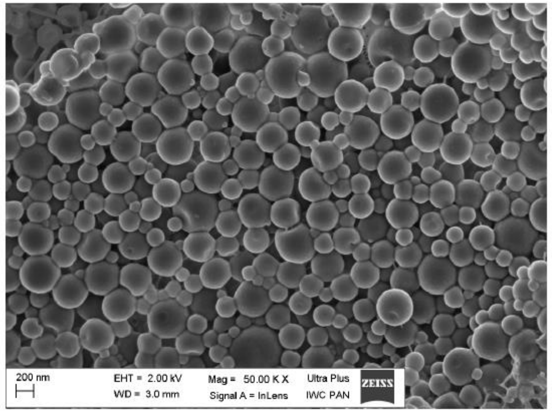
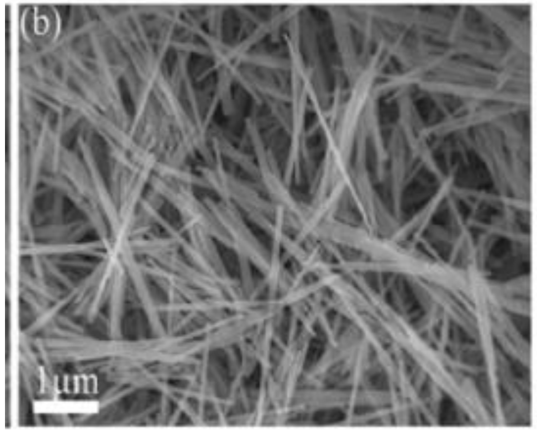
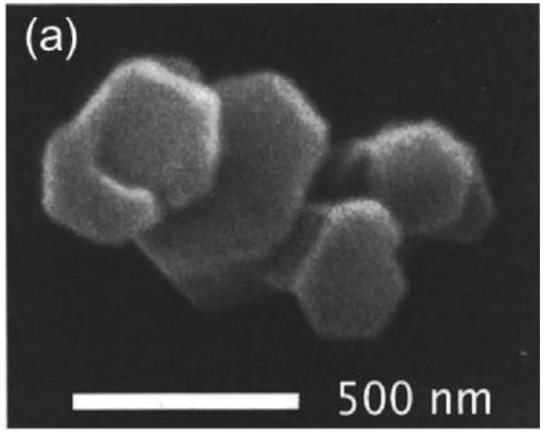
CaO

Nanomateriali nell'industria dei cementi e per la sostenibilità ambientale







Paola Comodi

Dipartimento di Fisica e Geologia

Università di Perugia

COLACEM

Perché i cementi ?

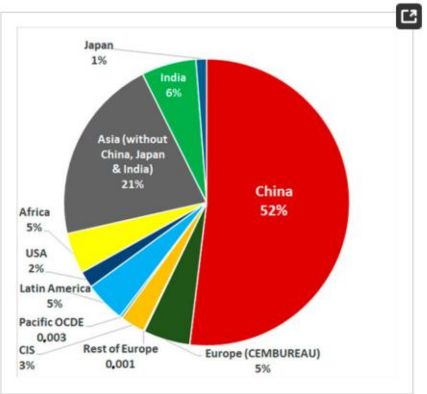
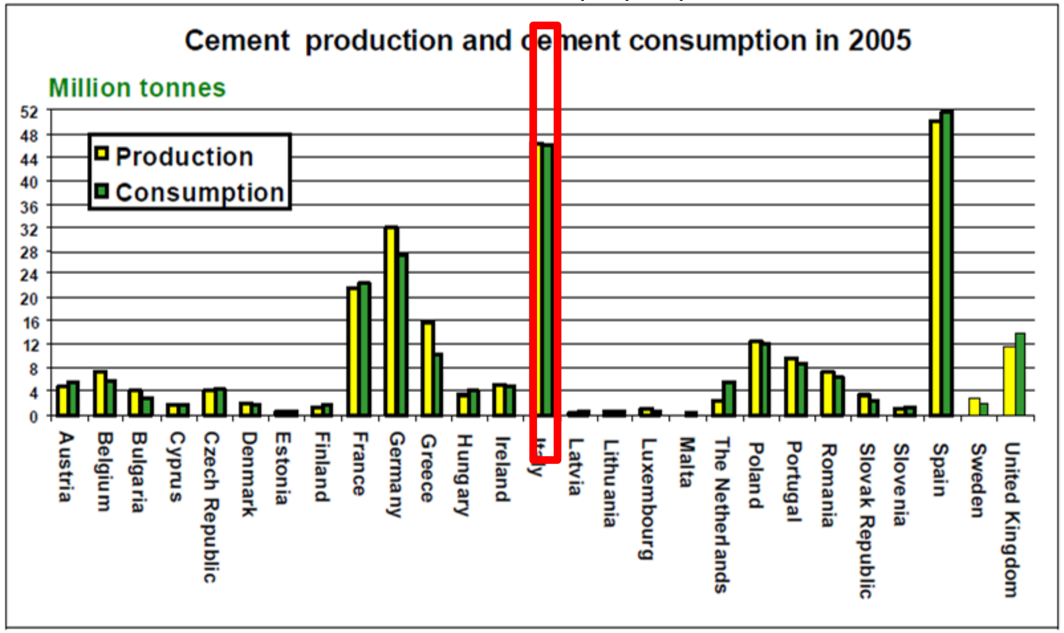


Figure 2. World cement production in 2016 by region and main countries (4.65 billion tons) [10].

concrete is ....

the most widely **used substance on the planet after water!!!!**

ITALIA → **Seconda** nazione in Europa per produzione e consumo di cemento



ITALIA → **Tra le 18 nazioni al mondo** per produzione di cemento e portata di clinker (USGS Mineral Program Cement Report - February 2014)

World Production and Capacity:

	Cement production 2012	Cement production 2013[e]	Clinker capacity[e] 2012	Clinker capacity[e] 2013
United States (includes Puerto Rico)	74,900	77,800	106,000	105,000
Brazil	68,800	70,000	57,000	60,000
China	2,210,000	2,300,000	1,800,000	1,900,000
Egypt	46,100	46,000	46,000	46,000
Germany	32,400	34,000	31,000	31,000
India	270,000	280,000	270,000	280,000
Indonesia	32,000	35,000	47,500	50,000
Iran	70,000	75,000	75,000	80,000
Italy	33,000	29,000	46,000	46,000
Japan	51,300	53,000	55,000	55,000
Korea, Republic of	48,000	49,000	50,000	50,000
Mexico	35,400	36,000	42,000	42,000
Pakistan	32,000	32,000	42,500	42,000
Russia	61,500	65,000	80,000	80,000
Saudi Arabia	50,000	50,000	55,000	55,000
Thailand	37,000	35,000	50,000	50,000
Turkey	63,900	70,000	66,900	67,000
Vietnam	60,000	65,000	68,000	70,000
Other countries (rounded)	524,000	597,000	312,000	291,000
World total (rounded)	3,800,000	4,000,000	3,300,000	3,400,000

Perché i cementi ?

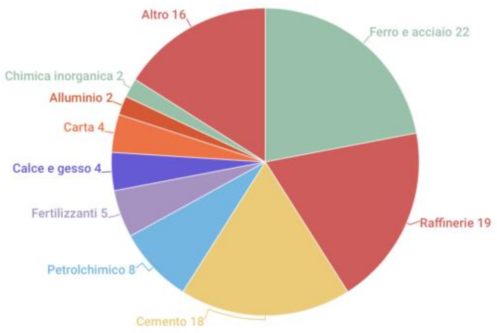
New global standards:

Infrastrutture ultrahigh performanti: aumento di

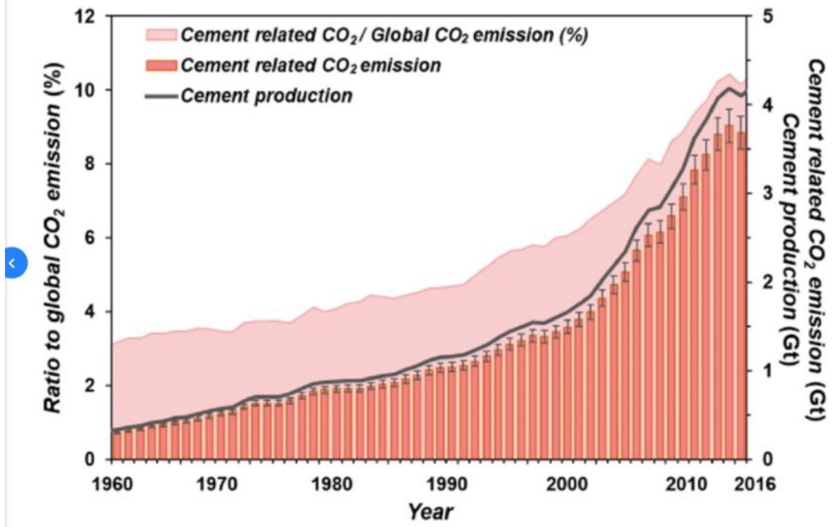
- Funzionalità
- Caratteristiche meccaniche,
- Resistenza a trazione
- Resistenza a sforzi di taglio
- Resistenza all'alterazione

Cementi green che riducano il consumo di energia e la produzione di CO_2

Dall-8-10 % della CO_2 di origine antropica nel mondo viene dalla manifatture del cemento
Rilasciata sia per il combustibile 220 kg di carbone per 1 ton cemento) sia per la de-carbonatazione delle materie prime



Percentuale di CO2 prodotta dai vari settori industriali in Europa



CO2 emissions related to the production of cement and its ratio to total CO2 emissions. Reproduced with permission from Thomas D. Kelly and Grecia R. Matos, Historical statistics for mineral and material commodities in the U.S.; published by the United States Geological Survey (USGS), 2015 [85].

Cementi rispondenti al new global standard

Che siano. ...

Più perfomanti però.....

