



SOLPART

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

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Deliverable D1.4

WP1 – Assessment of technologies for solar particle processing and storage at high temperature

Deliverable D1.4. Report on chemical behavior of natural phosphate during calcination.

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Annex 1

1. Phosphate Minerals

1.1. Background information

Phosphate rock and its derived upgraded phosphates are important minerals. 97% of the world production of phosphate ores is located in 16 countries, each producing multi-million ton/year [Jasinski, 2005 and 2007], and arranged in descending order of their production capacities including: USA, Morocco, China, Russia, Tunisia, Jordan, Brazil, Israel, Syria, South Africa, Egypt, Australia, Senegal, India, Togo and Canada. Only 5 Mt/yr are produced by all other countries. Since the origin of these phosphate rocks differs, their mineralogy and composition varies widely, as illustrated for some deposits in Tables 1 and 2 [Abouzeid, 2008]. Data for Morocco are not included, since dealt with in section 1.2. Depletion of current economically exploitable reserves are estimated at somewhere between 60 to 130 years. Increasing demand and increasing prices will make more reserves economically exploitable [Evans and Johnston, 2004]. Based upon the current rate of extraction (~150 Mt/yr) and the available extractable reserves (180,000 Mt), the life time of these known reserves is about 120 years [Jasinski, 2007].

Table 1: Mineralogical composition of phosphate ores (in %) [Abouzeid, 2008]

Phosphate ore	Apatite *	Calcite	Dolomite	Quartz	Kaolinite	Feldspar/ Mica
Algeria	84		10	2.5		
Tunisia 1	85	2	3	3		
Tunisia 2	90	4	1.5	1.5		
Tunisia 3	85	6	1	6		
Jordan-mean	74	11		12		
Senegal	83	3		11		
Togo-mean	87			8	1.5	
Brazil, Patos	55			30	2.5	2/5
Brazil, Bahia Inglesa	62			18		13/1.5
China, Jingxian	46	8	21	23		1/-
China, Jinning	58		11	27		-/3

* Apatites are mostly fluor-apatite [$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$] and hydroxy-apatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$].

The ability of anions to substitute phosphate in apatite is not restricted to F^- and OH^- , but also CO_3^{2-} , silicate, aluminate, titanate and arsenate may also occur. Likewise, calcium may be replaced in part by trace metals such as uranium, rare earths, cadmium, magnesium, strontium and barium. [USGS, 2003].

Table 2: Chemical composition of phosphate ores (in %) [Abouzeid, 2008]

Phosphate ore	P ₂ O ₅	CaO	MgO	CO ₂
Algeria	28.90	47.95	1.46	7.66
Tunisia 1	29.55	48.23	0.47	6.14
Tunisia 2	30.29	49.63	0.51	5.88
Tunisia 3	28.12	47.39	0.45	6.59
Jordan-mean	30.53	48.51	0.26	4.75
Senegal	35.51	50.05	0.06	1.96
Togo-mean	52.01	44.21	0.20	1.55
Brazil, Patos	25.45	31.40	0.21	0.45
Brazil, Bahia Inglesa	17.22	28.88	0.72	3.92
China, Jingxian	19.24	35.47	3.93	12.30
China, Jinning	21.39	30.98	0.95	2.67

1.2. Phosphates in Morocco and the OCP Group

1.2.2. The OCP Group

The OCP Group is a world leader in the phosphate and phosphate derivatives market with nearly 30% of the global market share. The company is active across 5 continents with 22,000 people employed. As the largest exporter of phosphate rock and phosphoric acid, as well as one of the world's largest producers of fertilizer, OCP is a major agricultural development player. OCP provides innovative solutions to important issues, such as agricultural output, the use of fertilizer suited to the needs of different soils and crops, and, especially, the unrelenting search for solutions that do not have an impact on the environment and natural ecosystems.

