Towards a sustainable future

Study of new technologies for wastes management and CO_2 emissions reduction

Azzurra Zucchini, Paola Comodi

A.D. 1308 unipg UNIVERSITÀ DEGLI STUDI DI PERUGIA

A.D. 1308 unipg DIPARTIMENTO DI FISICA E GEOLOGIA

Dipartimenti:

- **Ingegneria**
- **Scienze Farmaceutiche**
- **Chimica, Biologia e Biotecnologie**
- **Scienze agrarie, alimentari e ambientali**

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Kick-off Meeting

Piano Triennale della Ricerca e Terza Missione (2021-2023)

Dipartimento di Fisica e Geologia

10-11 gennaio 2022

VOLUME DEGLI ABSTRACT

Comitato scientifico e organizzatore:

Bertucci Bruna, Cirilli Simonetta, Di Matteo Lucio, Paciaroni Alessandro, Perugini Diego, Scopetta Sergio

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Aula A - Di

The Research Team…past and present


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Prof. Costanza Cambi


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Dr. Maximiliano Fastelli


Prof. Francesco Frondini


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- **Dr. Giada Santarelli**
- **Dr. Giulia Guidobaldi**
- **Dr. Silvia Gentili**
- **Dr. Serena Casagrande**


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Aula A -

#1 The Circular Economy

- ☑ To reduce the consumption of natural raw materials
- ☑ To protect human health and the environment

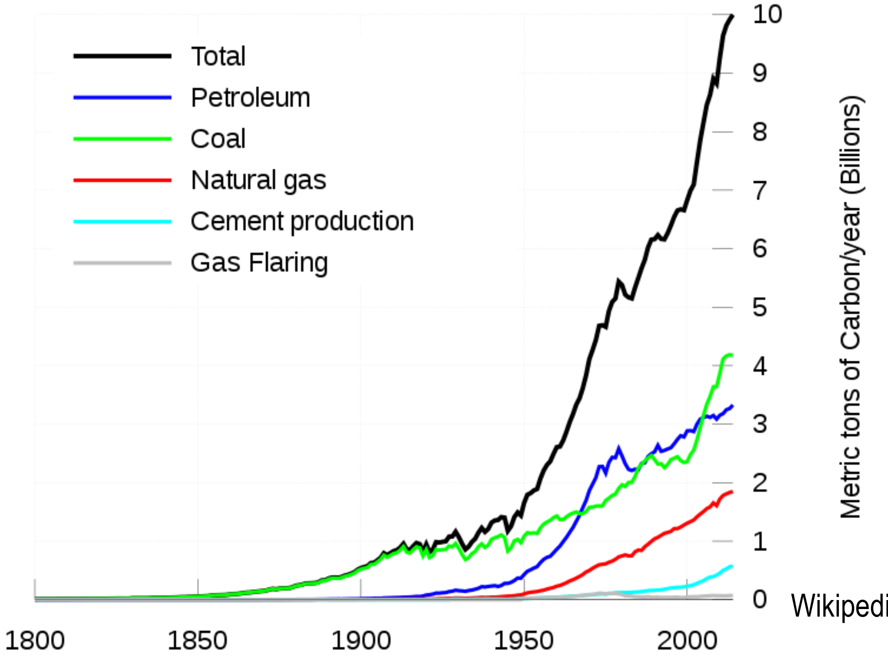
Global Recycling Day 18 • 03

Global Recycling Foundation

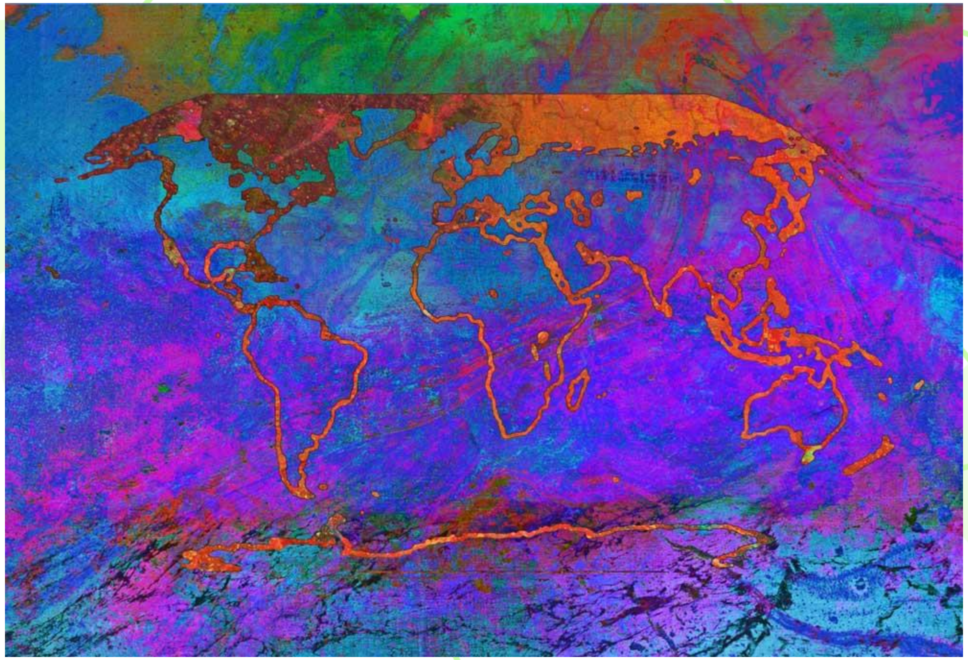
Parlamento Europeo 2015

Protagonisti:
"geomateriali"

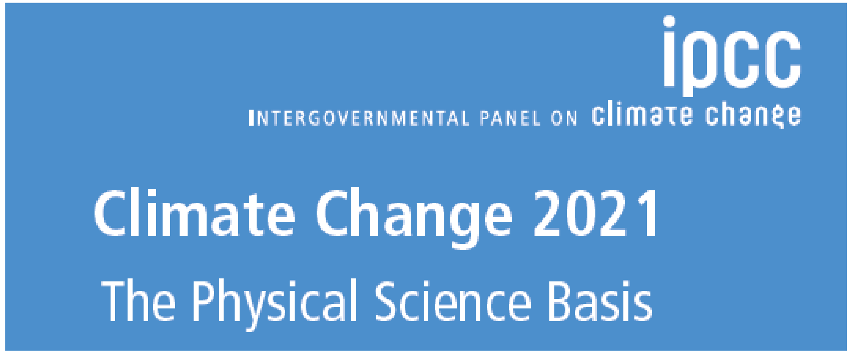
#2 The anthropic CO_2 emissions



Wikipedia.org



Changing by Alisa Singer
"As we witness our planet transforming around us we watch, listen, measure … respond."
www.environmentalgraphiti.org – 2021 Alisa Singer.



A.1 It is unequivocal that human influence has warmed the atmosphere, ocean and land. Widespread and rapid changes in the atmosphere, ocean, cryosphere and biosphere have occurred.

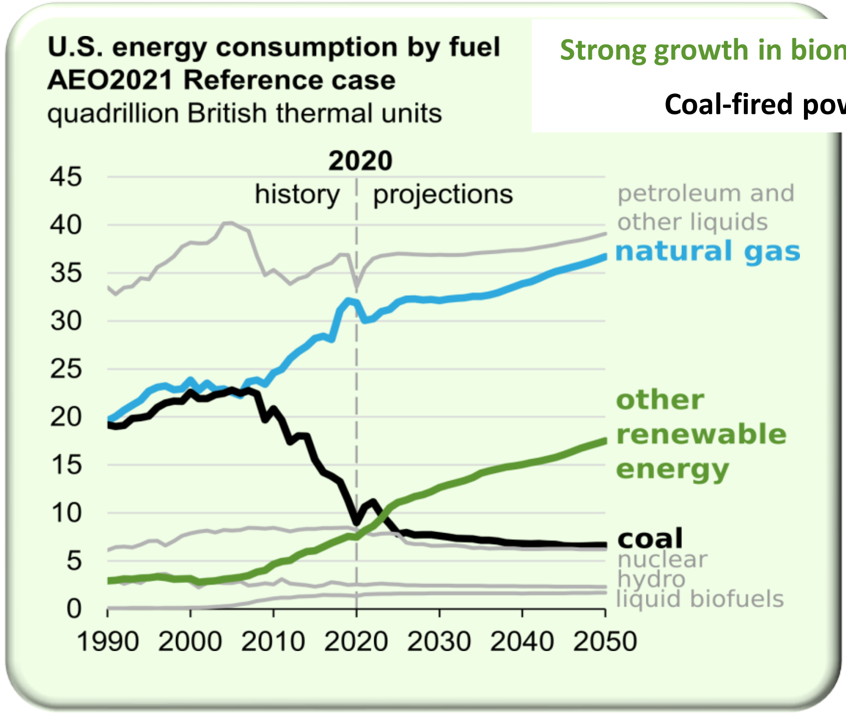
"Observed increases in well-mixed greenhouse gas (GHG) concentrations since around 1750 are unequivocally caused by human activities. Since 2011 … concentrations have continued to increase in the atmosphere, reaching annual averages of 410 ppm for carbon dioxide (CO_2), 1866 ppb for methane (CH_4), and 332 ppb for nitrous oxide (N_2O) in 2019. Land and ocean have taken up a near-constant proportion (globally about 56% per year) of CO_2 emissions from human activities over the past six decades…".

