State-of-the-art, opportunities and challenges for nanotechnology in concrete materials

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Nano Innovation 2016 Rome, 20-23 September
Conference & Exhibition

Cement and concrete

- **Cement and nanotechnology**

- **Cement-based material and nanotechnology**

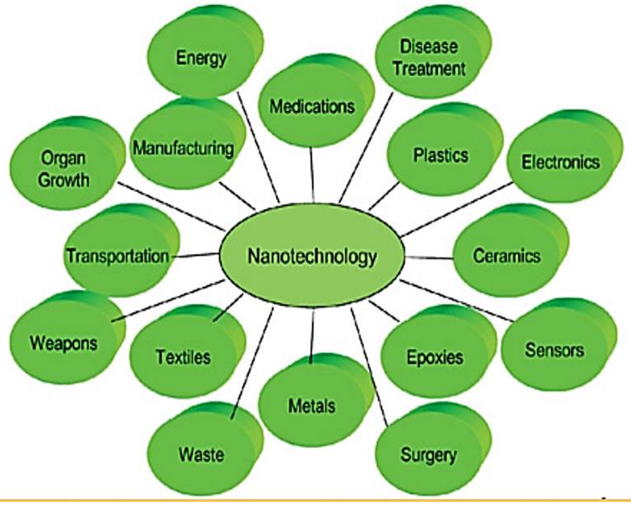
- **Cement-based materials and carbon nanotechnology**

Cement and nanotechnology

Nanotechnology

- **~30 years old:** -1959, *R.Feymann*, building things from the bottom up with atomistic precision
  - 1974, N.*Taniguchi*, first use of the term
  -1980s, *K.E Drexler*, popularization and awareness of nanotechnology concepts
  G.Binning and H.Roher, scanning tunnelling microscope invention
- **Nanoparticles**: - from 1 to100nm (National Nanotechnology Initiatives, U.S)

Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nanometers, where unique phenomena enable novel applications (EU commission).



Rakesh Kumar, **Renu Math, Arun Kumar Mishra**, Opportunities & Challenges for Use of Nanotechnology in Cement-Based Materials

Cement and nanotechnology

Nanotechnology applied to cementitious materials:

1817 L.Vicat: artificial cement by burning an intimate mixture of chalk and clay
1824 J.Aspdin: proto-Portland cement

To make cement and concrete a product of nanotechnology we must be able to **understand and control** type, amount, structure and location of the:
- **nano-products**
- **nano-scale pores**
- **nano-ingredients**

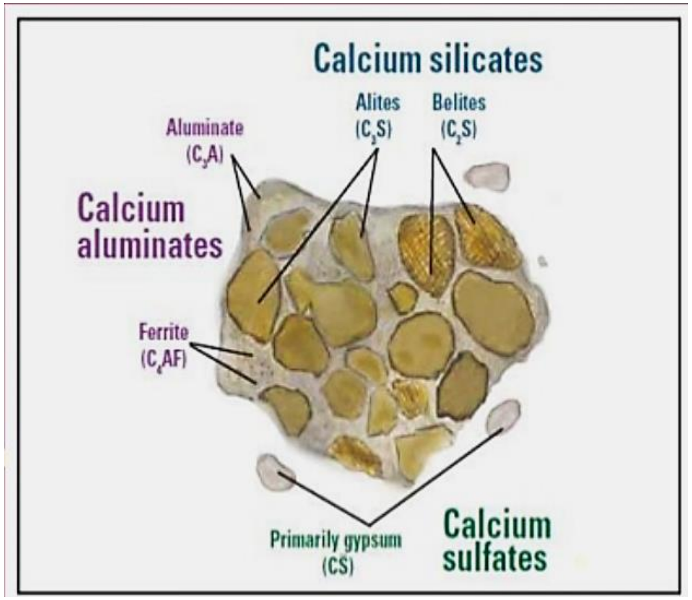
to create materials with fundamentally **new properties and functions.**

Anhydrous cement

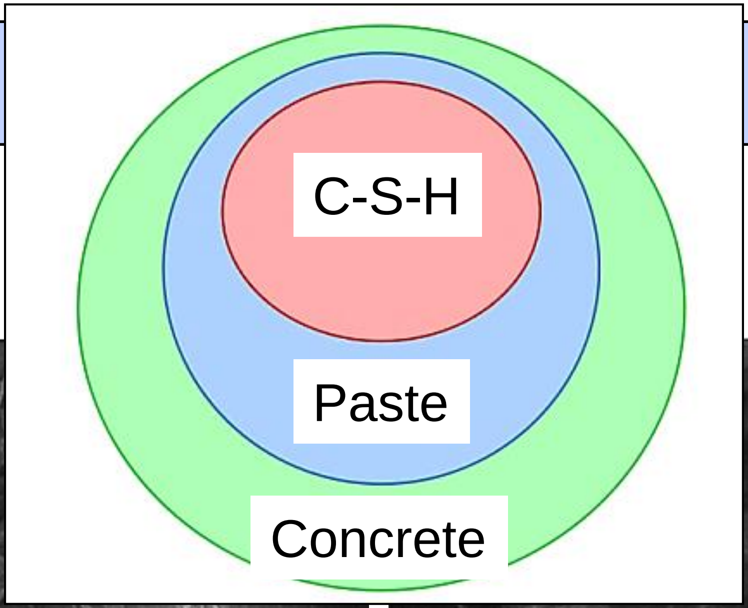
Calcium aluminate
-tricalcium aluminate **C_3A**, 8-12% bwc
-calcium aluminoferite **C_4AF**, 6-12% bwc

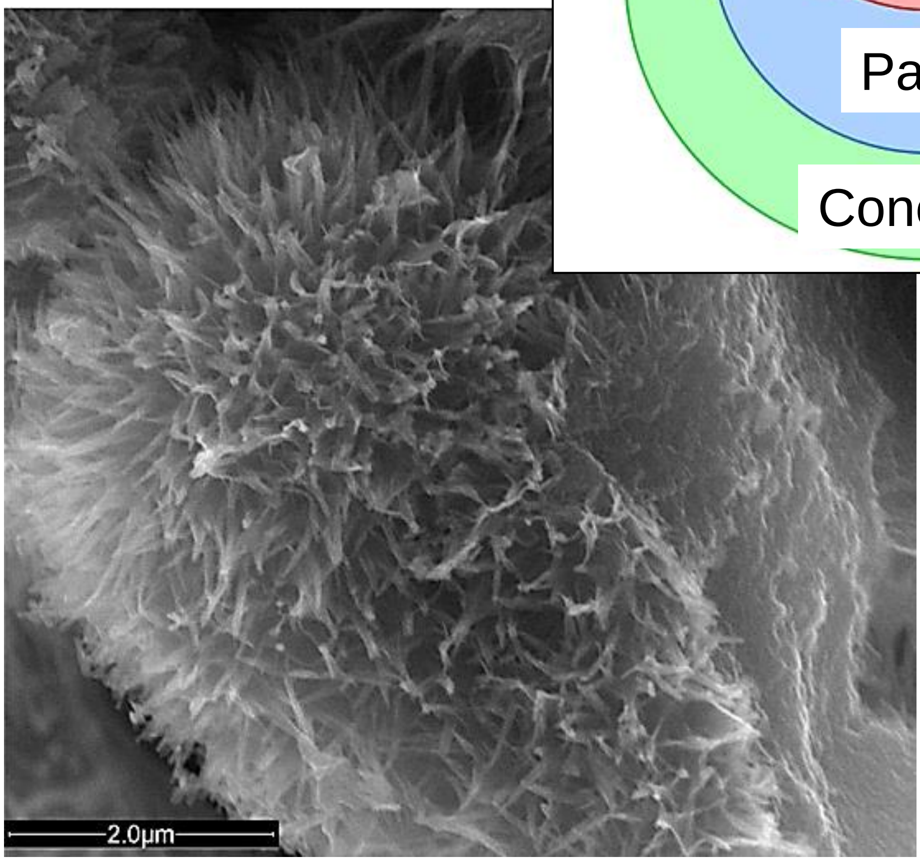
Calcium silicate
-tricalcium silicate **C_3S**, 55-65% bwc
-dicalcium silicate **C_2S**, 15-25% bwc