OCP is the world largest producer of phosphate rock, with an annual mining capacity of 36.6 million metric tons. The Group's mining operations are focused in three regions in Morocco, with 6 mining sites in Khouribga (near Daoui, Merah El Ahrach, Sidi Chennane, and Beni 'Amir), 3 in Gantour (Ben Guerir, Bouchane, and Mzinda), and 1 in Boucraâ. The quality of the rock mined at the Group's different sites grants it a prominent place on the world fertilizer stage. The concentration of P₂O₅ in the phosphate rock produced in Morocco varies between 5% and 45%. The average concentration has risen to 31.5%. According to the OCP estimation, the Khouribga reserves represent approximately 44% of the total available Moroccan reserves, whereas those of the Gantour and Boucraâ sites make up 36% and 2% respectively. OCP offers a wide range of high-grade phosphate rock for various uses, as described in Table 3 below:

Table 3: Phosphate deposits of OCP (Morocco)

Origin	Quality	%P ₂ O ₅	BPL*
Khouribga	K02	29.75	65
Khouribga	K09	31.12	68
Khouribga	K10	32.04	70
Khouribga	K12**	32.04	70
Khouribga	K20	32.95	72
Gantour	YCC	34.32	75
Gantour	Y1	31.12	68
Gantour	BG4 : Direct application	29.75	65
Boucraâ	PB	36.15	79

* Bone Phosphate of Lime
 **SSP production adapted (and other specific uses)

1.2.2. Quality of the OCP phosphates

While visiting the Youssoufia phosphate plant of OCP on 01 December 2016, samples were taken and analyzed subsequently. Table 4 shows the results of the chemical analyses.

The OCP phosphate mineral is indeed of excellent quality, with average P₂O₅ concentrations of nearly 32 wt%. Compared to the data of Table 2, only 2 smaller deposits of African countries (Senegal, Togo) score better.

Table 4: Chemical composition of the mixed OCP mineral treated at the Youssoufia plant

Elements	Wt%
P ₂ O ₅	31.72
CaO	51.73
CO ₂	5.90
SO ₃	1.54
SiO ₂ -total	1.88

Al ₂ O ₃	0.29
Fe ₂ O ₃	0.10
MgO	0.49
Na ₂ O	1.12
F	4.11
Organic C	0.23

The particle size of the raw and crushed phosphate rock ranged from ~0 to 640 μm, with a 50% particle size of 172 μm. In comparison with other minerals dealt with within the SOLPART project, the average and maximum particle size are coarse. The particles belong to the Geldart B or near-D classification, against C for Cement Raw Meal, and A to near-B for all other minerals (e.g. limestone, dolomite).

1.2.3. Upgrading of the phosphate ores

The techniques for upgrading the phosphate ores are diverse. They include a size reduction and screening, attrition scrubbing and classification, electrostatic separation, magnetic separation, chemical dissolving of carbonates, pyrite flotation and other physico-chemical treatments [Abouzeid, 2008].

These techniques, or part of them in combination, are commonly applied, and outside the scope of the SOLPART research. The final upgrading of some of the ores is however performed through thermal processes (calcination), where solar irradiance could replace the use of fossil fuels.

Thermal treatment of phosphate ores

The main objectives behind the thermal treatment of the ores are:

-removing water	120-150 °C	Drying
-removing organic matter	650-750 °C	Calcination
-dissociation of the carbonates	850-1000 °C	Calcination
-removal of fluorine	up to 1510 °C	Defluorination

Drying, which is a required step in wet processing of phosphate ores, is included in the thermal treatment, although operated at moderate temperatures only.

Calcination of the phosphate ores is necessary for obtaining a phosphate product suitable for the production of light green phosphoric acid, which is in turn used in the production of pure, edible, super phosphoric acid. This last product is used in the preparation of pure chemicals, food, soft drinks, or pharmaceutical preparations.

Defluorinated phosphates are produced by adding defluorinating agents such as phosphoric acid and soda compounds, and calcining the mix between 1370 and 1510 °C. Fluorine is driven off. The resulting phosphate is essentially a solid solution of calcium phosphates as well as calcium silicate, and suitable as an animal feed supplement.

Defluorination occurs in dedicated rotary kilns, at temperatures not readily achievable in a solar furnace.