Fly ashes and their employment in civil engineering and agriculture

The Circular Economy

Biomass fly ashes: **amount of solid, inorganic residue left after the complete burning of biomasses.**

(James et al. 2012 DOI: 10.3390/en5103856, Torquati et al. 2016 DOI:10.1016/j.biombioe.2016.09.017, Cavalaglio et al. 2020 DOI: 10.3390/su12166678)



Modified from EIS's Annual Energy Outlook 2021

Strong growth in biomass plants → production of large quantities of ash

Coal-fired power plants → undergoing decommissioning

+

Geotechnical engineering, industrial processes and agriculture: sometimes problems in raw materials supplying

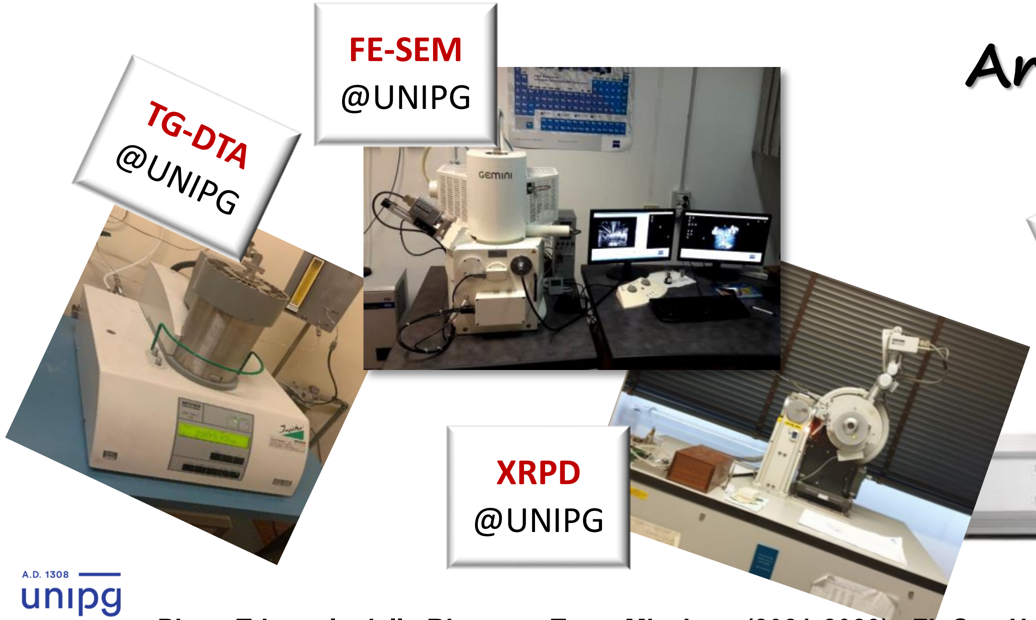
Fly ashes and their employment in civil engineering and agriculture

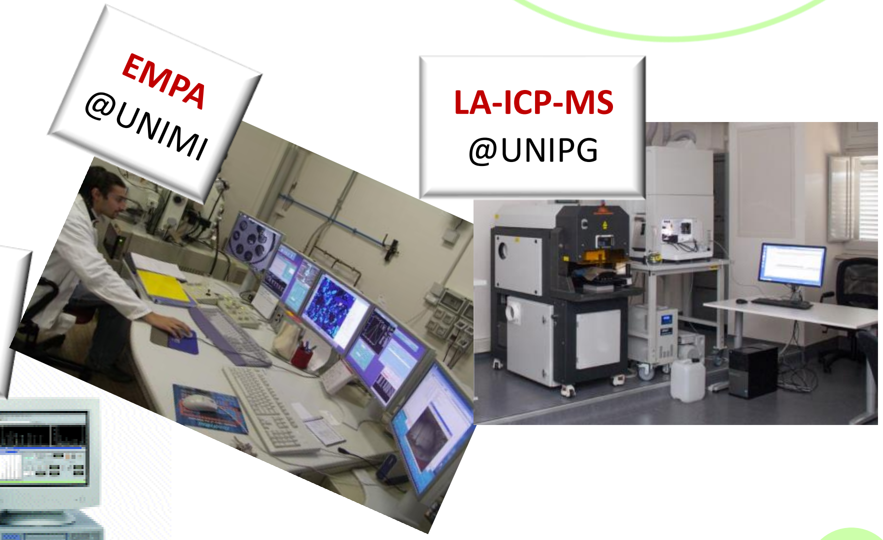
The Circular Economy

Biomass fly ashes

Code	Origin
#1	Gasification power plant, Magione (PG) Italy
#2	Grapevine prunings, Torgiano (PG) Italy
#3	Wood pellet
#4	Olive tree prunings
#5	Cardoon plants

Analytical techniques





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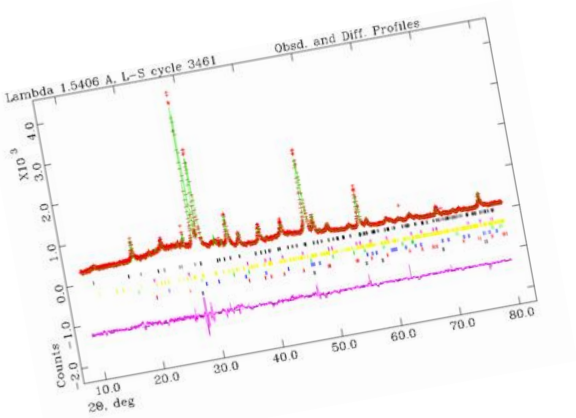
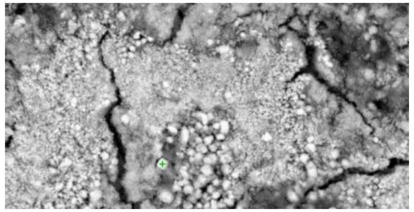
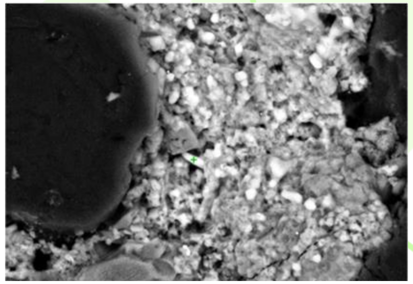


Results

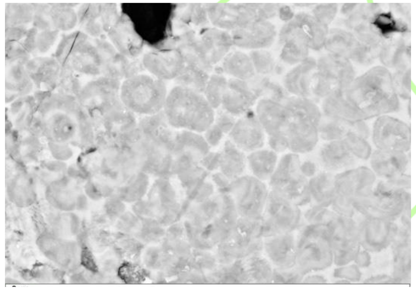
Comodi et al. (2021) 10.3390/su13116052



Apatite crystals
roundly shaped at sub-micrometric to deci-micrometric sizes



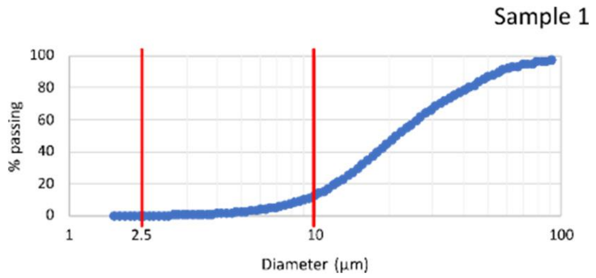
Elongated **K_2O and KCl crystals**



Devitrification structures

Apatite and sylvite
Small dimensions

→ **High P and K content.**



Red lines: positions of the **2.5 and 10 µm diameter particles**. They identify the **inhalation properties**.

- Less than 1 vol% of particles with dimensions under 2.5 µm .
- Particles with diameters less than 10 µm vary from 5 to 40 vol%.

Large reaction surface, one the most important parameters for **bioavailability**.
Good fertilizer for agricultural lands.

High Ca content
Supposedly stored in the amorphous phase

→ Biomass fly ashes could be used in combination with or as **substitutions for traditional binders** (e.g. CaO) in soil stabilization.
Good amendments in soils, usually clayey soils, with low geotechnical properties

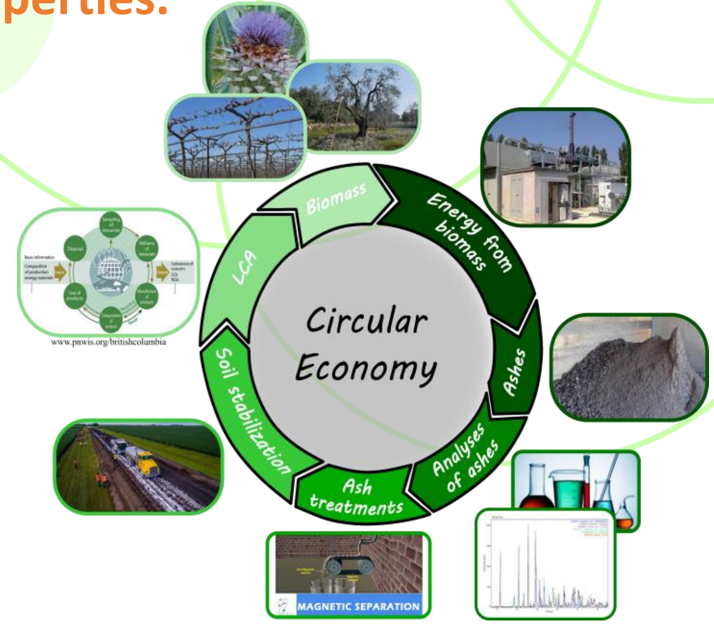
Fly ashes and their employment in civil engineering and agriculture