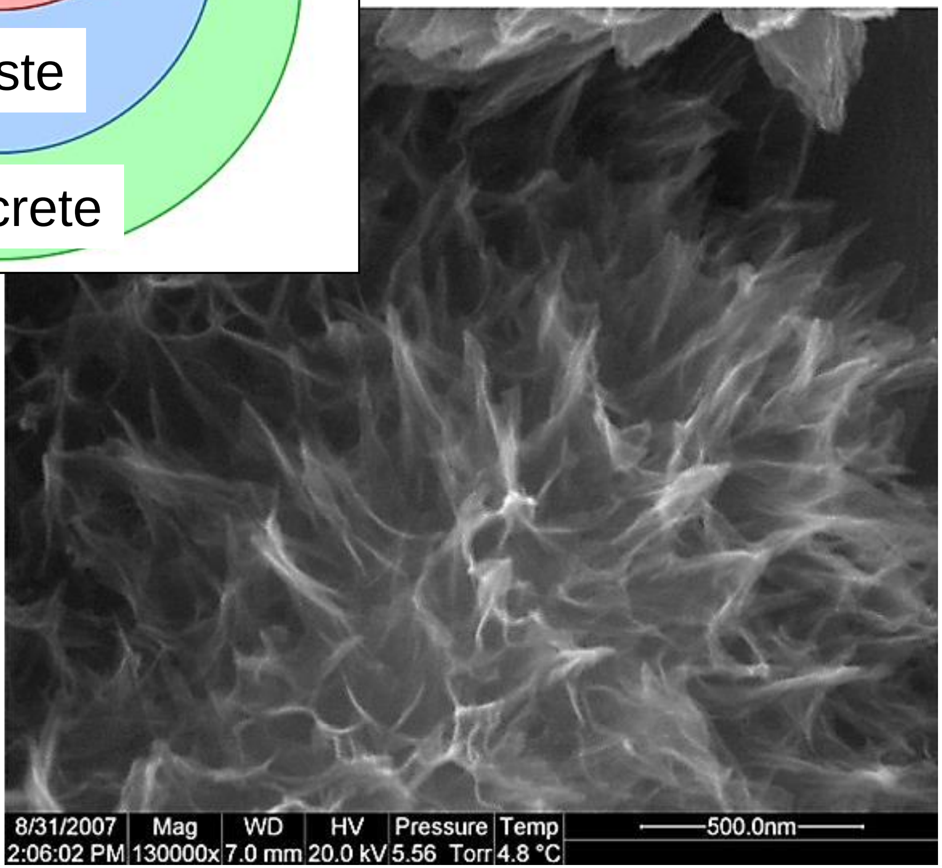
Calcium sulfates
-gypsum or hemihydrate



Hydrated cement: C-S-H





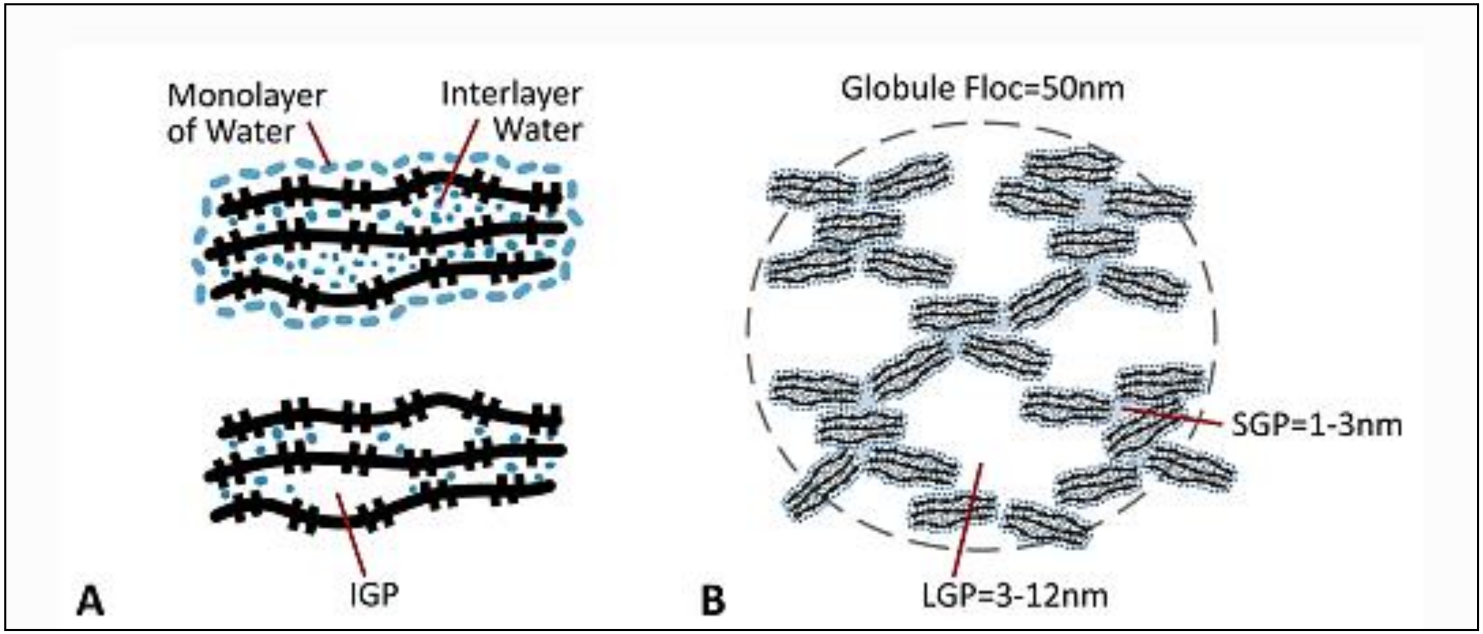


Hydrated cement: C-S-H

C_3S, C_2S $\xrightarrow{H_2O}$ C-S-H + CH

J-model for C-S-H (2008)

Variable, nanoscale composite material itself, based on colloidal particle with a layered substructure modifyed by a multinetwork of hierarchycal capillary pores and cracks



a. **Particles** >5nm*30-60nm outer surface and internal porosity
b. **Gel pores** (IGP intragranular, SGP small, LGP large gel pores)
c. **Clusters of globules**: **HD** C-S-H, **LD** C-S-H

Resolving C-S-H

C-S-H

- **nanoscale** dimensions;
- the most **abundant** reaction product, ~50% of paste volume;
- not intrinsically strong or stable;
- **70% LD C-S-H**: 21.7GPa; **30% HD C-S-H**: 29.4GPa *(Constantinides and Ulm, CCR 34,2004)*
- forming a continuous layer binding together the original cement particles into a cohesive whole
- all the other hydration products being discrete crystals not forming strong connections to the solid phases they are in contact with and so not contributing much to the global strength.

"Understanding" C-S-H should open the door to the potential "control" of fundamental and engineering properties:

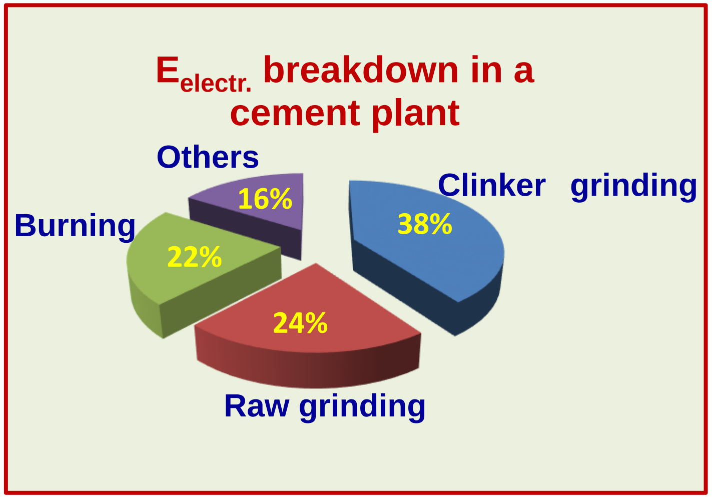
- tensile strength;
- shrinkage cracking potential;
- ions substitution/interactions (e.g Al) and effect on bulk properties;
- chemical compatibility with inorganic material additions (e.g fly-ash);
- permeability;
- in depth structural modifications

Challenge !!!

