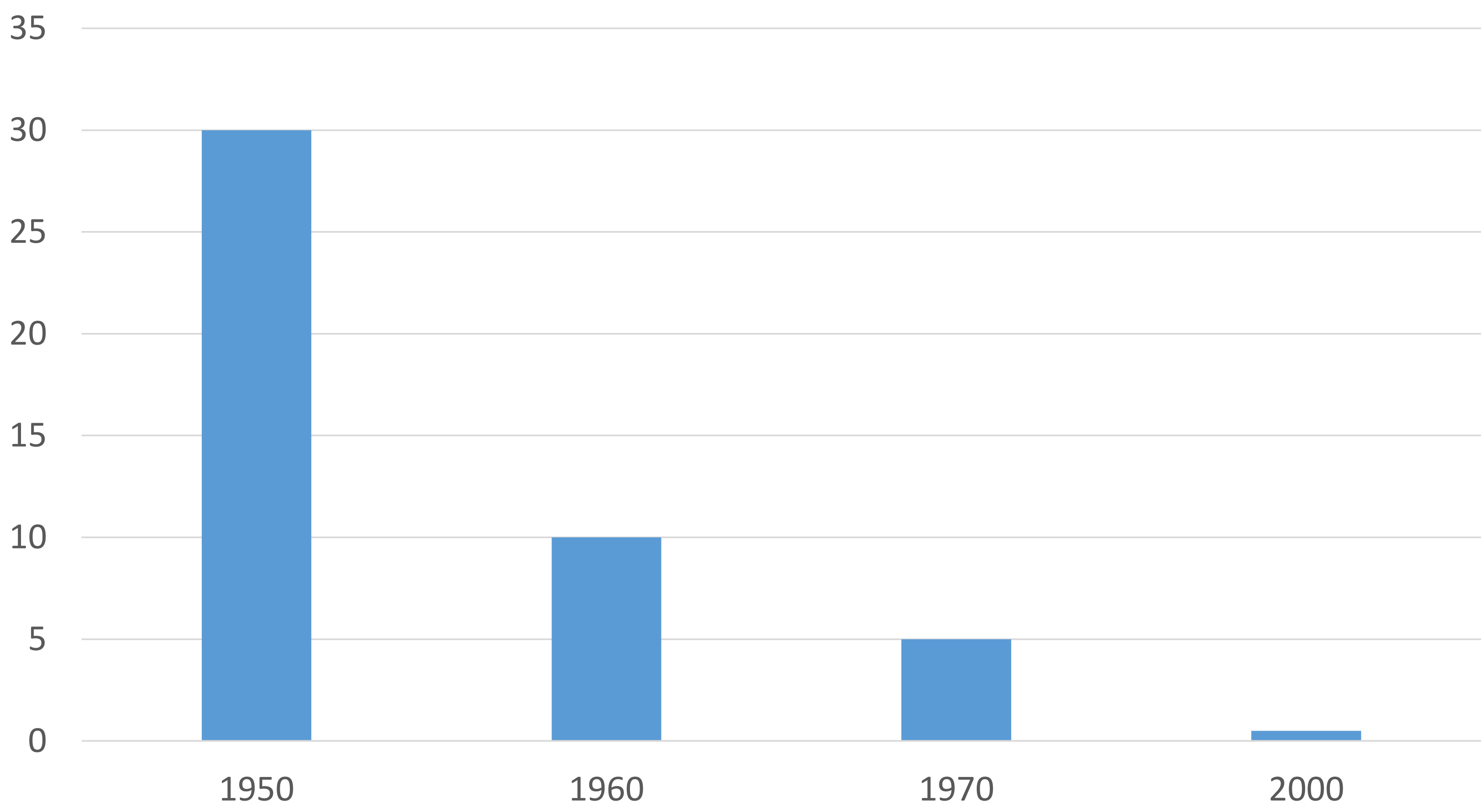



Figure 4 Compressive strength of portland cement CEM I and multimodal Portland cement (MPC)

(Sanytsky et all. 2015)

# Refractory Castables Binder Content




Lee et all Castable refractory concretes **Int Materials Reviews** 2001 Vol. 46 No. 3

# LEAP approach in structural concretes

How much binder is needed for structural ?concrete

# Binder Intensity

$$BI = \frac{\text{Binder content (kg/m}^3\text{)}}{\text{Compressive Strength (MPa)}}$$