The Circular Economy

To move on…towards Circular Economy

1. Addition of Ca from biomass fly ashes in soils with poor geotechnical properties.

2. Biomass fly ashes used as agricultural fertilizes.



The above-mentioned scenarios fit well with the principles of the

Circular Economy

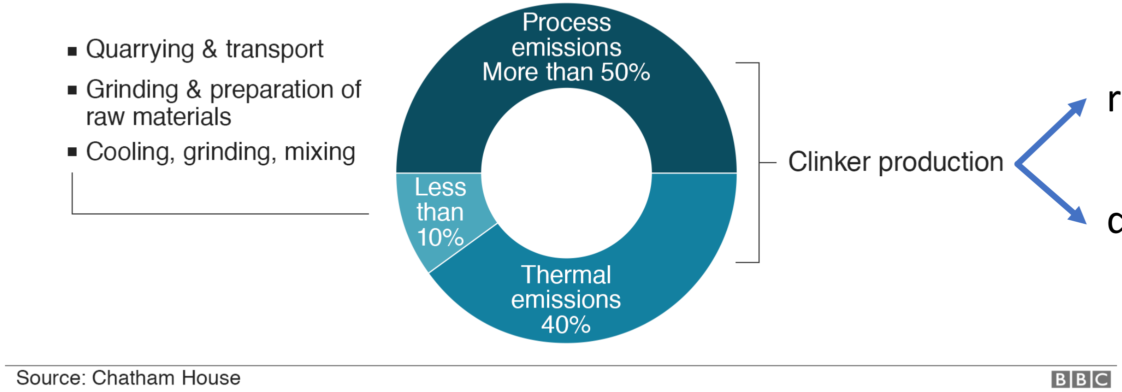
Waste materials, such as biomass fly ashes, are recycled and used as second generation products.

Collocazione PTSR 2021-2023:
Ambito di ricerca nuovo: 1
«Earth System and Global Changes»

Nanomaterials: a way to decrease the CO_2 emissions in cement industry

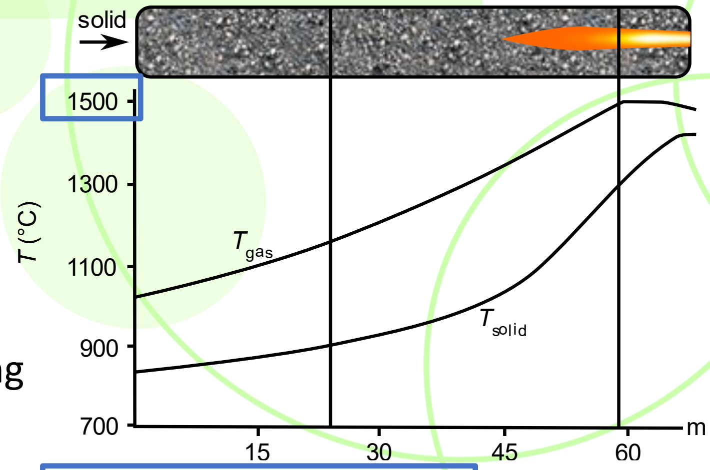
CO_2 emissions reduction

The production of "clinker" accounts for most of the CO2 emissions of cement production



rotary kilns feeding

decarbonation during firing



$CaCO_3 \rightarrow CaO + CO_2\uparrow$

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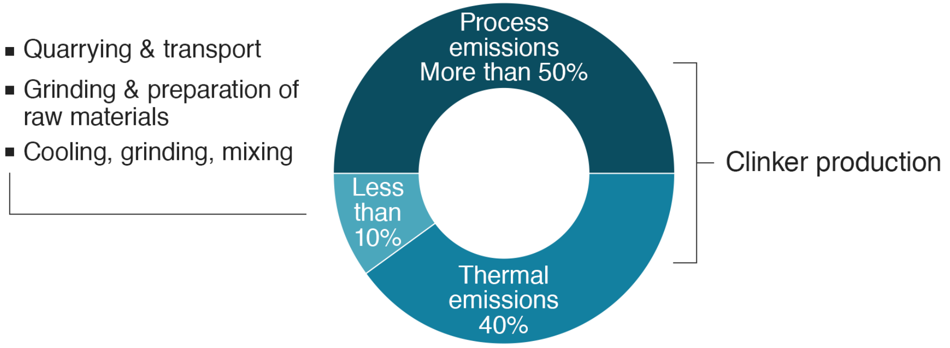
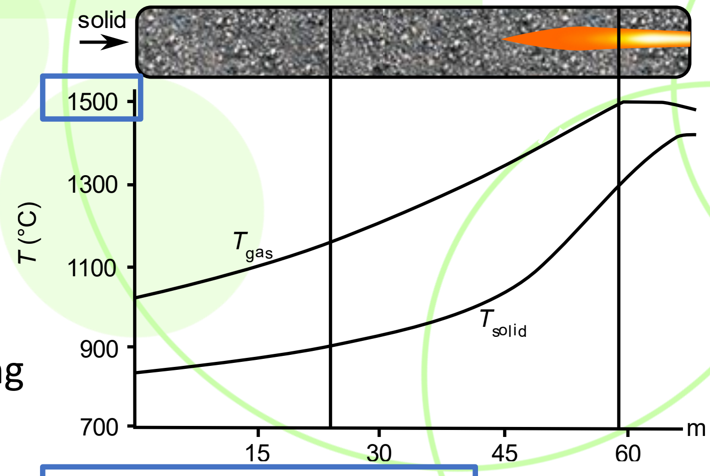


Source: Chatham House

BBC

rotary kilns feeding

decarbonation during firing



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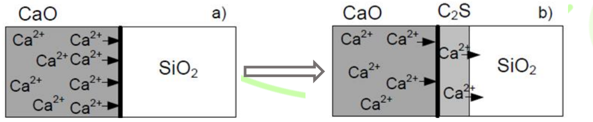
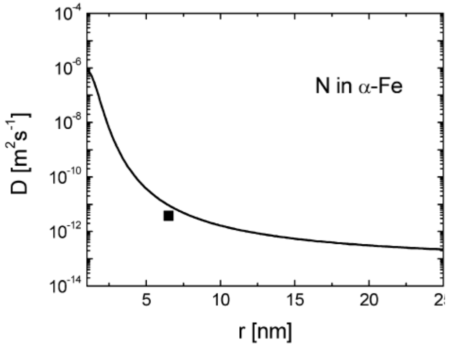
Ca^{2+} diffusion is the driven mechanism for clinker minerals formation

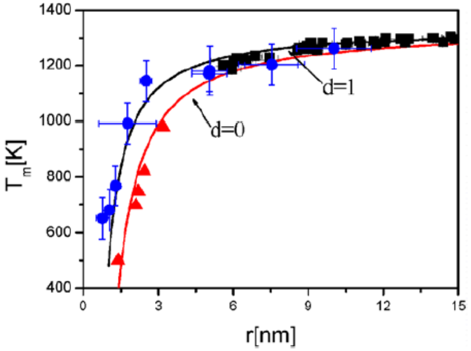


Telschow (2012) Clinker Burning Kinetics and Mechanism - PhD thesis

Our IDEA



self-diffusion coefficient



size-dependent melting *T*

Dimension to nm

↓ **Melting *T***

↑ **Diffusion coefficient**

Cohn (1948) DOI: 10.1021/cr60133a002
Jiang et al. (2004) DOI: 10.1016/j.ssc.2004.03.033

Nanomaterials: a way to decrease the CO_2 emissions in cement industry

CO_2 emissions reduction

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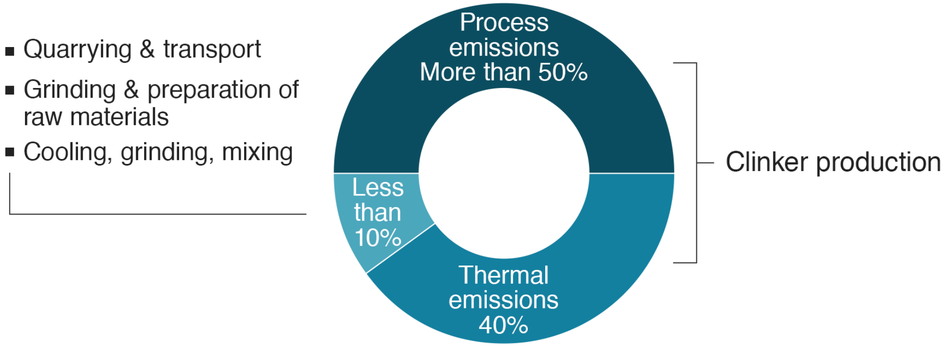
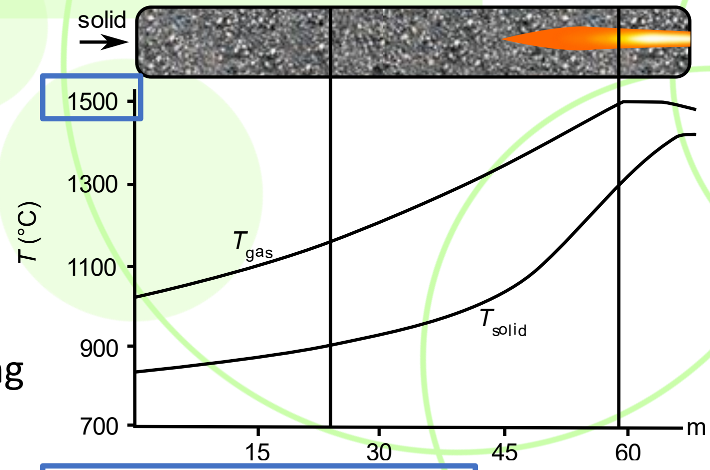


Source: Chatham House

BBC

rotary kilns feeding

decarbonation during firing



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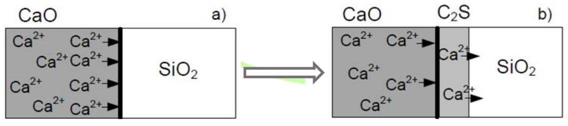


Telschow (2012) Clinker Burning Kinetics and Mechanism - PhD thesis

Limestone + Clay + Nano-materials

Nano-CaO ?