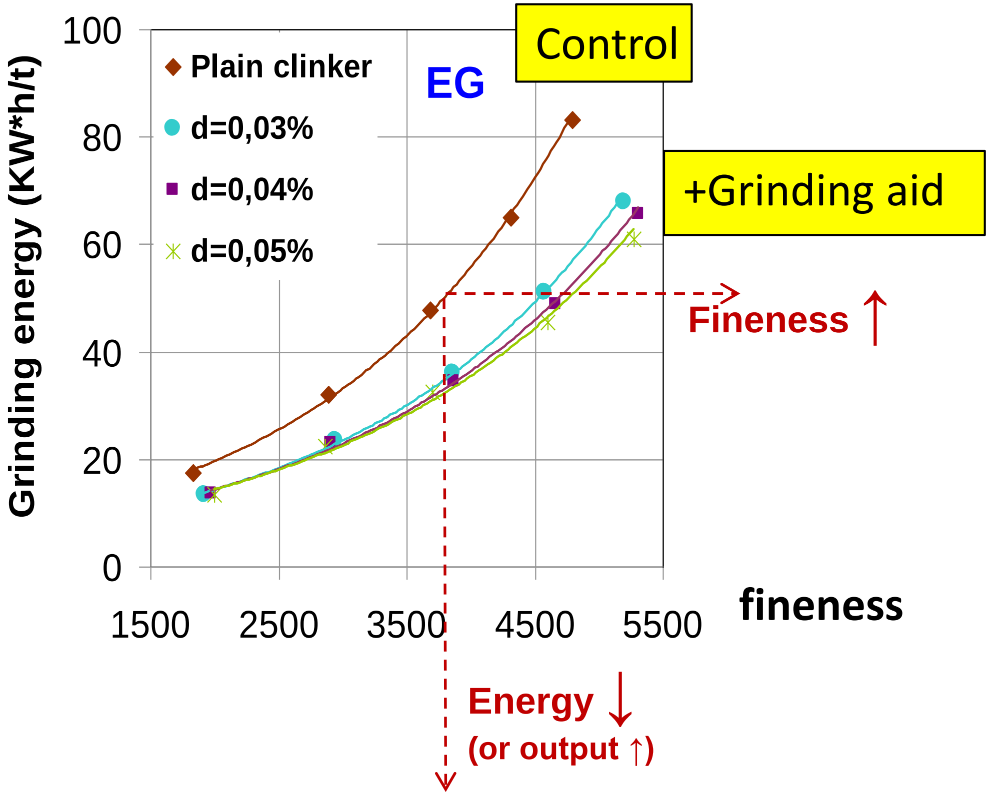
Anhydrous clinker: grinding (1)

- **Clinker grinding: ~40%** (of electrical plant demand)

- **Organic compounds (GA):** able to reduce energy consumption (glycols and amines)

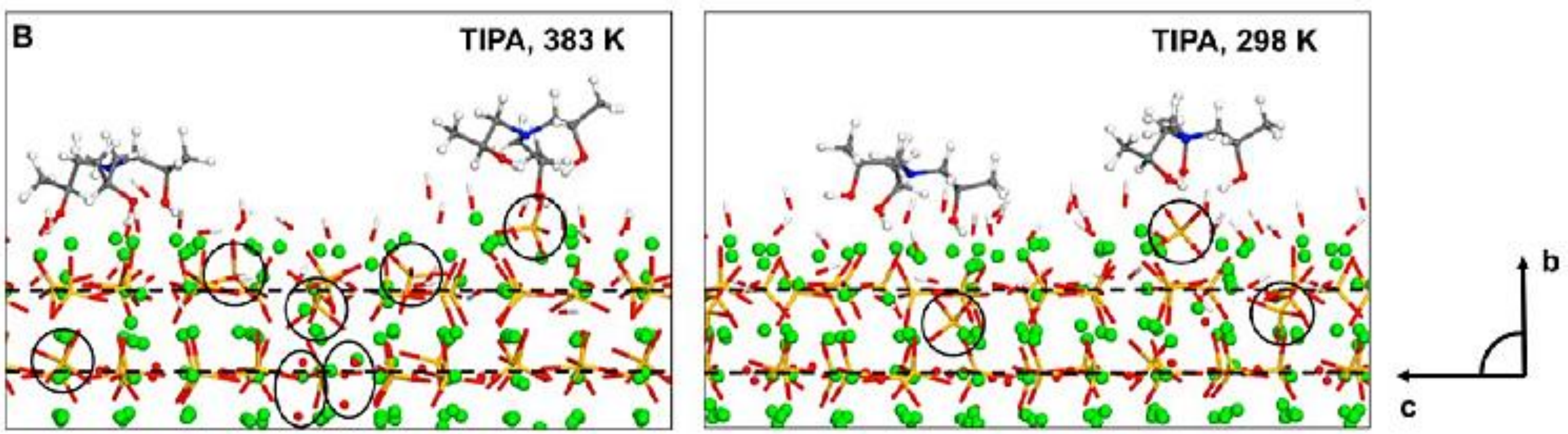


Grinding aid



Anhydrous clinker: grinding (2)

- **Design and prediction behaviour:** need adsorption and agglomeration energy values
- **Recent progress** by computer-aided simulation

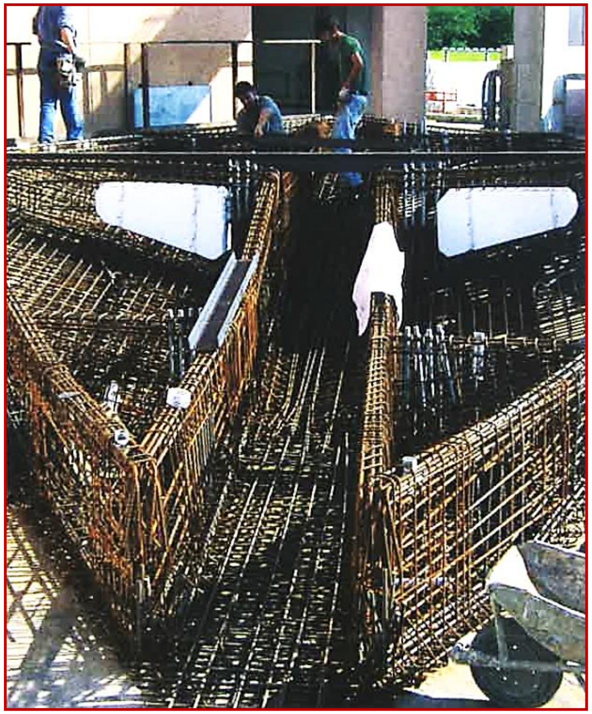


Mishra R.K, Flatt R.J, Heinz H., J.Phys.Chem. C 2013,117, 104127/10432

Hydrated cement: paste dispersion (1)

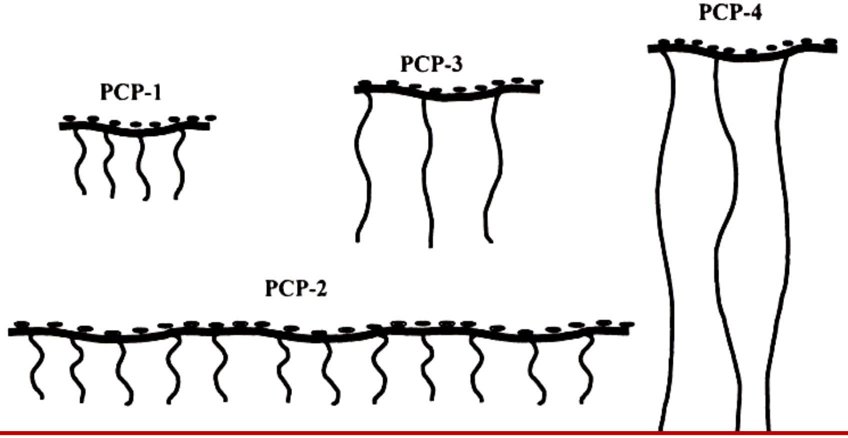
Superplasticizer

- Paste initial dispersibility
- Paste dispersibility over time
- Mixture with low water added



Hydrated cement: dispersion (2)

PCE



Structure

- **type of monomer in the trunk chain**
- **length of trunk chain**
- **length of graft chain**
- **degree of grafting**
- **MWD of the polymer**

Fundamental components of comb-type SPs :
-**carboxylic groups** of the trunk chain, as adsorbing sites, bonded to Ca^{++} on the cement particles
-**polyether graft** chains able to reduce attractive forces between the cement particles by their steric hindrance effect.