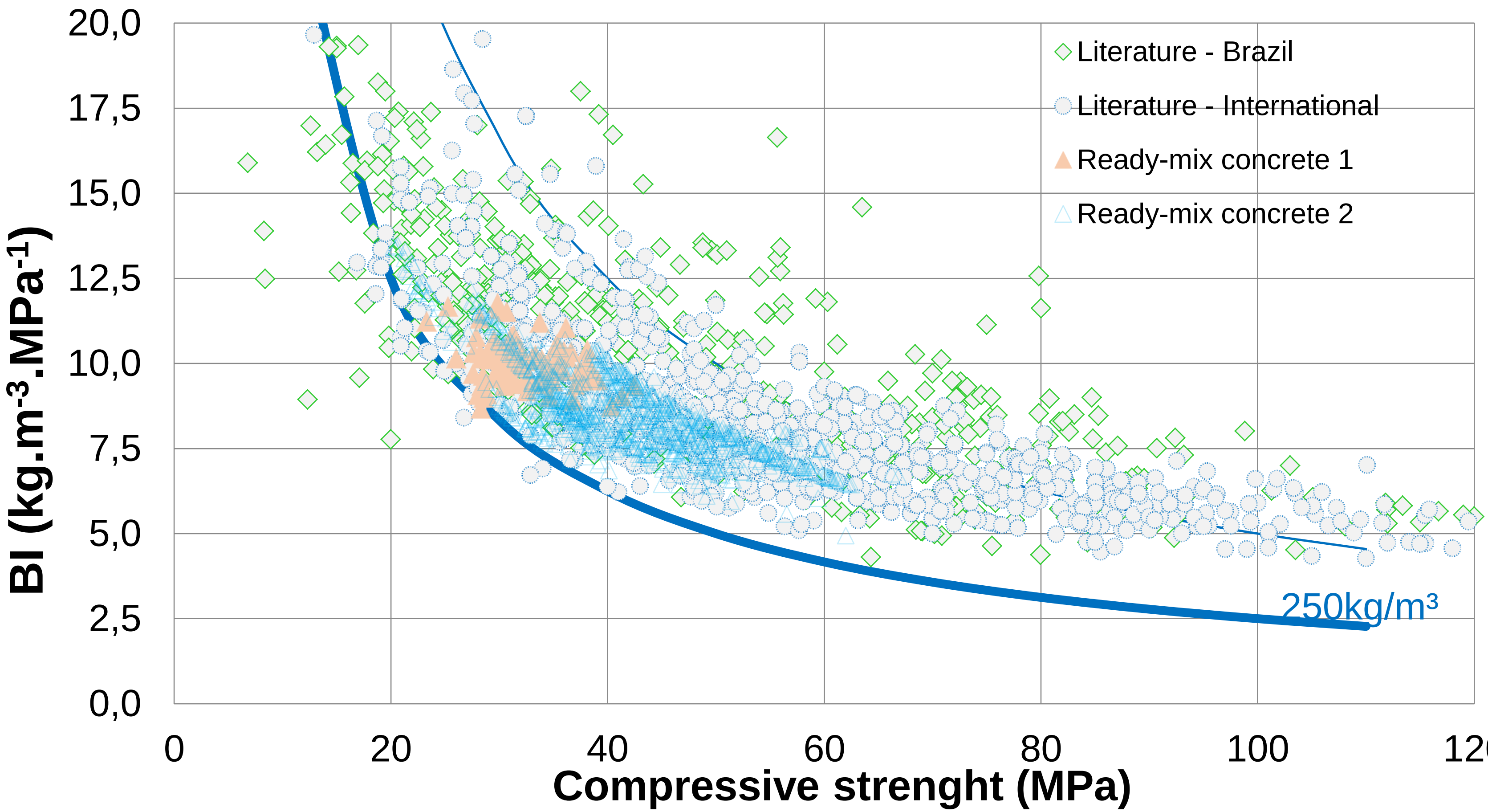
- Binder: reactive materials
  - clinker, gypsum, slag, pozzolans
  - No limestone filler
- Performance:
  - Compressive strength, cylinder, 28 days
  - Service life...

# $CO_2$ Intensity

$$CI = \frac{CO_2\ \text{emissions}(kg/m^3)}{\text{Compressive Strength (MPa)}}$$