Nanomaterials: a way to decrease the CO_2 emissions in cement industry

CO_2 emissions reduction

Clinker production in Lab



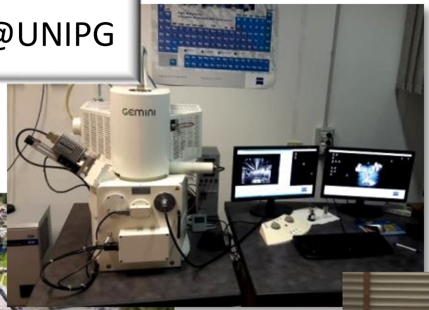



Analytical techniques

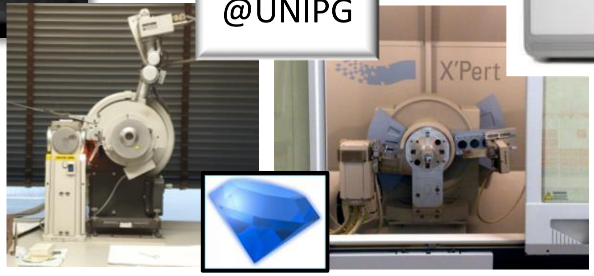
SEM
@UNIPG

µm-TC
@ELETTRA

FE-SEM
@UNIPG



XRPD
@UNIPG



DLS
@UNIPG

artisantg.com

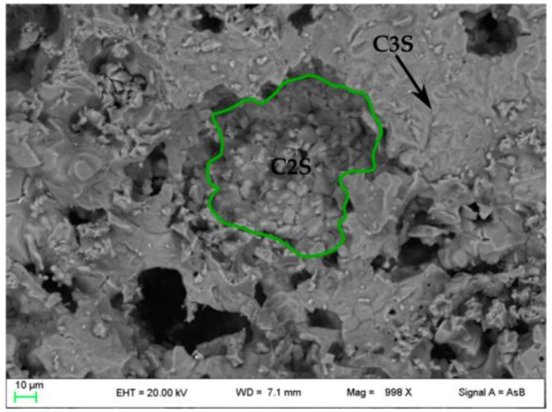
azonano.com

Nanomaterials: a way to decrease the CO_2 emissions in cement industry

CO_2 emissions reduction

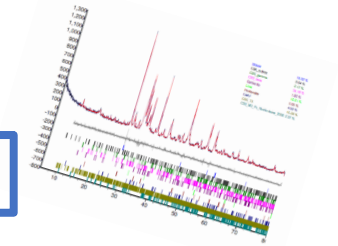
Results

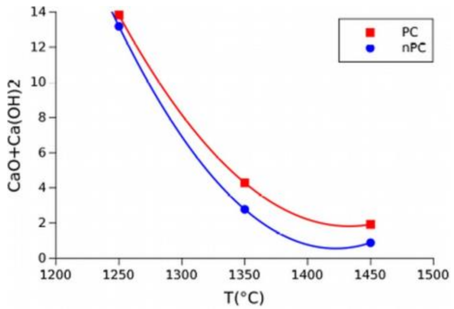
Zucchini et al (2019) DOI: 10.3390/ma12111787



Belite nest @ 1350°C with nano-CaO

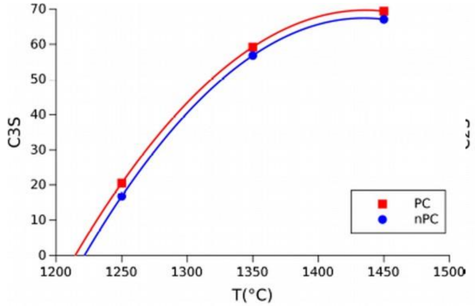
Higher **crystallinity** **of the nano-added clinker**

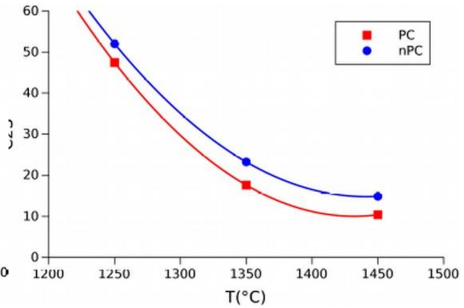




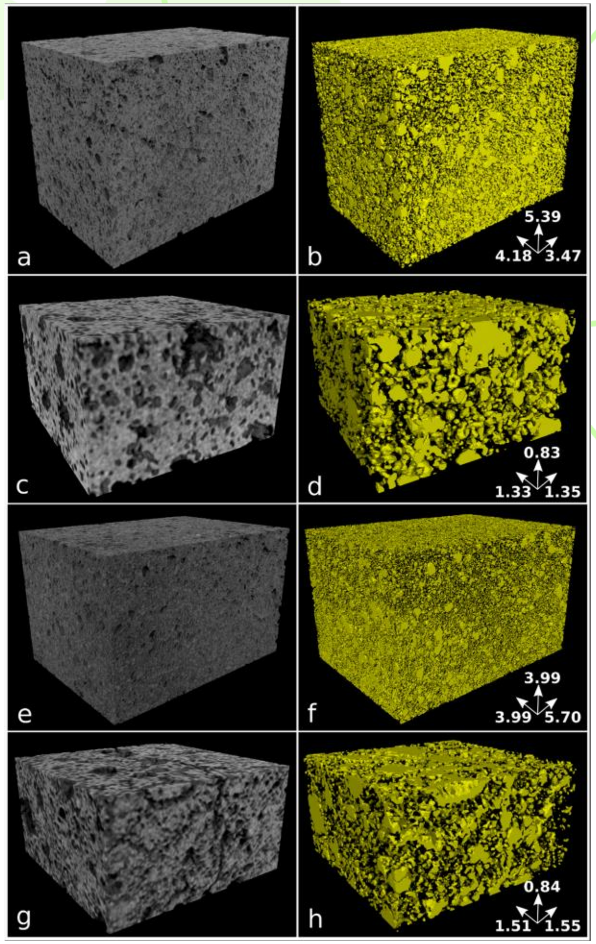
Decrease of free lime

Improvement in the nano-added clinker **cooking efficiency**





Higher **reactivity** **of the nano-added clinkers**



1450°C with nano-CaO

1450°C

1350°C with nano-CaO

1350°C

Decrease in the total **porosity**
of the clinker prepared by using nano-CaO

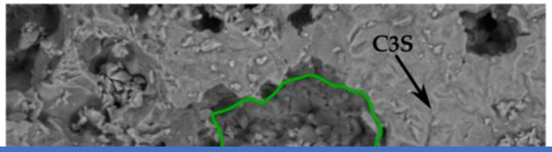
Nanomaterials: a way to decrease the CO_2 emissions in cement industry

CO2 emissions reduction

Results

Zucchini et al (2019) DOI: 10.3390/ma12111787

Collaborative actions



Belite nest @ 1350°C
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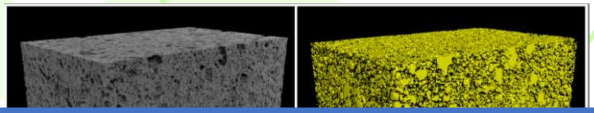
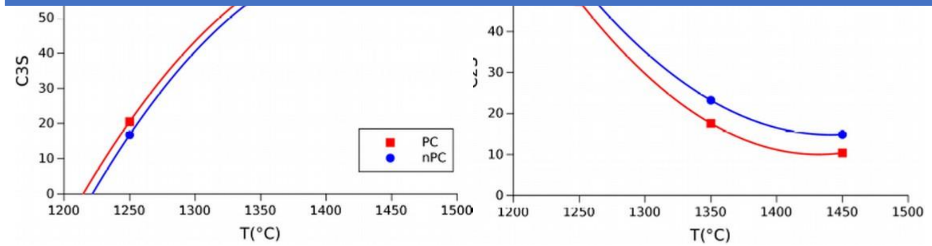
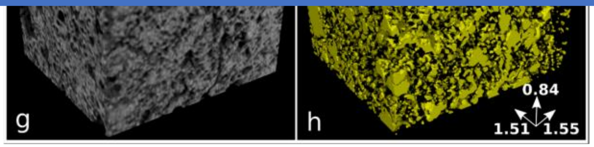


Increase of the nano-added clinkers cooking efficiency

- Decrease of the cooking *T* of approximately 100°C means **low energy requirement for the minerals formation reactions** during Portland clinker production.
- **Decrease of the CO_2 emissions** from both the **pre-treatment of starting materials** and from the **cooking process**
- **Increase of the plant productivity**