Cement and concrete

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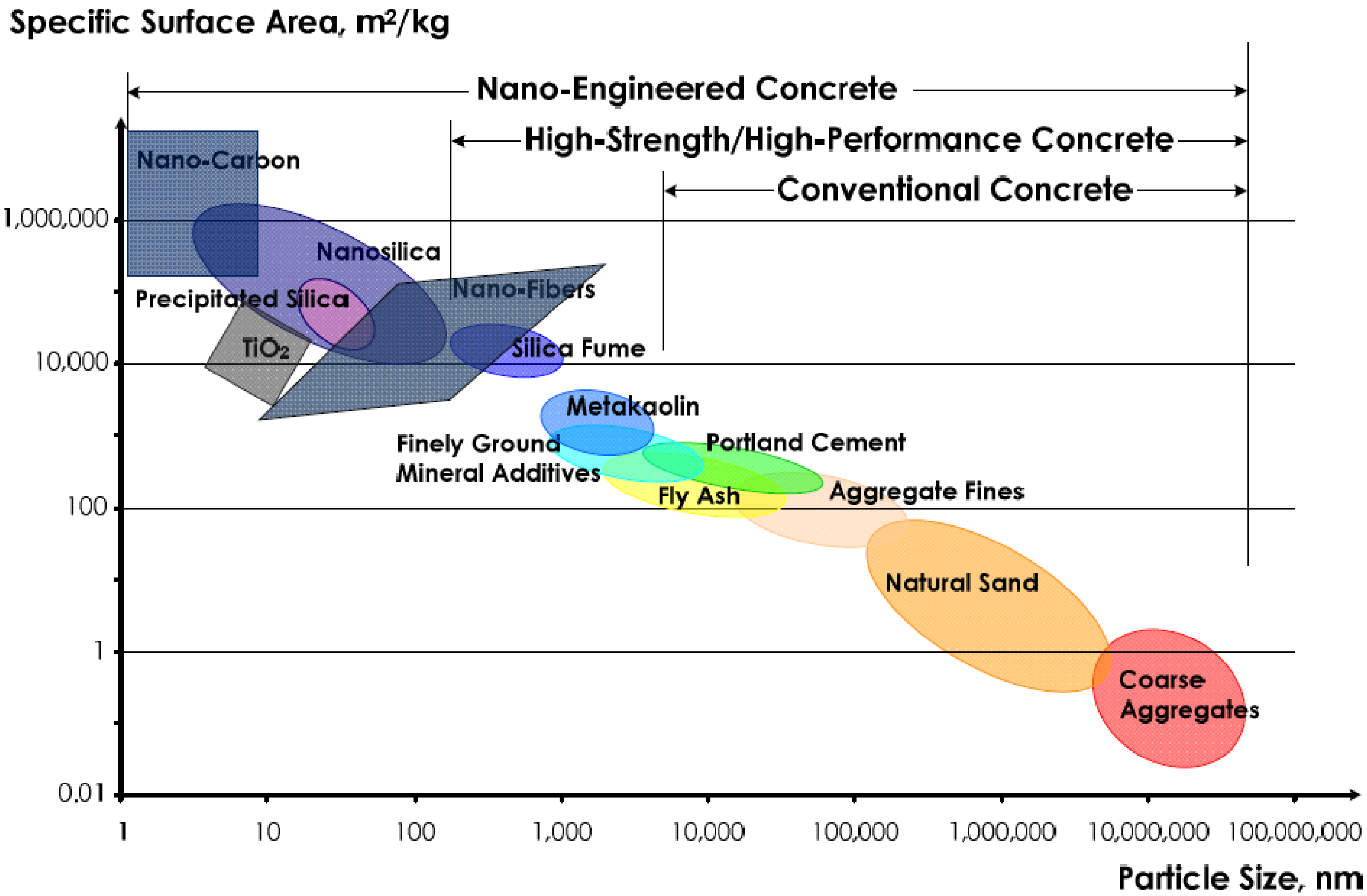
Additions of nanosized materials (1)

Main nanoparticles

- **colloidal SiO_2**
- **TiO_2**
- **nano-$CaCO_3$**
- **nano-Al_2O_3** (fibers)



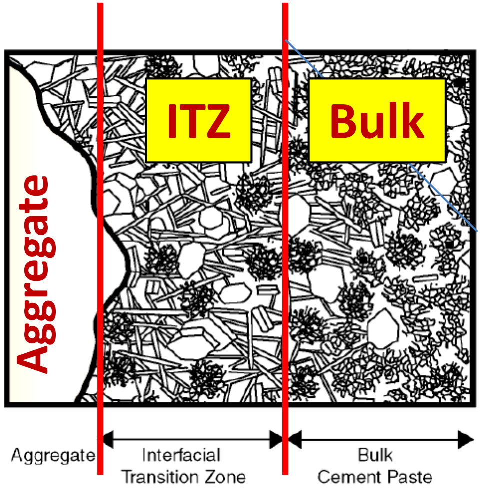
Additions of nanosized materials (2)

Nanoscale particles: high surface area-to-volume ratio
high reactivity (some)

Formation of denser microstructure

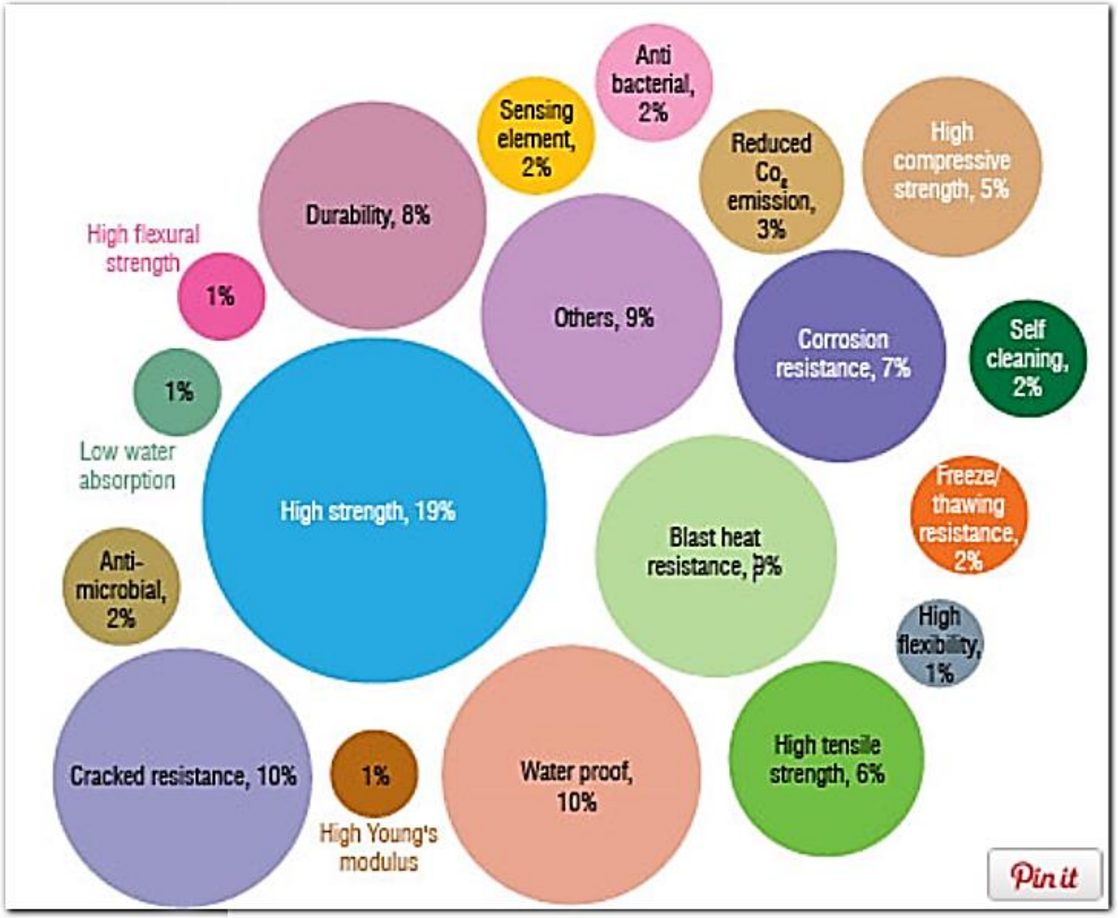
- nanoparticles act as centers of crystallization of hydration products
- filling the nanosize pores of cement paste
- improve structure of the aggregate contact zone (ITZ)
- generation more C-S-H through pozzolanic reaction