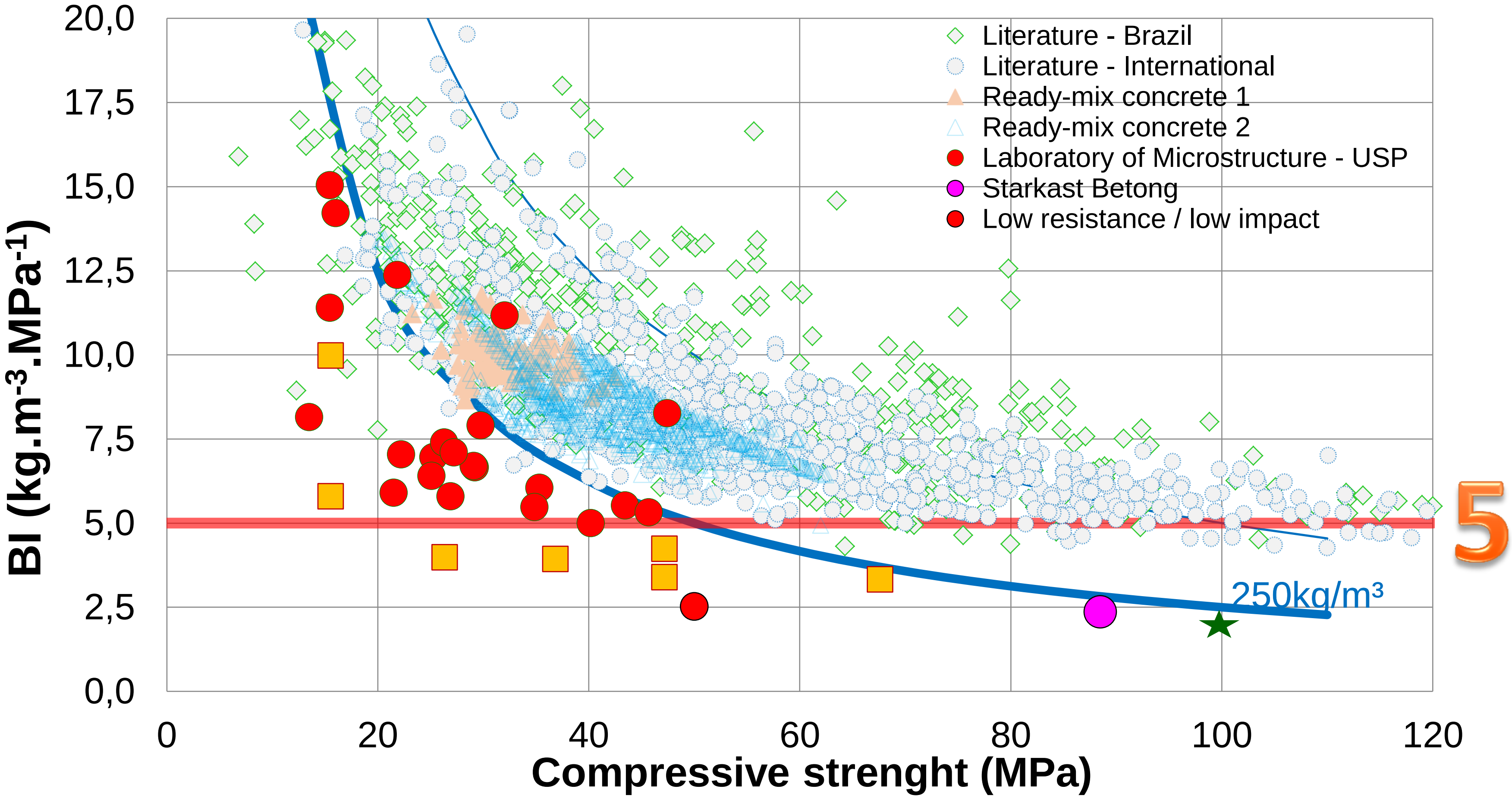
- $CO_2$: cradle to gate
  - clinker, gypsum, slag, pozzolans
- Performance:
  - Compressive strength
  - Service life...

# Conventional technology
# Binder intensity 29 Countries




DAMINELI, B. L. KEMEID, F. M. AGUIAR, P. S.; JOHN, VANDERLEY M. Measuring the eco-efficiency of cement use. **Cement and Concrete Composites**, v. 32, n. 8, p. 555-562, 2010.