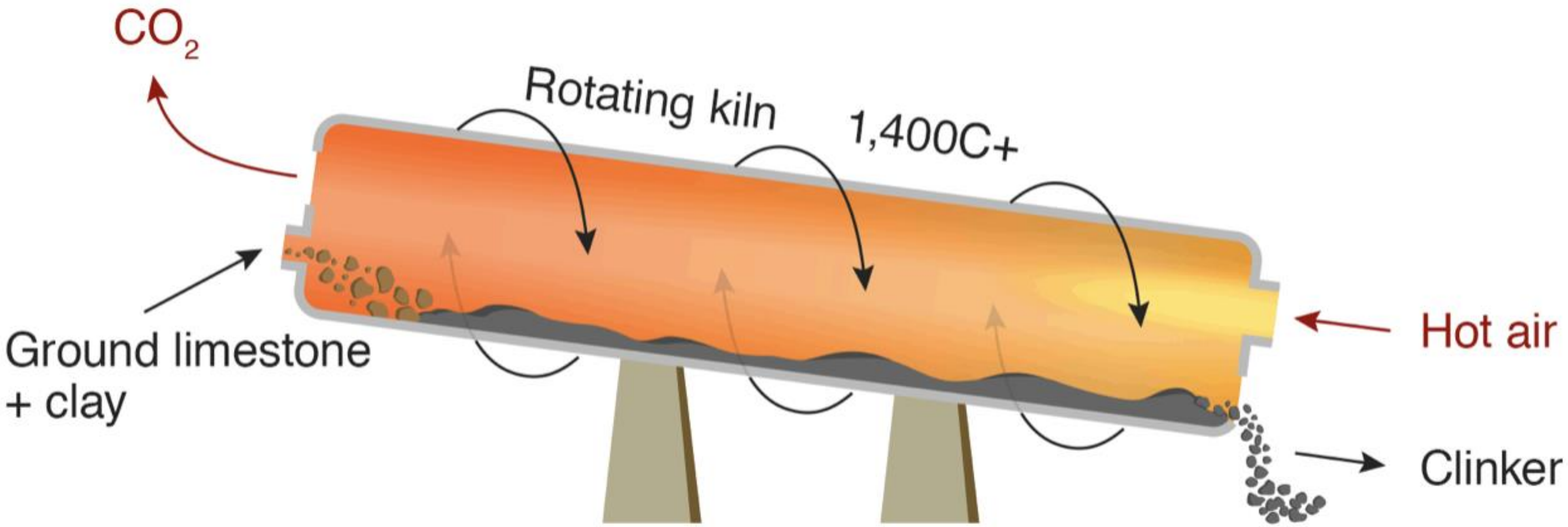
....Che producano meno $CO_{2....}$

$_{....}$Che consumino meno materie prime

Come fare ????

Cosa sono i cementi ?

Cemento Portland



Le materie prime

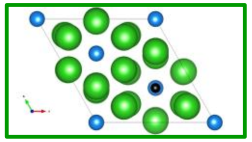
Calcari ed argille

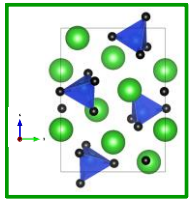
Cosa è il clinker?

Clinker Portland

BELITE

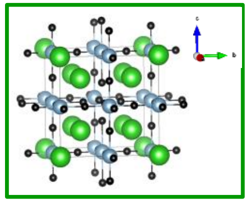
ALITE

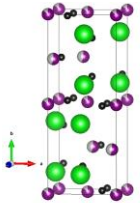


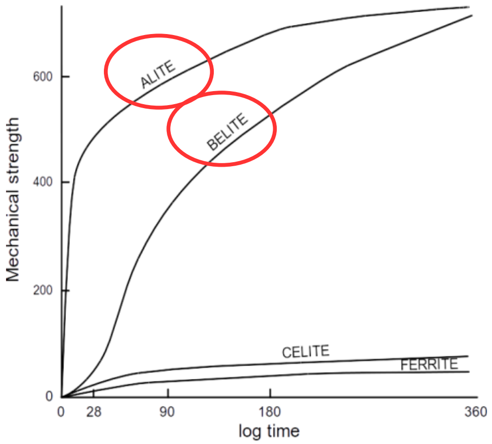


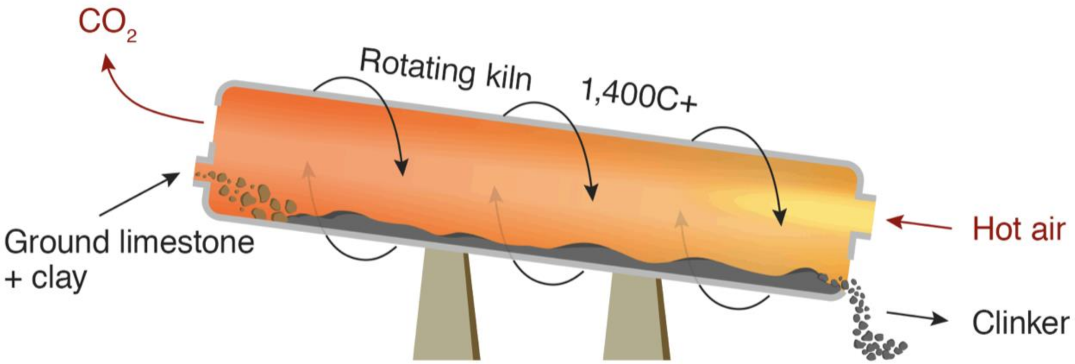
FERRITE

CELITE



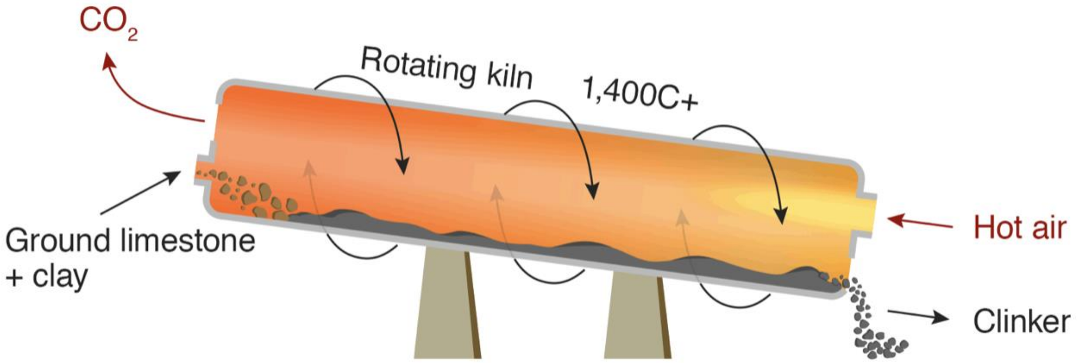


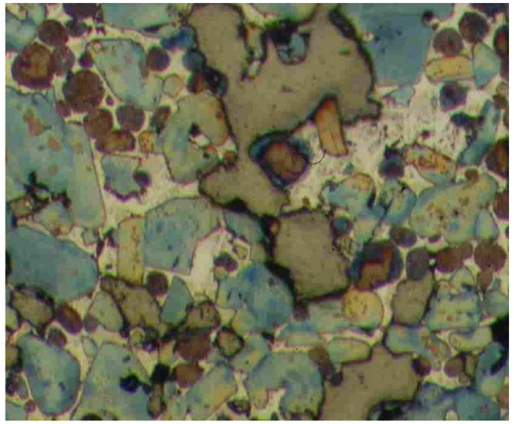


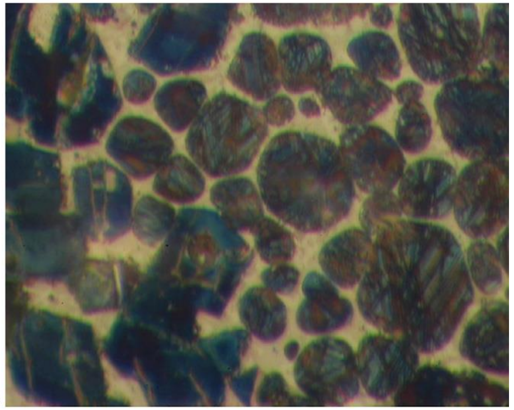


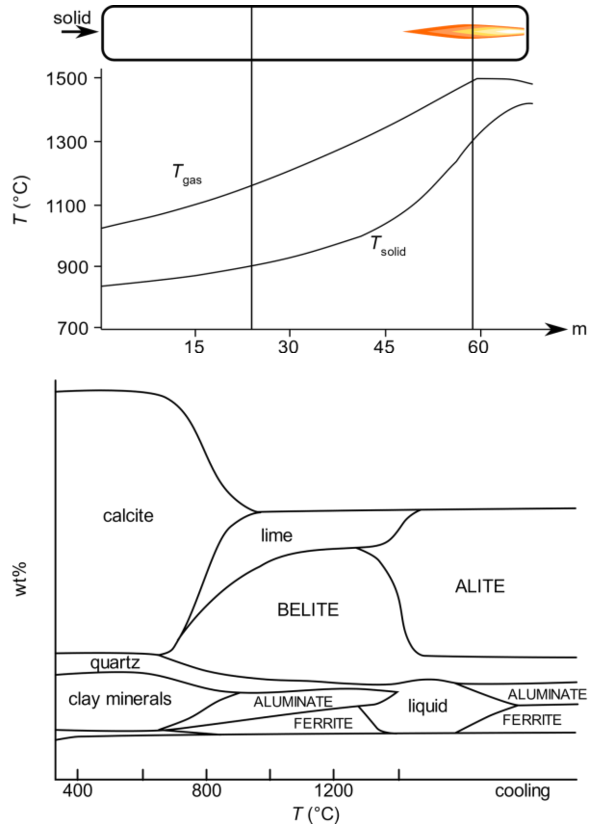
Formula	Ossidi	Abbreviazione	Nome	$\%_p$
Ca_3SiO_5	$3CaO \cdot SiO_2$	**C3S**	**Alite**	50-70
Ca_2SiO_4	$2CaO \cdot SiO_2$	**C2S**	**Belite**	13-30
$Ca_3Al_2O_6$	$3CaO \cdot Al_2O_3$	**C3A**	**Celite**	5-10
$Ca_4Al_2Fe_2O_{10}$	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	**C4AF**	**Ferrite**	5-15