$$\text{Pozzolan} + \text{CH} + \text{H} \xrightarrow{\text{SLOW}} \text{C-S-H}$$



- favour formation of small-sized crystal ((CaOH)2 and Afm) and small-sized clusters C-S-H
- arrest crack and create interlock effect between slip planes

Additions of nanosized materials (3)



Percentage-wise distribution of patents based on characteristic property imparted by the added nanomaterials. *NanoWerk spotlight, dec. 2012*

Advantages

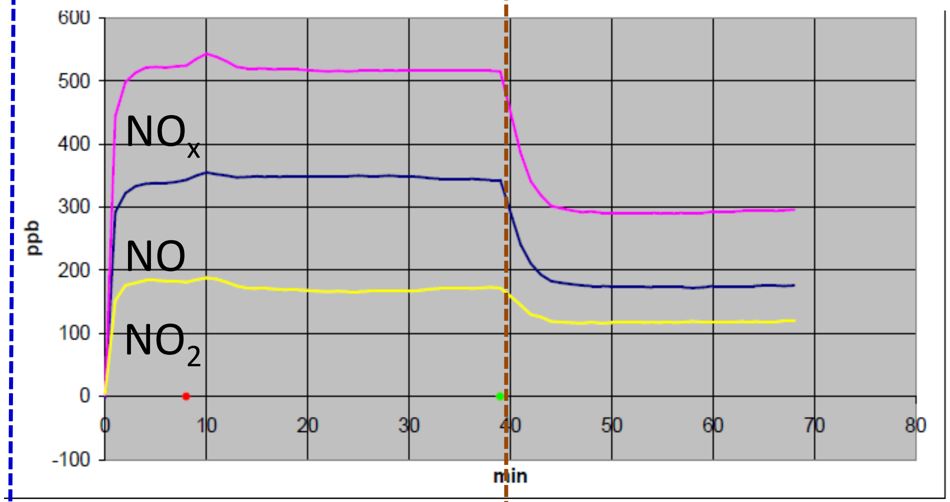
- mechanical properties ↑
- durability ↑
- reactivity ↑
- industrial footprint ↓

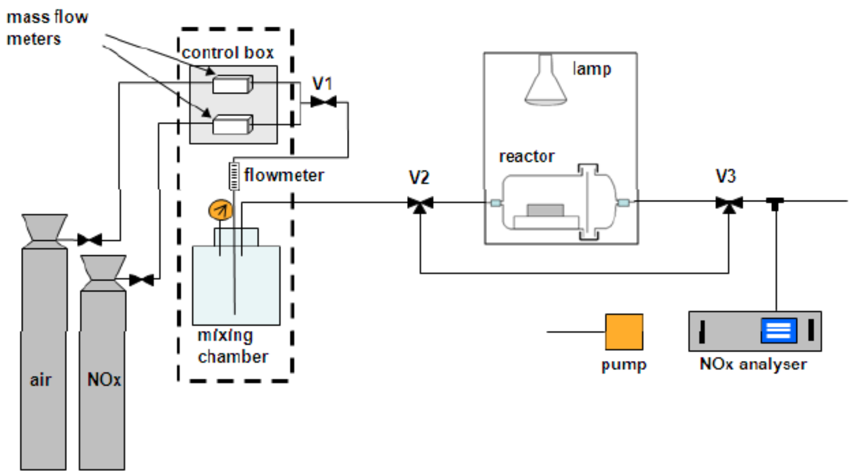
TiO_2: de-polluting property

Photocatalytic cement

TiO2: effective in pollutants reduction
(NOx, aromatics, ammonia and aldehydes)