# Cement use efficiency
# LEAP - low binder concretes

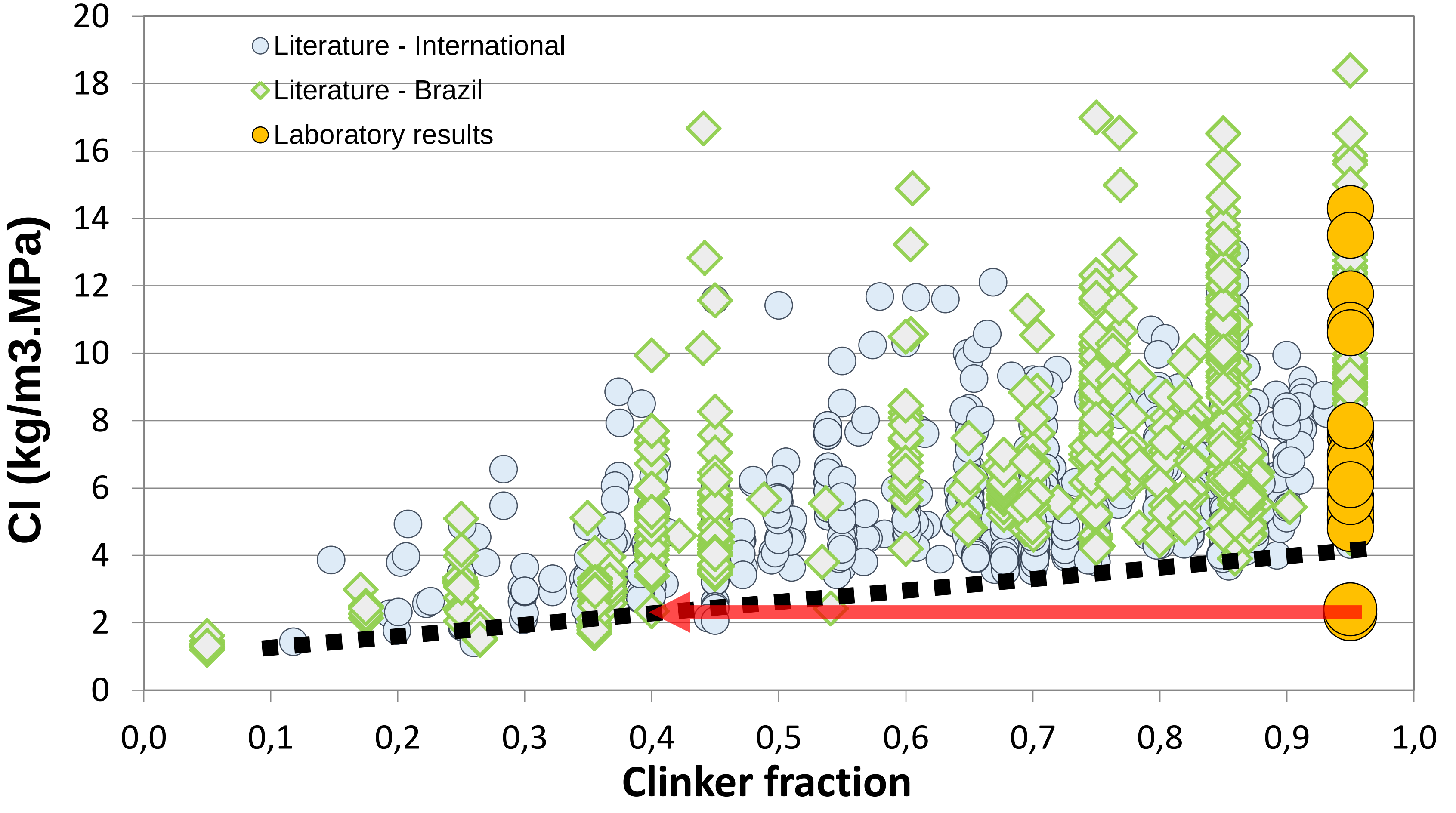



DAMINELI, B. L. - D.Sc. Thesis, 2013 (to be published) . Slump> 150mm

Proske et al. Approach for eco-friendly concretes with reduced water and cement content. ICCS 2013. p288 . Slump> ~55mm