Produzione clinker




(a)


(b)



Idratazione del Cemento Portland

1. $C_3A + H_2O \xrightarrow{\text{molto veloce}} \text{C-A-H}$
2. $C_4AF + H_2O \xrightarrow{\text{veloce}} \text{C-A-H + C-A-F-H}$

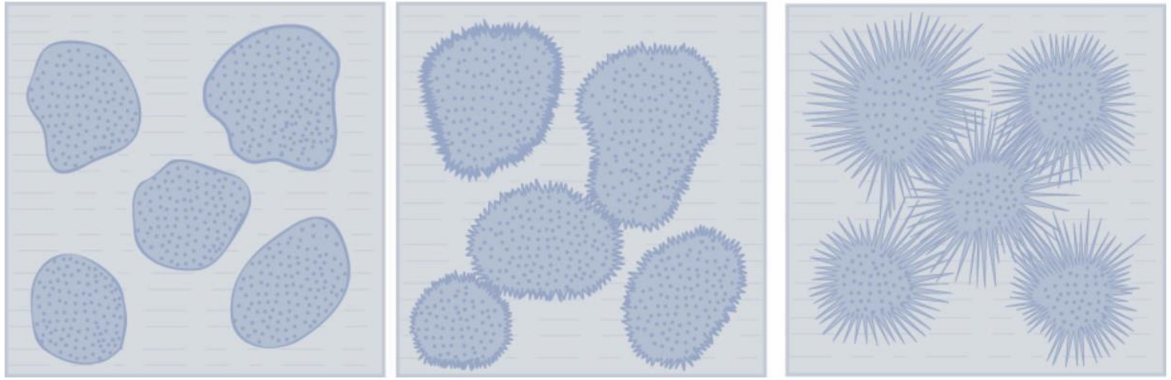
Presa

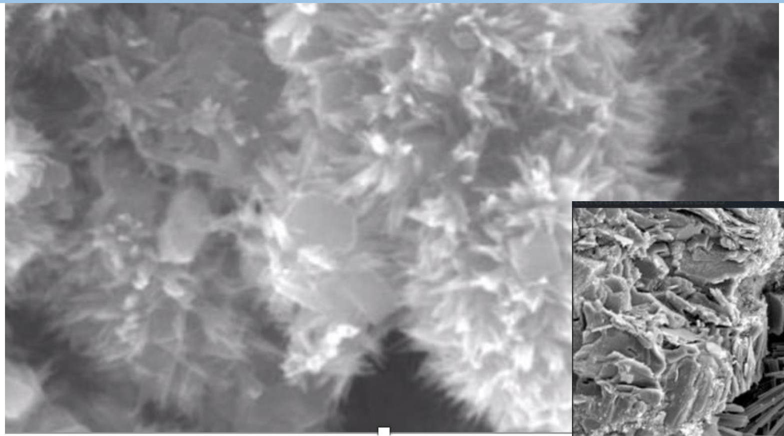
3. $C_3S + H_2O \xrightarrow{\text{lenta}} \text{C-S-H + CH}$
4. $C_2S + H_2O \xrightarrow{\text{molto lenta}} \text{C-S-H + CH}$