Higher reactivity of the nano-added clinkers



1350°C

Decrease in the total porosity
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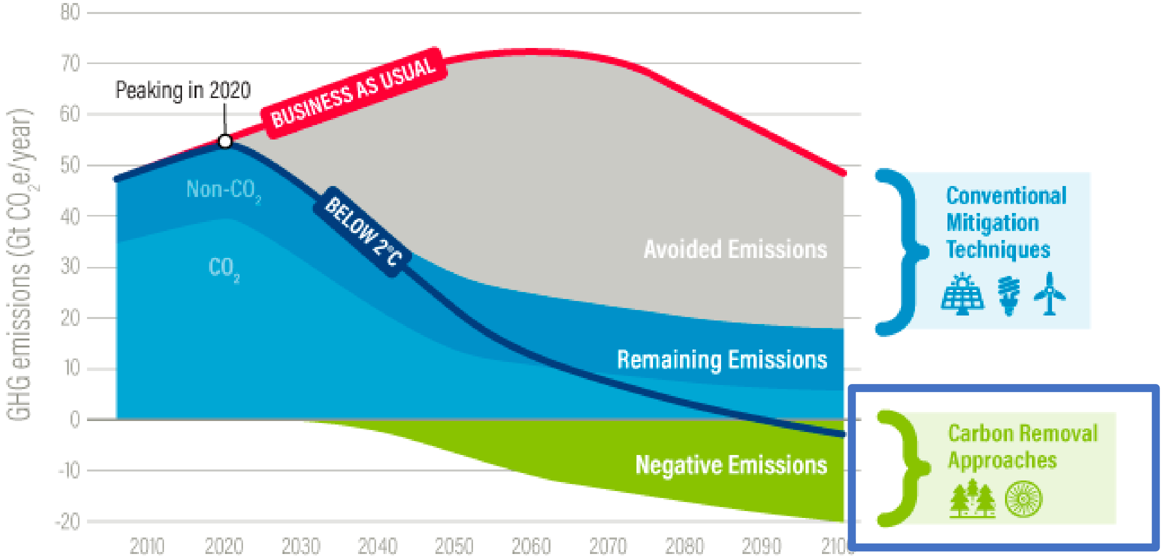
Nanomaterials: a way to increase the kinetics of the CO_2 Mineralization

CO_2 emissions reduction

To move on…towards Negative emissions



Source: Adapted from UNEP 2016.
For more information, visit wri.org/carbonremoval.

WORLD RESOURCES INSTITUTE

Ex-situ CO_2 Mineralization Reactions (CMRs)

Reaction between **CO_2 and natural silicate minerals (pyroxenes, olivine and serpentine) producing at least one carbonate type.**

$$(Mg,Ca)_xSi_yO_{x+2y+z}H_{2z(s)} + xCO_{2(g)} \rightarrow x(Mg,Ca)CO_{3(s)} + ySiO_{2(s)} + zH_2O_{(l)}$$

Slow reaction kinetics

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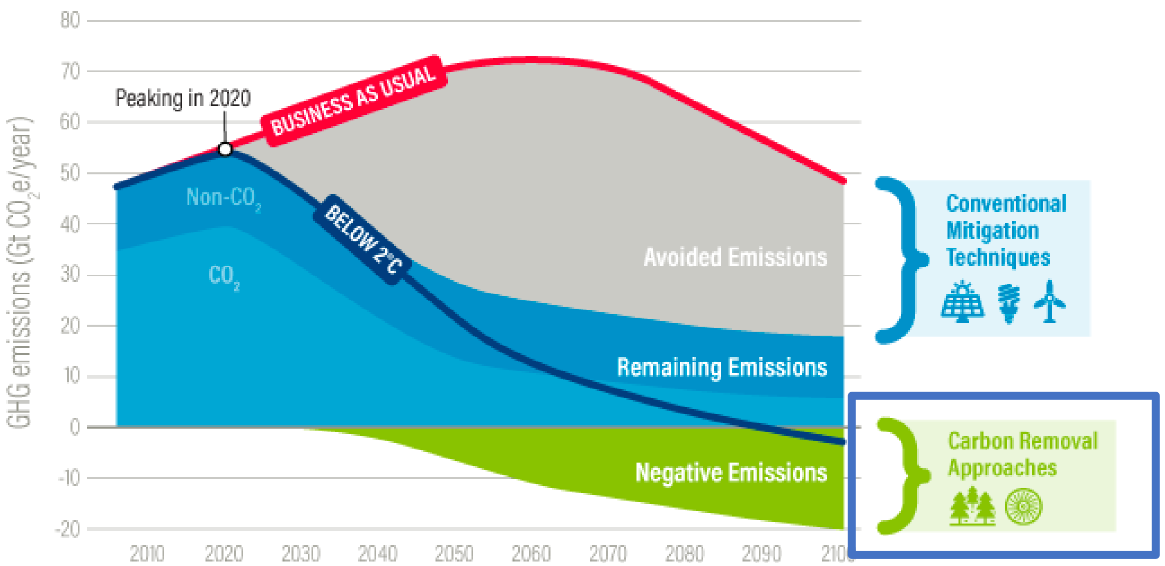
To move on…towards *Negative emissions*



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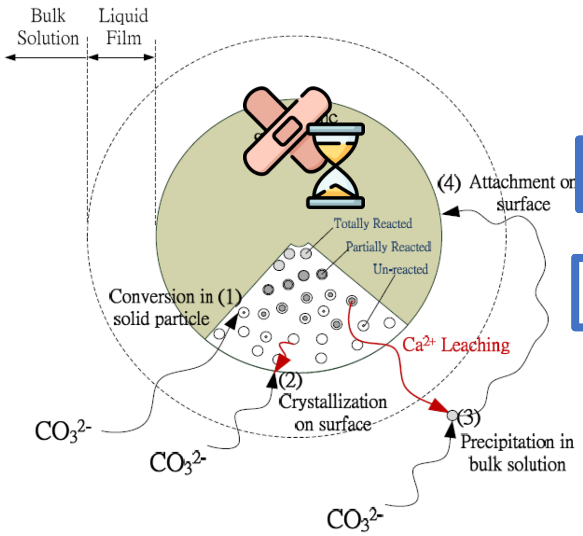

$$Ca(OH)_{2(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(l)}$$

$$Mg(OH)_{2(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)} + H_2O_{(l)}$$

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$$MgO_{(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)}$$

Pan et al. (2012) DOI: 10.4209/aaqr.2012.06.0149

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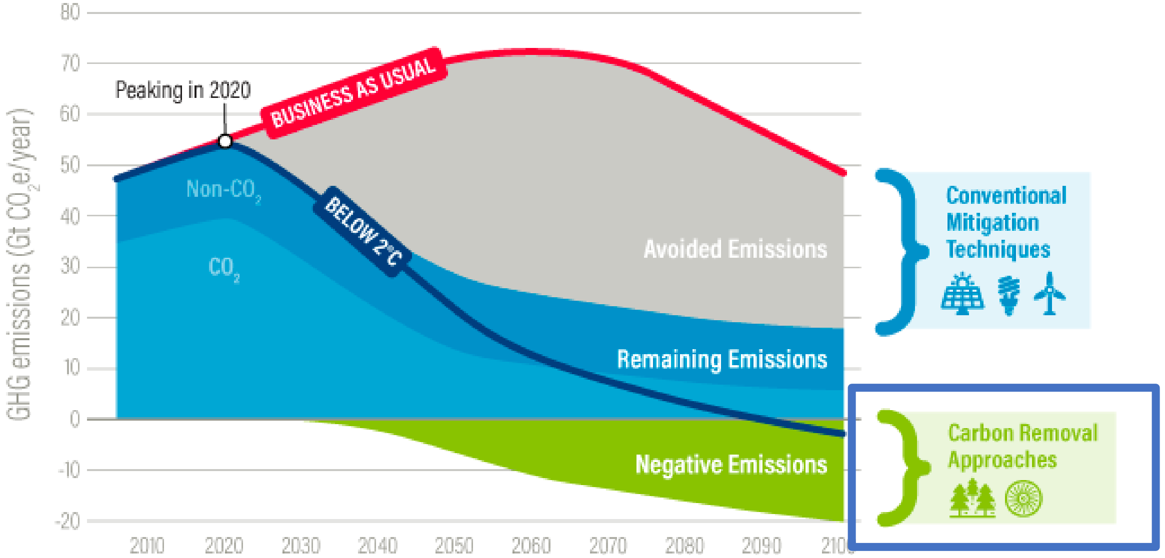

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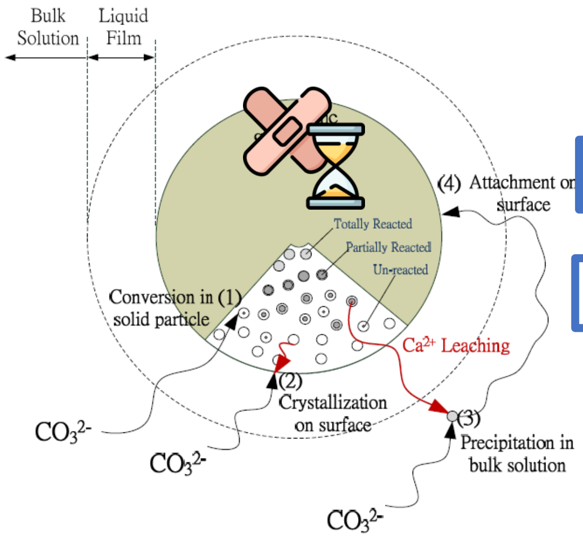

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$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$$

$$MgO_{(s)} + CO_{2(g)} \rightarrow MgCO_{3(s)}$$

Main mechanism that can affect the rate and extent of carbonation:

- ❑ transportation-controlled mechanisms such as **CO_2 and Ca^{2+}-ions diffusion to/from reaction sites;**