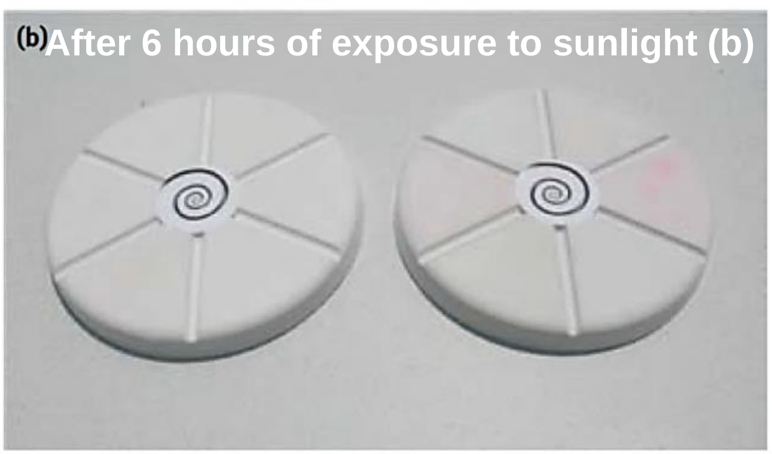
NOx abatement

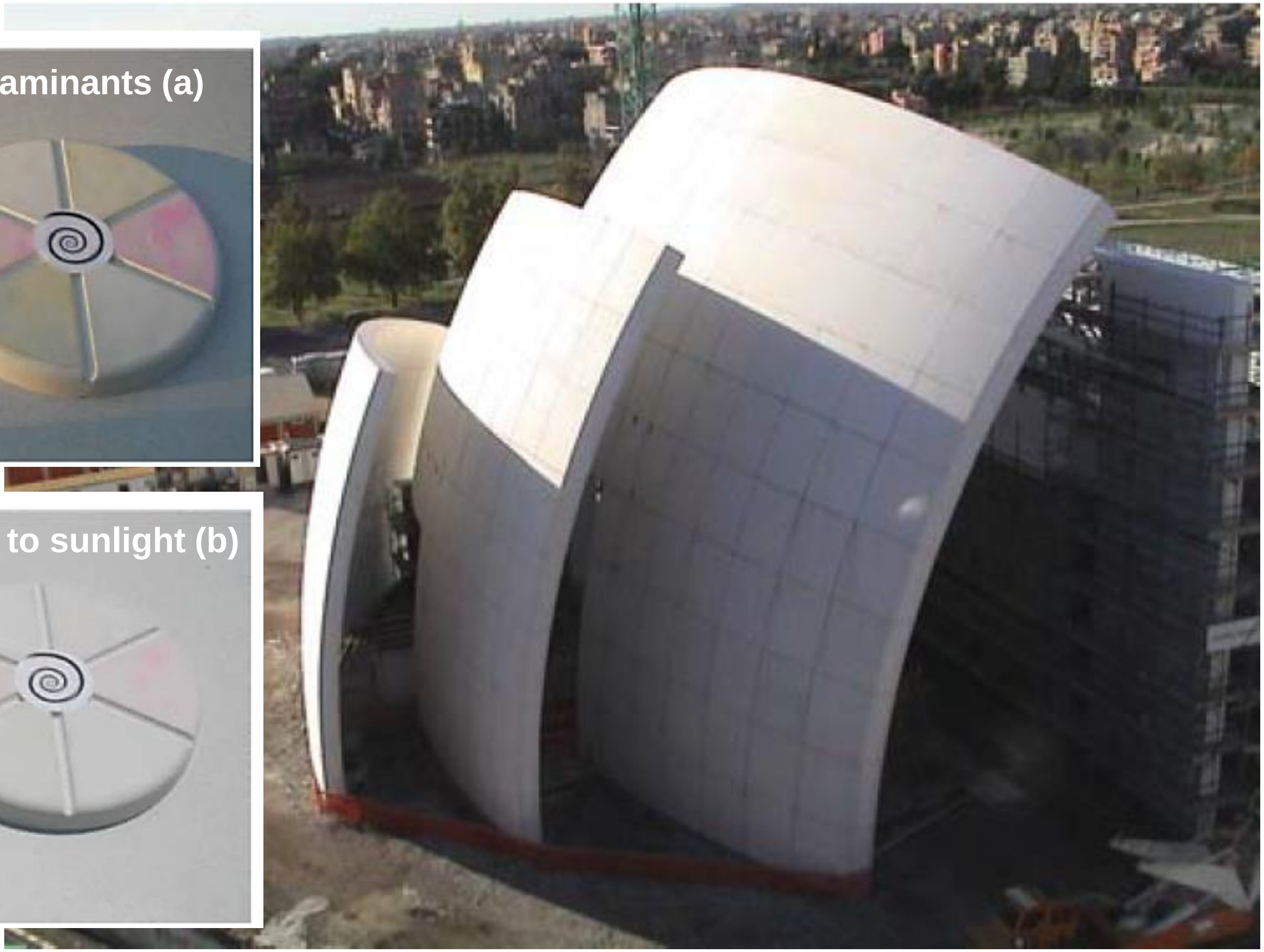




Continuous flow-method UNI 11247

TiO_2: self-cleaning property

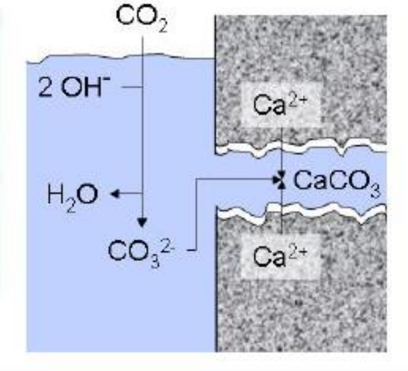


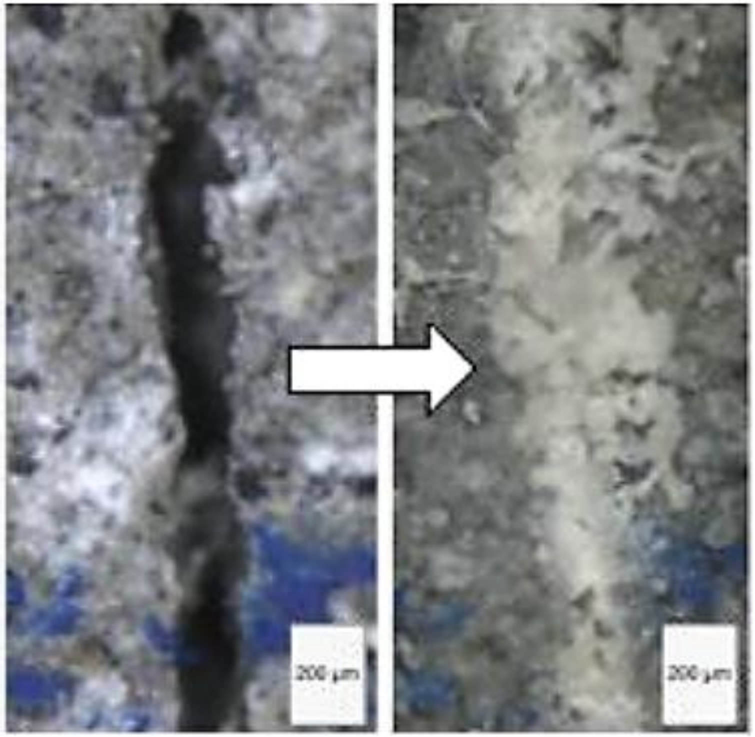


Self-healing materials

a. Autogeneous healing

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$





b. Healing by compound expansion

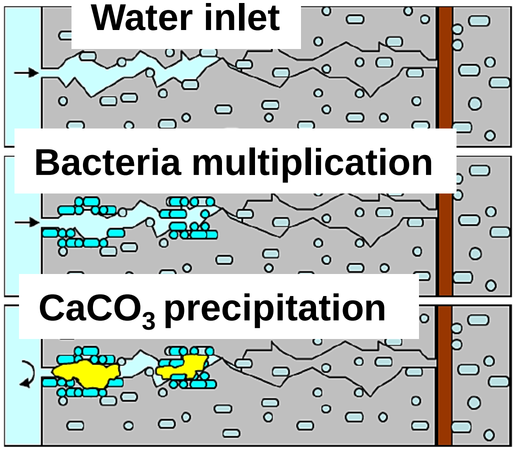
c. Healing by compound swelling

d. Bacteria

bacteria

$$\text{Lactate} + O_2 \xrightarrow{\text{bacteria}} \text{acetate} + CaCO_3 + CO_2$$

Metabolic conversion of Calcium Lactate $\text{---->} CO_2 \xrightarrow{Ca(OH)_2} CaCO3$



After *Klaas Van Breugel*

Cement and concrete

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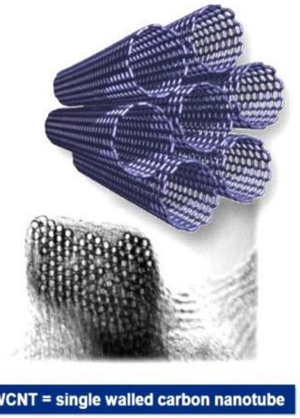
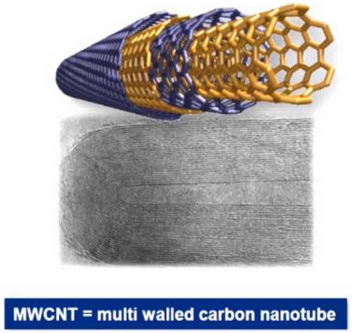
CNTs (1)