VOGT, C. Ultrafine particles in concrete:. KTH Dr. Eng. Thesis 2010. 155 p

# LEAP concrete - $CO_2$ Intensity
# (USP results only )




# Up to 60% reduction

# T Proske's (TU Darmstadt) Concretes

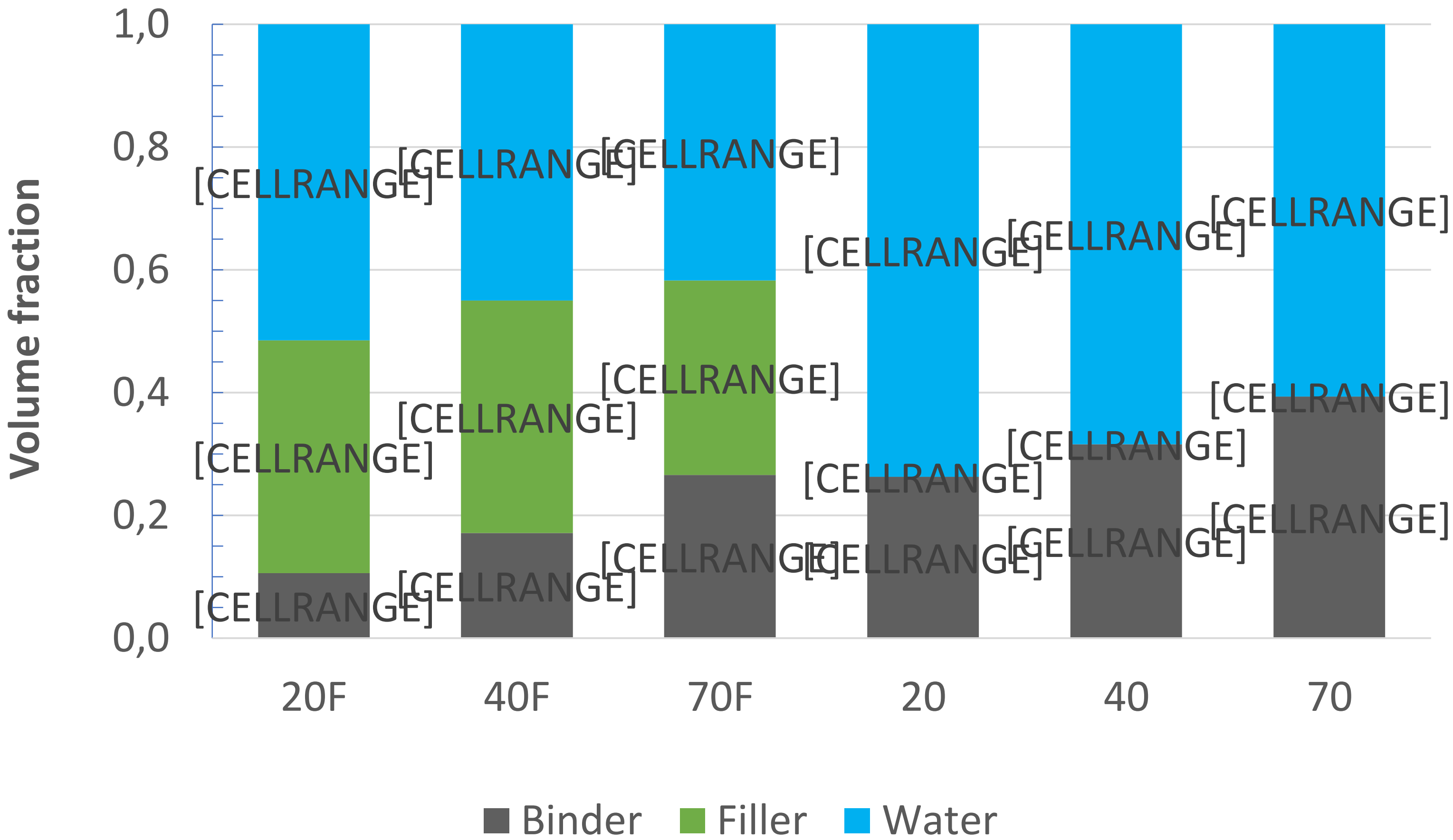
| CS (MPa) | Filler (%) | Paste kg/m³ | | | | w/c | Bi |
|---|---|---|---|---|---|---|---|
| | | Binder | Filler | **Cement** | Water | | |
| 20 (15,5) | **75** | 90 | 270 | **360** | 141 | 1,57 | 5,8 |
| | 0 | 220 | | 220 | 199 | 0,90 | 14,2 |
| 40 (37,8) | **60** | 145 | 269 | **404** | 123 | 0,85 | 3,9 |
| | 0 | 265 | | 265 | 185 | 0,70 | 7,2 |
| 70 (67,6) | **50** | 225 | 225 | **550** | 114 | 0,51 | 3,3 |
| | 0 | 330 | | 330 | 164 | 0,50 | 4,9 |

30-50% binder, low water, **more cement (50-66%)**

Proske et al. Approach for eco-friendly concretes with reduced water and cement content. ICCS 2013. p288 .

