INSTITUTO MEXICANO DEL CEMENTO Y DEL CONCRETO, A.C.

Application of Nanotechnology and Nanomaterials for High-Performance Cement Composites

Konstantin Sobolev
University of Wisconsin-Milwaukee
USA

Ismael Flores
Universidad Autonoma
de Nuevo Leon
Mexico

DEMAND FOR A NEW CONCRETE WHICH IS :

- stronger and more durable,
- with desired stress-strain behavior and
- possibly possessing the range of newly introduced smart properties such as:
  - electrical conductivity,
  - temperature-sensing ability,
  - moisture-sensing ability,
  - stress-sensing ability.
- sustainable,
- cost and energy effective.

SOLUTION:
NEW CONCRETE

can be developed due to:

- better understanding and precise engineering of an extremely complex structure of cement based materials at **nano-level**

WHAT IS NANOSCALE?

- Nano – one billionth of a unit of measure
- A strand of DNA is 2 nm wide
- A human hair is about 100,000 nm

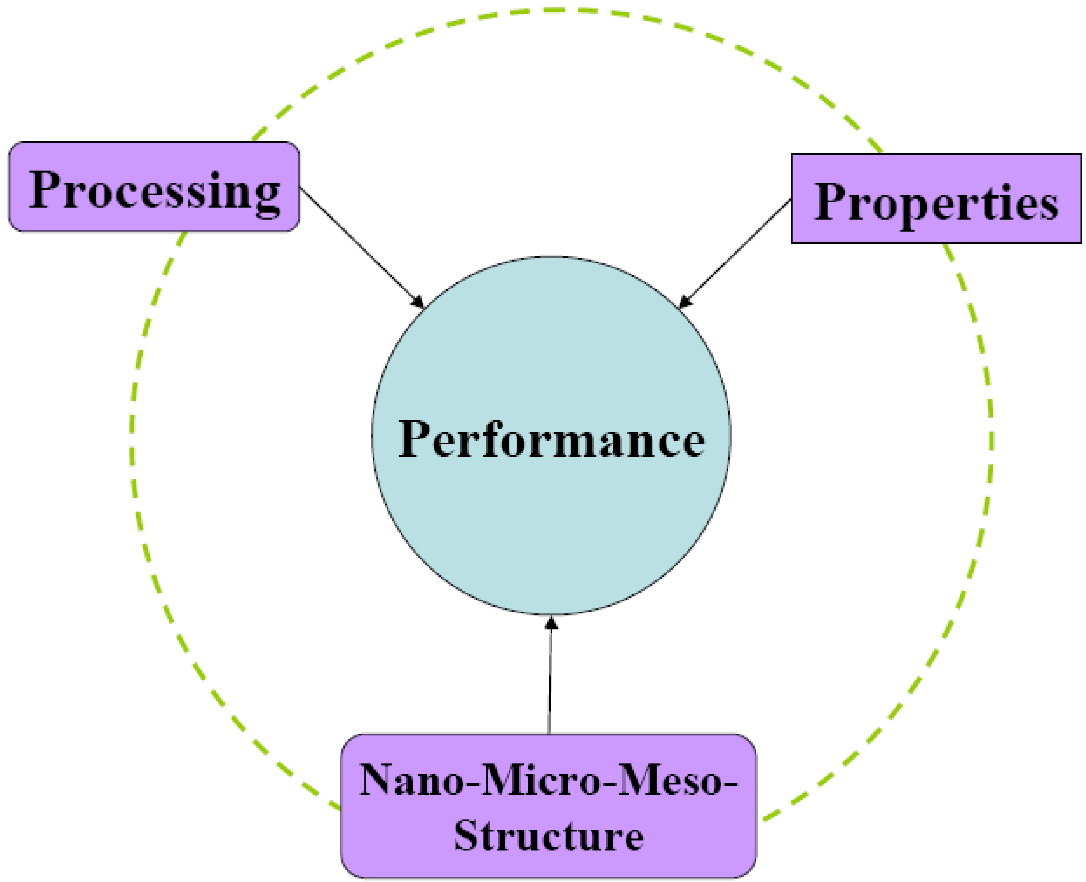
When matter is controlled at the nanoscale, the following fundamental properties can change completely:

- thermal
- electrical
- magnetic
- chemical reactivity

MATERIALS SCIENCE OF CONCRETE

How can Nanotechnology Help?

- Characterization
- New materials
- Sensors

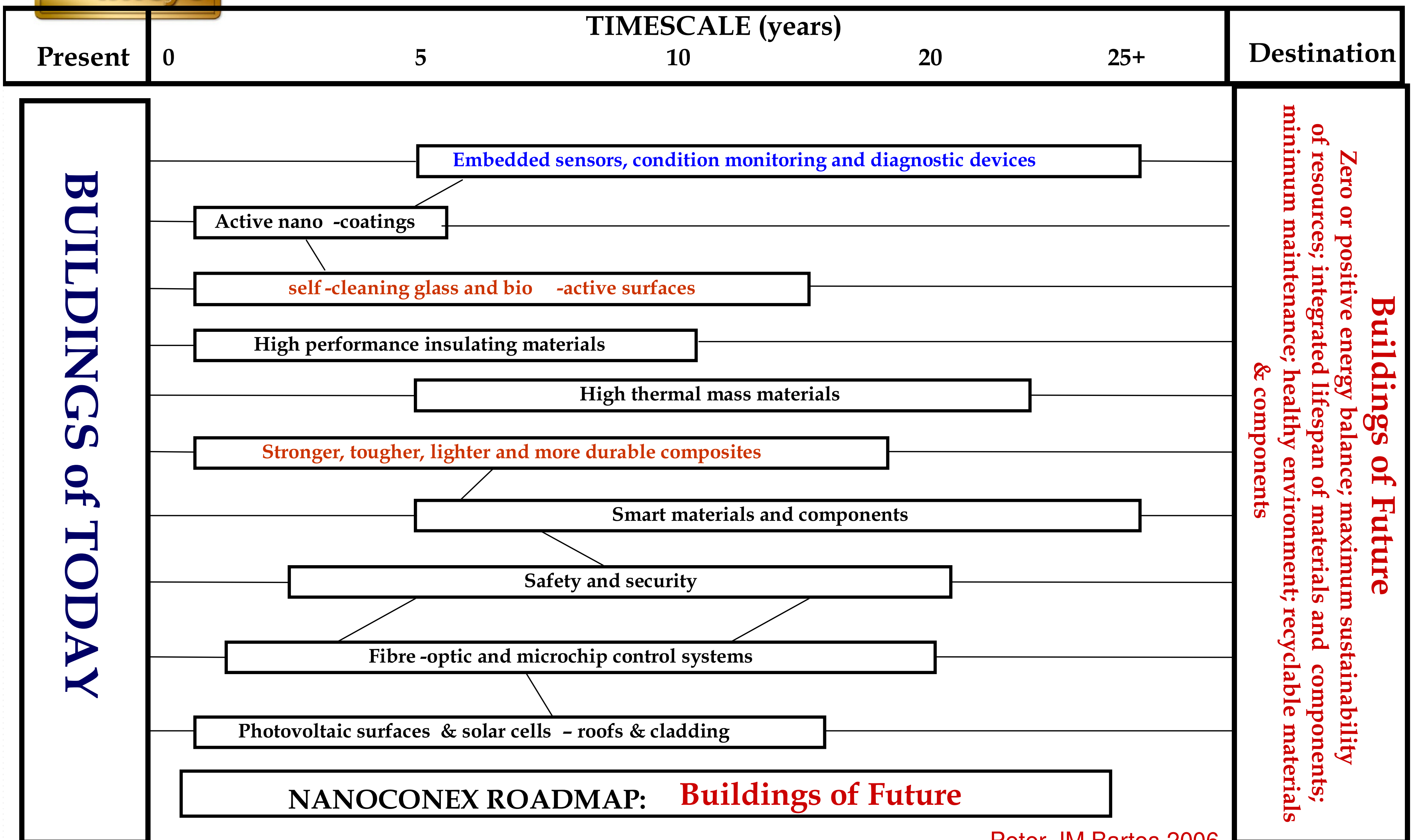


NANOSCIENCE FOR CONCRETE

- Nanoscience deals with the need to understand nano-scale phenomena and to improve our ability to control the nanostructure of materials

- Material properties and performance can be improved by controlling nano-scale processes and structures

Nanotechnology in Concrete: ACI Denver 7th November 2006



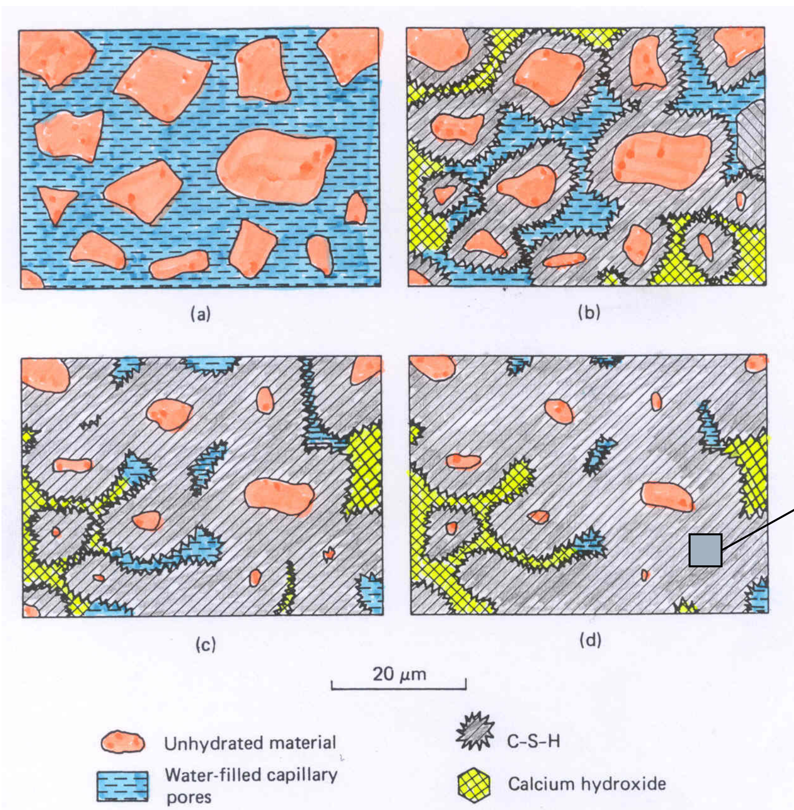
Peter JM Bartos 2006

INVESTIGATION OF MICRO- AND NANO-STRUCTURE

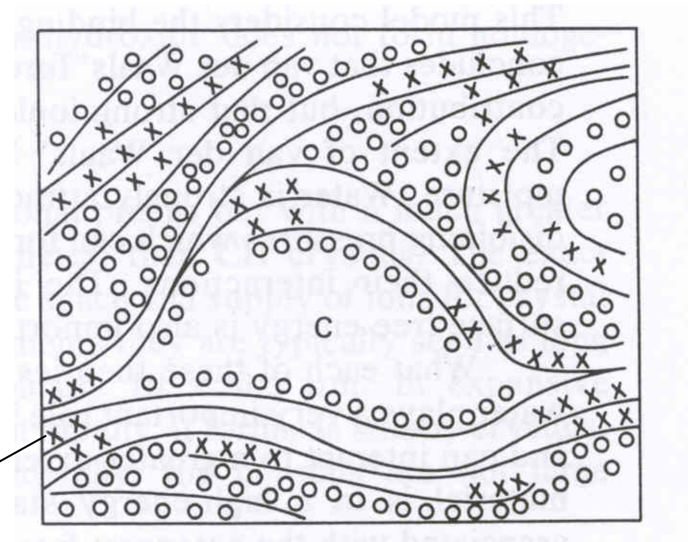
- Recent nano-research in construction focused on the investigation of the structure of cement based materials and their fracture mechanisms.
- With new advanced equipment it is possible to observe the structure at its atomic level and even measure the strength, hardness and other basic properties of the micro- and nano-scopic phases of materials.

