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Solar Thermal Treatment of Non-Metallic Minerals: the Potential Application of the SOLPART Technology

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High Temperature Solar-Heated Reactors for
Industrial Production of Reactive Particulates



SOLPART Project Objective

Develop, at a pilot scale, a high temperature (800–1000 °C) 24 h/day solar process suitable for particle treatment in energy intensive non-metallic minerals' industries.

SOLPART Project Concept

Supplying totally or partially the thermal energy requirement for CaCO_3 calcination by solar heat, which is 60% of the total required energy in a cement plant and 100% in a lime plant.

Examining similar thermal applications for other non-metallic minerals, e.g. dolomite, phosphate, kaolinite, and others.

SOLPART Project Partners

Participant No *	Participant organisation name	Short name	Organization type	Country
1	Centre National de la Recherche Scientifique	CNRS	Research organization	FR
2	CEMEX	CEMEX	Industry	CH
3	Deutsches Zentrum für Luft- und Raumfahrt EV	DLR	Research organization	DE
4	Abengoa Research	ABENGOA	Industry	SP
5	University Manchester	UMAN	High education	UK
6	European Powder & Process Technology	EPPT	SME	BE
7	COMESSA	COM	SME	FR
8	EURONOVIA	EURONOVIA	SME	FR
9	New Lime Development	NLD	SME	BE
10	Université Cadi Ayyad (& OCP as third party)	UCA	High education	MA

Expected Results and Impact

- Demonstrate a **pilot scale solar reactor** (about 30 kW_{th}) suitable for calcium carbonate decomposition and cement raw meal calcination (calcination reaction: $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$).
- Simulate at prototype scale a 24 h/day industrial process (TRL 4–5) thereby requiring a **high temperature (about 900 °C) particle transport and storage system**.
- Reduce the CO₂ emission by 40% in the lime and cement industry and by 100% if CO₂ capture and sequestration is applied. Inject 60% solar energy in cement processing.
- Develop a solar technology able to treat particles to about 900 °C and apply it to various minerals.



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Several minerals require a physical-chemical and thermal treatment prior to their application as mineral feedstock and use in the production of value-added products. The thermal processes are energy-consuming, partly due to the preheating of the minerals to their reaction temperature, but mostly due to the endothermicity of the reaction itself.

Conditions and objectives of thermal treatments of target minerals

Reaction system	T (°C)	Sensible heat reqd. kJ/kg of product	Reaction heat kJ/kg of product	Use
$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	850-950 f(P _{CO2})	500 to 2000, function of degree of heat recovery	3000-3200	Lime, Cement
$\text{MgCa}(\text{CO}_3)_2 \rightarrow \text{MgO} \cdot \text{CaO} + 2\text{CO}_2$	650-750 f(P _{CO2})	See above	2400-2700	Dolomite, Dolomitic Lime
Meta-kaolinite	550-900	300 to 500, function of degree of heat recovery	~700	Pozzolanic additive for cement and lime-mortar
Phosphate ore	700-1000	Max. 300, function of degree of heat recovery	Exothermic (combustion of C- contaminants); Mostly endothermic (calcite calcination)	Feed stock for Phosphate Industry
Clays, Sands with organic contaminants	600-700	~700	Slightly exothermic by combustion of organic contaminants	Ceramics, Pipes, Tiles, Concrete

- The total consumption energy in the target lime production processes is in the range of 3600 – 5000 kJ/kg of CaO, and in the range of 3100 - 4200 kJ/kg of clinker (cement industry) and represents 40% of the total production cost per ton of cement (dry rotary kiln with cyclonic pre-heaters) and up to 60% in the case of lime kilns.
- Substituting fuel by concentrated solar energy may result in up to 40% reduction of CO₂ emission in the lime industry. Since in the cement industry a high temperature sintering follows the pre-calcination process, the total reduction is about 20%.
- In the thermal treatment of phosphate ores and other minerals, the CO₂ emission from the reactions is less outspoken, since the carbonate content is far lower than in lime or cement raw meal,. CO₂ emission from fuel combustion is eliminated by using solar energy, representing e.g. 6.5 kg CO₂/ton phosphate.