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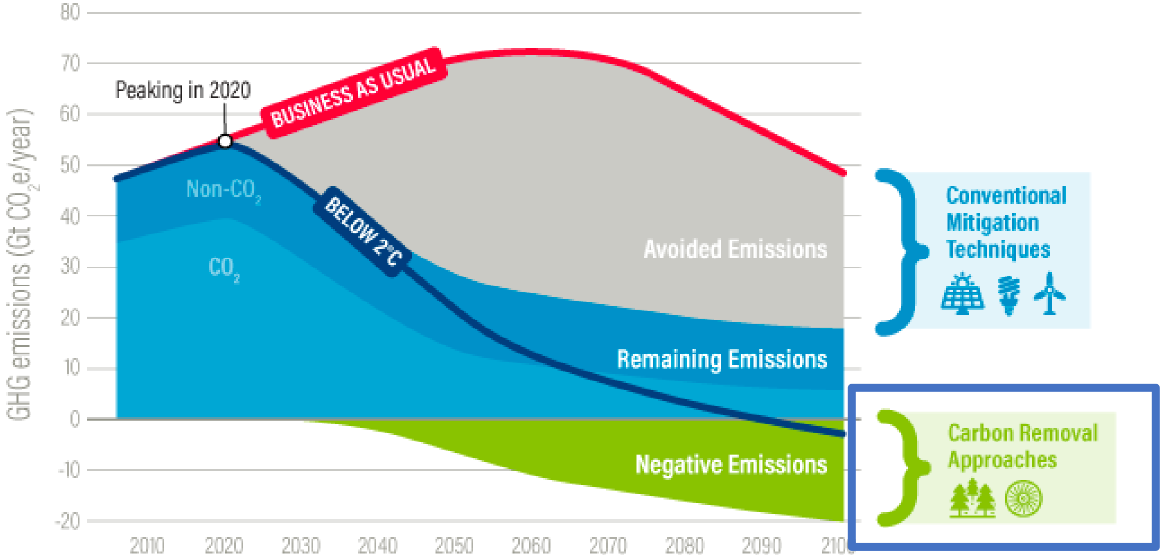

WORLD RESOURCES INSTITUTE

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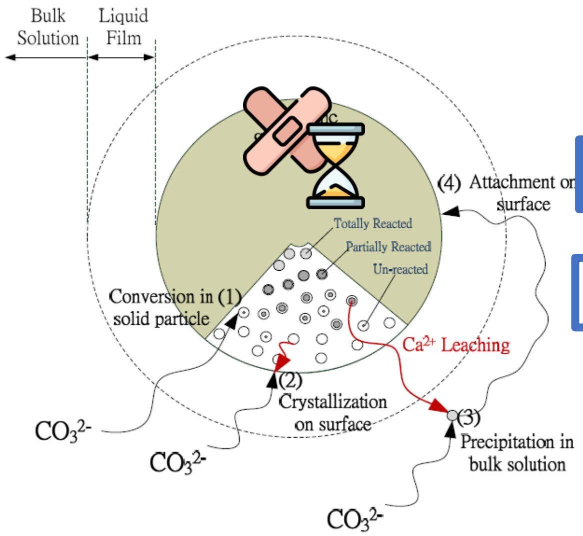

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$Ca(OH)_{2(s)}$ … $O_{(l)}$

$Mg(OH)_{2(}$ … $O_{(l)}$

$CaO_{(s)}$ + C…

$MgO_{(s)}$ + …

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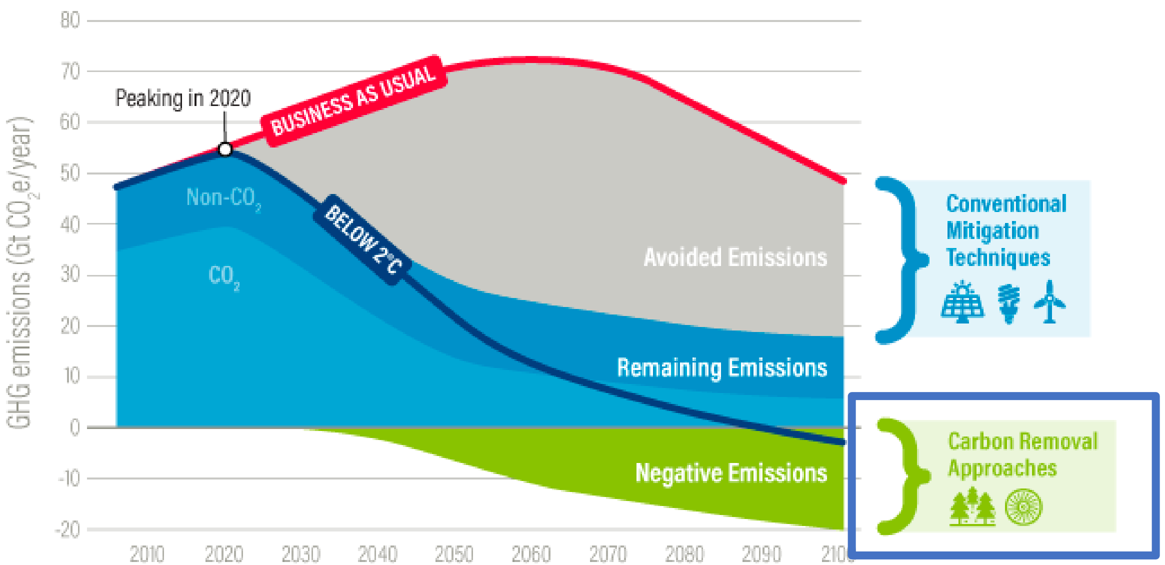
CO_2 emissions reduction

To move on…towards *Negative emissions*



Source: Adapted from UNEP 2016.
For more information, visit wri.org/carbonremoval.

WORLD RESOURCES INSTITUTE

Ex-situ CO_2 Mineralization Reactions (CMRs)

Reaction between **CO_2 and natural silicate minerals (pyroxenes, olivine and serpentine) producing at least one carbonate type.**

$$(Mg,Ca)_xSi_yO_{x+2y+z}H_{2z(s)} + xCO_{2(g)} \rightarrow x(Mg,Ca)CO_{3(s)} + ySiO_{2(s)} + zH_2O_{(l)}$$

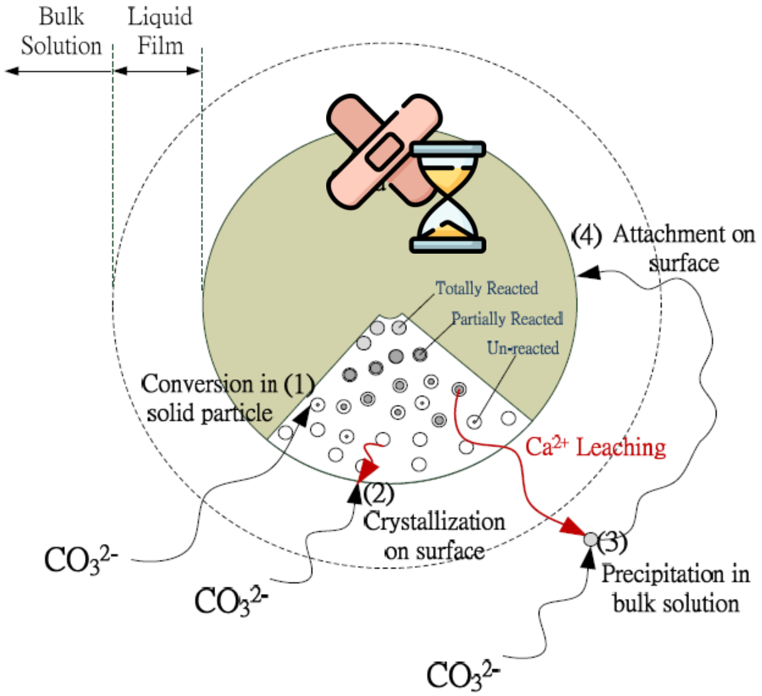
Slow reaction kinetics

Use of nano-materials to improve the kinetics of the CO_2 mineralization reactions.

The new IDEA

Collocazione PTSR 2021-2023:
Ambito di ricerca già attivato: 5
«Nanoscienze»
Ambito di ricerca nuovo: 1
«Earth System and Global Changes»

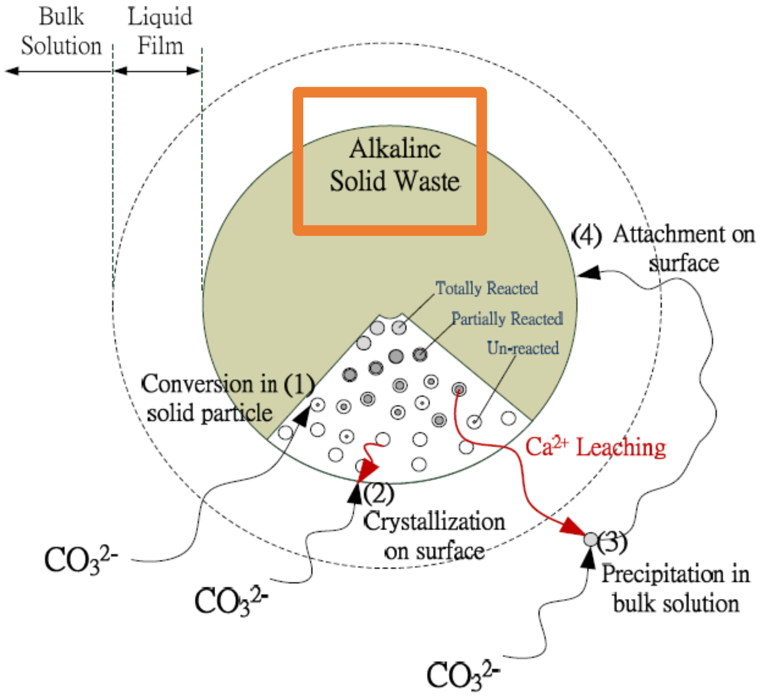
Joining Circular Economy and Negative Emissions