NANOSTRUCTURED NATURE OF CEMENT HYDRATION PROCESS

Hydration Process



C-S-H gel

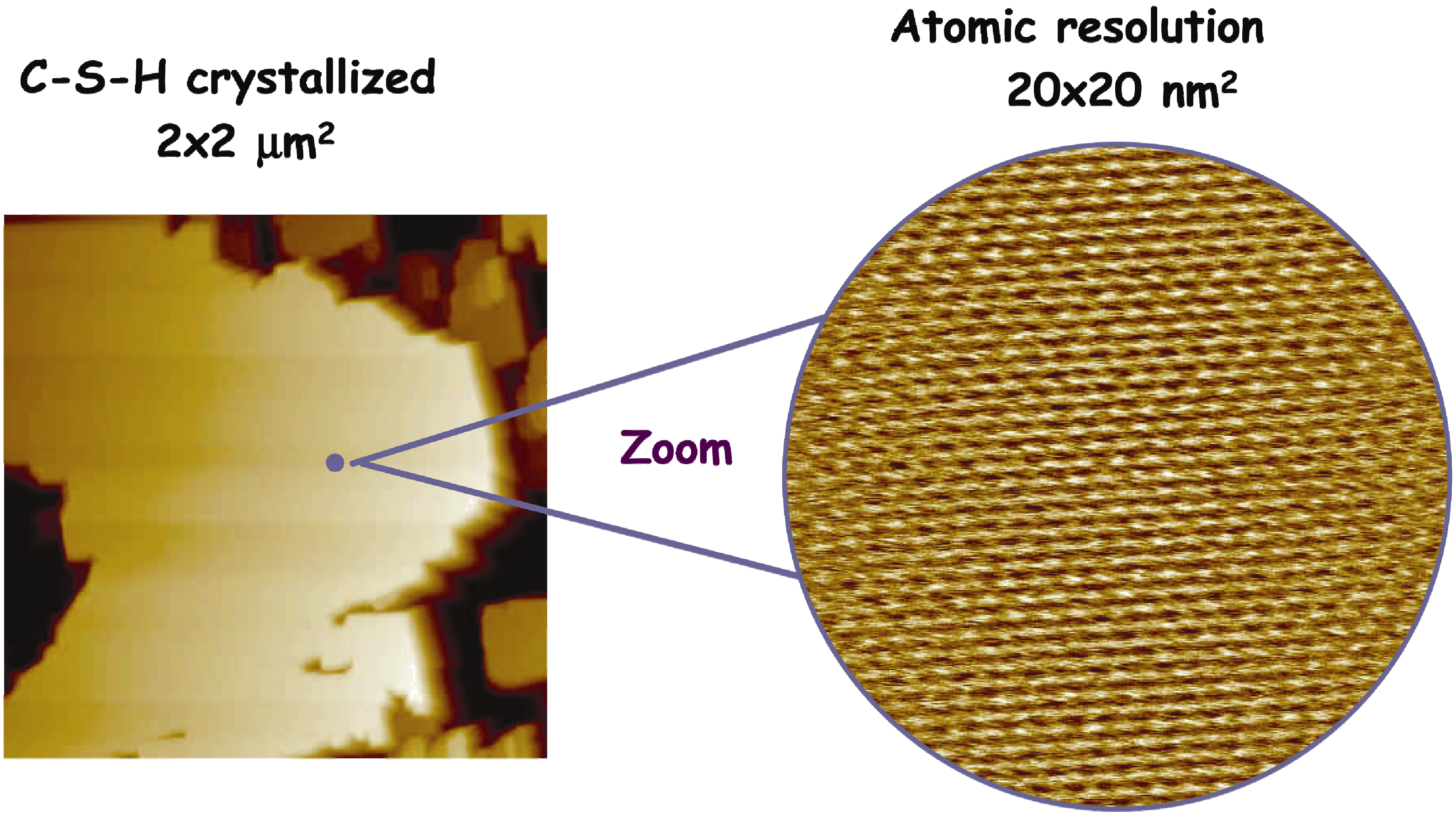


x inter-laminar water ○ adsorbed water
c capillary pore — C-S-H layers

All derived properties are consequence of its nanostructured nature

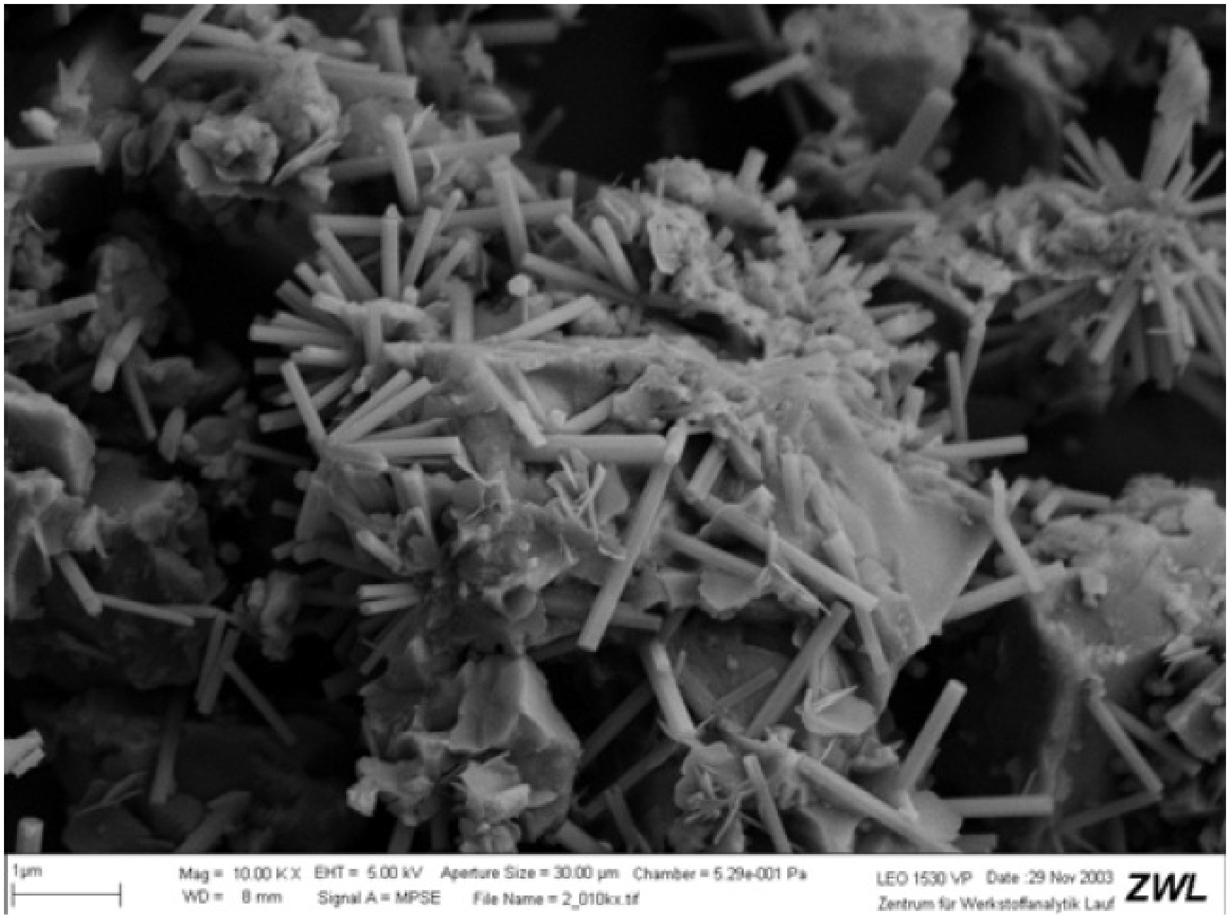
NANOSTRUCTURE OF C-S-H GEL

Ca/Si = 0.9



The application of AFM for the investigation of the "amorphous" C-S-H gel structure discovered that at nanoscale this product has a highly ordered structure (after C. Plassard et al.).

CEMENT HYDRATION PROCESS NANOSTRUCTURED NATURE

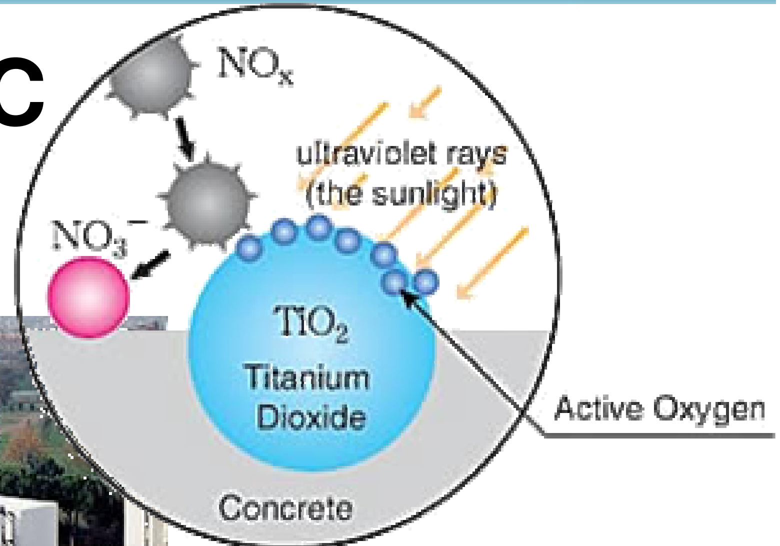


Hydration time: 10 min

NANODESIGN OF CONSTRUCTION POLYMERS

- Nano-chemistry with its “bottom-up” possibilities offers new products that can be effectively applied in concrete technology.
- One example is related to the development of new superplasticizers for concrete, based on polycarboxylic ether polymer.
- New superplasticizers can be nanodesigned targeting the extended slump retention of concrete mixtures or development of high early strength.

PHOTOCATALYTIC MATERIALS

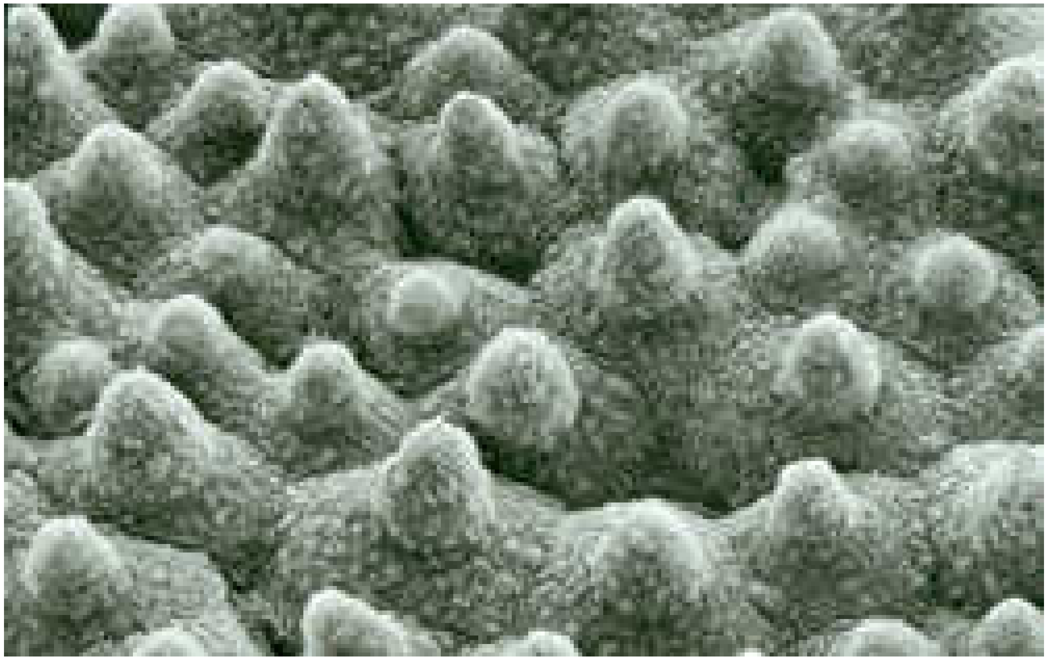


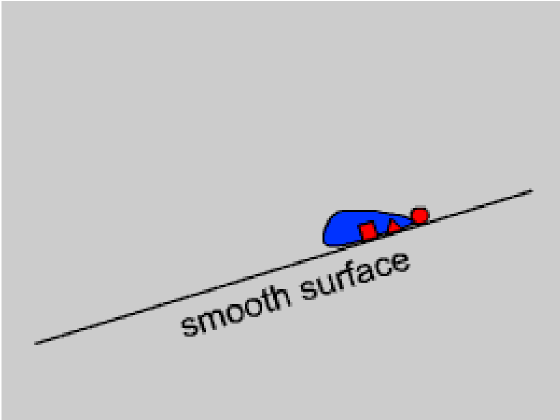
"*Dives in Misericordia*" church

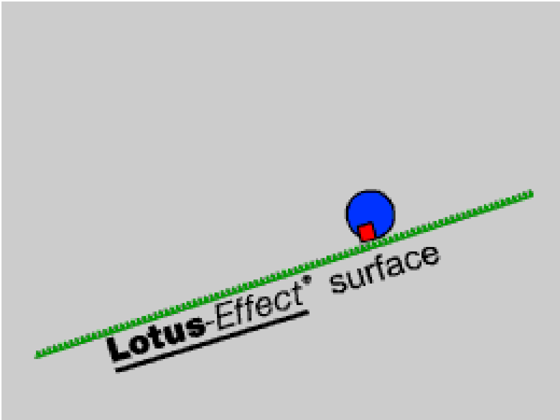
SELF-CLEANING SUPER-HYDROPHOBIC SURFACES

- The self-cleaning of super-hydrophobic micro-to nano-structured surfaces was observed to be a property of some plants
- This physico-chemical phenomenon was reproduced technically and named Lotus-Effect

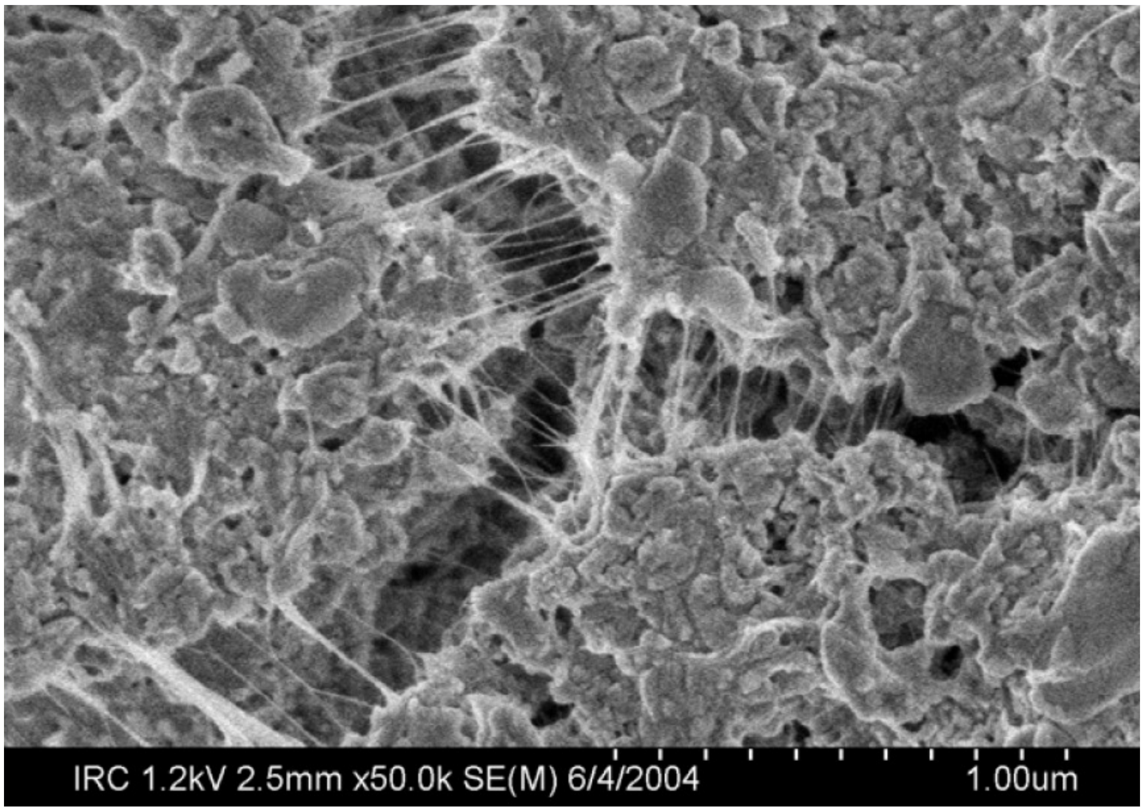
SELF-CLEANING SUPER-HYDROPHOBIC SURFACES







APPLICATION OF CARBON NANOTUBES



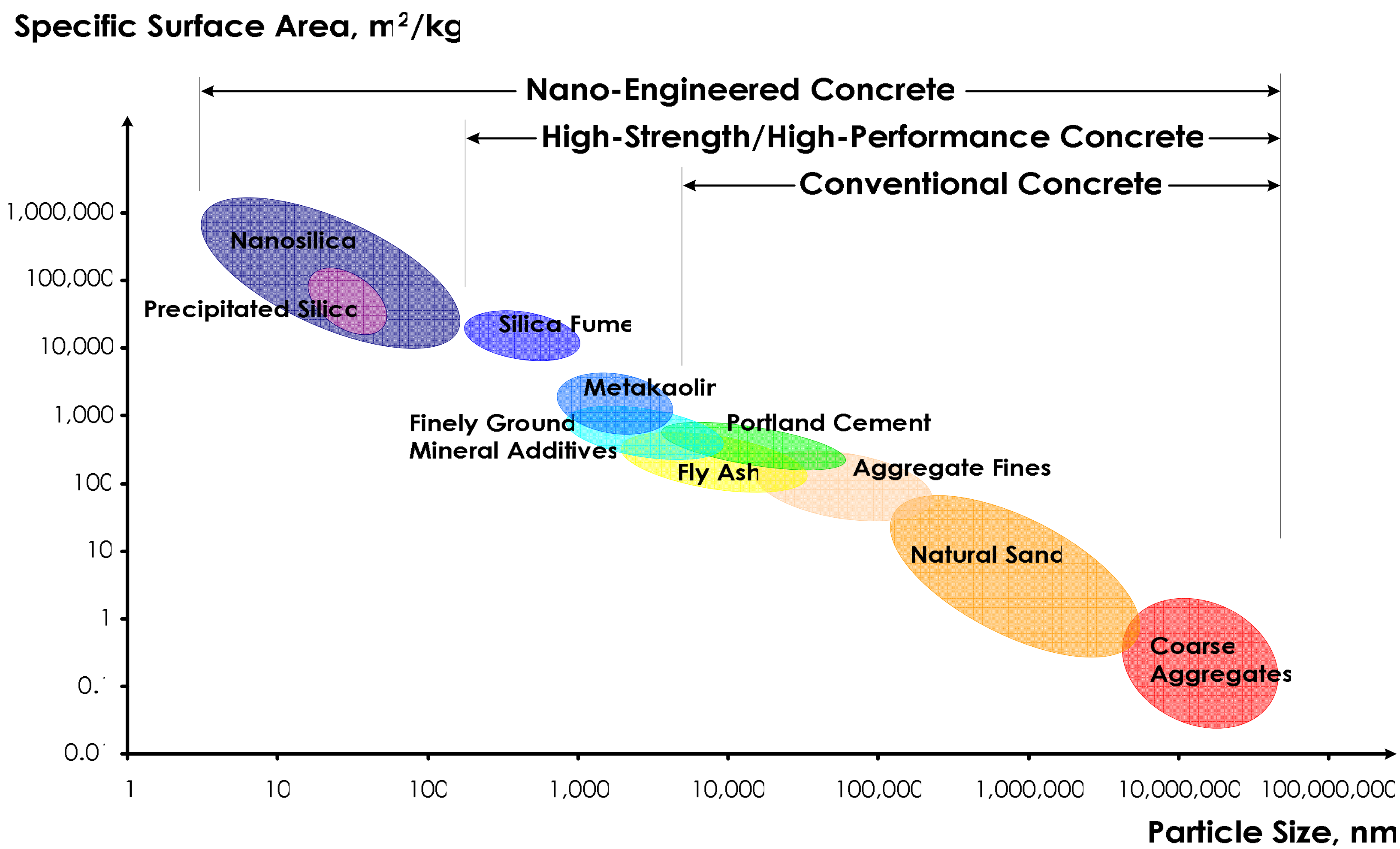
“Ultimate” reinforcing material:
- E ~ 1 TPa, UTS > 80 GPa
- 7-10% elastic deformation
- Very high electrical and thermal conductivity
- Very quick crack interruption