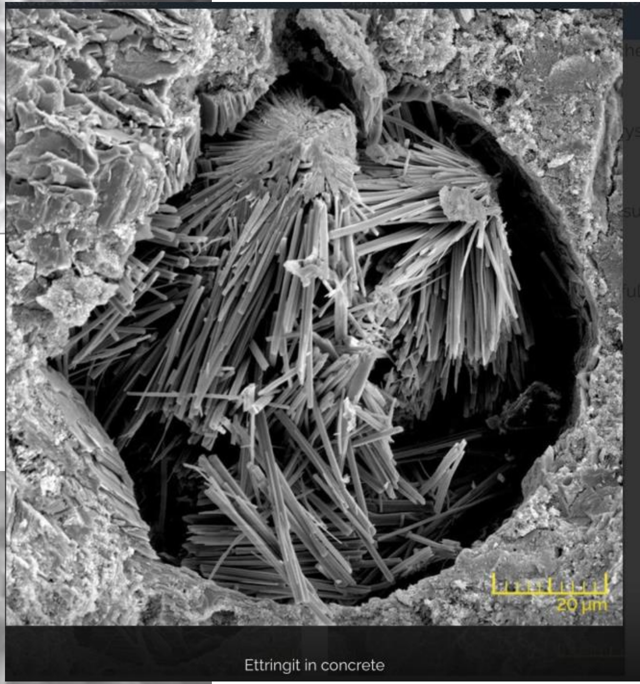
Indurimento

+

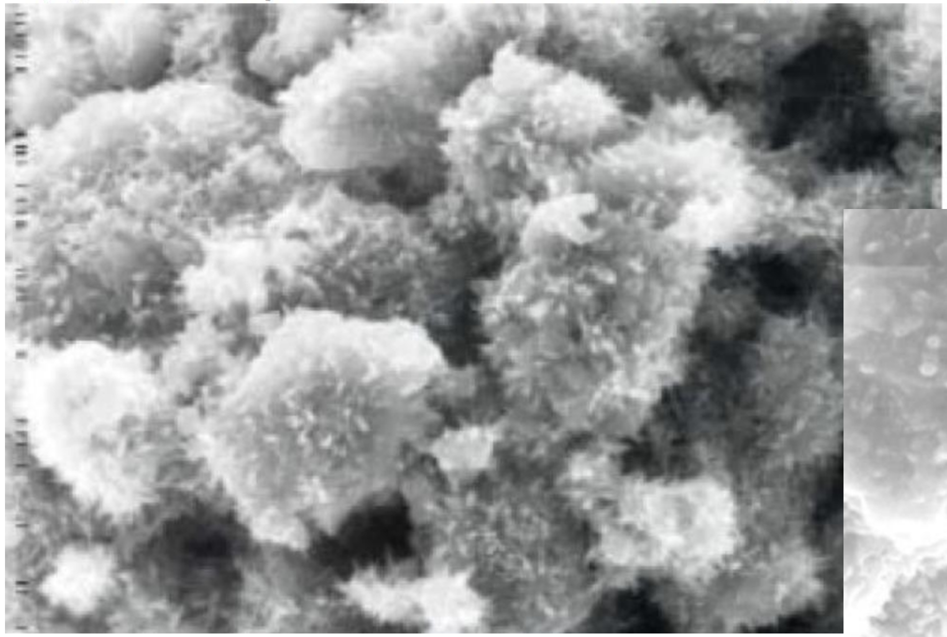
L'idratazione del clinker …. C-S-H

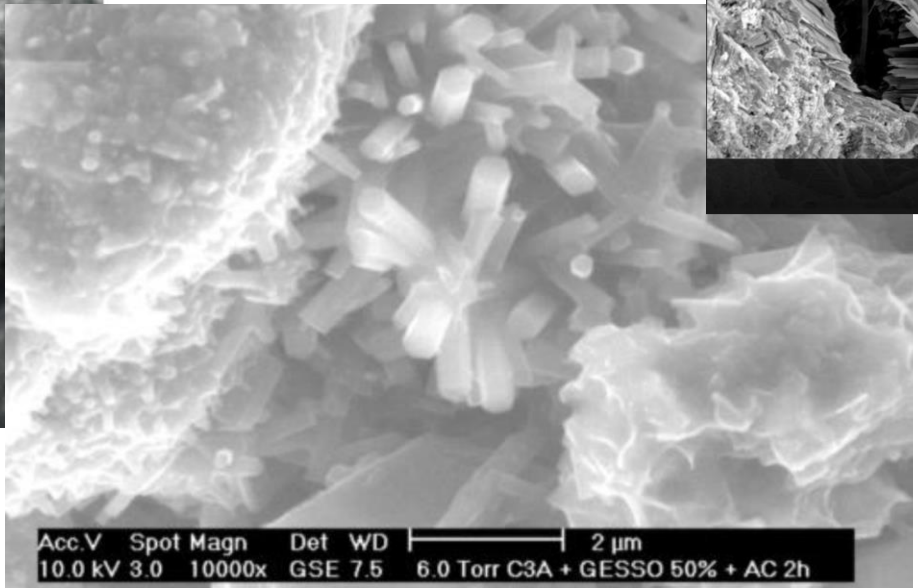




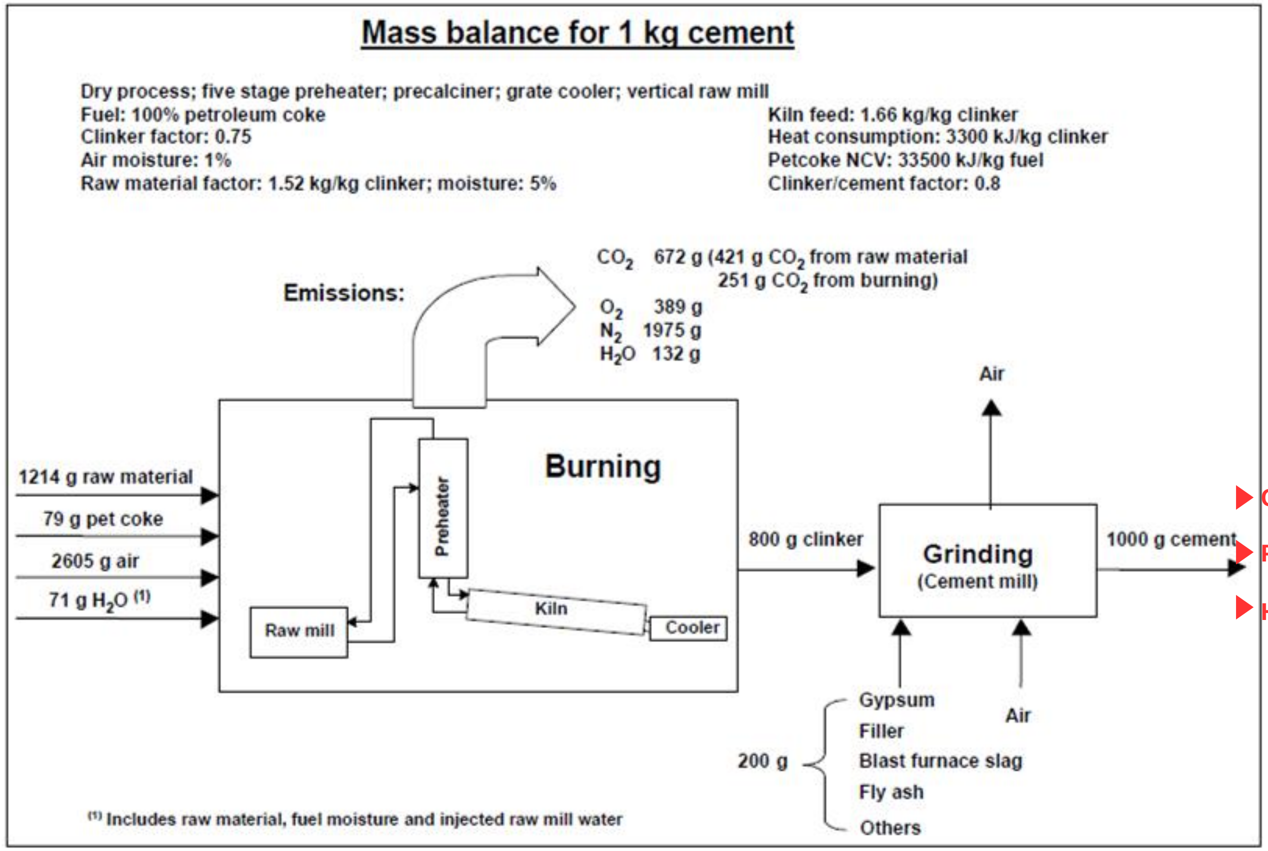


Ettringit in concrete





- **Wastes** as raw materials
- **Non-potable** water
- **Dry processes**



- **CO_2** emissions
- **Fuel** consumption
- **Heat** consumption

Mass balance for the production of 1 kg cement using the dry process [103, CEMBUREAU, 2006]

"Reference Document on Best Available Techniques in the Cement, Lime and Magnesium Oxide Manufacturing Industries" European Commission - May 2010

Come fare cementi per i…. new global standards

Cementi attivati con :

Scaglie ferrose
Fly ashes
Fumo di silice
Alluminati Ca

sustainability

Article

Use of Iron and Steel Slags in … Future Perspectives

Alan Piemonti [1], Antonio Conforti [1,*], Luca Comin… and Giovanni Plizzari [1]

Expansive Cement

Expansive cem… of drying shri… restrained exp…

Calcium Aluminate Cements

Karen L. Scrivener, Alain Capmas, in Lea's Chemis… Cement and Concrete (Fourth Edition), 1998

CONCRETE

Optimizing the Use of Fly Ash in Concrete

By: Michael Thomas, Ph.D., P.Eng., Professor of Civil Engineering, University of New Brunswick

Nanomateriali

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Construction and Building Materials

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Experimental Investigation on Strength and Durability of Graphene Nanoengineered Concrete

Sejal P. Dalal [a,*], Purvang Dalal [b]

[a] *Civil Engineering Department, SVIT, Gujarat, India*
[b] *Faculty of Technology, Dharmsinh Desai University, Nadiad, Gujarat, India*

ELSEVIER

Construction and Building Materials

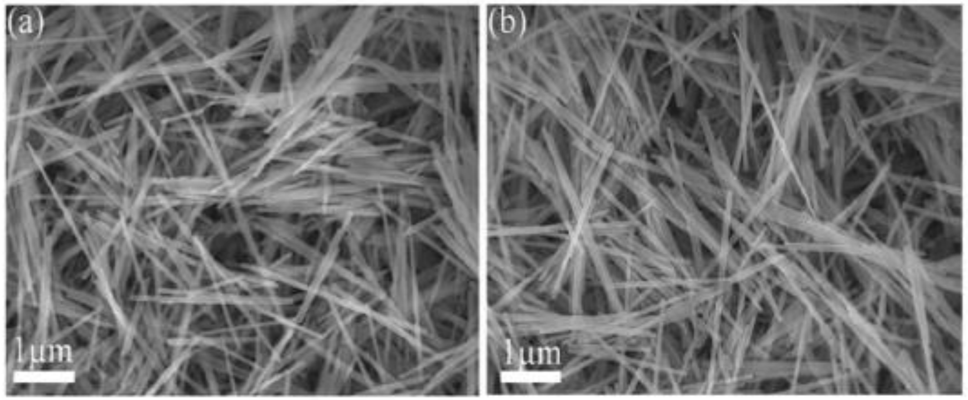
Volume 276, 22 March 2021, 122236

Experimental Investigation on Strength and Durability of Graphene Nanoengineered Concrete

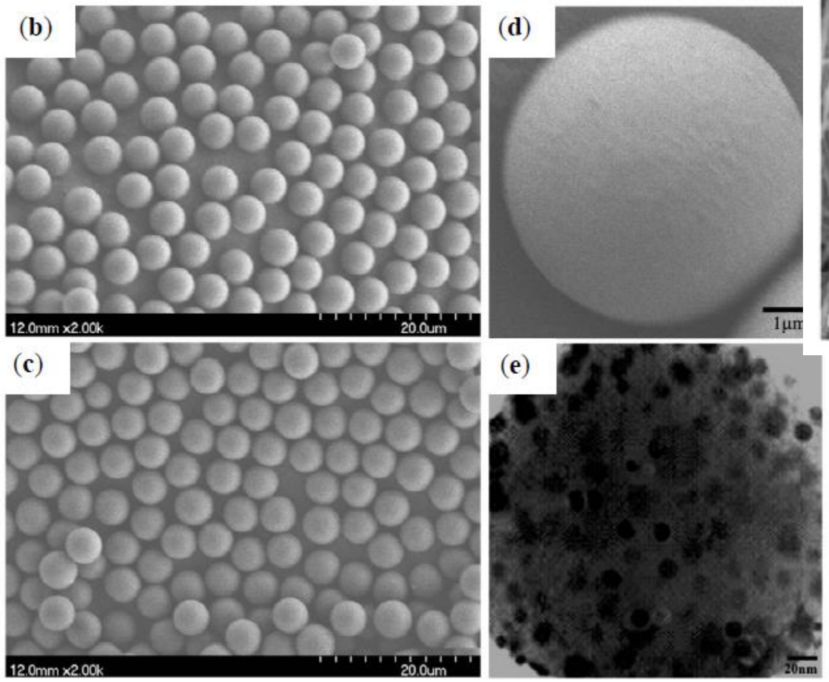
Sejal P. Dalal [a], Purvang Dalal [b]

Cementi nano-ingegnerizzati

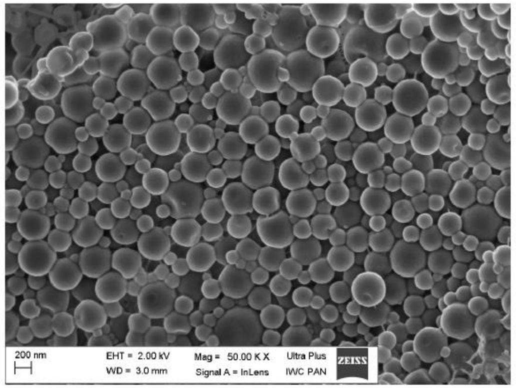
- Materials with a grain size **lower than 200nm**



Halayqa & Domańska, 2014, *Int. J. Mol. Sci.*, 15(12), 23909 – 23923



Nguyen et al., 2014, *Nanomaterials*, 4(3), 628 –



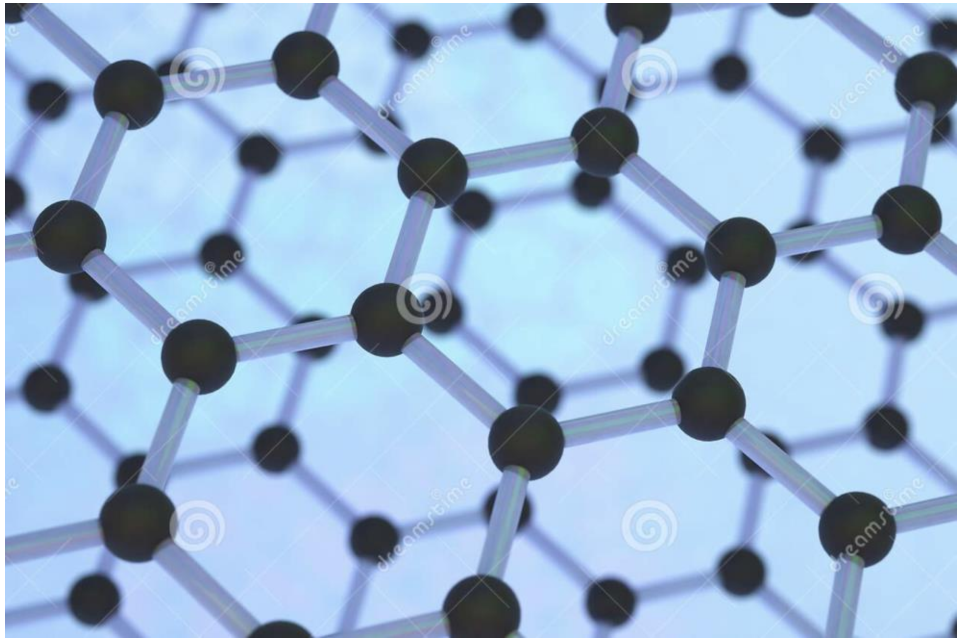
Shakir et al., 2014, *RSC Advances*, 4, 8741 – 8745

aumentare la durabilità e le proprietà meccaniche
Ridurre la porosità
Facilitare la formazione dei C-S-H

Ultrahigh Performance Nanoengineered Graphene–Concrete Composites for Multifunctional Applications

Dimitar Dimov, Iddo Amit, Olivier Gorrie, Matthew D. Barnes, Nicola J. Townsend, Ana I. S. Neves, Freddie Withers, Saverio Russo, Monica Felicia Craciun,

First published: 23 April 2018 | https://doi.org/10.1002/adfm.201705183 | Citations: 79



Ultrahigh performance multifuntional costruction materials.....