Target Particles

Free – flowing vs. Cohesive particles

Properties determined by

- Geldart classification
- Angle of Repose
- Ratio tapped/loose density (Hausner ratio)
- Balance of forces
- Yield limit

All but CRM are free – flowing

REACTION THERMODYNAMICS

Mostly $A \rightarrow B + \text{gas (CO}_2\text{)}$

▲ Thermodynamic equilibrium data

▲ Heat of reaction

Possible reaction pairs

Reaction $A \leftrightarrow B + C (+D)$	C_p (of A) [kJ/kgK]	T_{eq} (P=1 atm) [°C]	ΔH_r at T_{eq} [kJ/kg of A]
$\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$	$0.8227 + 0.000497T - 12,858.72/T^2$	839	1703
$\text{MgCO}_3 \leftrightarrow \text{MgO} + \text{CO}_2$	0.8387	303	1126
$\text{CaMg(CO}_3)_2 \leftrightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2$	0.92	490	868

For cement raw meal, as a mixture of ~85% of limestone, and 15% of alumina-silicates, the specific heat is about 1.05 kJ/kgK. The equilibrium temperature is ~839 K, and the reaction heat is ~1659 kJ/kg.

In the lower ranges of partial CO₂ pressures, the effect of pressure-induced changes of T_{eq} is significant, even of the order of 100 K at very low values of P. Only at high partial pressures does the value of T_{eq} remain nearly constant

REACTION KINETICS

- For conversion, both **reaction kinetics and residence time** in the reactor environment need to be assessed. For operation with a continuous feed of solids, the exit stream consists of particles of different ages and degrees of conversion. The average conversion of this stream is thus dependent upon (i) the rate of reaction of single particles in the reactor environment, and (ii) the residence time distribution of solids in the reactor.
- For small particles ($d \ll 200 \mu\text{m}$), chemical reaction determines the reaction rate (external + internal diffusion negligible)
- Mostly 1st order $k = A \exp\left(\frac{-E_A}{RT}\right) \quad \ln(1 - \alpha) = -kt$
- Since the decomposition must proceed against combustion gases and the CO_2 generated by the decomposition, the decomposition time τ will increase. It is therefore necessary to apply a correction coefficient so that:

$$\tau' = K_C \tau \quad \text{with} \quad K_C = \frac{1}{1 - \frac{P_{\text{CO}_2}}{P_{\text{EQ}}}}$$



EXPERIMENTAL INVESTIGATION

Both by dynamic (non-isothermal) and isothermal methods

- dynamic α f(T)
- isothermal α at specific T

For a first order reaction, the conversion expression is

$$\ln(1 - \alpha) = -kt = -A \exp\left(\frac{E_A}{RT}\right) t$$

1st-order reaction results for different reactions

Reaction	E _A [kJ/mol]	A [s ⁻¹]
<chem>CaMg(CO3)2 <=> MgO + CaO + 2CO2</chem>	219	1.15×10^{12}
<chem>CaCO3 <=> CaO + CO2</chem>	228	7.03×10^7
Cement raw meal	224	6.53×10^7

To achieve 95 % of conversion in a first order reaction, the required reaction time at indicates that the reactions can be completed for fine particles in less than a minute. This is however tentative only, and pilot/large scale experimentation is certainly required.

MASS AND ENERGY BALANCES

The mass balances determine the feed rate (kg/h) of raw material for the given target production, respectively 5 kg/h in lab-scale, and 30 kg/h in pilot-scale for the SOLPART project. For 5 kg/h of CaO, CaO·MgO and calcined CRM, respectively 9.2 kg/h of $\text{CaMg}(\text{CO}_3)_2$ and 8.3 kg/h of cement raw mix are required.

The maximum heat to be supplied, based upon the mass balance includes the sensible heat of the limestone feed, the sensible heat of the fluidization air, and the reaction heat. A total of 4.9 kW is required. For the pilot scale application, all values are multiplied by 6, leading to a net required heat supply of 29.6 kW.