Applications:
- Ultrahigh performance concrete: bridges, pre-stressed structures, blast resistant structures, power plants, dams
- Repair materials

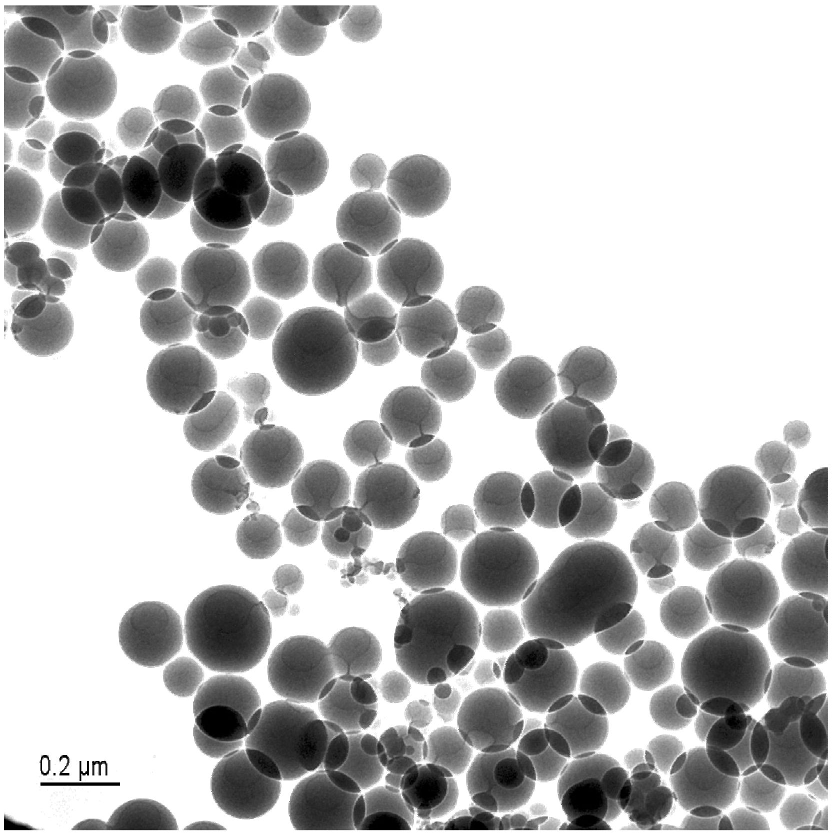
APPLICATION OF NANOPARTICLES

- When nanoparticles are incorporated into conventional building materials, such materials can possess advanced or smart properties required for the construction of high-rise, long-span or intelligent civil and infrastructure systems.

PARTICLE SIZE SCALE RELATED TO CONCRETE



APPLICATION OF NANOPARTICLES



Nanosilica under TEM

For example, silicon dioxide nanoparticles (or nanosilica) can be used as an additive for high-performance and self-compacting concrete improving workability and strength of concrete.

courtesy of Dr. Andri Vital,
EMPA Materials Testing and Research

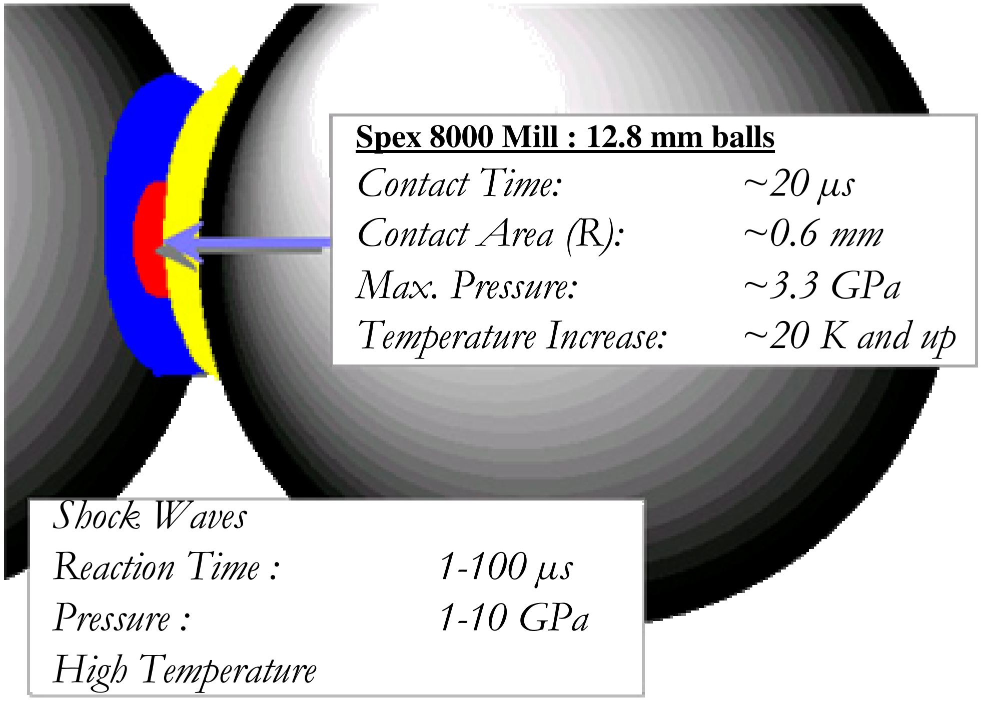
NANO-ENGINEERED CONCRETE

Research profile:

- high-performance cement composites
- mechano-chemical activation of cement
- design of nano-additives for cement
- eco-materials for utilization of industrial by-products
- advanced additives for cement and concrete
- investigation of rheology
- packing of particulate composites

MECHANO-CHEMICAL ACTIVATION

MECHANO-CHEMICAL ACTIVATION OF CEMENT

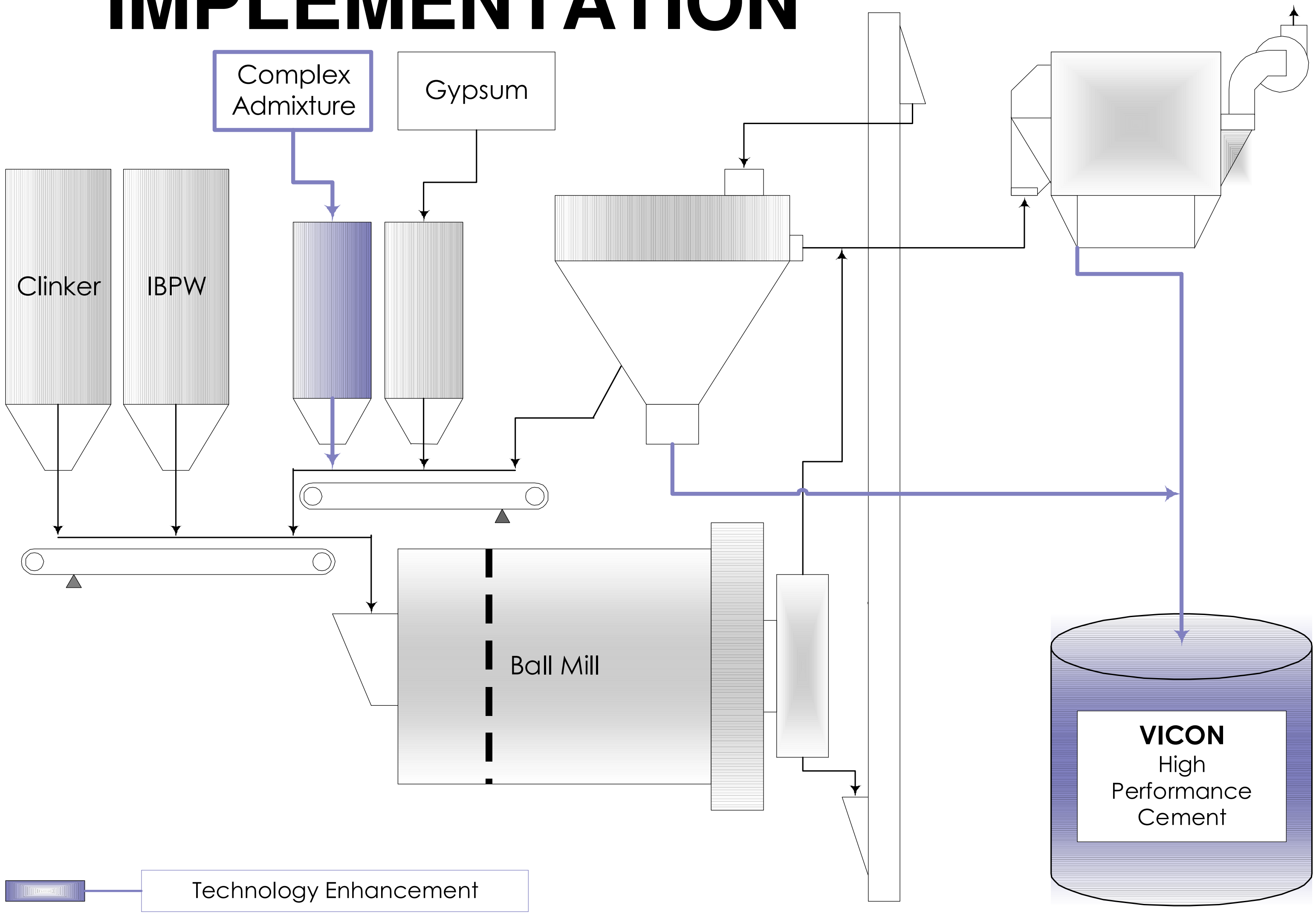


<u>Mechanism of Mechanically Induced Solid State Reactions</u>

The mechanical processing usually results in the formation of dislocations and other defects in the structure of the material.

In case of mechano-chemical activation, the mechanical impacts cause the development of elastic, plastic, and shear deformations leading to fracture, amorphization, and even chemical reactions in the solid state.

TECHNOLOGICAL IMPLEMENTATION



MATERIALS USED

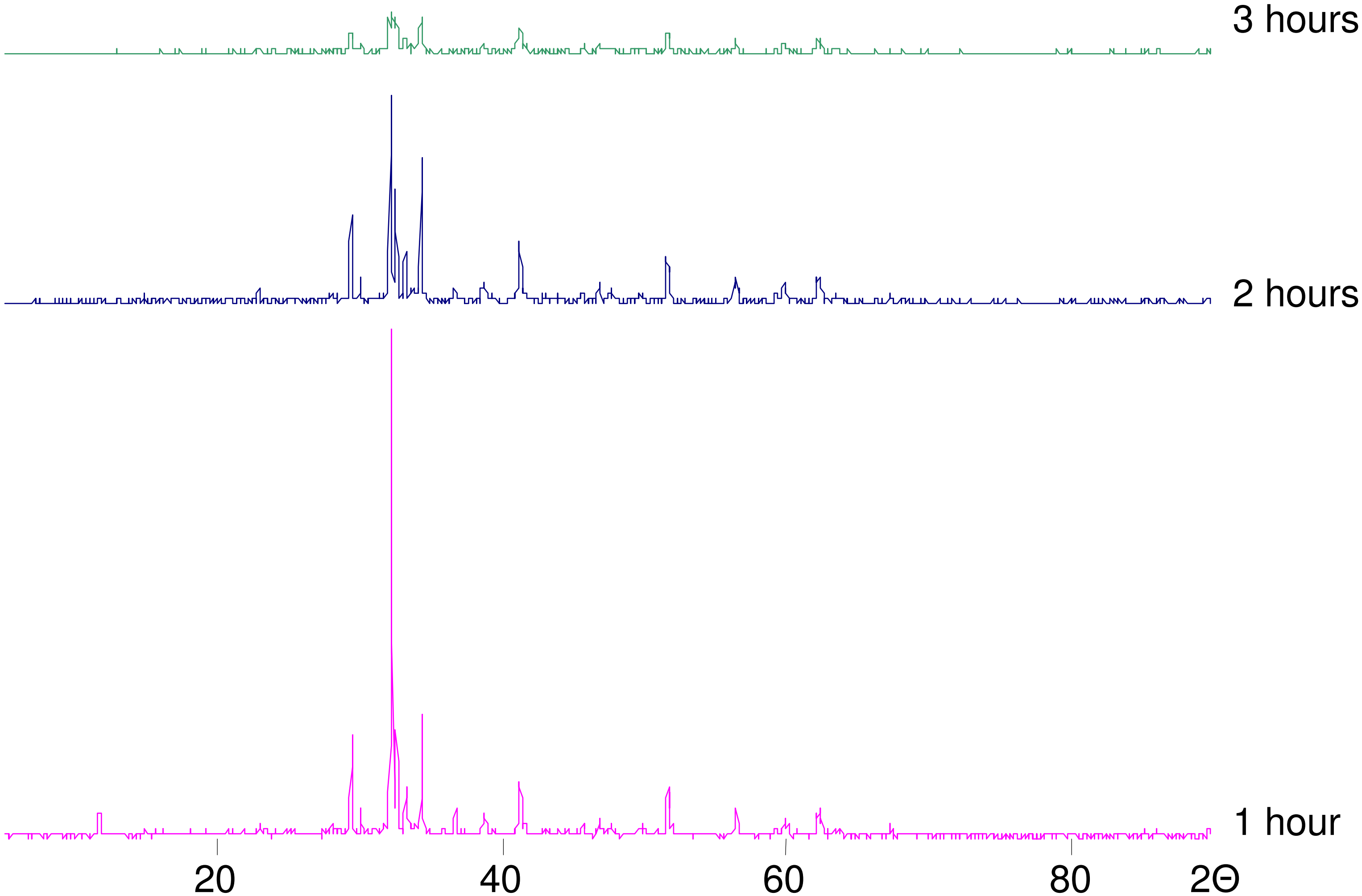
Composition, %	Silica Fume	Clinker	Gypsum
SiO_2	94.6	20.5	1.1
Al_2O_3	0.5	5.4	0.3
Fe_2O_3	1.1	1.9	0.1
CaO	1.1	65.8	38.5
MgO	0.3	1.7	0.1
SO_3	0.3	2.5	42.7
Na_2O	0.1	0.4	0.0
K_2O	0.4	1.2	0.1
TIO_2	0.0	0.2	0.0
P_2O_5	0.0	0.1	0.0
Mn_2O_3	0.0	0.0	0.0
SrO	0.0	0.1	0.1
LOI	1.6	0.2	16.9