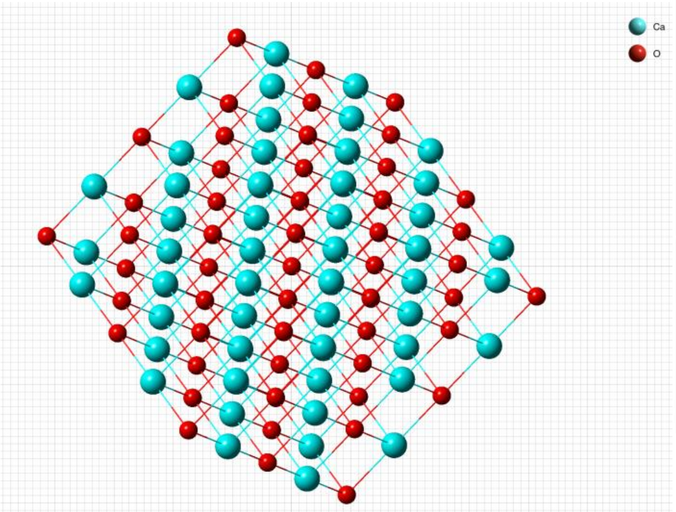
Nanoengineered concrete con graphene

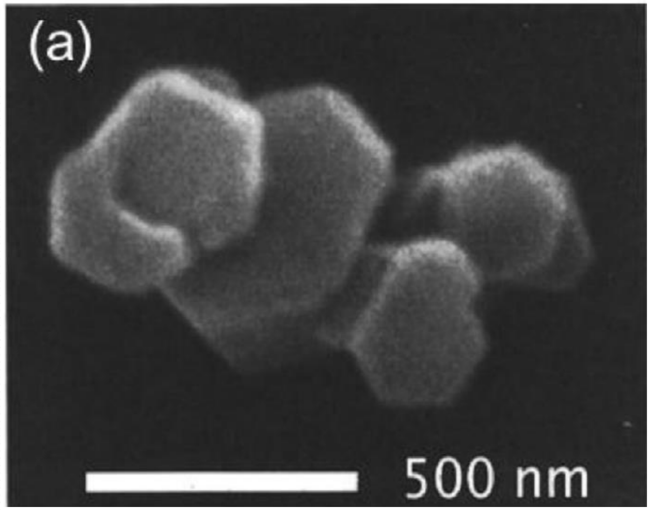
+146% resistenza compressione
+ 79.5 resistenza alla flessione/trazione
Aumento perfomance termiche ed elettriche
+ 400 % permeabilità all’acqua

Cosa sono i nCaO e $nCa(OH)_2$

Dimensioni particelle 50-250 nanometri
Stabili se disperse in alcoli
Si formano dalla decarbonatazione

$CaCO_3$ = CaO (**quick lime**) + CO_2



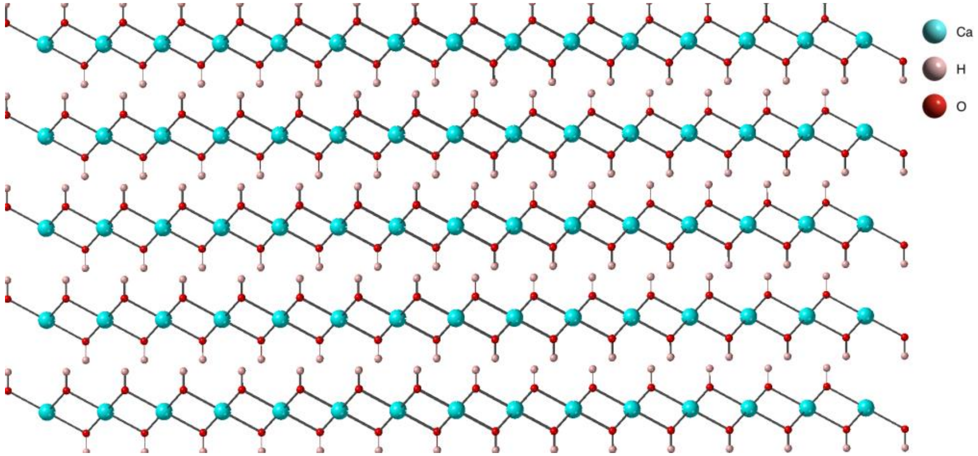


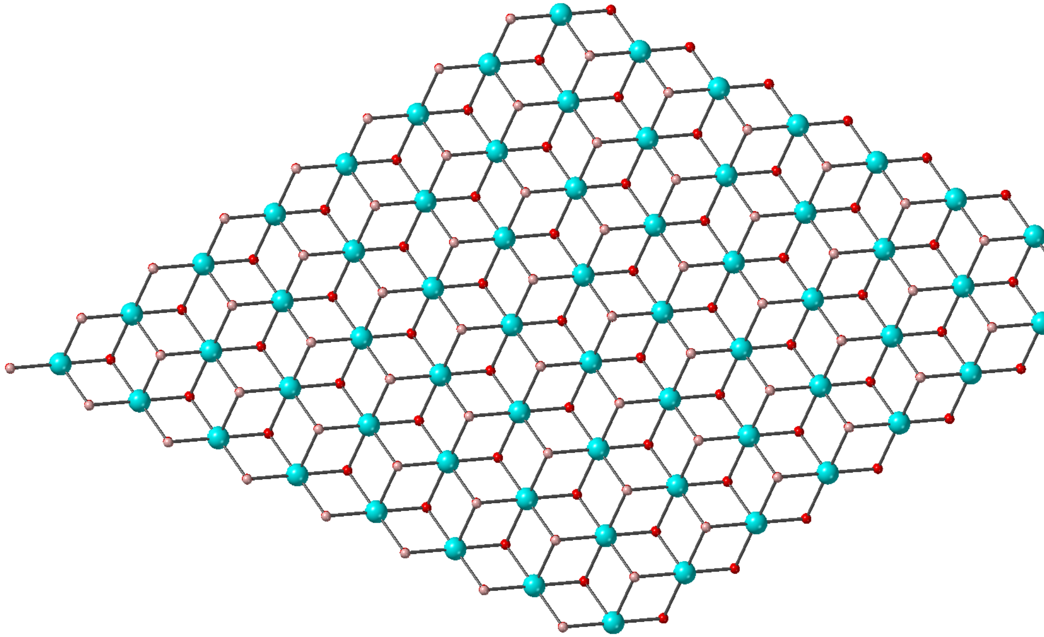
Tendeno ad idratarsi a formare nanoportandite

CaO + H_2O = $CaOH_2$ (**slaked lime**)

Riconverte facilmente in

$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$





A cosa serve il nCaO ....

Progetto NANOCOAT

Nuovi materiali e rivestimenti nanostrutturati: azioni di trasferimento tecnologico

INNOVAFVG

REGIONE AUTONOMA FRIULI VENEZIA GIULIA

Per il restauro e la conservazione delle malte e negli stucchi archeologiche a matrice carbonatica....

Riconverte facilmente in $CaCO_3$ $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$

Rispetto al trattamento tradizionale: completamento carbonatazione, profondità di penetrazione e minore acqua

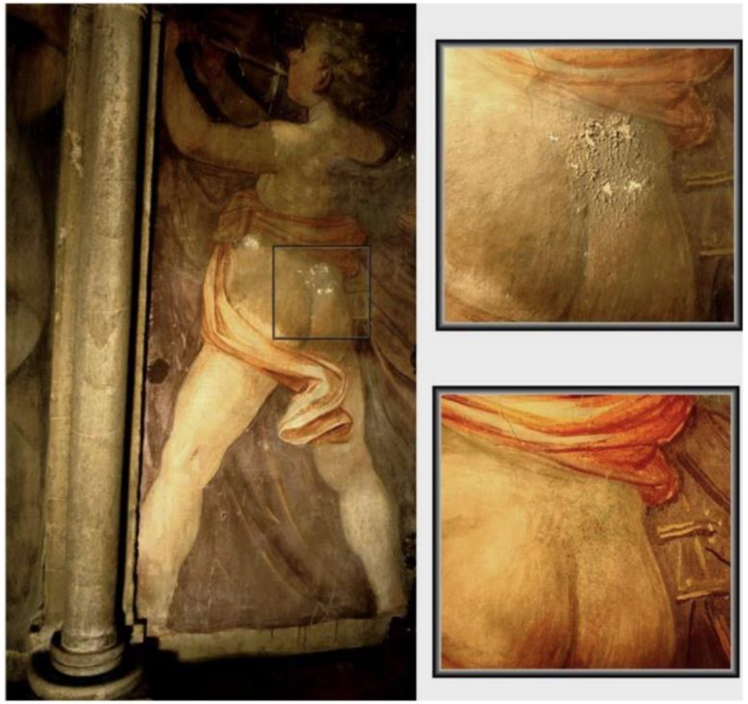


Figura 2.1.1. Affresco "Gli angeli musicanti" di Santi di Tito (16° sec.) sulla controfacciata del Duomo di Firenze. L'area selezionata e stata trattata con nanoparticelle di $Ca(OH)_2$ (in alto prima del trattamento, in basso dopo il trattamento) [Baglioni, P., *"Tecnologie del futuro per i tesori del passato. Le nanoscienze e la conservazione dei beni culturali"*, Dipartimento di Chimica e CSGI, Univerisitá di Firenze, Sesto Fiorentino, 2006].