Pan et al. (2012) DOI: 10.4209/aaqr.2012.06.0149

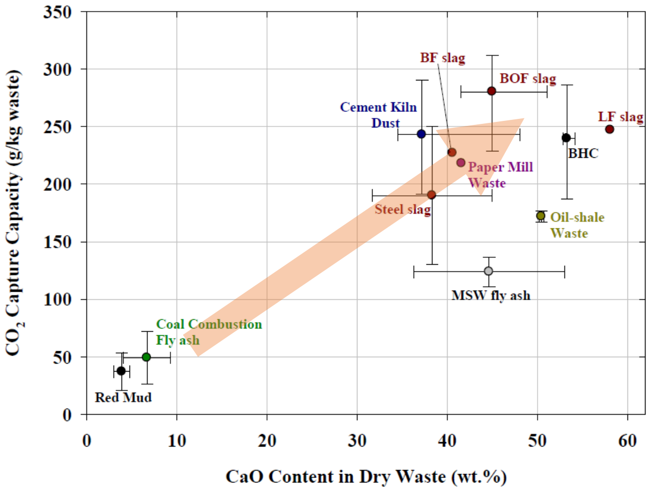
Joining Circular Economy and Negative Emissions

Ex situ CO_2 mineralization reactions by means of waste materials and nanomaterials



Pan et al. (2012) DOI: 10.4209/aaqr.2012.06.0149

Substitution of natural minerals with alkaline wastes



Pan et al. (2012) DOI: 10.4209/aaqr.2012.06.0149

- **Case study #1** Nano-CaO

- **Case study #2** Biomass fly-ashes
  Being enriched in CaO.

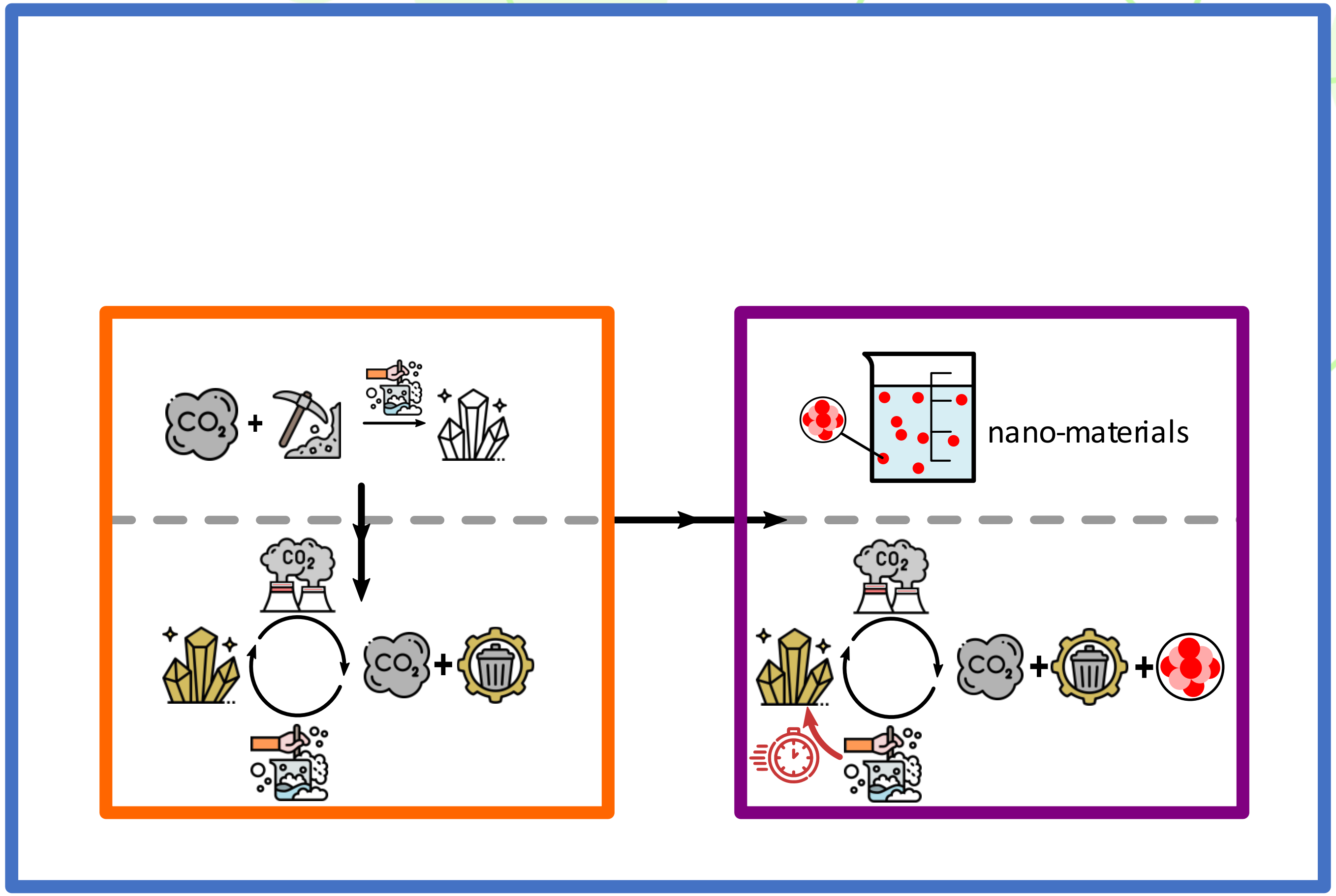
- **Joining #1 and #2**

Joining Circular Economy and Negative Emissions

Ex situ CO_2 mineralization reactions by means of *waste materials* and *nanomaterials*

2. Reagents at **low cost** that will also meet the status of **“end of waste”**

3. **Overcoming the slow reaction kinetics**



Joining Circular Economy and Negative Emissions

Ex situ CO_2 mineralization reactions by means of **waste materials** and **nanomaterials**

1. **Stable carbonate minerals**

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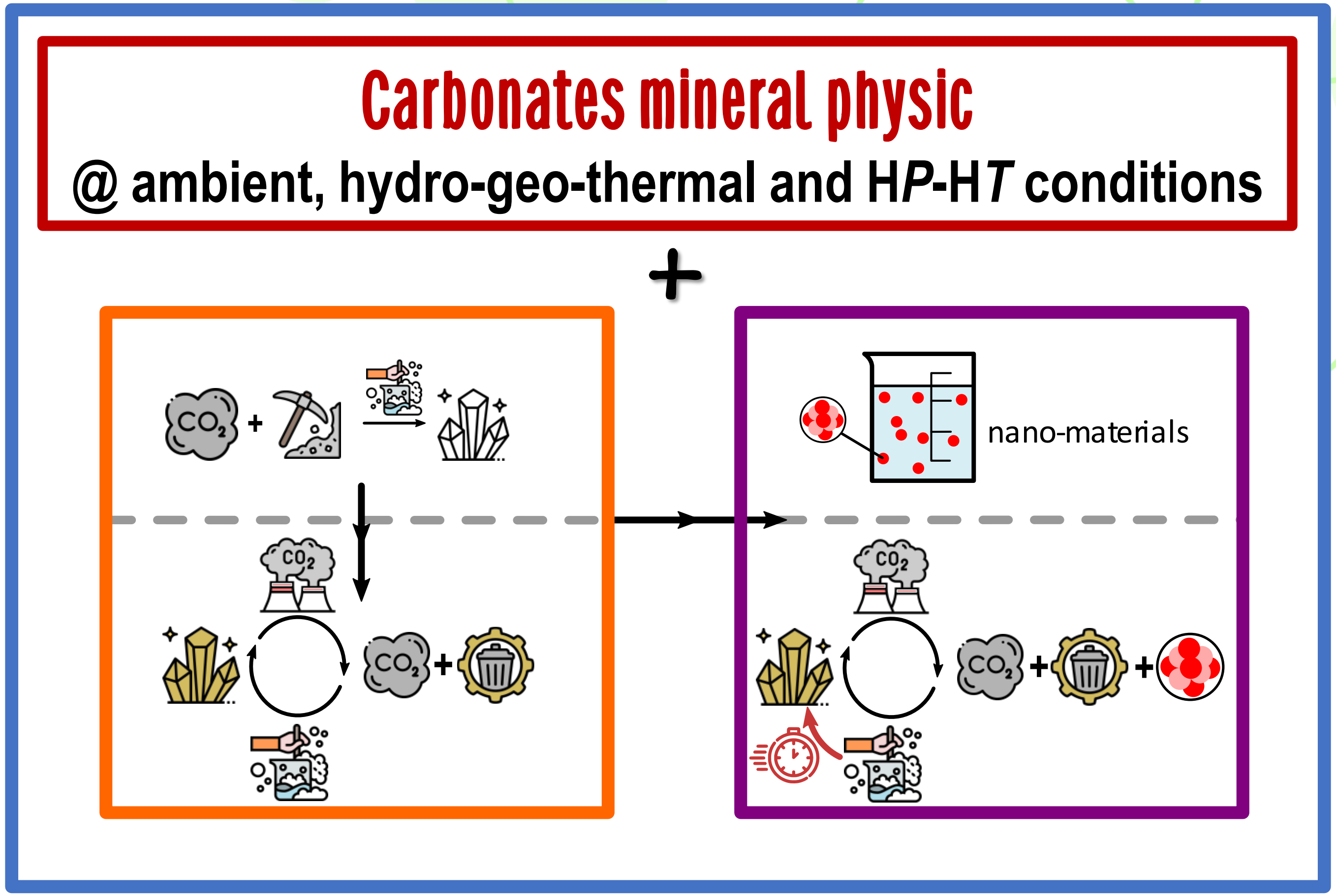
CO_2 mineralization reactions to an advanced state, efficient in terms of