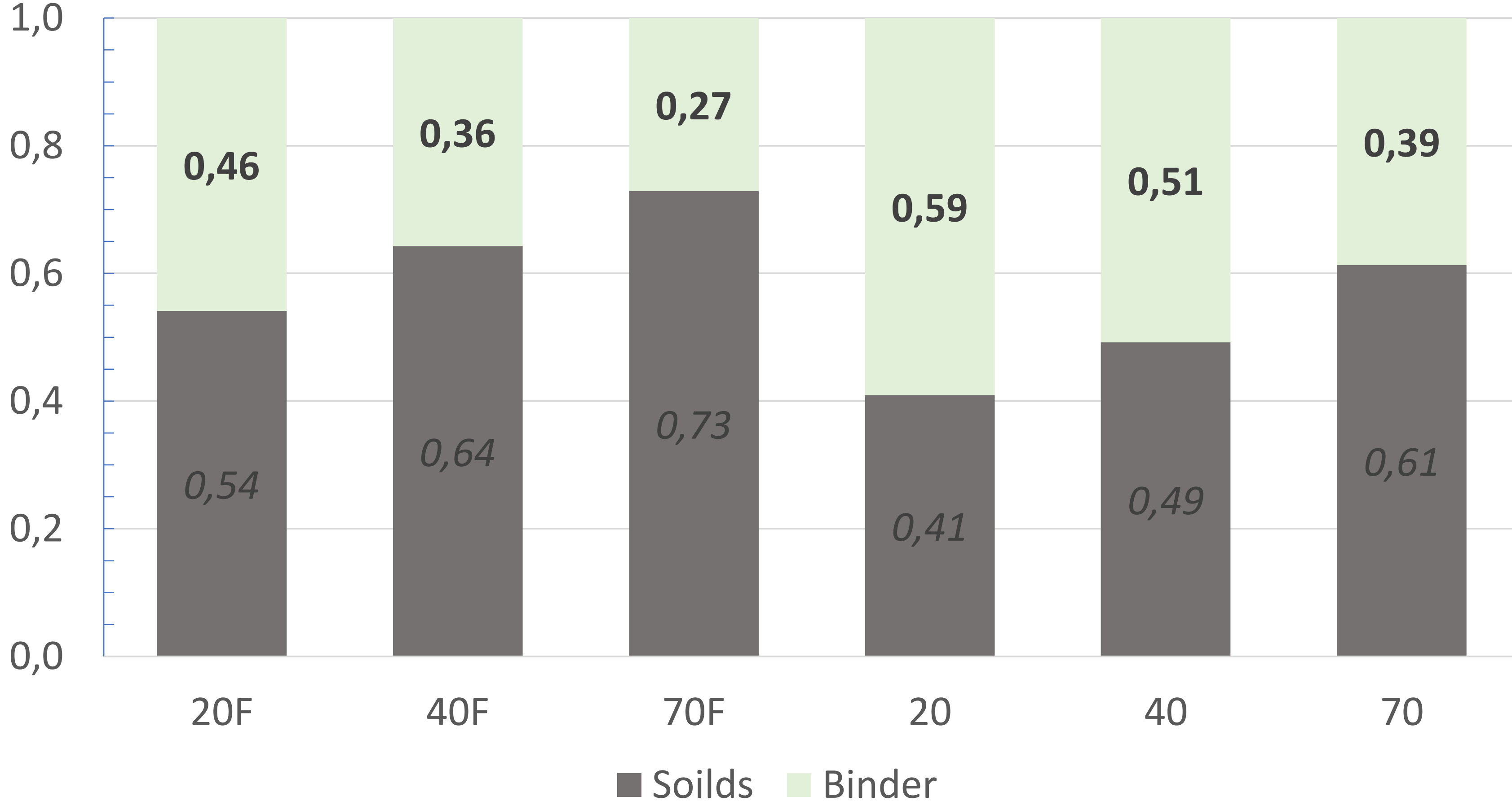
Slump ~55mm, CEM I 52,5 R, Paste volume 0,270m³/m³

# T Proske's Volume phase composition




Data from Proske et al. Approach for eco-friendly concretes with reduced water and cement content. ICCS 2013. p288 .

# T Proske's Cement Paste Porosity




*Data from Proske et al. Approach for eco-friendly concretes with reduced water and cement content. ICCS 2013. p288 .*