Figura 2.1.3. Dipinti Maya scoperti nella "Antigua Ciudad Maya de Calakmul", patrimonio mondiale dell'UNESCO (Campeche, Messico). Dispersioni di nanoparticelle di $Ca(OH)_2$ sono state utilizzate per consolidare lo strato dipinto decoeso e soggetto a polverizzazione. Dopo il restauro la superficie dipinta ha recuperato la sua tonalità di colore originale perché la ri-coesione dei pigmenti nello strato superficiale minimizza la diffusione della luce che aveva conferito opacità alle pitture murali [P. Baglioni, R. Giorgi, *Soft Matter* (2006) 2, 293].

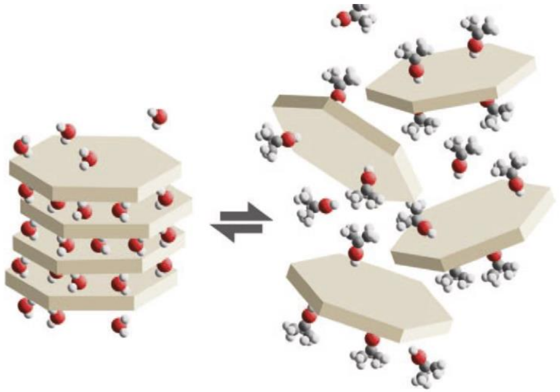
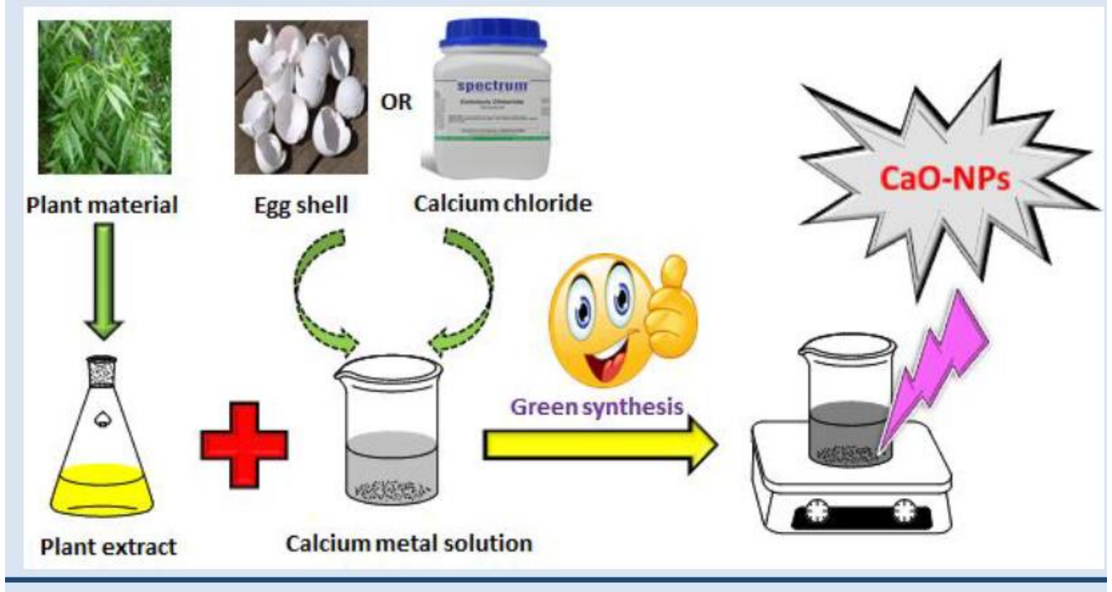


Figura 2.1.2. Sx: aggregazione delle nanoparticelle di idrossido di calcio in acqua; Dx: l'adesione delle facce è inibita grazie all'assorbimento del 2-propanolo, portando alla stabilizzazione della dispersione [P. Baglioni, D. Chelazzi, R. Giorgi, In: "*Nanotechnologies in the Conservation of Cultural Heritage A compendium of materials and techniques*", Springer (2015)].

A cosa serve il nCaO ....



PREPARATION AND CHARACTERIZATON OF CaO NANOPARTICLE FOR BIODIESEL PRODUCTION

Jharna Gupta[1,b)], and Madhu Agarwal[1,a)]
[1]Department of Chemical Engineering, MNIT, Jaipur, 302017, India
[a)]Corresponding author: madhunaresh@gmail.com
[b)]onlinejharna@gmail.com

Tahvildari *et al. Journal of Environmental Health Science & Engineering* (2015) 13:73
DOI 10.1186/s40201-015-0226-7

JOURNAL OF ENVIRONMENTAL HEALTH SCIENCE & ENGINEERING

RESEARCH ARTICLE Open Access

CrossMark

The study of CaO and MgO heterogenic nano-catalyst coupling on transesterification reaction efficacy in the production of biodiesel from recycled cooking oil

Kambiz Tahvildari[1], Yasaman Naghavi Anaraki[1], Reza Fazaeli[2], Sogol Mirpanji[1] and Elham Delrish[3*]

nCaO nei cementi per ridurre emissioni CO_2

65% delle emissioni di CO_2 del settore cementi viene dalla calcinazione

$$CaCO_3 \rightarrow CaO + CO_2$$

$$1\ \text{kg} \rightarrow 0.56\ \text{kg} + 0.44\ \text{kg}$$

In un 1 kg di clinker ci sono 0.65 kg di CaO

35 % delle emissioni CO2 viene dalla combustione

Cosa ci si può aspettare dal nCaO

Accellerare le reazioni con minore energia data la elevate superficie di reazion

Aumentare la cuocibilità

Diminure le temperature di reazione

Aumentare la resistenza e diminuire la compressione

Aumentare l’attività pozzolanica

Diminuire la porosità

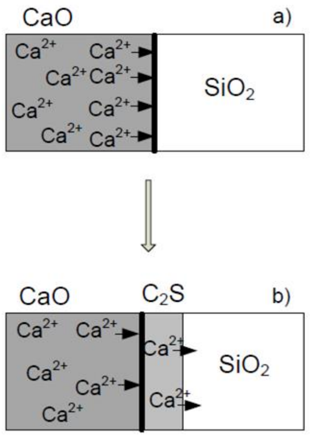
Calcare + Argilla + Nano-materiale

↓ **Dimensione**

↑ **Energia superficiale**

↓ ***T* di fusione**

↑ **Coefficiente di diffusione**



- **SiO_2 + CaO → C2S**
- **C2S + CaO → C3S**

Diffusione di Ca^{2+}

nano-CaO

Sostituzione di parte dei carbonati con CaO → diminuzione delle emissioni di CO_2

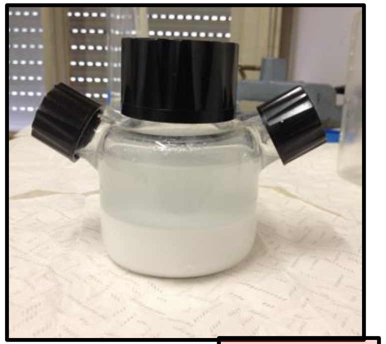
Aumento della diffusione di Ca^{2+} Diminuzione della *T* di clinkerizzazione

Quali nCaO?

The formation of the hydroxide particles occurs at the interface between the bubble and the liquid and the ultrasound accelerated the formation of $Ca(OH)_2$.
(Alavi & Morsali, 2013, *J. Exp. Nanosci.*, 5(2), 93 – 105)

Nano-materials

Nano-CaO



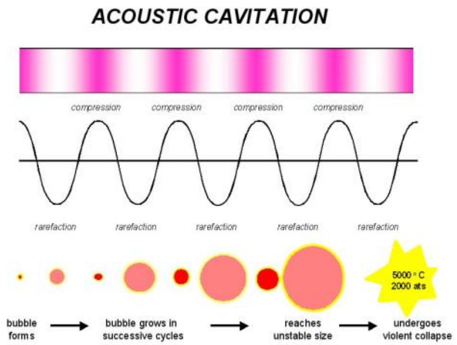
From Calcium Nitrate and Calcium Chloride

Waste from the Solvay process

Synthesis of nano-CaO by acoustic cavitation

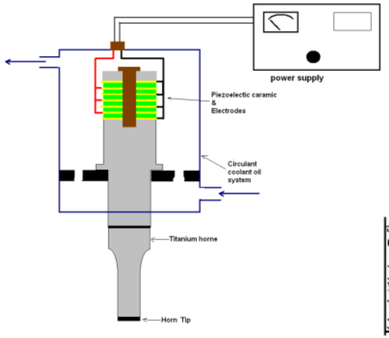
$$Ca(NO)_3 + 2NaOH \xrightarrow{)))} Ca(OH)_2 + 2NaNO_3$$

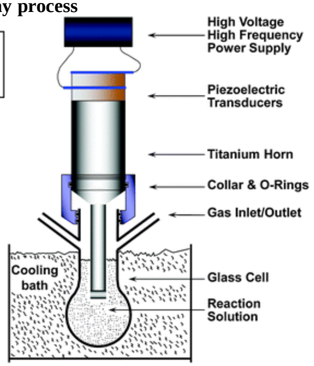
$$CaCl_2 + 2NaOH \xrightarrow{)))} Ca(OH)_2 + 2NaCl$$