CO_2 capturing **reaction kinetics**

stability of the final products

in the frame of

circular economy and sustainability



Joining Circular Economy and Negative Emissions

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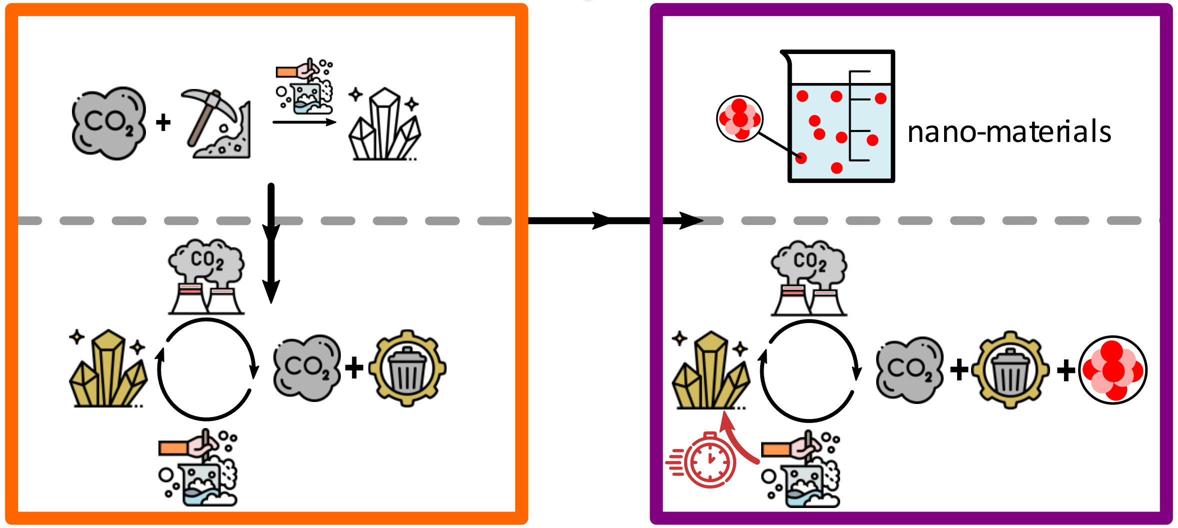
Collocazione PTSR 2021-2023
Ambiti di ricerca già attivati: 5 e 11
«Nanoscienze»
«Struttura dell'interno della Terra e geodinamica»
Ambito di ricerca nuovo: 1
«Earth System and Global Changes»

Carbonates mineral physic
@ ambient, hydro-geo-thermal and HP-HT conditions
+



Joining Circular Economy and Negative Emissions

Ex situ CO_2 mineralization reactions by means of *waste materials* and *nanomaterials*

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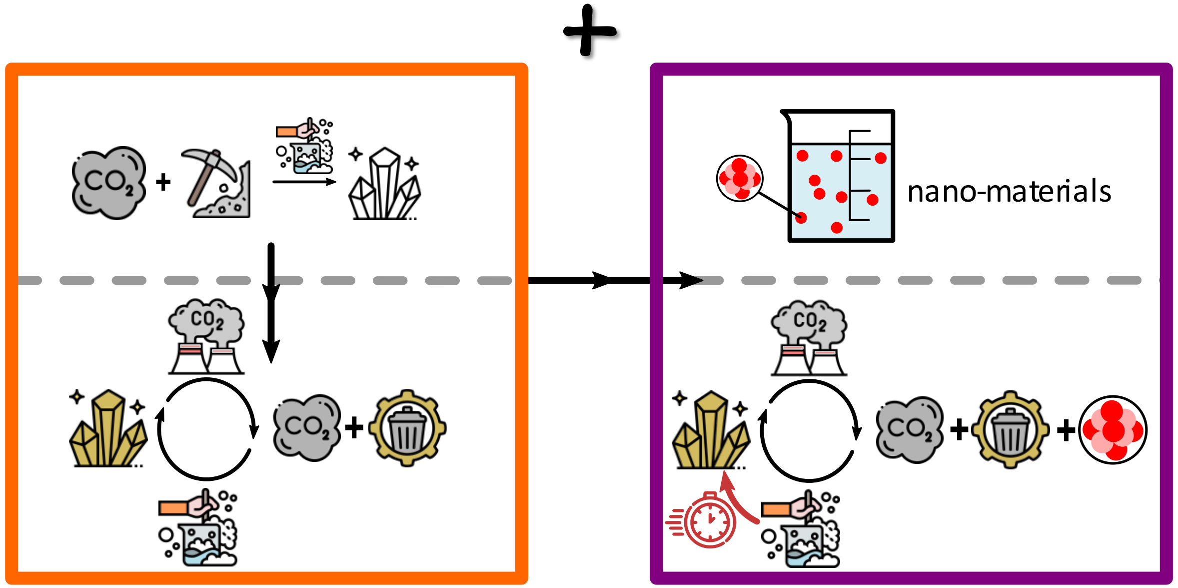
Submitted proposals

European Research Council
Established by the European Commission

Future proposals

Carbonates mineral physic

@ ambient, hydro-geo-thermal and HP-HT conditions



Joining Circular Economy and Negative Emissions

Ex situ CO_2 mineralization reactions by means of *waste materials* and *nanomaterials*

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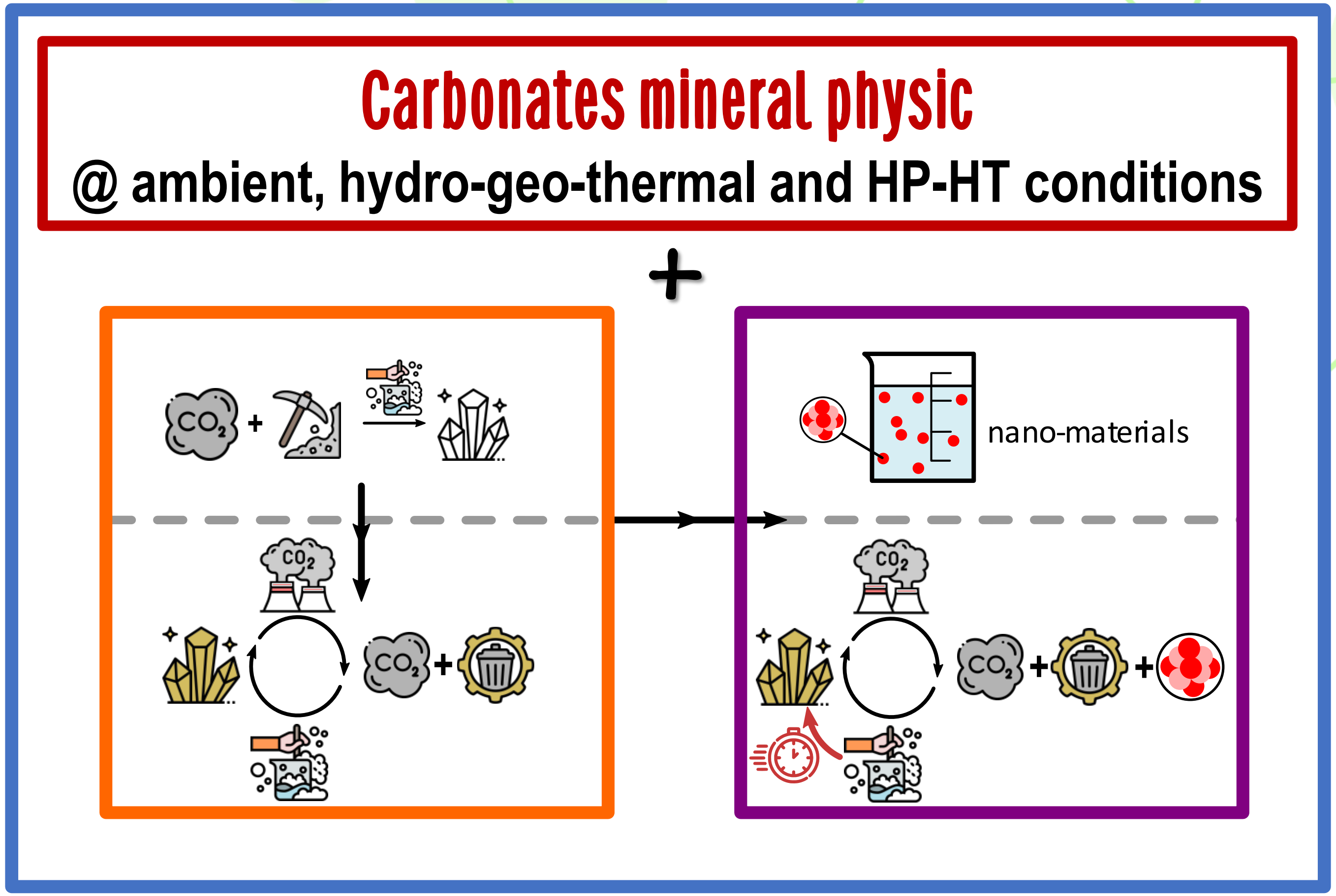

Collaborative actions

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- **Scienze Farmaceutiche**
- **Chimica, Biologia e Biotecnologie**
- **Scienze agrarie, alimentari e ambientali**

Thanks for your attention! !

Azzurra Zucchini, Paola Comodi

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European Commission

European Regional Development Fund 2014-2020 (ERDF 2014-2020)

European Social Fund 2007-2013 (ESF 2007-2013)