SWCNTs: 0.4-10nm diameter

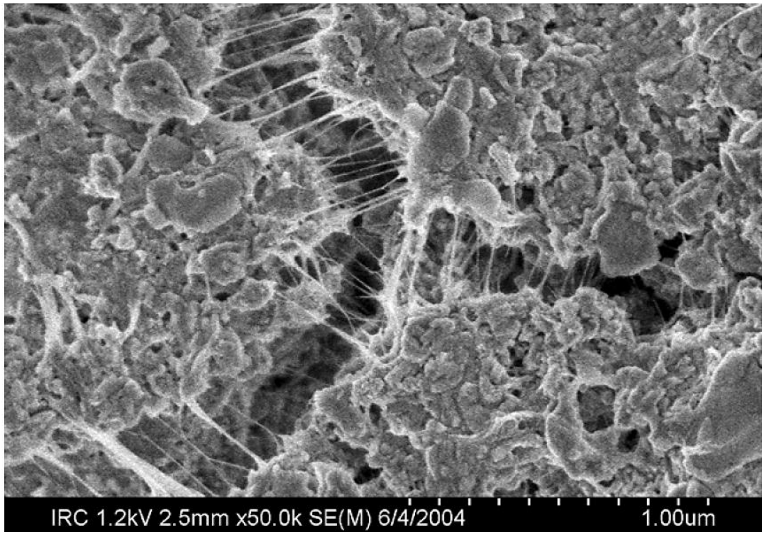
MWCNTs: 10-100nm diameter

Aspect ratio: 30 - many thousands

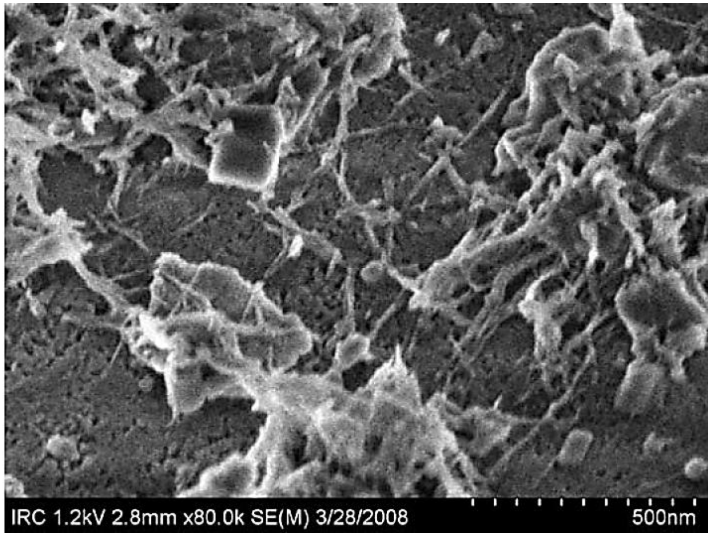




Nano reinforcement of cement-based composites (E~1TPa, Tensile strength~10-50GPa)
Potential: crack propagation resistance (finely diistribution throughout cement matrix, bridges across voids…) ↑, strength ↑, stiffness ↑, ductility ↑



Crack bridging in a SWCNT/hydrated OPC composite



Growth of C-S-H around SWCNT bundles at 135 min. of hydration of an OPC composite sample

Raki. L. et al, Materials, 3,918-942, 2010

CNTs (2)

Dispersibility in cementitious matrix: hydrofobicity

- surfactants (comb-polymer)
- functionalization (-COOH, -OH)
- synthesis on cement grain surface
- sonication

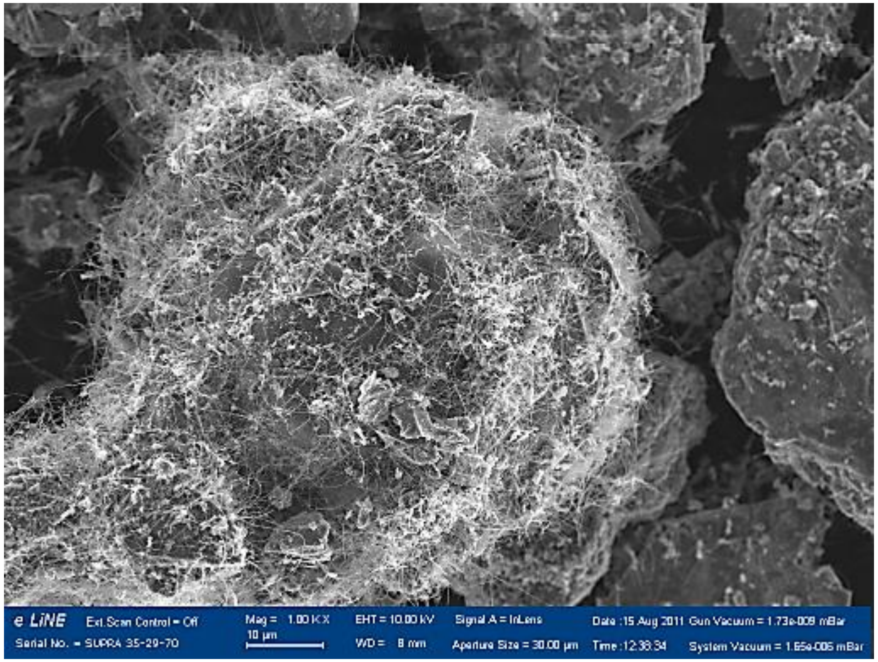
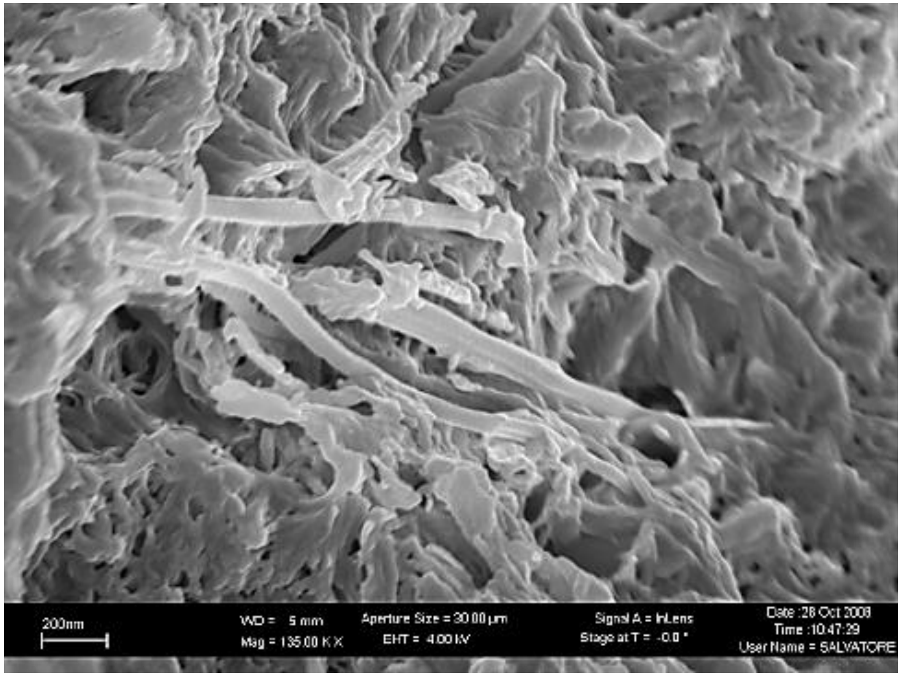


Figure 1: CNT synthesized on the surface of a cement grain. The image is 115 µm in width. Image by K. Hruška, Institute of Physics ASCR, Prague.

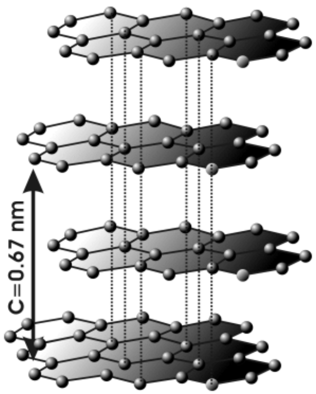


SEM micrograph of 0.4% MWCNT cement composite

Musso S. et al., Composites Science and Technology, 69 (2009), 1985

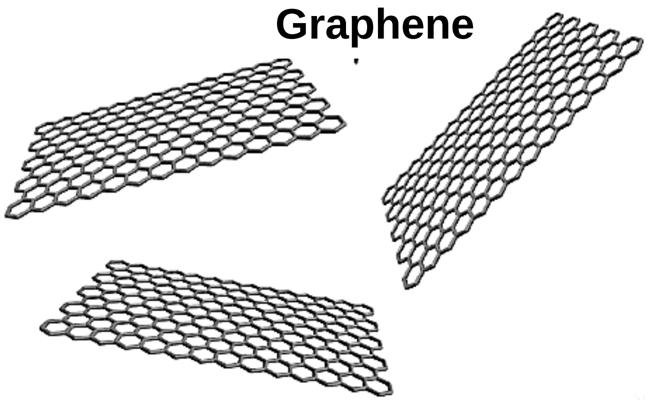
Graphene (1)

One-atom thick planar sheet of sp2-bonded carbon atoms, densely packed in a honeycomb crystal lattice. Graphite itself consisting of many graphene sheets stacked together.