# Binder content and durability

## Carbonation and chloride diffusion f(CS)

Wassermann et all (2009) binder > 220 kg/m³

Proske (2013) binder > ~170kg/m³

Materials and Structures (2009) 42:973–982
DOI 10.1617/s11527-008-9436-0

ORIGINAL ARTICLE

**Minimum cement content requirements: a must or a myth?**

R. Wassermann · A. Katz · A. Bentur

# Binder content and Carbonation

Desirable for concrete not steel reinforced

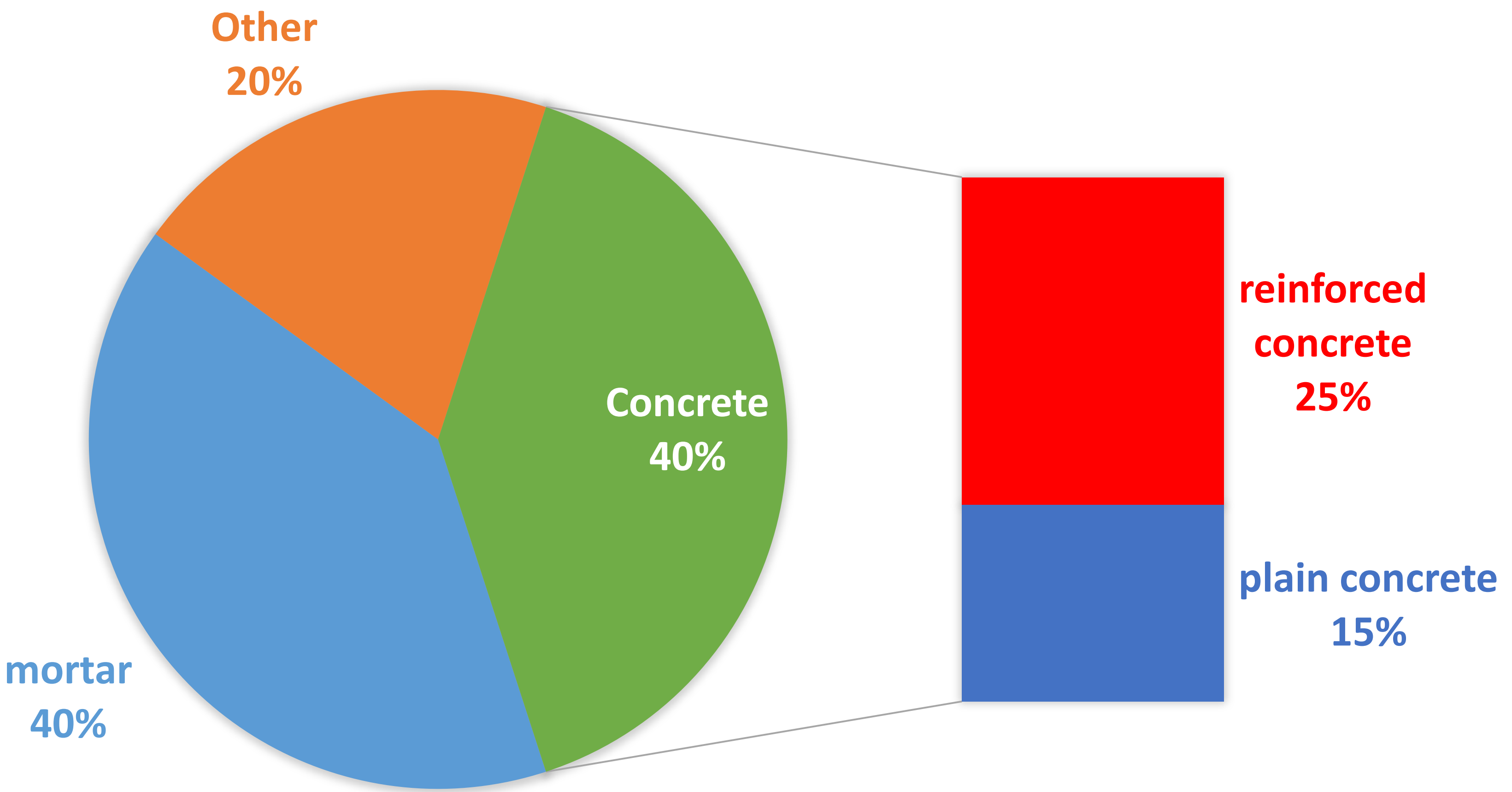
Mortar

Fibre-cement

Pavements

Can capture up to 60% of $CO_2$ from cement production!

# Cement in reinforced concrete (Brazil)




**25% of cement protect steel.**

# How much filler can we add?

## Conventional dilution

- **Up to 30-35%**
- All major players do have international experience
- **It is not reasonable keep filler amount bellow 35%**
- We have a social responsibility of an immediate action

## LEAP technology

- Depends on market
- Up to 70%
  - Mortar
  - Unreinforced structural concrete (even 70 MPa)
  - Reinforced concrete in dry environment
- A progressive approach: **l**earn, **i**mprove, **a**dvance.