MIXTURE PROPORTIONING

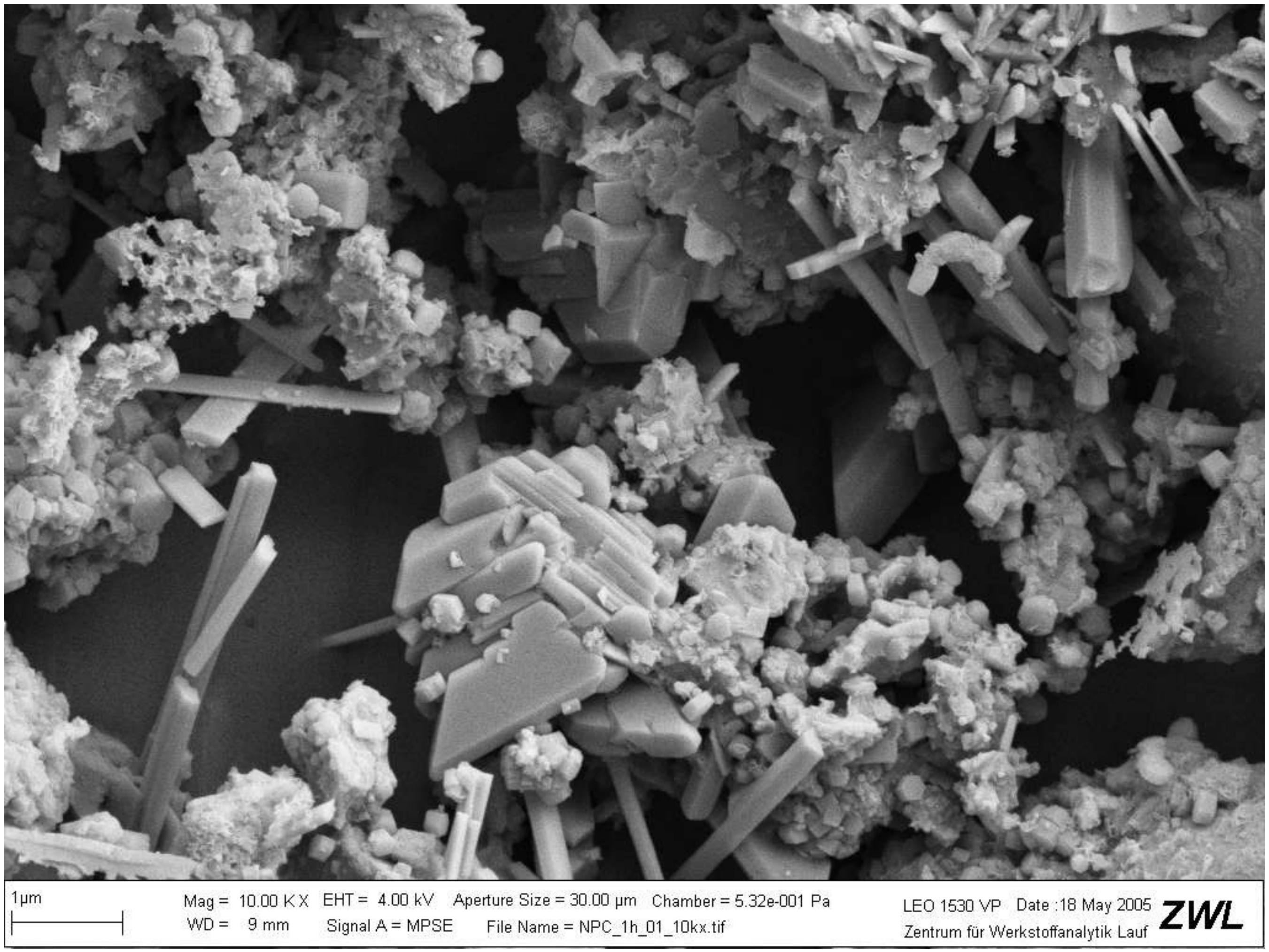
Composition	Portland Cement	SF Cement	HPC (SNF)	HPC (SMF)	HPC (PAE)
Clinker	96	88	88	88	88
Gypsum	4	4	4	4	4
Silica Fume	-	8	6.2	6.2	6.2
Water	-	-	1.2	1.2	1.2
SNF	-	-	0.6	-	-
SMF	-	-	-	0.6	-
PAE	-	-	-	-	0.6

EFFECT OF GRINDING: surface amorphization

HPC-N



CEMENT HYDRATION AT NANO-LEVEL



Portland Cement – hydration for 1 hour

CEMENT HYDRATION AT NANO-LEVEL

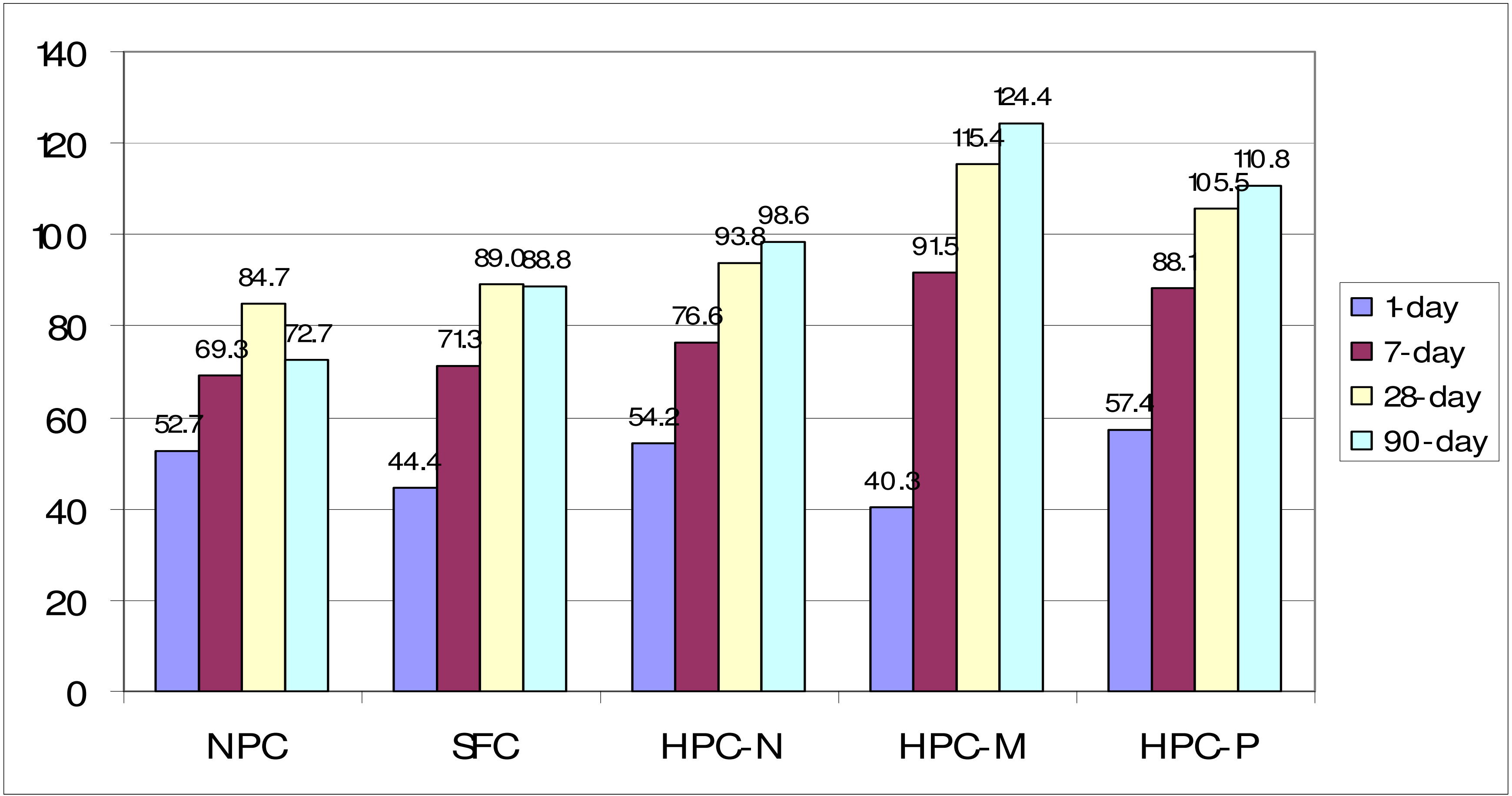
High-Performance Cement – hydration for 1 hour

MORTAR PROPORTIONING

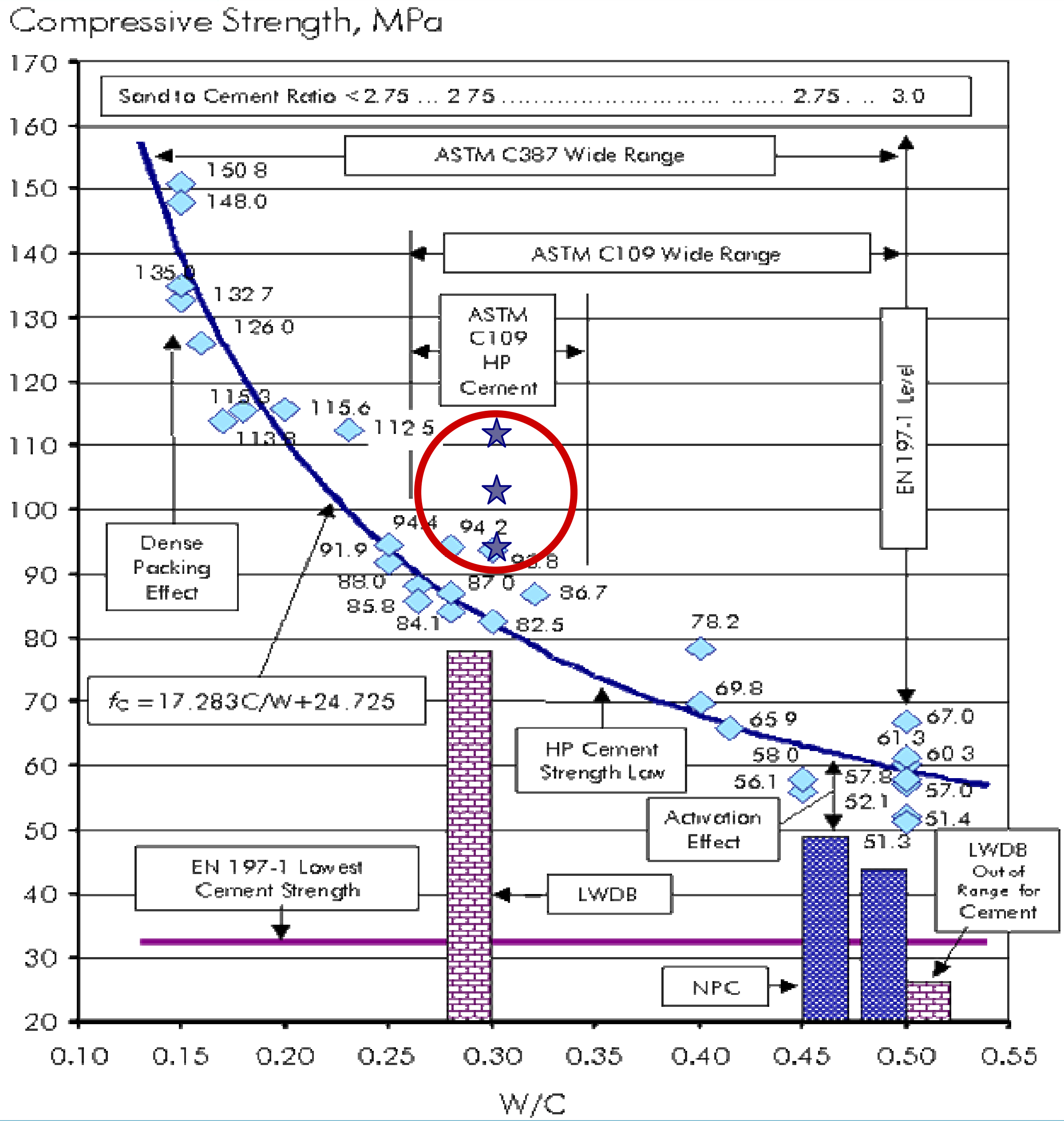
- Sand-to-cement ratio equal to 1
- Water-to-cement ratio equal to 0.3

STRENGTH DEVELOPMENT

Compressive Strength, MPa



LAW
of
W/C


Compressive Strength, MPa
Sand to Cement Ratio < 2.75 ... 2.75 ...... 2.75 ... 3.0
ASTM C387 Wide Range
ASTM C109 Wide Range
ASTM C109 HP Cement
EN 197.1 Level
150.8
148.0
135.0
132.7
126.0
115.3
115.6
113.3
112.5
94.4
94.2
93.8
91.9
88.0
87.0
86.7
85.8
84.1
82.5
78.2
69.8
65.9
67.0
61.3
60.3
58.0
57.8
57.0
56.1
52.1
51.4
51.3
Dense Packing Effect
$f_c = 17.283C/W + 24.725$
HP Cement Strength Law
Activation Effect
EN 197-1 Lowest Cement Strength
LWDB
LWDB Out of Range for Cement
NPC
W/C

CONCRETE WITH NANOPARTICLES

SYNTHESIS OF NANO-PARTICLES: SOL-GEL METHOD

- Sol-gel synthesis involves the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel).
- Usually, tetraethoxysilane (TEOS) is applied as precursors for synthesis of nanosilica.
- Sol-gel process can be simplified to four stages:

  - Hydrolysis;
  - Condensation and polymerization of monomers;
  - Growth of particles;
  - Agglomeration of particles, followed by the formation of networks and, subsequently, gel structure.

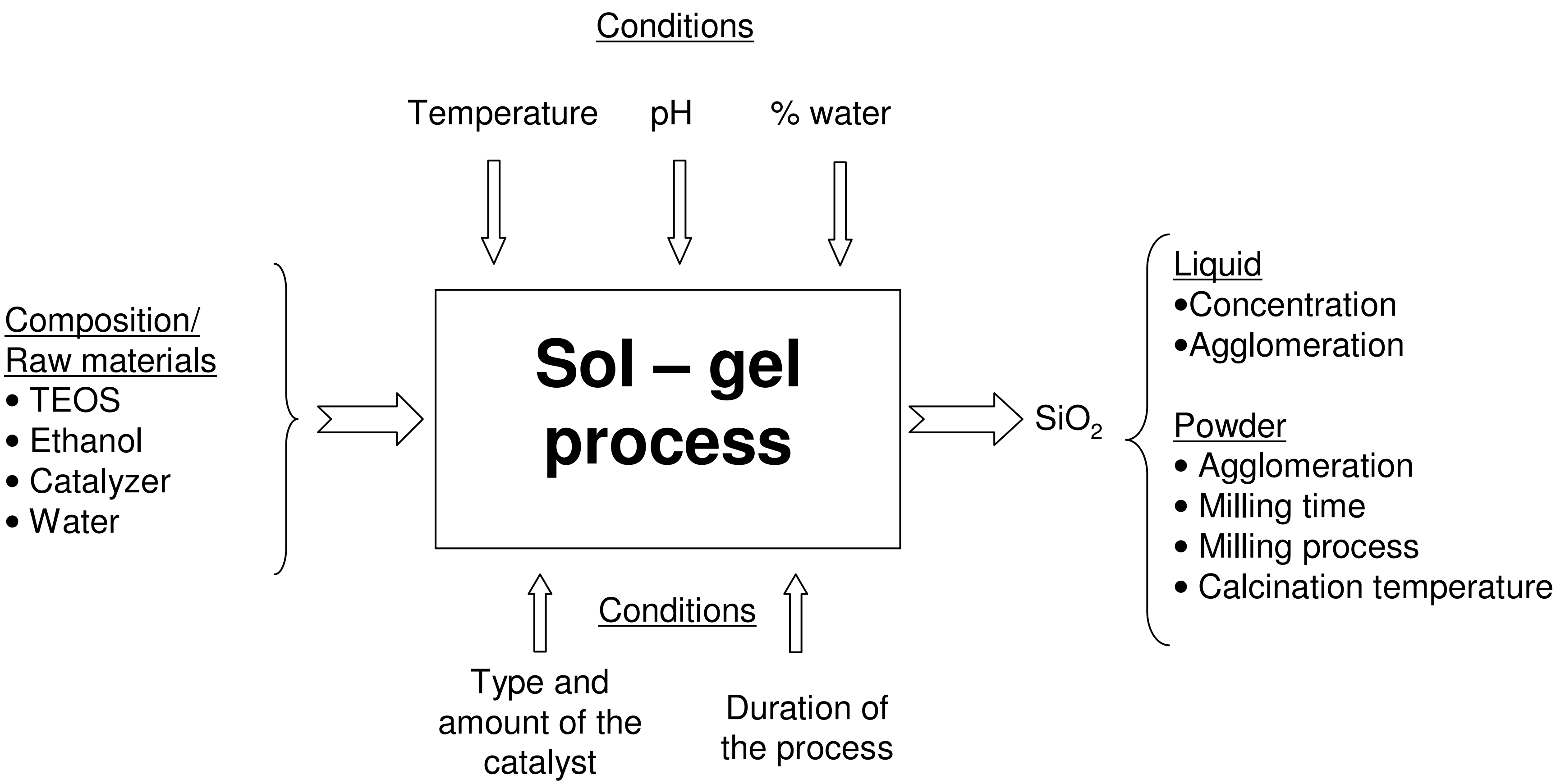
SYNTHESIS OF NANO-PARTICLES: SOL-GEL METHOD