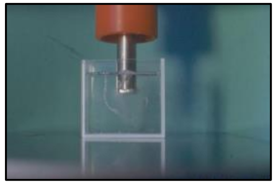


Possible re-agglomeration after calcination

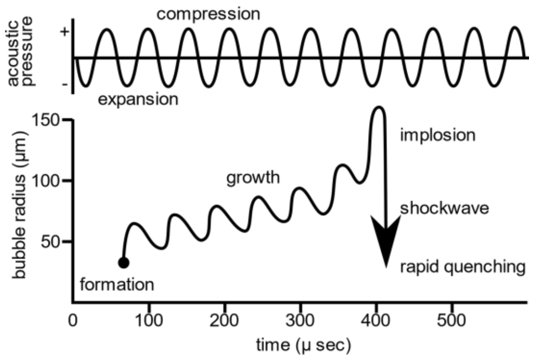
NO calcination → $Ca(OH)_2$





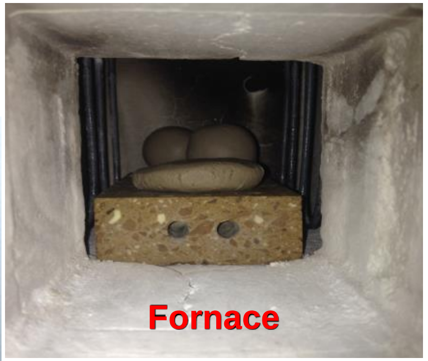


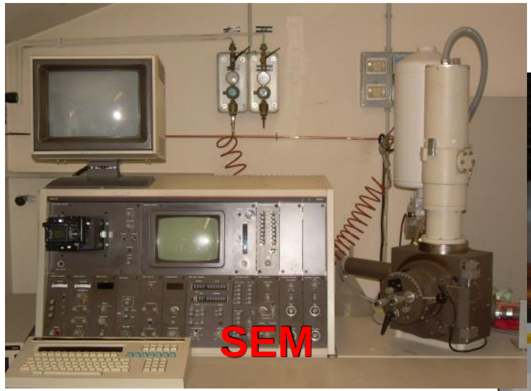
Ultrasound Generator:
Horn type 750 W

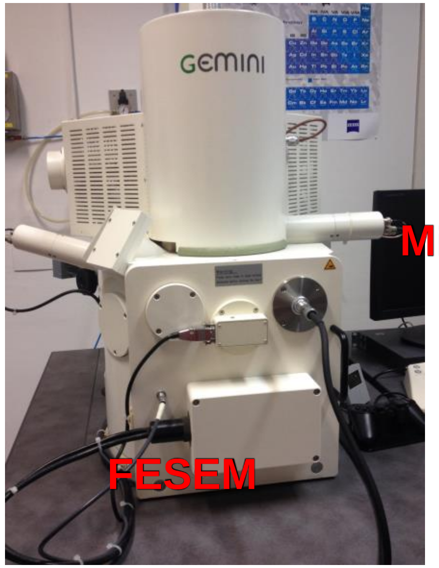


Suslick, 1990, *Science*, 247,1439 – 1445

Il clincker nei nostri labs





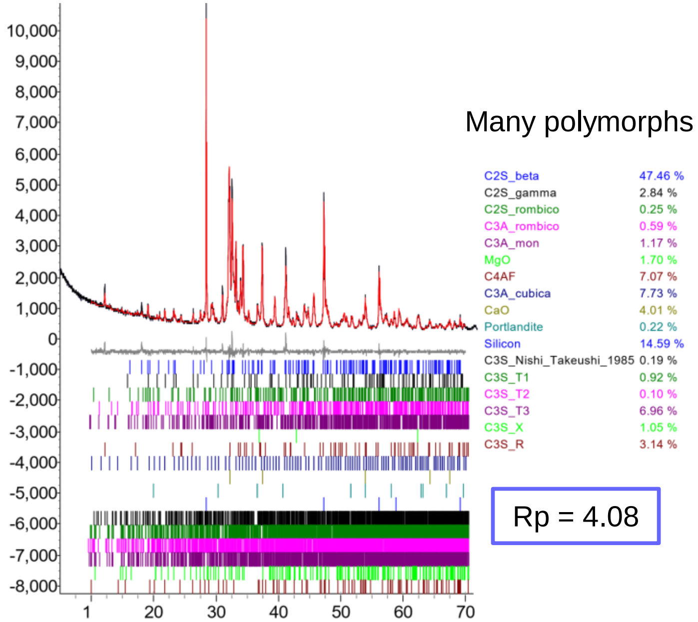


Il clincker ingegnerizzati con nCaO nei nostri labs

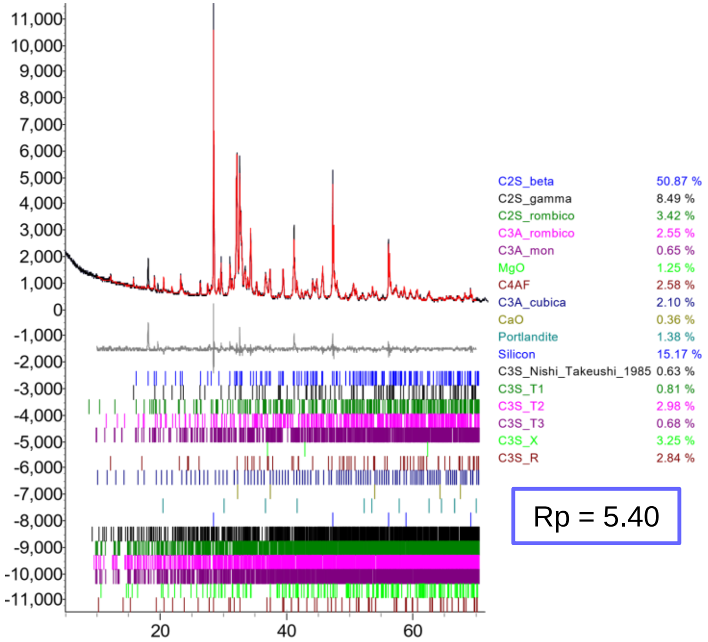
1250°C

Nano – $Ca(OH)_2$

Without nano – addition



With nano – addition



Il clincker ingegnerizzati con nCaO nei nostri labs

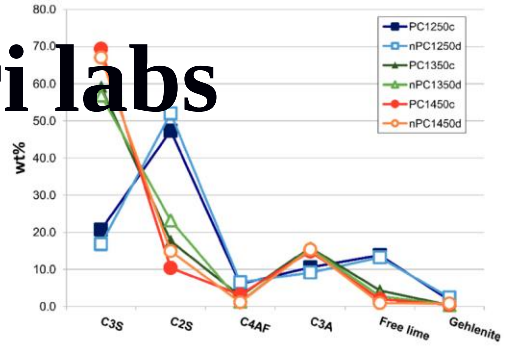


Figure 10. Spider diagram for the mineralogical quantitative analysis (Rietveld refinement Reference [46]) for the whole data set. Error bars in wt % are within the symbols.

1250°C

Nano – $Ca(OH)_2$

Without nano – addition

Phase	wt%	Rp
C2S	42.0(2)	4.08
C3S	7.0(3)	

With nano – addition

Phase	wt%	Rp
C2S	46.2(2)	5.40
C3S	5.3(3)	

Aumento della cuocibilità del clinker

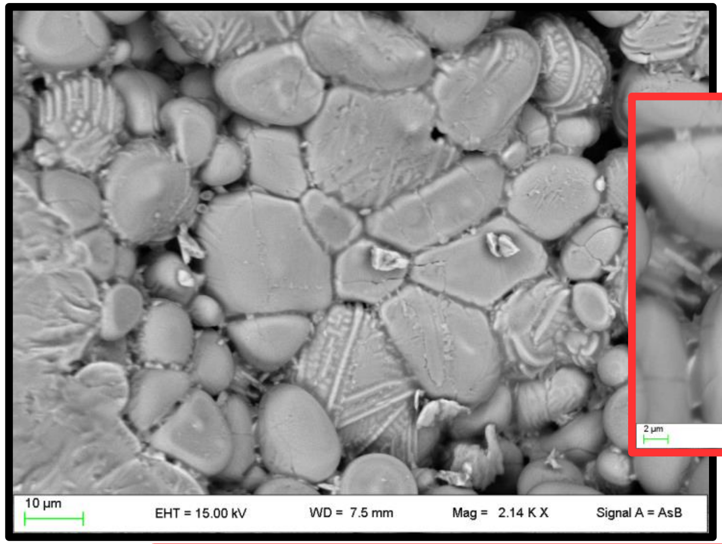
Miglioramento produttività impianto

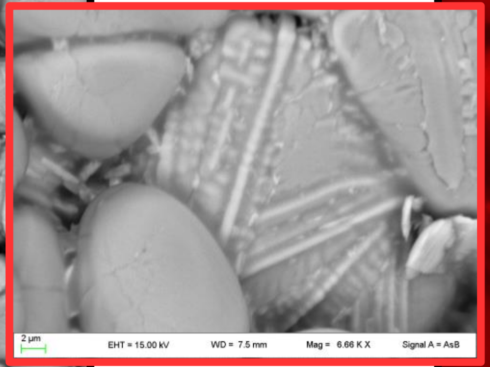
Minori emission di CO_2

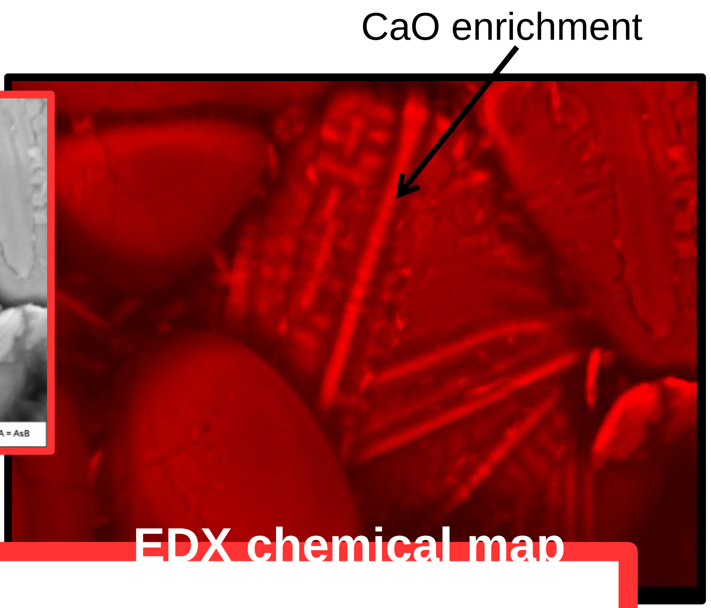
Il clincker ingegnerizzati con nCaO nei nostri labs

1350

Nano – $Ca(OH)_2$





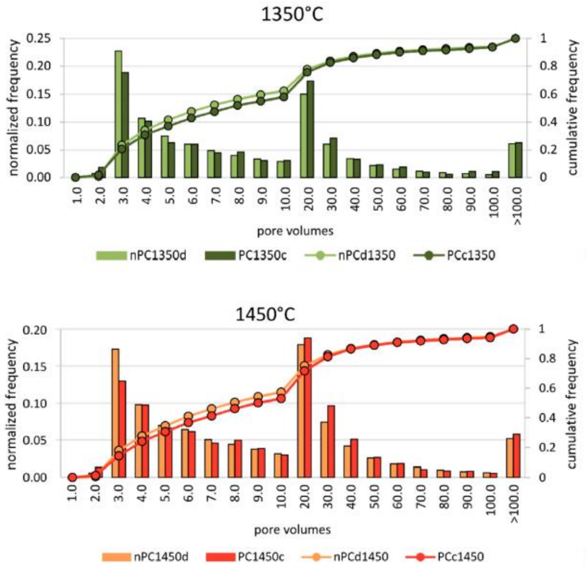


nCaO aumenta le superfici reattive favorisce

C2S + CaO

Il F

I clincker ingegnerizzati con nCaO al sincrotrone



(a)

(b)

Table 2. Results obtained by applying the Basic Analysis module of the Pore3D software library extracted from the laboratory X-ray μCT data.