The calcination itself proceeds at moderate to high temperature, both to remove organic contaminants and decompose the carbonates. It is a well-known technology, already described by Kunii and Levenspiel [1969]. The underlying principles are the oxidation of carbonaceous contaminants (exothermic reaction), and the endothermic decomposition of $MgCO_3/CaCO_3$, the major compounds considered in the SOLPART research. The worldwide phosphate calcining capacity is around 20 Mt/yr. Although different types of phosphate calciners have been described in literature (vertical shafts, rotary kilns; traveling grate kilns, flash calciners), about 75 to 80% of world calcination is treated in fluidized bed reactors, with design capacities between 2,000 and 9,000 t/day, and with major references in Algeria, Morocco and the USA (Idaho, Wyoming, North Carolina).

At the Youssoufia plant, OCP operates 3 parallel calcination lines. Each production line includes:

-Fluidized bed N°1: Drying operated at 320-350°C using flue gas from the calciner (heat recovery). The total feed rate is 300 ton/hr. After drying, approximately 70 ton/hr are withdrawn for OCP's own use.

-Fluidized bed N°2: Calcination of 230 ton/hr, operated at 750-790°C, to burn off the carbonaceous contaminants and decompose the carbonates. The final product is 170 to 180 ton/hr of calcined phosphate. The heavy fuel consumption in the calciner is 70 to 80 ton/day. At 42,000 kJ/kg of fuel, the average consumption is about 570 kJ/kg feed, or 750 kJ/kg of calcined phosphate.

-Fluidized beds N°3: Cooling beds of the calcined phosphate (with heat recovery to feed the drying and preheat part of the calciner fluidization air), operated in 3 stages from ~500°C, to 300°C and finally 120°C.

Photographic illustration of the Youssoufia plant is included in the Minutes of the 12th. Monthly Meeting in Marrakech (November 30th and December 1st).

The SOLPART-developed techniques might be able to partly or wholly substitute or complement the current calcination processes, with concentrated solar heat being capable to supply the sensible heat of the phosphate ore pre-heating to reaction temperature, and the endothermic carbonate decomposition heat, as will be demonstrated through thermal and kinetic analyses of the samples taken.

2. Reaction characteristics of the OCP phosphate mineral

2.1. Principles of the reactions

The schematics of the SOLPART reactions was already developed in Deliverable D1.1. Only essentials are repeated below. *Figures hereafter were experimentally determined by EPPT for the sole purpose of the SOLPART project.*

In the specific case of OCP's phosphates, different aspects need to be included:

- the sensible heat required for the phosphate preheating to reaction temperature ($= m.C_p.\Delta T$, from ambient temperature to $\sim 750-790^\circ\text{C}$)
- the heat required to remove the moisture from the samples
- the reaction heat (exothermal) of burning the C-contaminants
- the reaction heat (endothermal) required for the decomposition of the carbonates, with CO_2 release, and expected to occur around $650-750^\circ\text{C}$ for MgCO_3 , and $850-900^\circ\text{C}$ for CaCO_3 . These different phenomena are illustrated in the experimental results, as illustrated below.

2.2. Loss of Weight and occurring reactions as determined by TGA, DTG and DSC.

In this research, a DTG 60A Thermogravimetric Analyser was used at atmospheric pressure with a nitrogen flow of 50 mL/min for the reduction reactions. The weight was recorded every second with an accuracy of 0.001 mg and the TGA pan was made of aluminium. The weight of the samples was between 15 and 20 mg. Different temperature ramps (heating rates, β , in K/min) were used for the experiments and all the experiments were repeated at least three times. The average results are given with a standard deviation of maximum 5 %. The TGA experiments result in a plot of the weight loss in function of the temperature.

Illustration of obtained results are given in Figure 1.