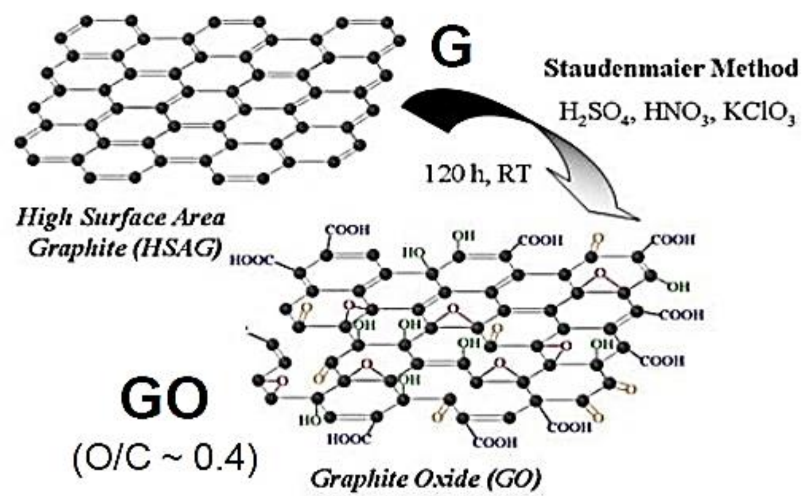


Graphite

Graphene



Hydrophobic material dispersibility in aqueous environment ?



Graphene (2)

GO interaction with cement

a. Microstructure

7d: flower-like crystalline form

15d: clear tendency for aggregates of flower-like and rod-like crystals to form a planar structure

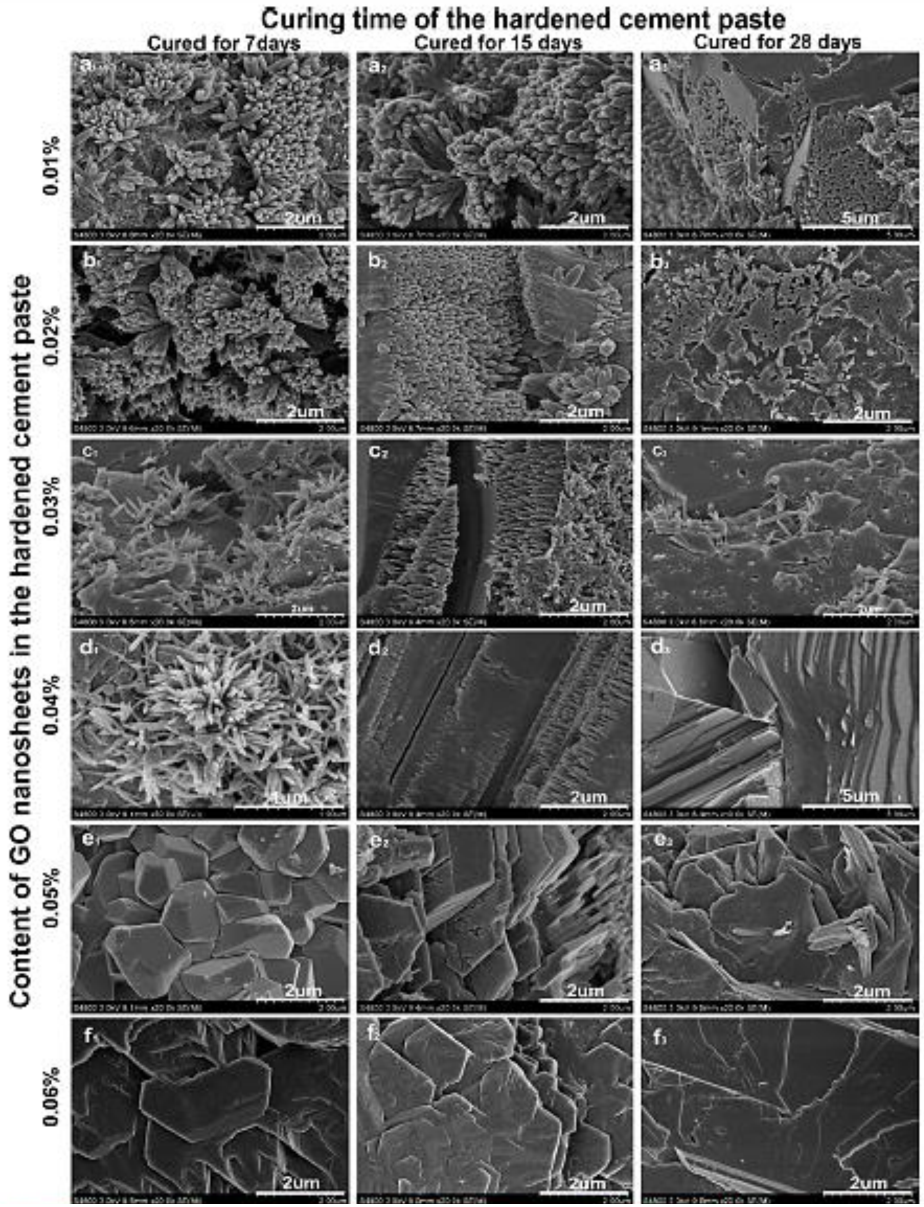
28d: a compact structure is formed, and rod-like crystals can hardly be seen in hardened cement paste with any GO content

flower-like crystalline form

⬇

polyhedron-like crystals

Shengua Lv et al., CrystEngComm., 2014, 16, 8508



SEM images of fractured surface of hardened cement paste

Graphene (3)

GO interaction with cement

b. Porosity

GO content (wt/wt%)	Porosity (%)
0.01	31.84
0.02	23.56
0.03	15.41
0.04	12.62
0.05	9.38
0.06	6.24

c. Strength

Table 5 Flexural and compressive strength and elastic modulus of hardened cement pastes with different GO contents

GO content (wt/wt%)	Compressive strength (MPa)/rate of increase (%)		Flexural strength (MPa)/rate of increase (%)	
	7 days	28 days	7 days	28 days
0 (control sample)	36.74/0	59.31/0	5.63/0	8.84/0
0.01	45.31/23.3	69.65/17.4	8.85/57.2	12.34/39.6
0.02	49.51/34.75	77.82/31.2	9.21/63.6	13.68/54.8
0.03	55.56/51.22	86.62/46.1	9.93/76.4	14.72/66.5
0.04	58.61/59.5	92.36/55.7	9.88/75.5	14.74/67.1
0.05	62.25/69.4	93.38/57.4	9.37/66.4	13.53/53.1
0.06	63.27/72.7	94.26/58.5	9.19/63.2	12.63/42.9

Shengua Lv et al., CrystEngComm., 2014, 16, 8508

Carbon nanotechnology: ITC and Graphene

10/2014-03/2016: ramp-up phase
Task: T10.12 of WP 10, Composites for catalysis in building applications

04/2016-03/2018: core 1 project
Task: T 13.3.4.12 of WP 13, Coatings for photocatalytic applications

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Archivio Comunicati e notizie
Approfondimenti

Dei/Sole 24 Ore - UE: sceglie Italcementi per progetto Graphene

Italcementi selezionata dalla Commissione Europea per entrare nel Graphene Flagship Project

di Redazione

(Il Ghirlandaio) Milano, 24 giu. Italcementi è stata selezionata dalla Commissione europea per entrare a far parte del 'Consorzio Graphene Flagship Project', un'iniziativa di ricerca avviata in Europa sullo sviluppo di nuove tecnologie legate ai materiali. Il progetto prevede dieci anni di ricerca e un finanziamento complessivo di un miliardo di euro.

Italcementi Group
Governance
Sustainable Development
Investor Relations
Media and Communication
Research and Innovation
Research
Research Projects
Technical Assistance
Laboratories
Graphene Flagship Project

Research and Innovation

Italcementi heads EU project to develop new materials with graphene

GRAPHENE FLAGSHIP

Italcementi is leading the way in the graphene revolution, the new material that promises to bring cross-sector innovation in the field of materials. Italcementi has been selected to take part in the **Graphene Flagship Project Consortium**, one of the most important research projects ever launched in Europe on the development of new material technologies. The unprecedented initiative will entail ten years of research, with overall financing for one billion euro. The goal is to fully develop the potential of graphene and other recently discovered two-dimensional materials, boosting the growth of new technologies in an effort to revolutionize a wide range of industrial sectors and foster economic development through job creation across Europe.

Thank you