- The chemical reaction for synthesis of nanosilica can be summarized as following:

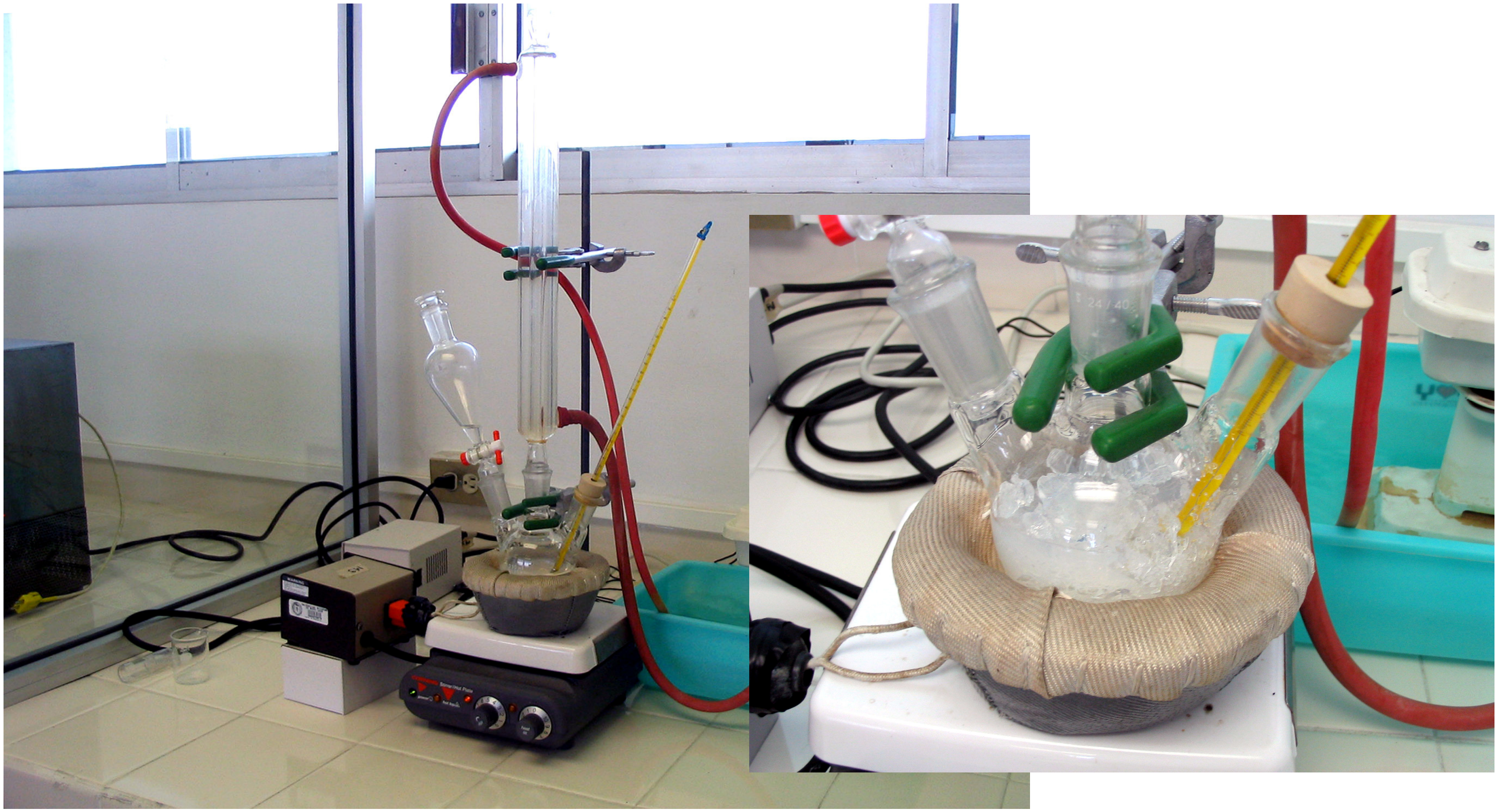
$$n\mathrm{Si(OC_2H_5)_4} + 2n\mathrm{H_2O} \xrightarrow[\mathrm{NH_3}]{\mathrm{C_2H_5OH}} n\mathrm{SiO_2} + 4n\mathrm{C_2H_5OH}$$

- There are a number of parameters affecting the process including pH (must be more than 7), temperature, concentration of reagents, H_2O/Si molar ratio (between 7 and 25), type of catalyst.
- When precisely executed, this process is capable of producing perfectly spherical nanoparticles of SiO_2 within the size range of 1-100 nm.

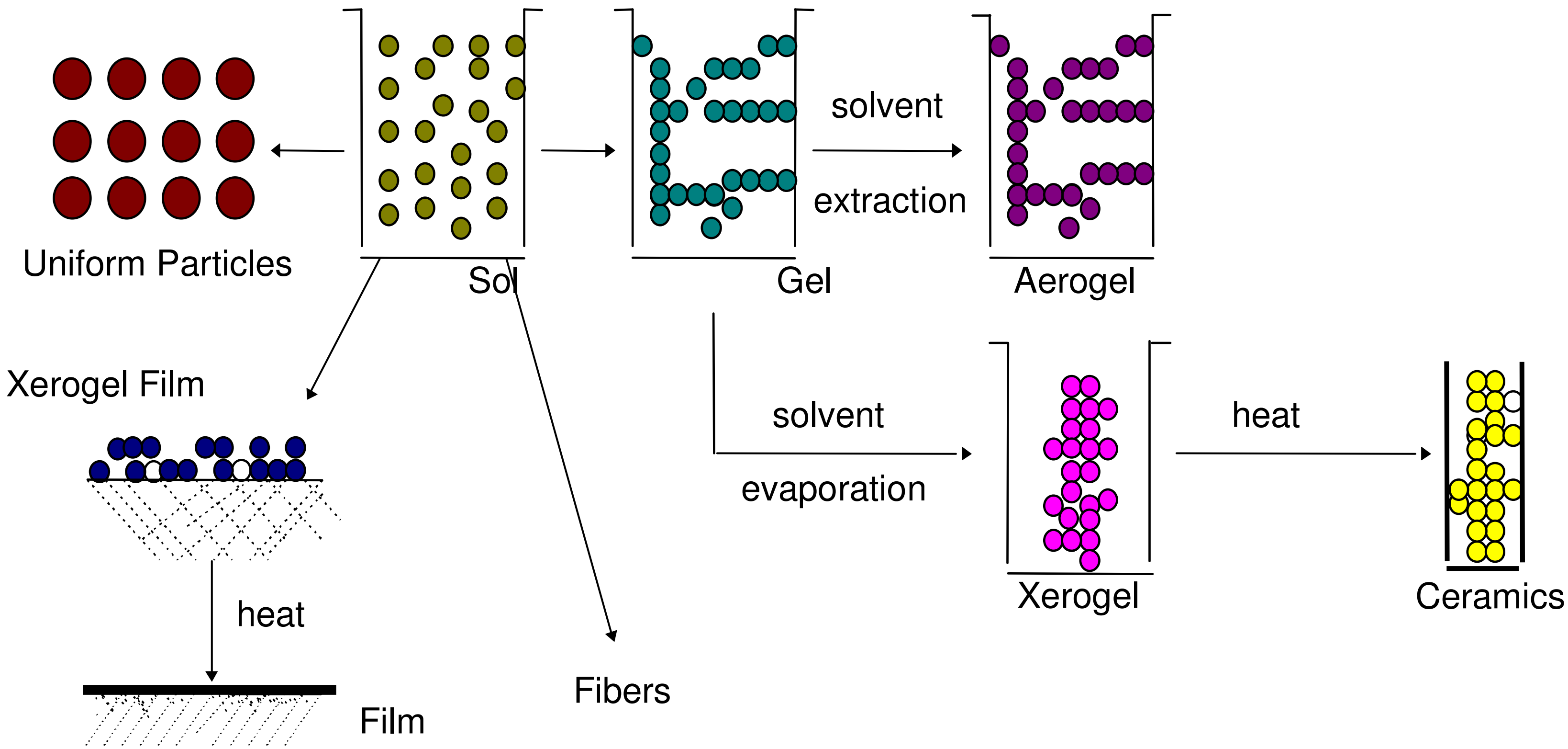
SOL-GEL METHOD: EXPERIMENTAL SETUP



SOL-GEL METHOD: EXPERIMENTAL SETUP



SOL-GEL METHOD: PRODUCTS RANGE

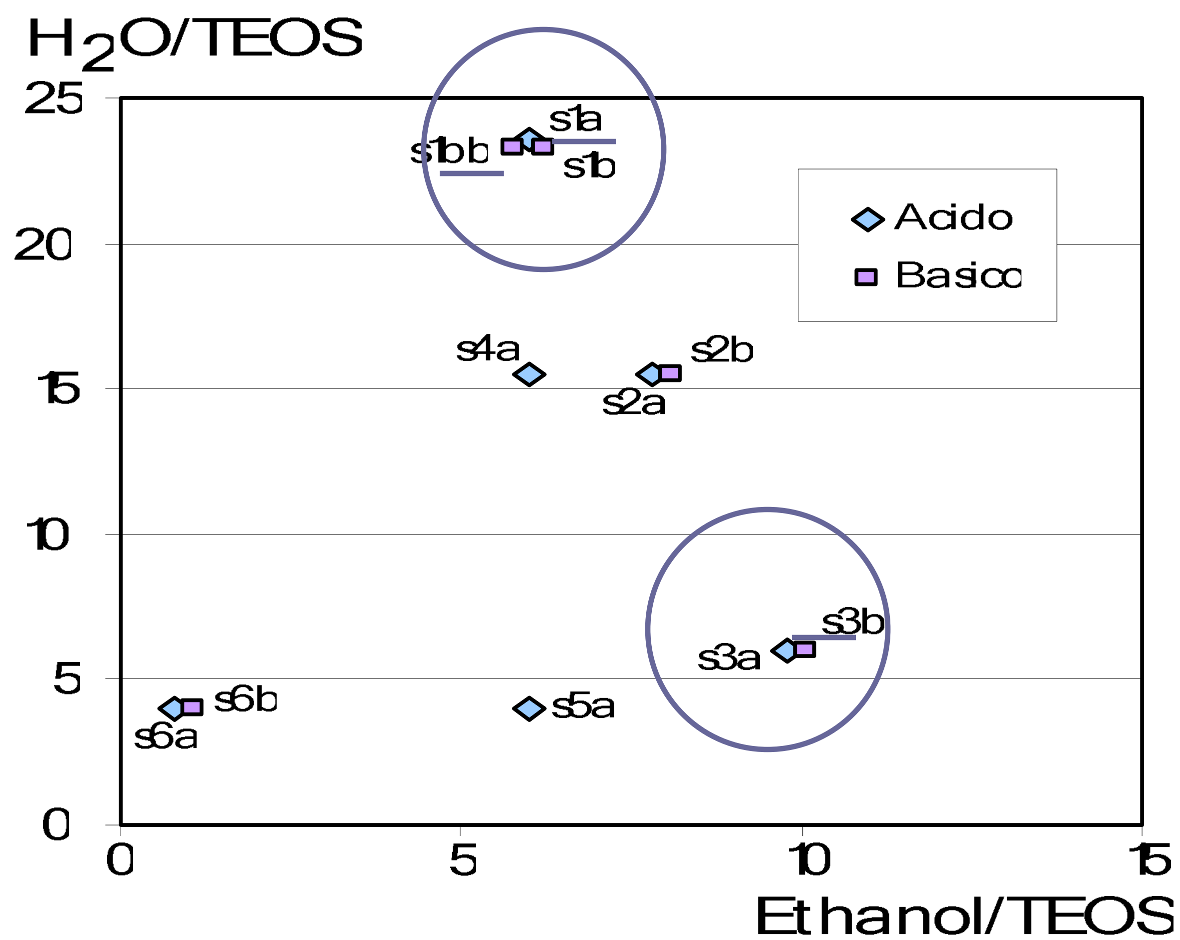


SOL-GEL METHOD: REACTION CONDITIONS

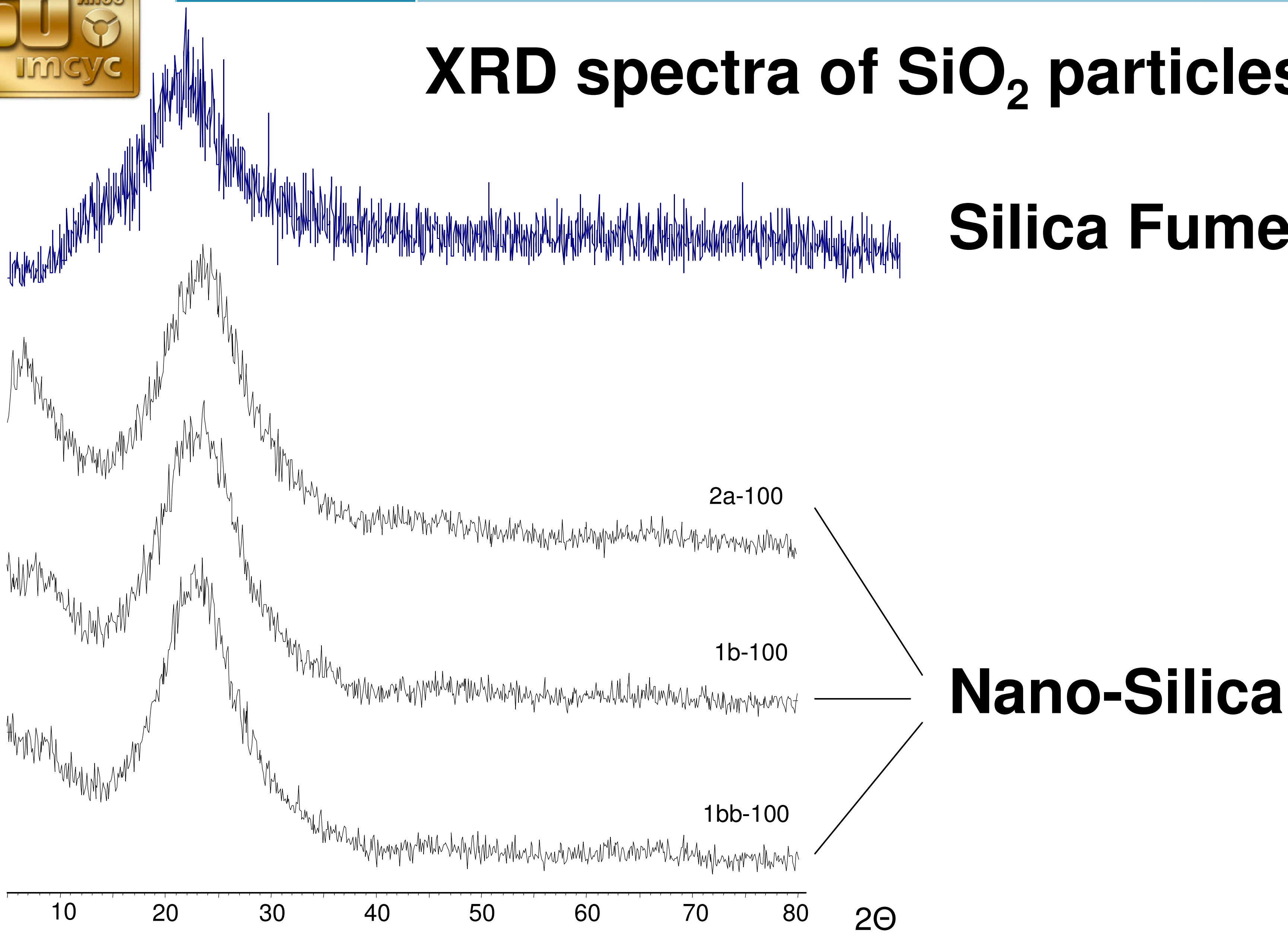
No.	Code	TEOS Etanol H2O	Catalyzer	Temperature ° C	Size of Cristallyte nm	Pore Size nm	BET Area m^2/kg
1	No. S 1b	1/ 6 / 23.25	Base	100	1.7	-	-
2	No. S 1bb	1/ 6 / 23.25	Base	100	1.8	-	27,000
				400	1.1	1	510,000
				600	1.0	4	482,000
				800	1.2	5	80,000
3	No. S 1a	1/ 6 / 23.25	Acid	100	1.7	-	-
4	No. S 2a	1/ 8 / 15.5	Acid	100	1.3	-	-
5	No. S 2b	1/ 8 / 15.5	Base	100	1.6	-	-
6	No. S 3a	1 / 10 / 6	Acid	100	1.2	-	-
7	No. S 3b	1 / 10 / 6	Base	100	2.5	-	-
8	No. S 4a	1 / 6 / 15.5	Acid	100	1.5	-	-
9	No. S 5a	1 / 6 / 4	Acid	100	1.7	-	-
10	No. S 6a	1 / 1 / 4	Acid	100	1.4	-	-
11	No. S 6b	1 / 1 / 4	Base	100	1.1	-	-