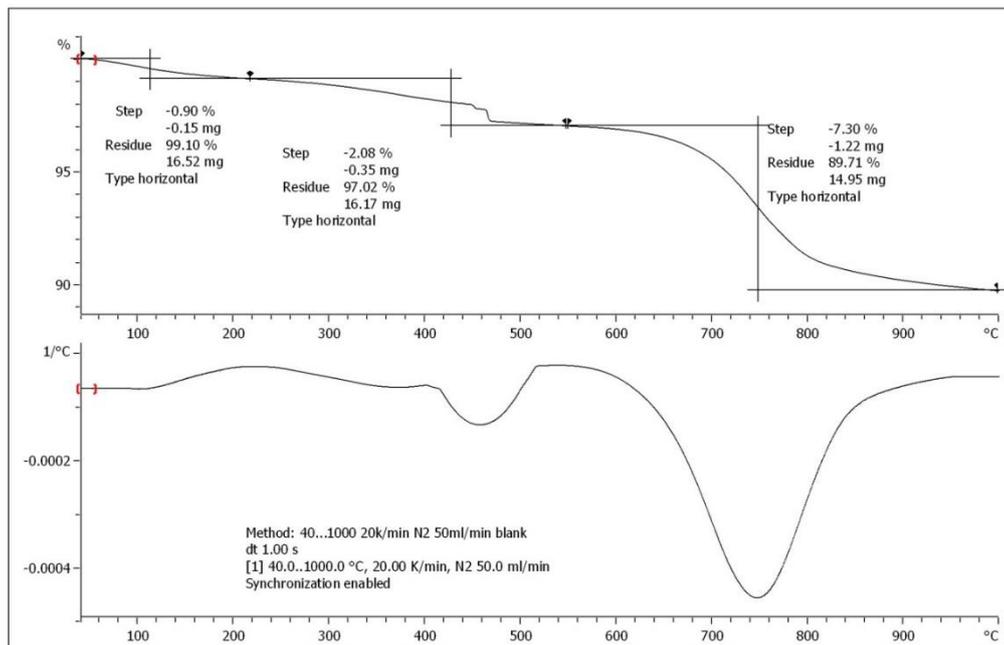


Figure 1. TGA and DTG analysis of OCP phosphate ore

The Figures demonstrate the different successive phenomena:

- removal of water, 0.9 wt%
- volatilisation and combustion of the carbonaceous contaminants (300-500°C)
- decomposition of the carbonates, between 600 and 900°C.

To obtain a more explicit and quantified expression of the heats involved, and reaction times required, a Differential Scanning Calorimetry (DSC) was carried out, as illustrated in Figure 2. It should be remembered that in this Figure, all heat developments above the 0 W/g datum line are exothermal processes, whereas those below the datum line require heat to proceed.