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SELECTED SOLAR REACTOR TECHNOLOGY

Different type of solar reactor were tested in the framework of the SOLPART project. CNRS and DLR initially tested the upflow bubbling fluidized bed, UBFB, and solar rotary kiln respectively. Problems of dust formation, difficulties to meet the required residence in a single pass operation, the effect of high CO₂ partial pressures in the reactor environment, and the cohesiveness of some of the required raw materials were major drawbacks.

A shallow cross-flow bubbling fluidized bed (CfBFB) was hence developed by BUCT, EPPT and CNRS.

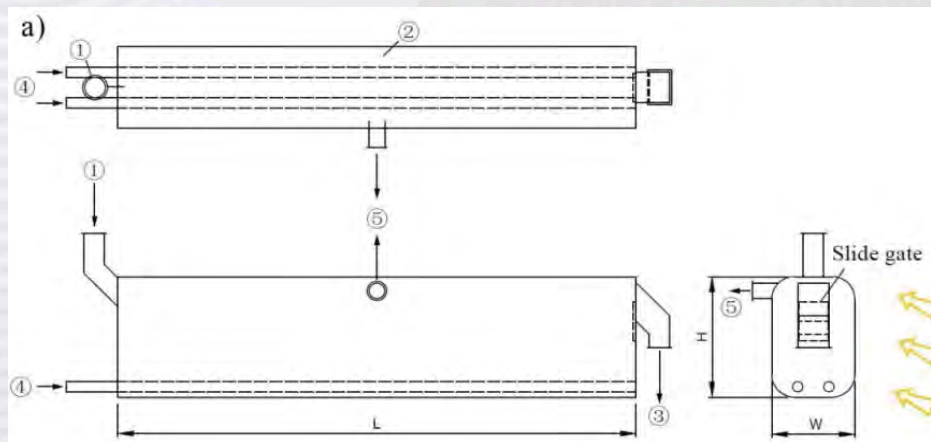
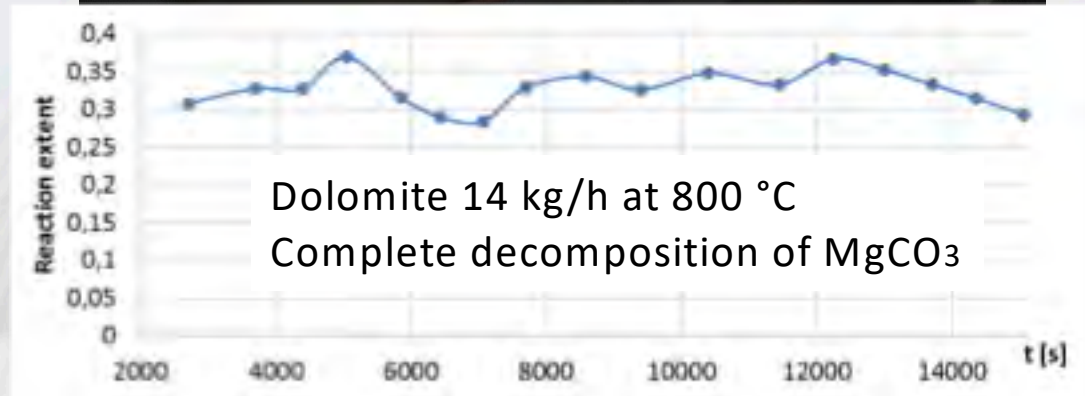
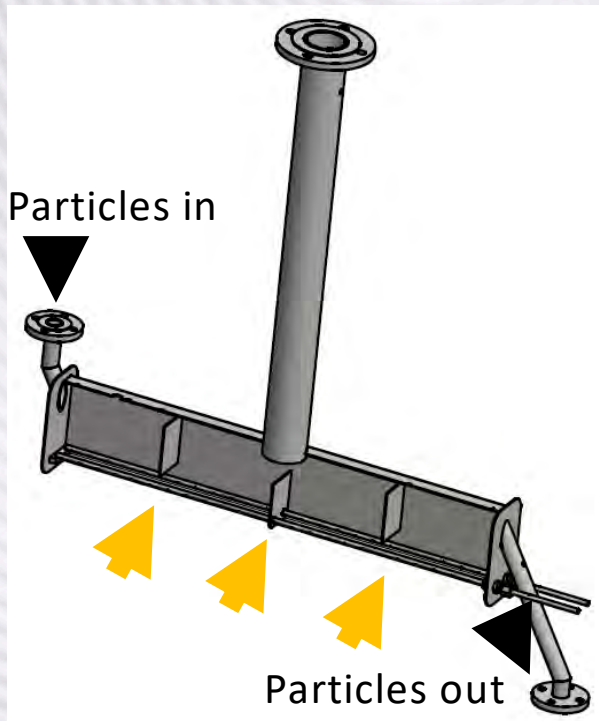
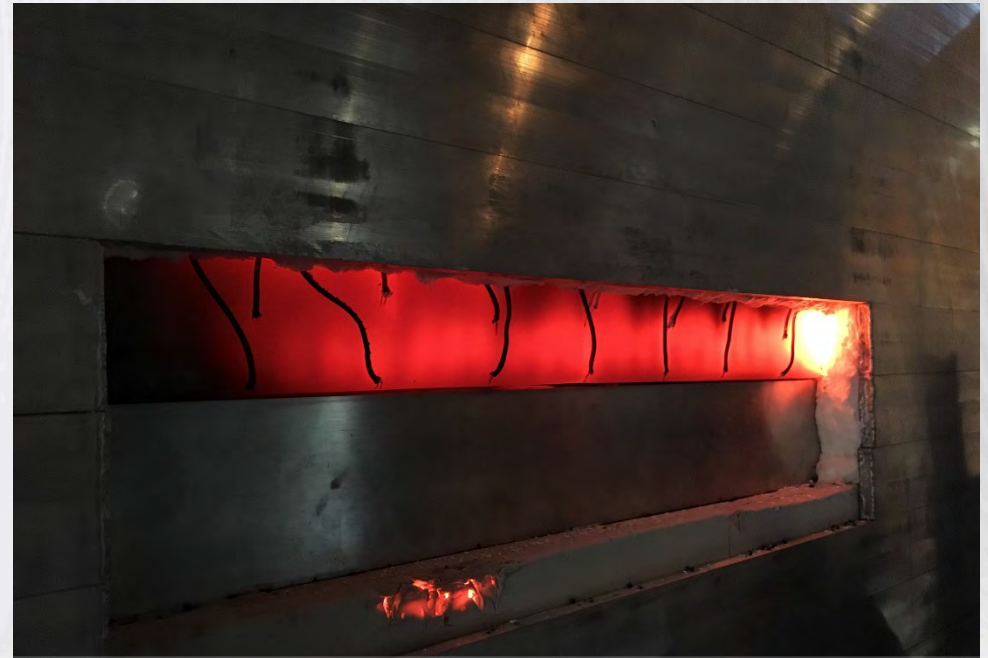