- Basic: Ammonia (NH4OH, Ammonium Hydroxide)
- Acidic: Nitric Acid (HNO_3)

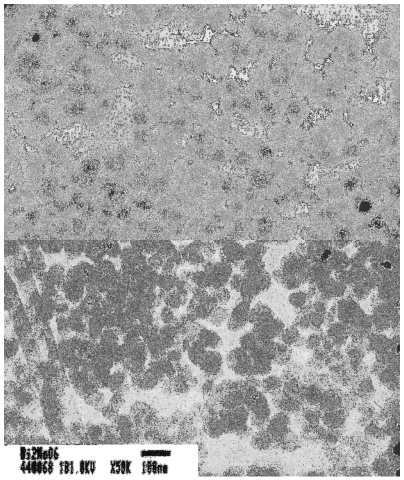
SOL-GEL METHOD: EXPERIMENTAL SETUP

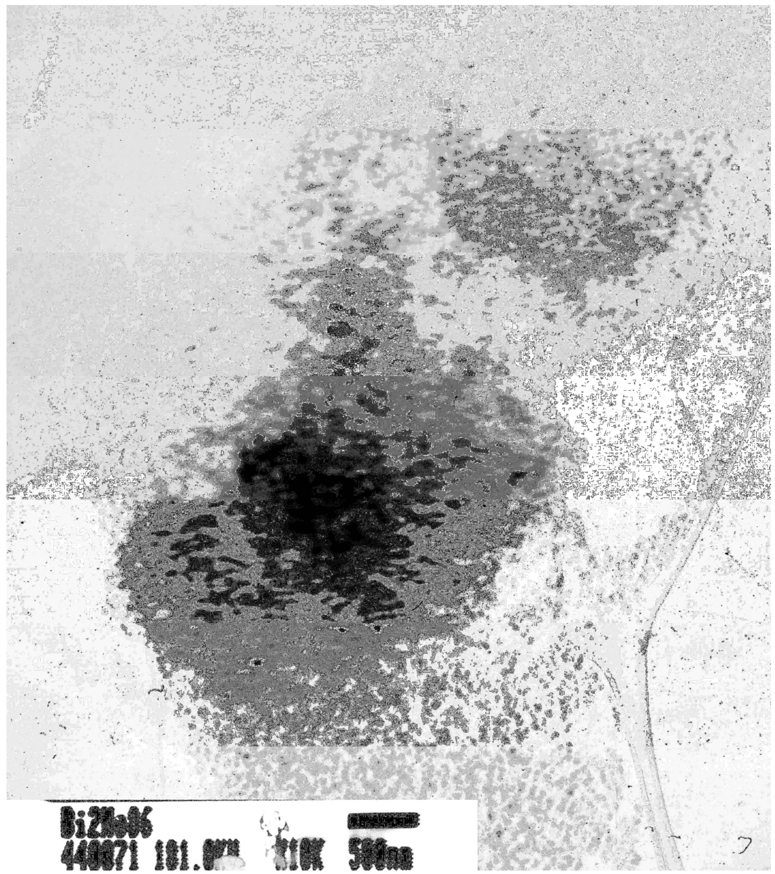


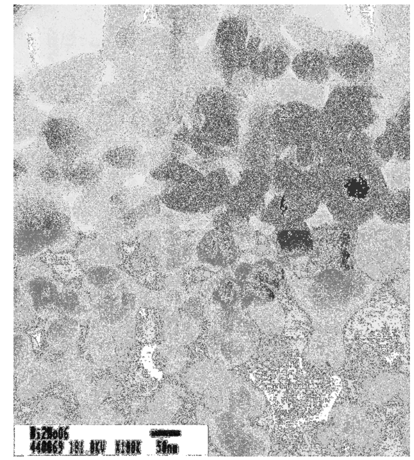
XRD spectra of SiO_2 particles

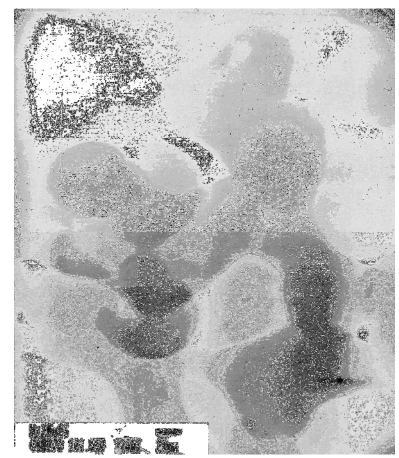


NANOPARTICLES OF SiO_2 UNDER TEM



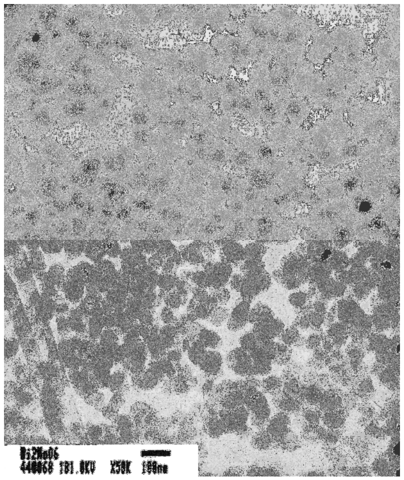


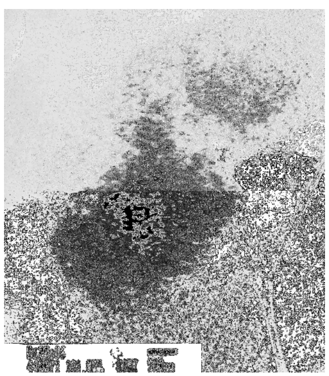


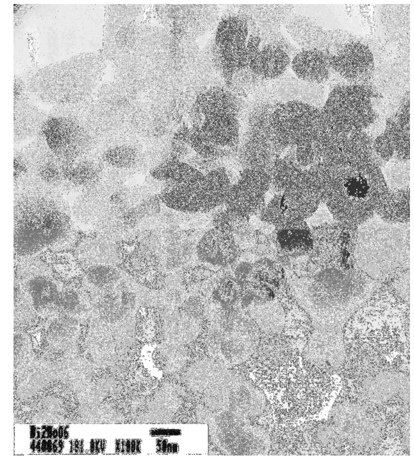


Nano-Silica
Sample 1bb

NANOPARTICLES OF SiO_2 UNDER TEM







Nano-Silica Sample 1bb

SOL-GEL METHOD: EXPERIMENTAL SETUP

Composition

- Portland cement (Type I)
- Standard sand
- Superplastizicer (PAE)
- SiO_2 (sol-gel)
- Silica fume

Water / cementitious materials

Sand / cementitious materials

MORTARS

Type and amount of superplastizicer

Type and amount of SiO_2

Mechanical Behavior
- Compressive strength
- Flexural strength

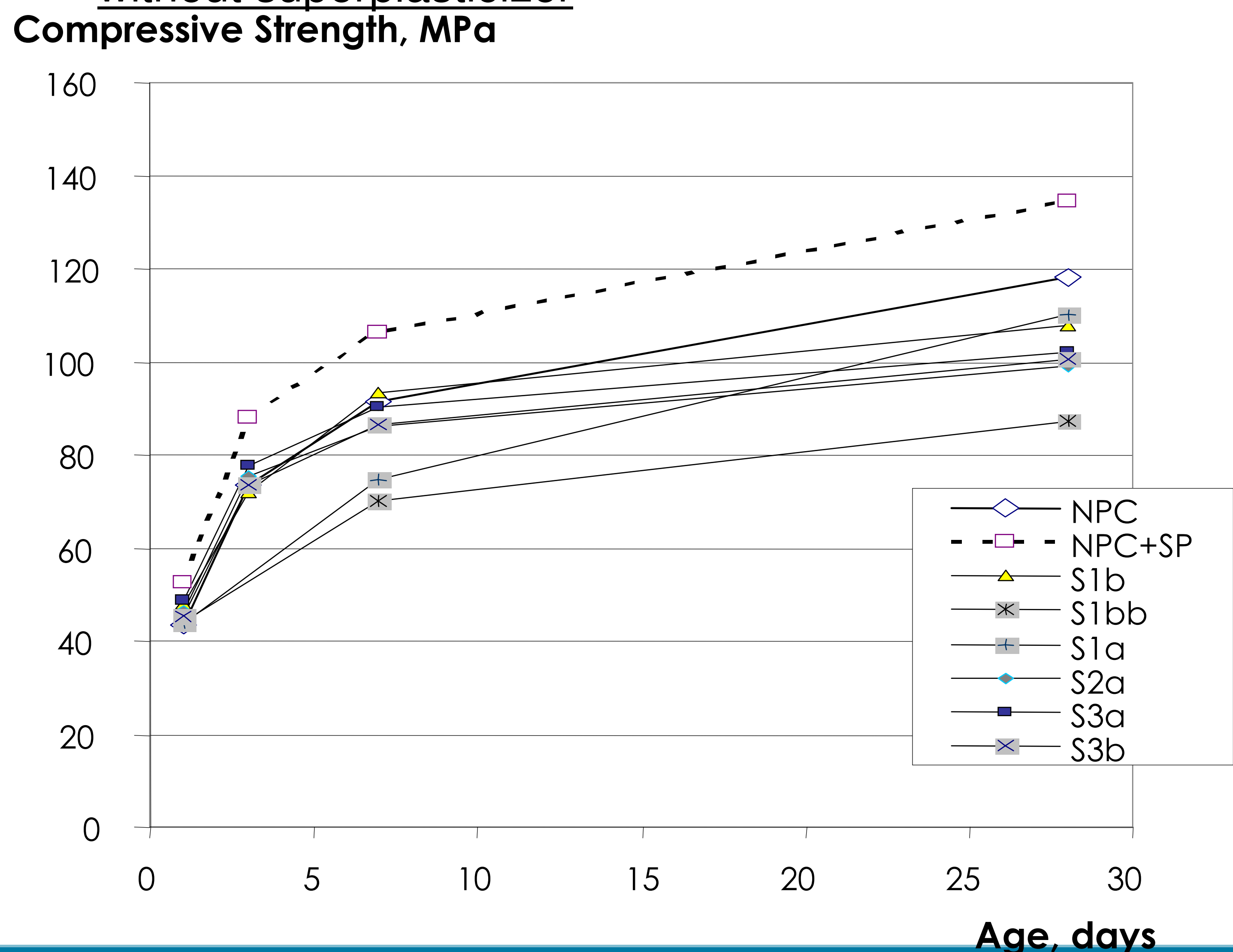
Rheological Behavior
Flow

MORTAR PROPORTIONING

- Sand-to-cement ratio equal to 1
- Water-to-cement ratio equal to 0.295
- Nano-SiO_2 dosage 0.25%
- Superplasticizer dosage 0.1% (to keep the flow of 200%)

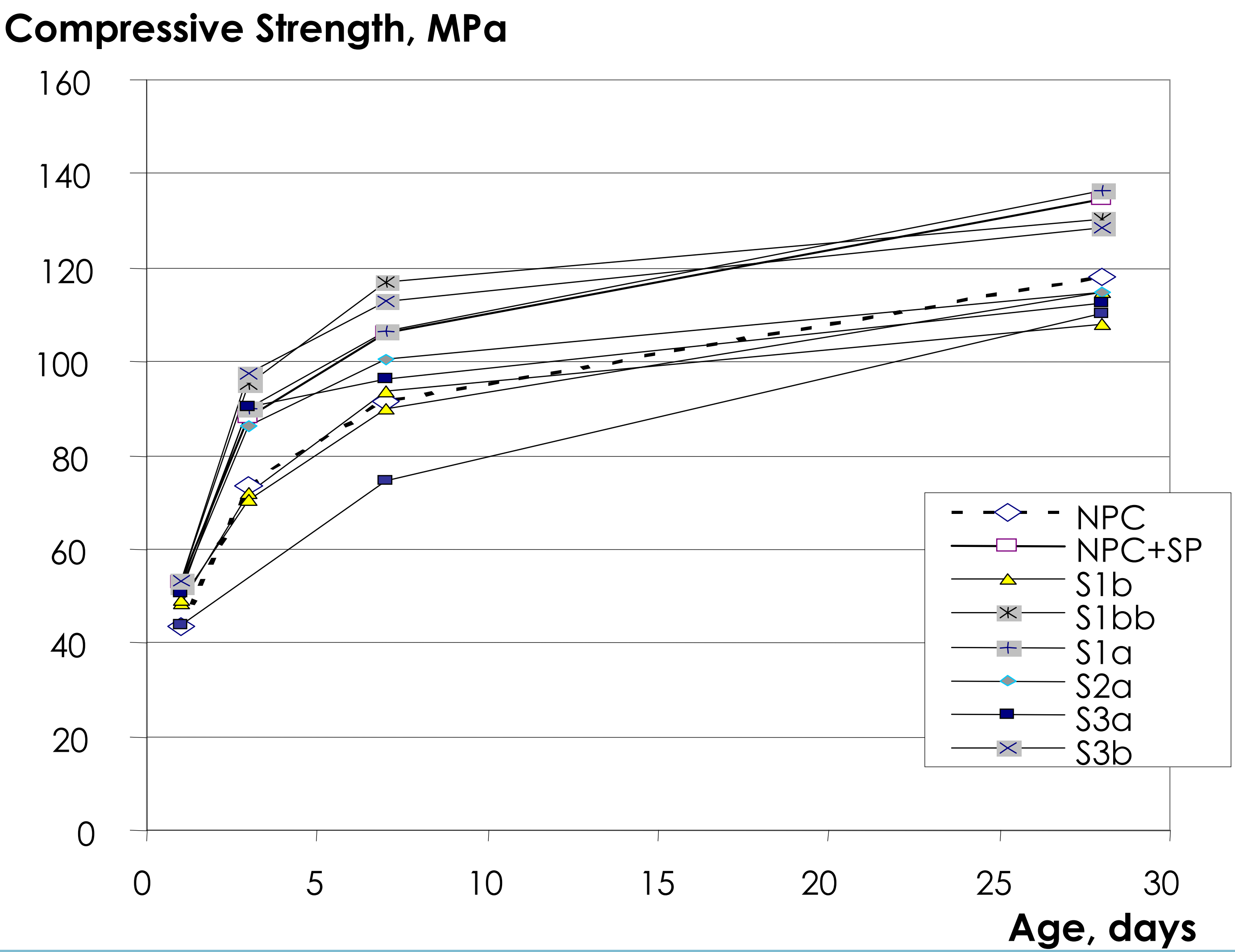
STRENGTH DEVELOPMENT:

without superplasticizer

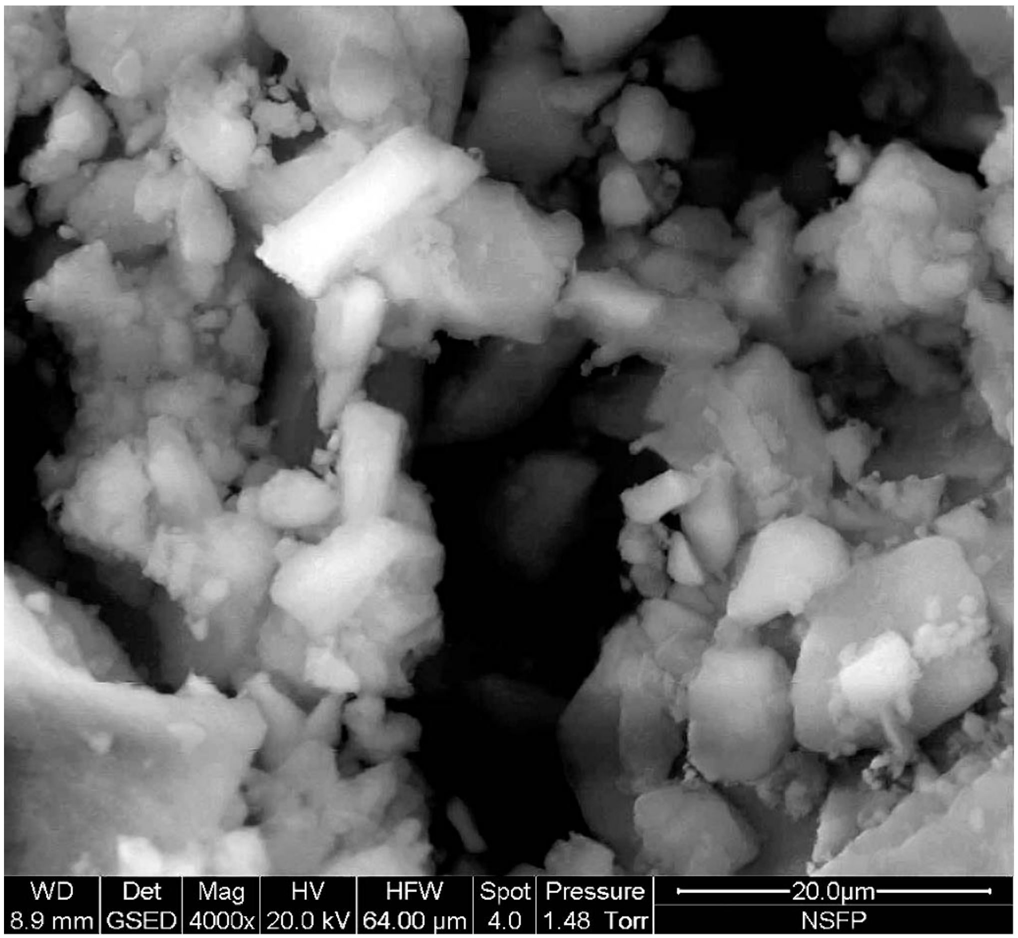


STRENGTH DEVELOPMENT:

with superplasticizer



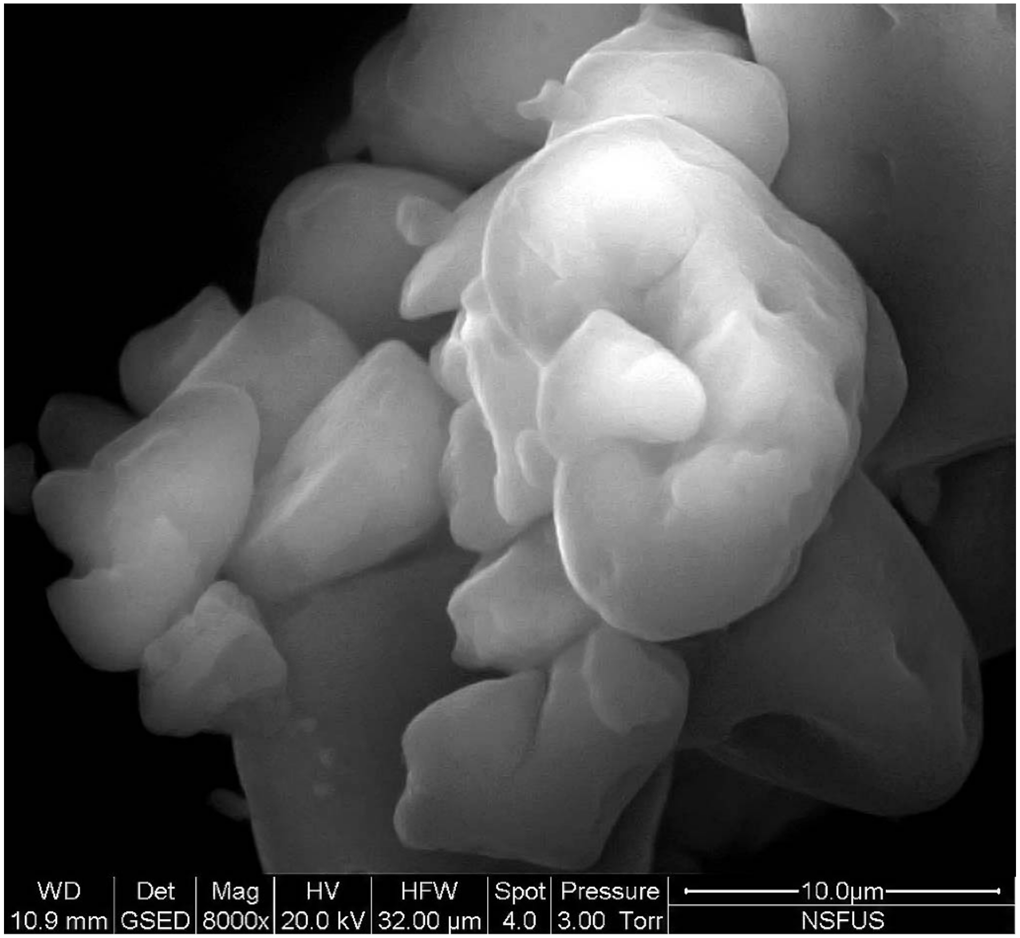
NANOPARTICLES OF SiO_2



Agglomerates of Nano-Silica after drying

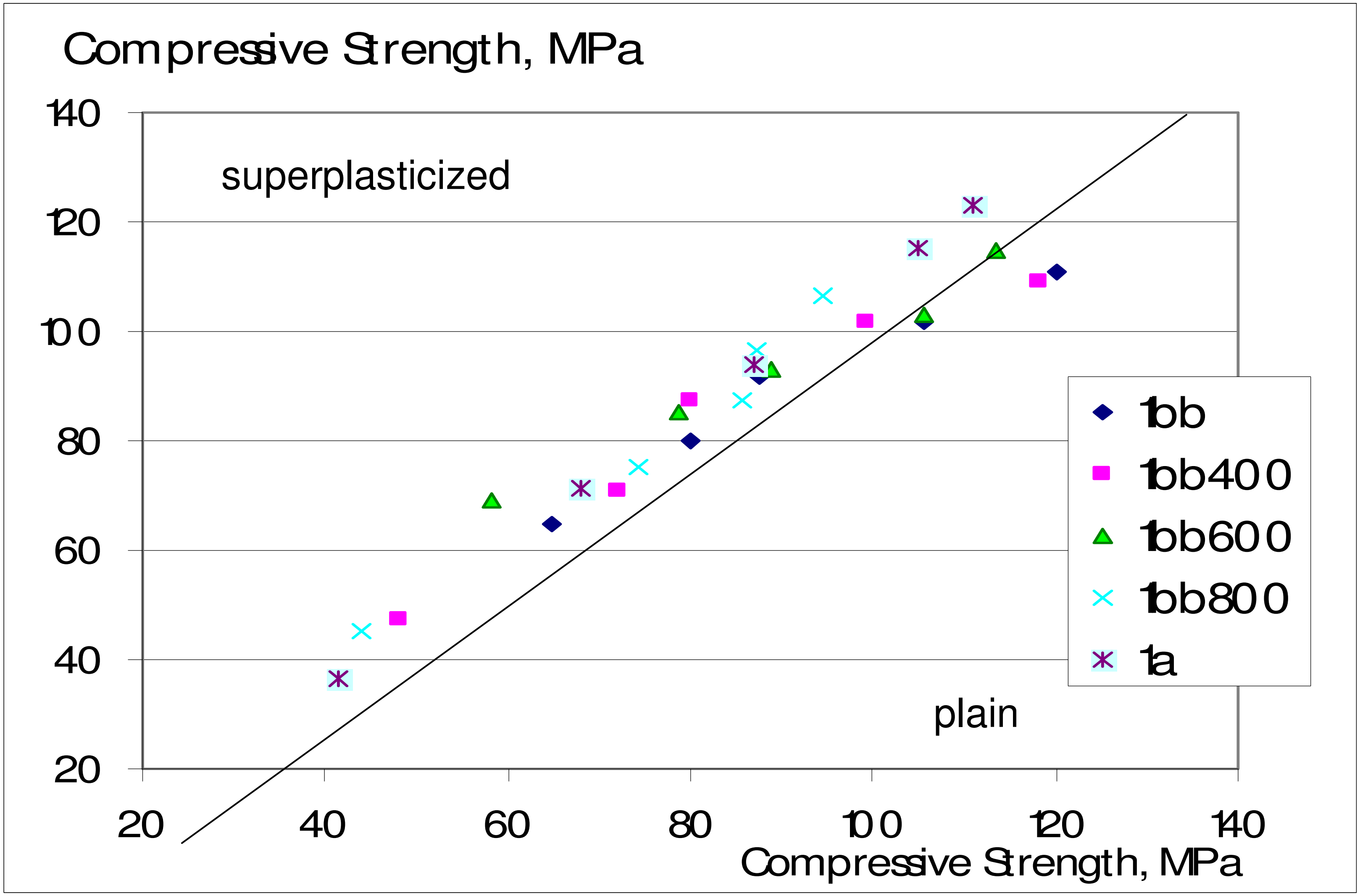
NANOPARTICLES OF SiO_2

Agglomerates of Nano-Silica after ultrasonification



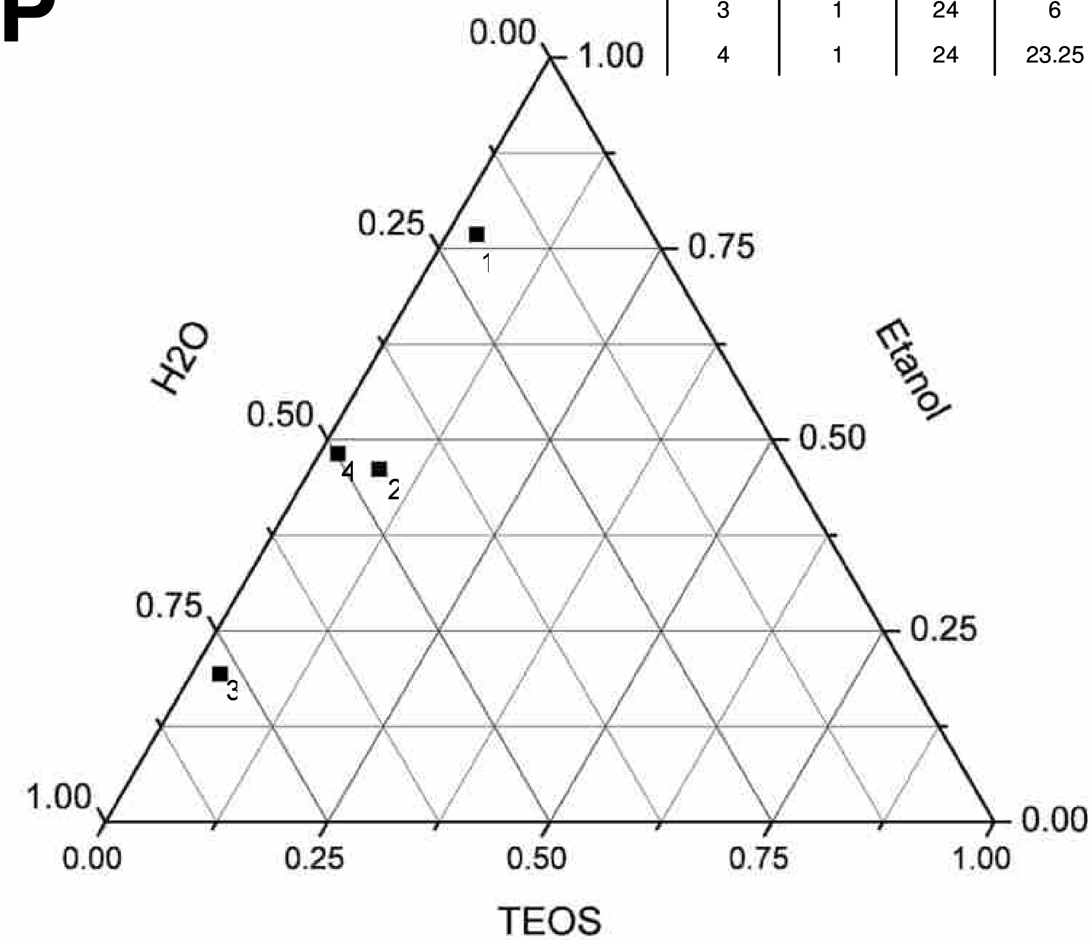
STRENGTH DEVELOPMENT:

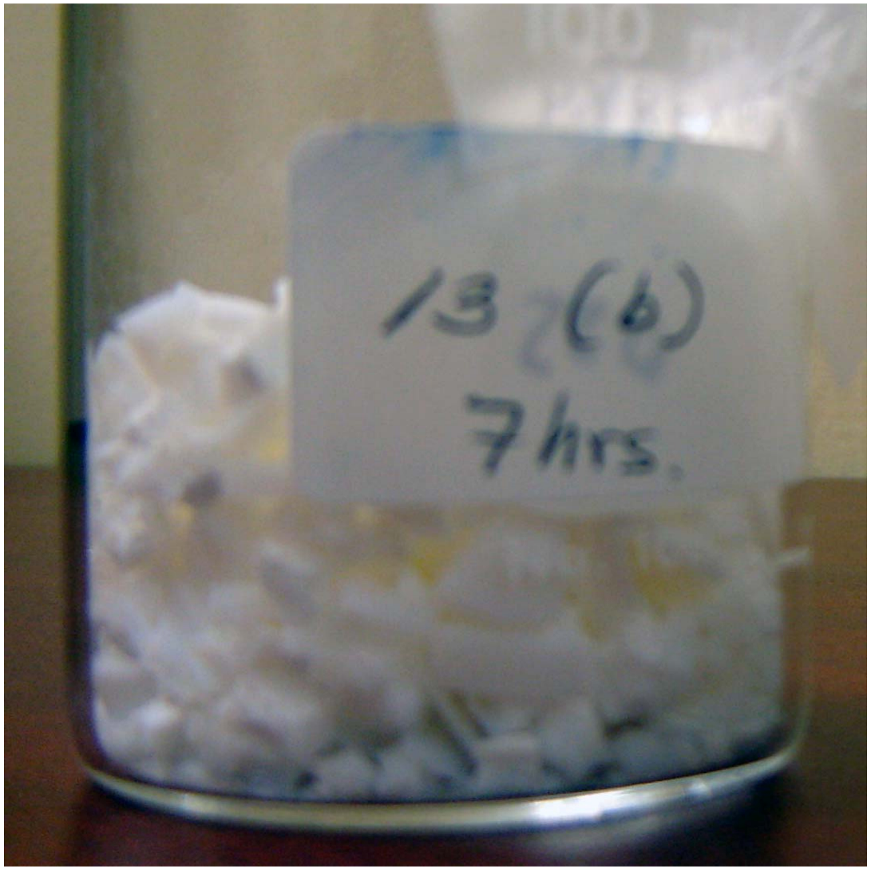
effect of ultrasonification

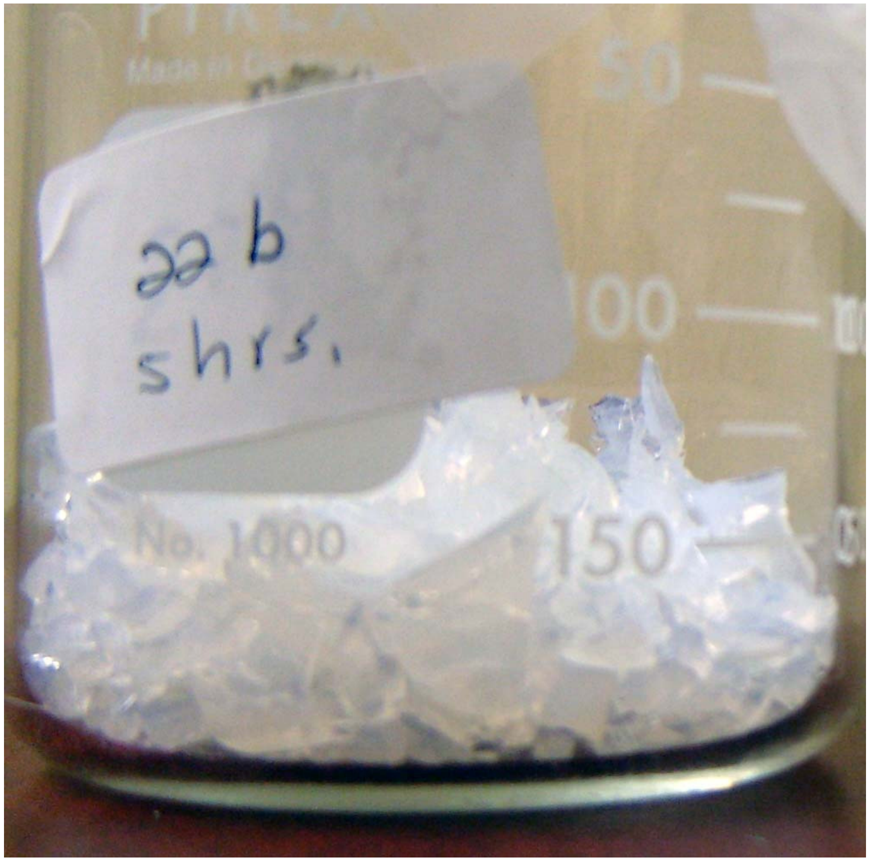


EXPERIMENTAL SETUP

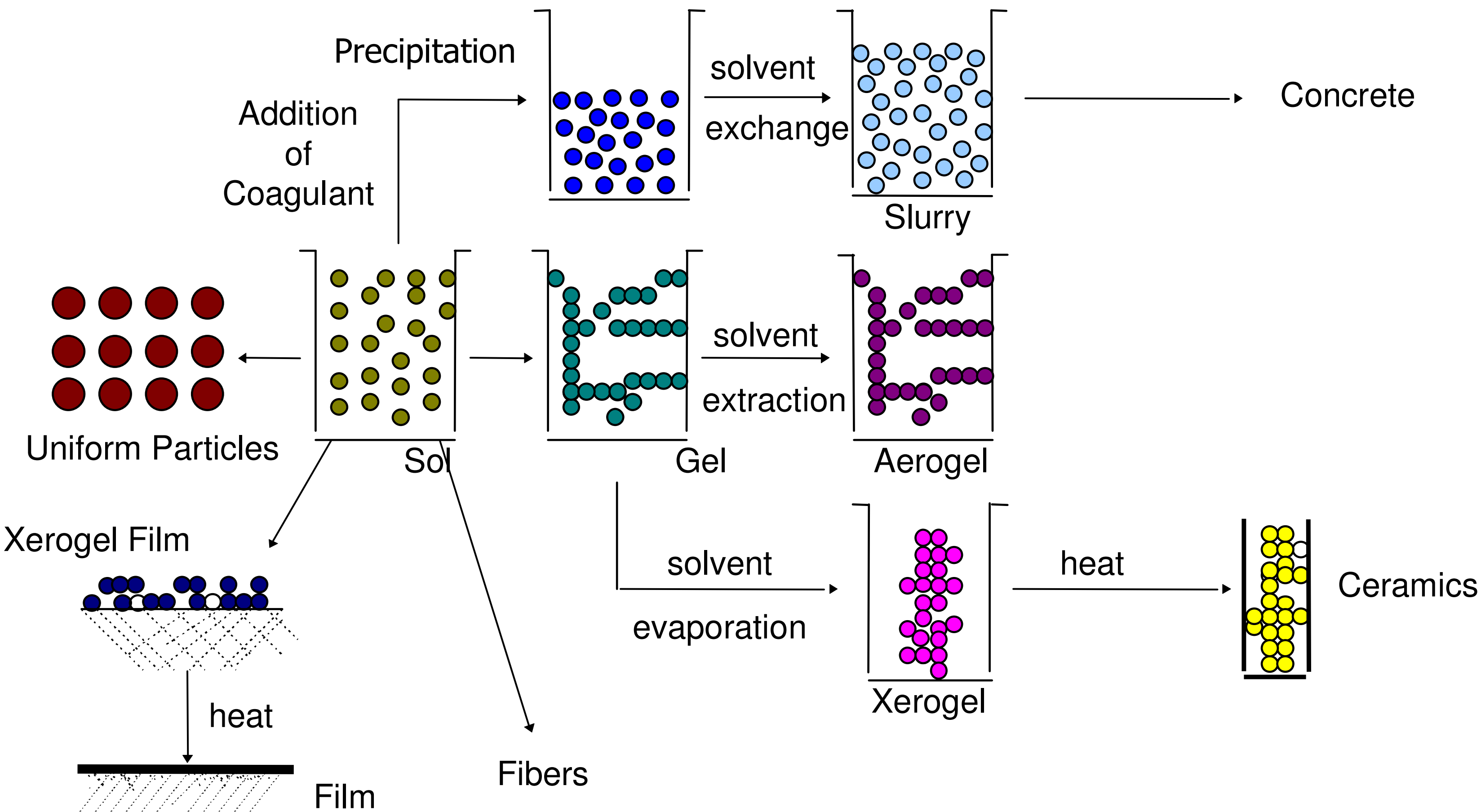
No.	Relación molar			% Relación molar		
	TEOS	H_2O	Etanol	TEOS	H_2O	Etanol
1	1	6	23.25	3.31	19.83	76.86
2	1	6	6	7.69	46.15	46.15
3	1	24	6	3.23	77.42	19.35
4	1	24	23.25	2.07	49.74	48.19



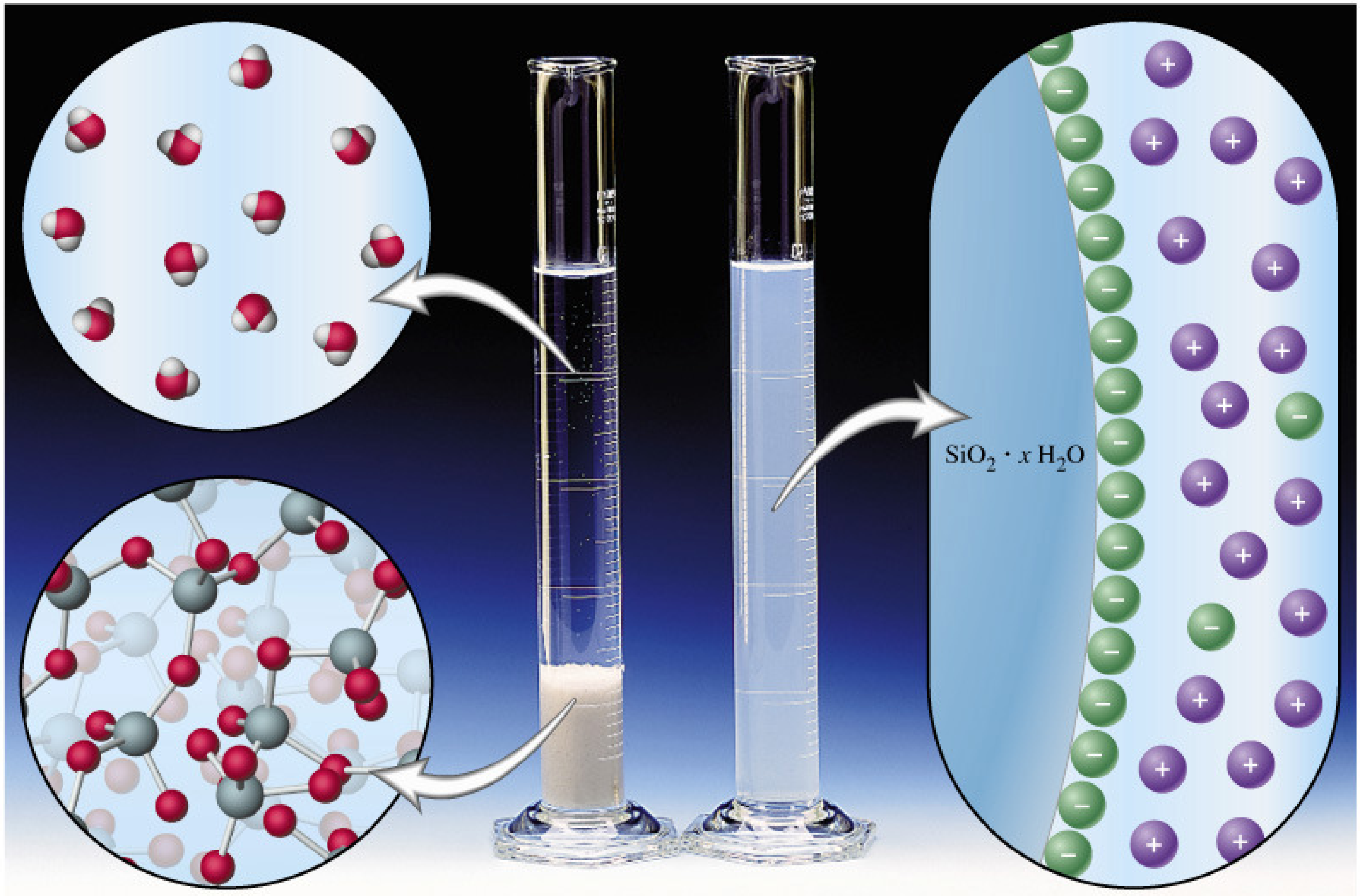

13 (b)
7 hrs.


22 b
No. 1000
50
150

SOL-GEL METHOD: THE NEXT STEP



FROM MACRO TO NANO



THE POSITIVE EFFECT OF NANOPARTICLES

- Well-dispersed nano-particles increase the viscosity of the liquid phase helping to suspend the cement grains and aggregates, improving the segregation resistance and workability of the system;
- Nano-particles fill the voids between cement grains, resulting in the immobilization of “free” water (“filler” effect);
- Well-dispersed nano-particles act as centers of crystallization of cement hydrates, therefore accelerating the hydration;

THE POSITIVE EFFECT OF NANOPARTICLES

- Nano-particles favor the formation of small-sized crystals of $Ca(OH)_2$, AFm and uniform clusters of C-S-H;
- Nano-SiO_2 participates in the pozzolanic reactions, resulting in the consumption of $Ca(OH)_2$ and formation of an “additional” C-S-H;
- Nano-particles improve the structure of the aggregates’ contact zone, resulting in a better bond between aggregates and cement paste;
- Crack arrest and interlocking effects between the slip planes provided by nano-particles improve the toughness, tensile and flexural strength of cement based materials.

CONCLUSIONS

- Mechano-chemical activation of cement, nano-binders and nano-engineered cement based materials with nano-sized cementitious component or other nano-sized particles may be the next ground-breaking development.
- Nanotechnology is still in its pre-exploration stage; it is just emerging from fundamental research onto the industrial floor and thus the full-scale construction applications are very limited. But the potential of nanotechnology to improve the performance of construction materials and processes is most promising.

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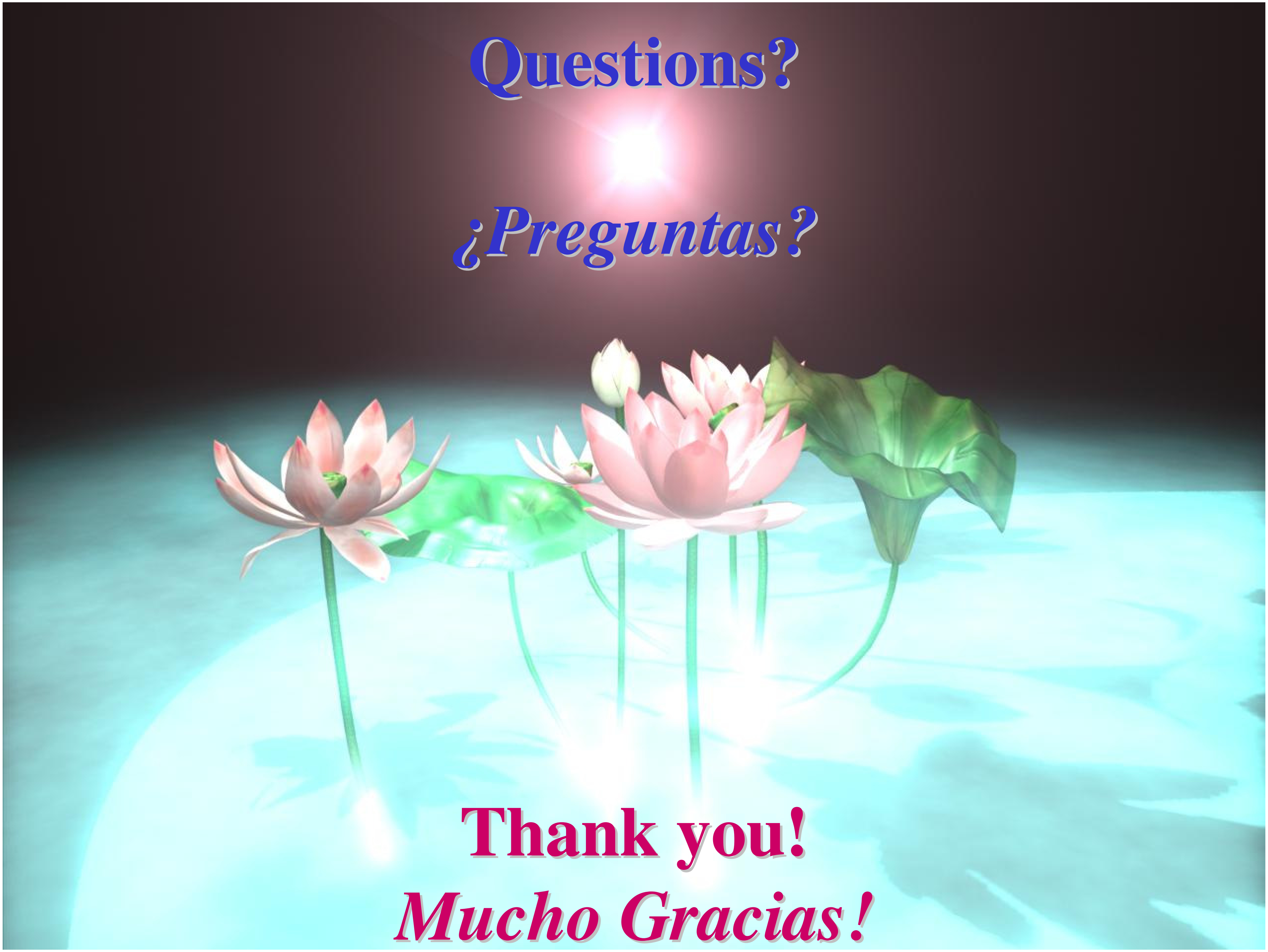
Questions?
¿Preguntas?
Thank you!
Mucho Gracias!