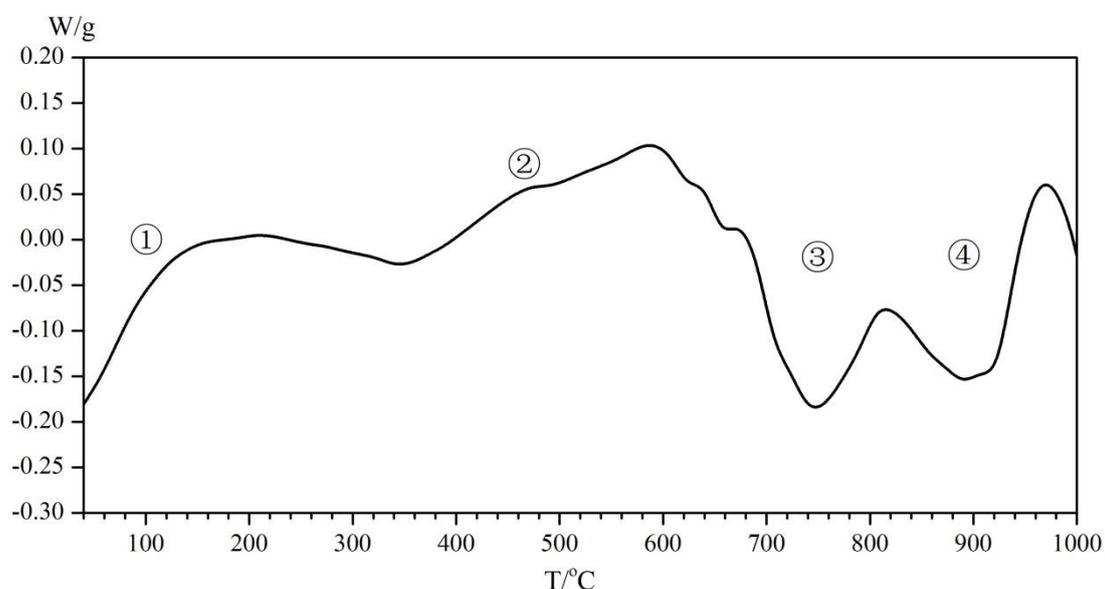


Figure 2. DSC analysis of OCP phosphate ore: 1- water evaporation; 2- combustion of C-contaminants; 3- decomposition of $MgCO_3$; 4- decomposition of $CaCO_3$ (at temperature ramp of $20^\circ C/min$).

Recorded weight losses were 0.9% around $100^\circ C$ through moisture evaporation, 2.08% between 420 and $510^\circ C$ as a result of burning C-contaminants; and 7.32 % between 620 and $900^\circ C$ from the de-carbonation reactions. The combustion of C generated ~ 180 kJ/kg phosphate. Preheating phosphates and fluidization air to reaction temperature consumes 719 kJ/kg phosphate (sensible heat). The heat for de-carbonation is 263 kJ/kg phosphate. The net heat is hence 802 kJ/kg phosphate. The required treatment time is ~ 45 minutes. Since SOLPART reactors operate at air velocities < 0.05 m/s against the current ~ 1 m/s, the heat required to preheat the air is negligible. Using an efficient phosphate preheating on SOLPART exhausts, the required heat can be reduced by over 70%. The solar treatment of raw phosphate will therefore require a solar energy input of maximum 300 kJ/kg phosphate, a reduction by nearly 65% in comparison with the current solution (750 kJ/kg).

2.3. Kinetics of the reactions.

As shown in Figure 2, reactions are fairly slow, due to the particle size under scrutiny (average 172 μm , largest particle size 640 μm). Contrary to reactions of small particles, such as limestone, dolomite and Cement Raw Meal, the diffusion of both heat and reaction products will be rather slow, resulting in a phenomenon whereby the reaction zone is restricted to a thin front that moves from the outer surface into the particle. This is generally represented by the unreacted core model for solids of unchanging size, as previously detailed in Deliverable 1.1. The detailed derivation of the reaction rate expression is given elsewhere [Kunii and Levenspiel 1969, Yagi and Kunii, 1961]. The conversion equations are usually expressed in terms of a characteristic time τ , the time to completely convert an unreacted particle into product.

For the Shell-model with control by diffusion through product layer, the direct application of Fick's law for diffusion through the product blanket gives the progression of the reaction with time as:

$$t/\tau = 1 - 3(1 - X_A)^{2/3} + 2(1 - X_A)$$

For $X_A = 98\%$, and $\tau = 45$ minutes, the required reaction time t should be 37 minutes.

Solar energy capture and subsequent heat release require a fast heat transfer from the exchanger wall to the particles or vice versa. This heat transfer is conditioned by the degree of gas and solid turbulence achieved in the systems. The heat transfer coefficient depends on the gas/solid contacting mode. It ranges from 10 $\text{W}/\text{m}^2\text{K}$ for a static bed, to 50 - 150 $\text{W}/\text{m}^2\text{K}$ in a fixed bed with forced gas circulation as in TGA, and several hundreds of $\text{W}/\text{m}^2\text{K}$ for bubbling fluidized bed and circulating fluidized bed [Zhang et al., 2016]. This again confirms that fluidized beds are specifically considered as one of the top technologies for solar energy systems, in general, and for minerals' conversion specifically. In a TGA, the temperature ramp, β , will vary from ~ 0.2 to 1.5 K/s ; in a rotary kiln, it will be close to 10 K/s ; whereas in a fluidized bed, heating rates of 10-100 K/s have been measured [Baeyens and Geldart, 1980].

Due to the very low concentration of CO_2 in the reaction products, no real impact of the flue gas composition is expected on the reaction rates, implying that a correction factor as proposed by Vosteen (D1.1) is not required.