Illustration of a cross-flow bubbling fluidized bed: (a) in a solar thermal application with ① feed of particles, ② horizontal fluidized bed, ③ discharge of particles, ④ multi-orifice air distributors, ⑤ exhaust air.

First experiments on lab-scale, using dolomite, gypsum and mete-kaolinite were completed and prove that the required conversion can be obtained in a single pass operation. Results with limestone are ongoing.

Lab-scale Solar Reactor Development and Testing

Shallow, cross-flow fluidized bed (patentPending), Credit PROMES-CNRS



MARKET PROSPECTS (1)

Calcination of Limestone, Dolomite and CRM

The limestone-lime market outside China is dominated by 2 international groups, i.e. Carmeuse and Lhoist: Lhoist = mostly in Europe (limited solar potential), Carmeuse = Europe + the Middle and Far East, Africa, USA and South America.

- Carmeuse offers several options for joint development of the technology in Italy (Carrara), Turkey (4 plants), Oman, Florida, and Colombia. Initial study for a 40 ton/day plant for both limestone and dolomite was conducted for the Carmeuse Soma-site in Turkey, where the solar irradiance pattern is excellent outside the winter season. A hybrid solar-biomass kiln offers a high potential. Investments were estimated, with costs of 1.9 M€ (Heliostats and solar tower), 1.3 M€ (Calcination reactor, cooling and preheating) and 0.65 M€ (Site layout, utilities).
- The calculated production cost of quicklime was about 30% lower than the cost of fossil-fuel produced product. The pay-back period was less than 5 years.
- Additional contacts with other lime producers in Spain, Algeria, and South Africa.
- Cemex is part of the SOLPART consortium, and their plant in Alicante (Spain) has been selected for the industrial demonstration. No contacts outside Cemex were made.

MARKET PROSPECTS (2)

Phosphate Calcination

- Solar energy seems a valid alternative, since major phosphate producing countries also experience high values of DNI, Morocco being an example.
Heat requirements and reaction kinetics were determined by TGA and DSC.
- A solar energy input of ~ 300 kJ/kg phosphate is needed, a reduction by nearly 65% in comparison with the current solution.
- Considering annual average DNI-values and the duration of solar irradiance, two alternatives are being studied : either a solar reactor of ~ 40 MW_{th} operated during the daytime at 480 ton/hr, or a continuous hybrid 17 MW_{th} reactor (fossil fuel for night time and sun-lean days).
- Both solutions will significantly reduce the fossil fuel consumption and result in a reduced CO₂ emission of 72,000 to 84,000 ton/year.
- Considering the required investment for a 40 MW_{th} receiver-reactor and the costs of consumed fuel oil and electricity, the payback period is estimated at 3 to 4.5 years.

OTHER MINERALS

- Additional experiments were conducted and industrial contacts were made with various manufacturers (clays, sand, meta-kaolin, cristobalite). With reserves of high purity clays in Europe being slowly depleted, alternative clay resources need to be exploited and imported.
- Since target supplies investigated are from North Africa, the use of solar calcination offers a potential for a clean and energy-friendly process. Tests are currently performed to investigate this process (650 – 750 ° C), and will be reported upon.
- Meta-kaolin needs de-hydroxilation (removal of chemically bound water) at a temperature of 500 to 650 ° C, when the aluminosilicate structure becomes amorphous or weakly crystalline and develops a pozzolanic reactivity (possible use in grouts as a blend with lime or dolomitic lime, in pozzolanic cements and mortars, etc.
- Due to current shortages of high quality sand in Europe, new resources need to be developed. The Sahara desert offers this possibility, as was previously demonstrated by DLR, with the aim of replacing up to 15% of the total amount of sand in concrete products by desert sand.
- Finally, NLD developed a specific hybrid solar system for calcining and sintering dolomite. Initial contacts were made with BCB (Algeria) for a possible 300 t/day hybrid process. Details will be made available in the presentation.



Major Challenges and Barriers

- Develop solar reactors able to process continuously reactive particles with various size and reaction temperature.
 - Design and test conveying and storage systems at 900 °C.
 - Design a solar process that can be integrated in existing plants (cement, lime, phosphate).
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- ✓ High temperature materials
 - ✓ Residence time / reaction time
 - ✓ Dust formation and management
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- Scale-up to MW_{th} production facility



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CONCLUSIONS

The solar horizontal bubbling fluidized bed concept developed within the SOLPART research project can be used as a solar receiver-reactor.

The SOLPART project paves the route to applications of solar heat at up to 900°C in the mineral industry.

Although many challenges remain, this application offers a considerable industrial potential, as illustrated in the paper.

The most demanding application is the calcination of limestone, either as pure calcite, or as 85% mix in cement raw meal.

Other thermal treatments (e.g. dolomite, gypsum, phosphate rock, meta-kaolin, clays, etc.) are less demanding since occurring at a lower temperature and with an endothermic reaction heat that is significantly lower than the reaction heat of CaCO_3 = the relevant test case.



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Thank you for your kind attention

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