# LEAP technology may be captured by filler producers

- Cost reduction on products formulation
  - Cement R$350-400/t
  - Filler R$160/t
  - Admixture
- Some filler suppliers

SIBELCO

IMERYS
TRANSFORM TO PERFORM

PROVALE

OMYA

# Calcined clay + limestone filler

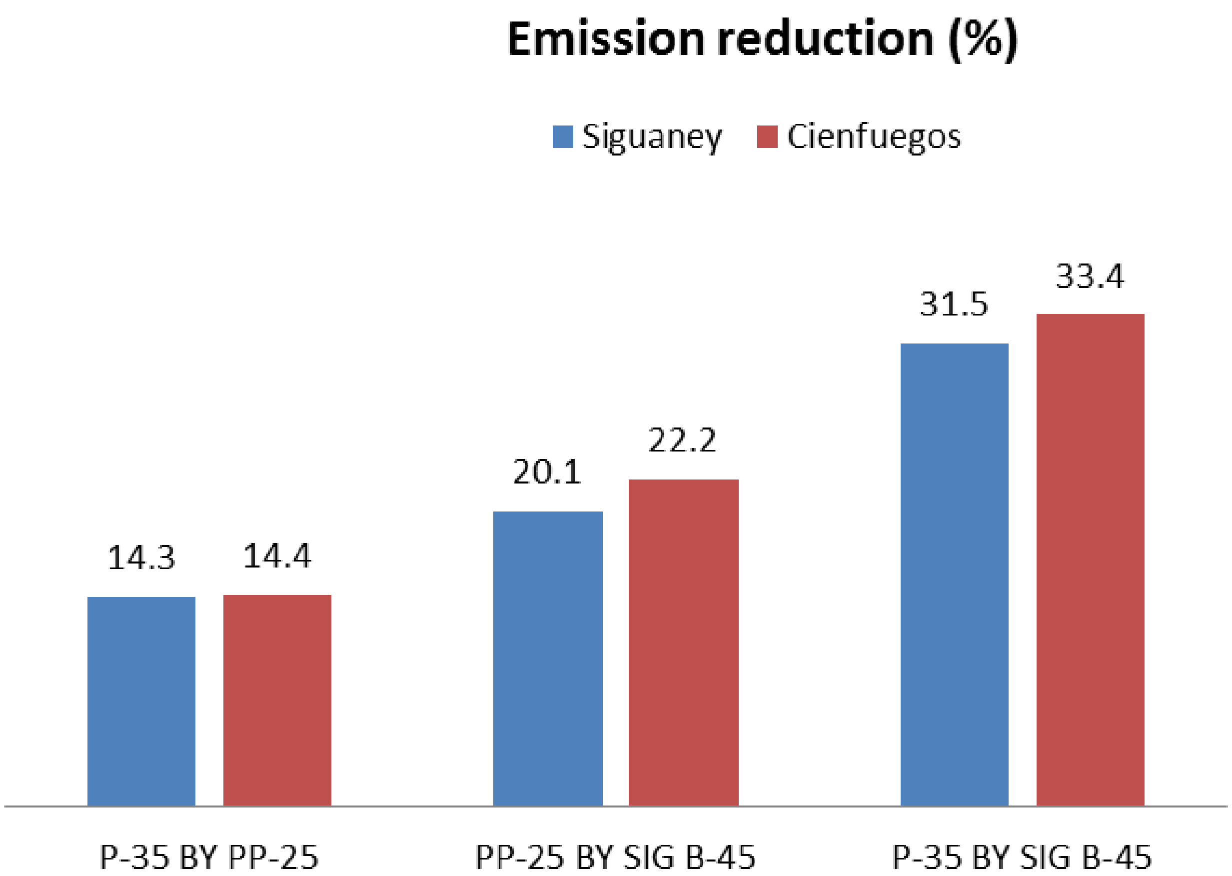
- Rheology improvement: less water, better strength
- Chemical reaction – monocarboaluminate

$$A + C\hat{C} + 3CH + H \Rightarrow C_3A \cdot C\hat{C} \cdot H_{12}$$

- Proportion
  - Stoichiometric  > 2 pozzolan : 1 limestone
  - Rheology ?
- Need to adjust standard immediately

Antoni et all. *Cement substitution by a combination of metakaolin and limestone*
**Cem Concr Res 42 (2012) 1579–1589**
http://dx.doi.org/10.1016/j.cemconres.2012.09.006

# $CO_2$ mitigation
# Calcined Clay + Limestone Filler




Sanchez, UCLV Cuba, K. Scrivener EPFL,

Emission reduction for two trial production in Cuba (Siguaney and Cienfuegos)

Limestone Calcined Clay Cement

www.lc3.ch

# High-filler & $CO_2$

- Lower CO2 in cement production (up to 65%).
- Lower CO2 in cement-based materials.
- Lower production costs (~35%).
- Higher CO2 capture rate.
- Higher cement sales.

# Filler in the Roadmap – a reasonable proposition

- Ambition: no increase in absolute $CO_2$ emission
- Immediate adoption European standard 35% filler
- ~15-20% average in 2020
- 30% average 2030
- 40% average 2050

- Research plan do solve problems
  - Durability engineering
  - Robustness of admixture

# Thank you!

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