Particles are however non-spherical (~ 0.75 - 0.9). The shape of the particle is very important for reaction kinetics and heat transfer. It is to be expected that a flake or a rod will decompose faster than the equivalent volume sphere of limestone and this affects the required time for complete decomposition, τ . In practice, the τ values must be corrected for phosphate shape (K_S) and

$$\tau^* = K_C \tau$$

Wührer [1958] indicates shape coefficient K_S as 0.83 for cubes and 0.44 for rods.

3. Conclusions and recommendations for the SOLPART project

For the phosphate ores, the elimination of carbonaceous contaminants, and the decomposition of Mg/CaCO_3 are the dominant factors in the thermal treatment. Both contributions of the sensible ($C_p \Delta T$) and reaction heat ΔH_r need to be considered in the thermal balance of the operation. The sensible heat will normally for 70 to 80% be supplied by pre-heating the feedstock using exhaust gases from the calcination and/or cooling stages (multi-stage operation, e.g. [Baeyens et al, 1989]). Solar heat will supply the balance of the sensible heat and the reaction heat.

In phosphate ore thermal treatment, fluidized beds are already the preferred technique. Solar reactors can be applied in a fluidized bed mode, and could hence substitute the current fossil-fuel fired fluidized beds. Its design can be based upon correlations found in literature [e.g. Smolders et al., 2001; Pitié et al., 2013]. Referring to D1.1, the strategy of Figure 3 will also apply.