Sample	Volume (voxels)	Voxel Size (μm)	Volume (mm^3)	Pores Thresholds	Eulerian Characteristics (mm^{-3})	Internal Mean Curvature (mm^{-2})	Specific Surface Area (mm^{-1})	Pore Fraction
nPC1450d	946 × 610 × 734	5.7	52.95	91	573	712	22.51	0.24
PC1450c	271 × 267 × 167	5.0	1.51	93	885	711	20.72	0.20
nPC1350d	700 × 700 × 1000	5.7	61.25	91	2048	711	16.77	0.16
PC1350c	303 × 168 × 311	5.0	1.98	76	1013	560	18.09	0.23

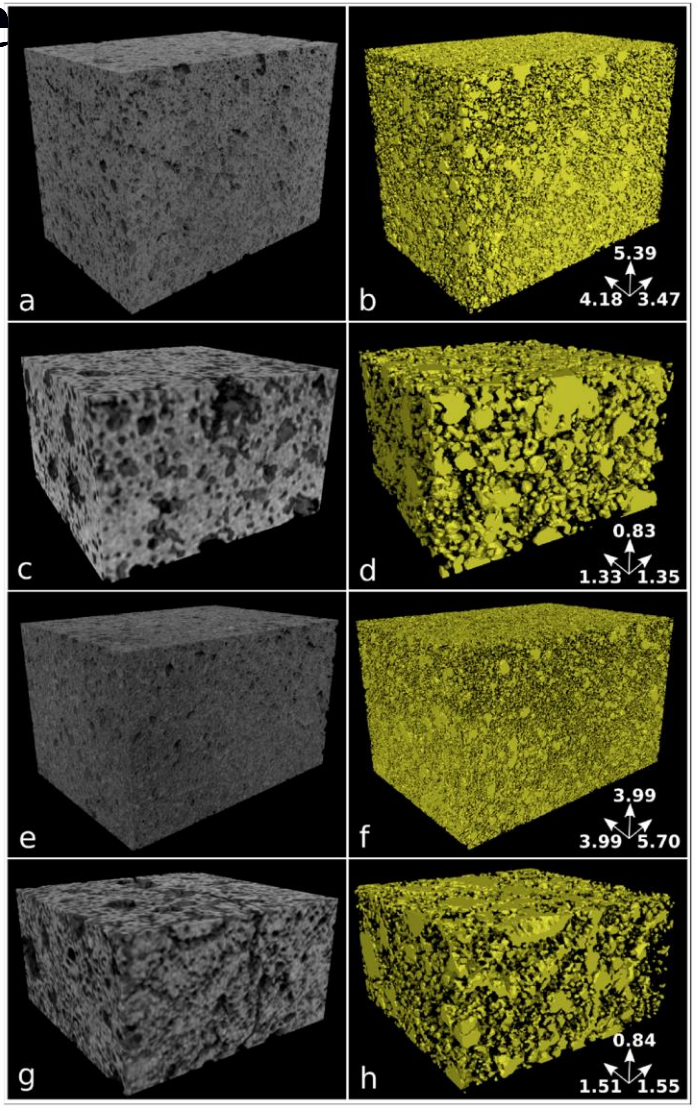


Figure 7. Volume renderings of the extracted VOIs from reconstructed images (left column) and corresponding iso-surface renderings of the pore phase in yellow (right column) for samples nPC1450d (**a**,**b**), PC1450c (**c**,**d**), nPC1350d (**e**,**f**), and PC1350c (**g**,**h**). Samples nPC1450d and nPC1350d have been reconstructed with an isotropic voxel size of 5.7 μm, while an isotropic voxel size of 5.0 μm has been used for samples PC1450c and PC1350c. The size of analyzed VOIs is reported in Table 2. The dimension of the sample edges is reported in mm.

Diminuzione porosità con nCaO

Conclusioni ... ad oggi

uso dei nano CaO nei cementi … la nostra esperienza ci dice:

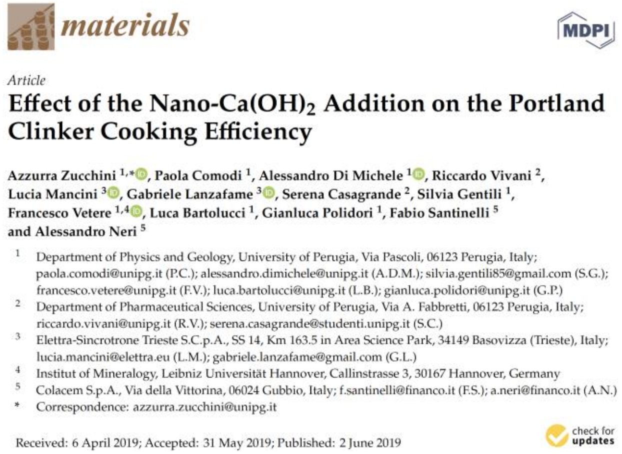
Vantaggi:

1) Uso di CaO invece di $CaCO_3$ riduce emissioni di CO_2 in partenza perché è già un materiale decarbonatato.. Non occorre la reazione $CaCO_3 = CaO + CO_2$

2) I nano-materiali costituiscono un ottimo catalizzatore di reazione nella produzione clinker favoriscono la formazione di belite a più basse temperature, riduzione di energia e produzione CO_2

3) Diminuzione della calce libera …del 35% a 1350 °C e del 55% a 1450 e quindi un miglioramento della cuocibilità (CaO residua produce della porosità secondaria indesiderata)

4) Importante cambio nella porosita



materials MDPI

Article

Effect of the Nano-$Ca(OH)_2$ Addition on the Portland Clinker Cooking Efficiency

Azzurra Zucchini [1,*], Paola Comodi [1], Alessandro Di Michele [1], Riccardo Vivani [2], Lucia Mancini [3], Gabriele Lanzafame [3], Serena Casagrande [2], Silvia Gentili [1], Francesco Vetere [1,4], Luca Bartolucci [1], Gianluca Polidori [1], Fabio Santinelli [5] and Alessandro Neri [5]

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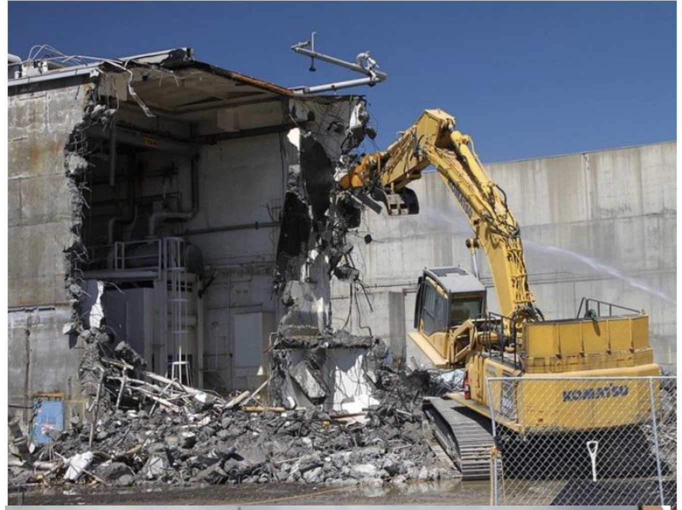
Nel libro dei desideri….

Cementi nano-ingegnerizzati basati su materiali da

Costruction and Demolition Waste C&DW



Stretta collaborazione
Con esperti di diverse discipline e …
con imprese del settore

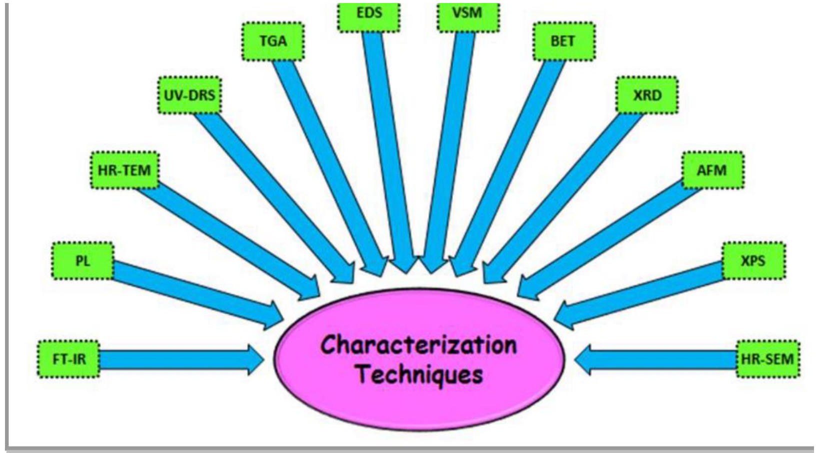


Figure 5. Characterization techniques for NPs.

Grazie per l’attentione