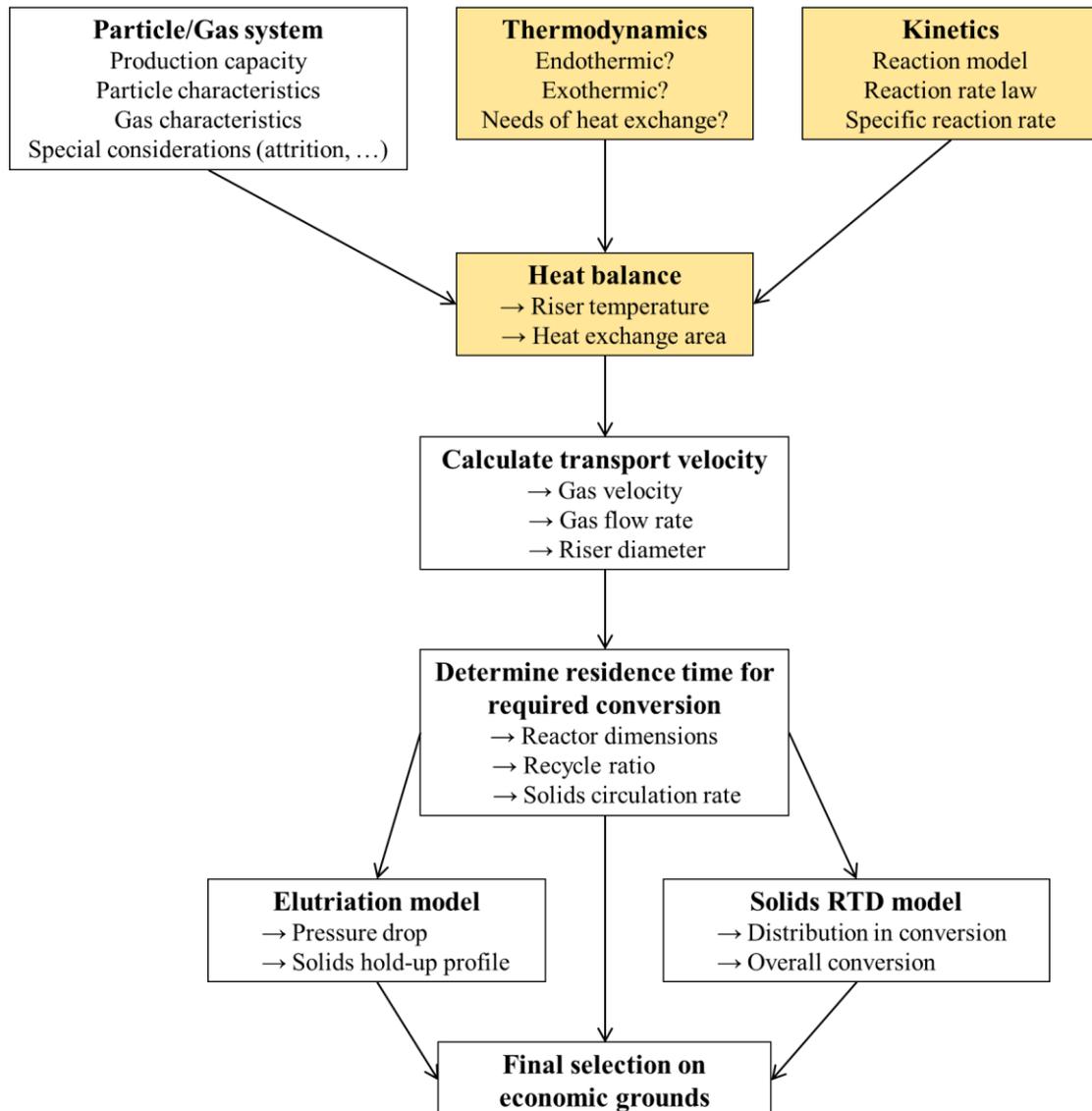


Figure 3: Design strategy of WP 1.2. Highlighted items were covered by D1.4.

The design procedure will start with gathering data concerning production capacity, particle and gas characteristics, reaction kinetics and heat transfer necessities.

Experimental work reported above defined the reaction kinetics and thermal requirements. The *heat balance* over the reactor determines the necessary rate of heat exchange. At sufficiently high solids mixing rates (fluidized beds > rotary kiln >> pneumatic conveying), the reactor can be assumed to be isothermal. Considerations of reaction kinetics and heat transfer effects will result in an optimum temperature for a required conversion. A specific focus of the SOLPART research will be the heat supply from direct solar irradiance, of major influence on the heat balance, and to be examined during the SOLPART testing.

Based upon the obtained results, a preliminary assessment of the SOLPART application has been made in the form of a paper, submitted to/and accepted by the 4th International Symposium on Innovation and Technology in the Phosphate Industry. The Abstract is added in Annex 1. Clearly, the solar thermal treatment of phosphate ores offers major advantages towards the reduction of required fossil fuel and the associated CO₂ emissions.

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Annex 1

4th International Symposium on Innovation and Technology in the Phosphate Industry [SYMPHOS 2017]

Solar Thermal Treatment of Phosphate Ore, a key target of the SOLPART EU project

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Phosphate ore is thermally converted into industrial feedstock by drying, burning carbonaceous contaminants, and dissociating carbonates. De-fluorination is achieved at ~1510 °C, thus outside the scope of solar processes. The current fuel-fired fluidized beds emit considerable tonnages of CO₂. The application of solar energy seems a valid alternative since major phosphate producing countries also experience high values of DNI, Morocco being an example. OCP samples were analyzed. The average particle size is 172 μm. Heat requirements and reaction kinetics were determined by TGA and DSC. Recorded weight losses were 0.9% around 100°C through moisture evaporation, 2.08% between 420 and 510 °C as a result of burning C-contaminants; and 7.32 % between 620 and 900 °C from the de-carbonation reactions. The combustion of C generated ~180 kJ/kg phosphate. Preheating phosphates and fluidization air to reaction temperature consumes 719 kJ/kg phosphate. The heat for de-carbonation is 263 kJ/kg phosphate. The net heat is hence 802 kJ/kg phosphate. The required treatment time is ~45 minutes. Since SOLPART reactors operate at air velocities < 0.05 m/s against the current ~1 m/s, the heat required to preheat the air is negligible. Using an efficient phosphate preheating on SOLPART exhausts, the required heat can be reduced by over 70%. The solar treatment of raw phosphate will therefore require a solar energy input of maximum 300 kJ/kg phosphate, 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 both the required investment for a 40 MW_{th} receiver-reactor, and the costs of currently consumed fuel oil and electricity, the payback period is estimated at 3 to 4.5 years.

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