COMPASsCO2

COMPONENTS' AND MATERIALS' PERFORMANCE FOR ADVANCED SOLAR SUPERCRITICAL CO2 POWERPLANTS

Particle optimization by modifying chemical composition

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WP2: Development and testing of particles

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ABOUT THE PROJECT

COMPASsCO$_2$ is a 4-year HORIZON2020 project started on 1.11.2020. It is led by the German Aerospace Center (DLR), with eleven additional partners from seven European countries.

COMPASsCO$_2$ aims to integrate CSP particle systems into highly efficient s-CO$_2$ Brayton power cycles for electricity production. In COMPASsCO2, the key component for such an integration, i.e. the particle/s-CO$_2$ heat exchanger, will be validated in a relevant environment. To reach this goal, the consortium will produce tailored particle and alloy combinations that meet the extreme operating conditions in terms of temperature, pressure, abrasion and hot oxidation/carburization of the heat exchanger tubes and the particles moving around/across them. The proposed innovative CSP s-CO$_2$ Brayton cycle plants will be flexible, highly efficient, economic and 100% carbon neutral large-scale electricity producers.

The research focus of COMPASsCO2 is on three main technological improvements: development of new particles, development of new metal alloys and development of the heat exchanger section.

DISCLAIMER

This project has received funding from the European Union's Horizon 2020 Research and Innovation Action (RIA) under grant agreement No. **958418.**

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LIST OF ABBREVIATIONS

COMPASsCO2	Components' and Materials' Performance for Advanced Solar Supercritical CO2 Power Plants
CST	Concentrating Solar Thermal

EC	European Commission
EU	European Union
CSP	Concentrating Solar Power
SGCREE	Saint-Gobain
DLR	German Aerospace center
DFI	DECHEMA-Forschunginstitut
sCO_2	Supercritical carbon dioxide
S.O.A.	State-of-the-art
SEM	Scanning Electron Microscopy
DLR	Deutsches Zentrum für Luft- und Raumfahrt e.V.
GEN2	Generation 2

1 ABSTRACT

Work Package 2 of COMPASsCO2 is mainly focused on the development and testing of particles and is divided in different tasks. This report concerns its first task, which is dedicated to the particle optimization by modifying the chemical composition and/or surface texture.

Deliverable 2.2 from this work package allowed us to optimise and characterize new particles materials. Two types of new ceramic particles / media exhibiting different chemical compositions and textures were developed and characterized taking into account the specificities of the heat exchange system and the cost.

2 INTRODUCTION

Over the last years, Saint-Gobain Research Provence have been contacted by several key players in the thermal energy storage market to co-develop with them innovative solutions for compact heat storage and filed some patents on media enabling high performances in terms of efficiency and storage volume. Indeed, a novel composition was developed internally based on iron-rich oxide composition and exhibiting high bulk density >4.5g/cm^3.

Saint-Gobain ZirPro is also one of the world's leading manufacturers of ceramic grinding media for surface treatment and micro-grinding applications (https://www.zirpro.com/). These medias can be produced through various manufacturing platforms in different sizes and compositions and are specially engineered to meet the requirements of the most demanding milling or surface treatment applications.

Based on the previous experiences, it was decided to pursue the development done on the hematite-calamine composite or doped calamine using the manufacturing processes commonly used by Saint-Gobain ZirPro business.

3 NOVEL PARTICLES DEVELOPED BY SAINT-GOBAIN

Two different novel particles are proposed by Saint-Gobain in this project:

- **Granulated particles** made by high shear granulation followed by a sintering step,
- And **fused particles** made by an electrofusion process.

These two processes are available at lab scale and pilot scales. Consequently, the particles can be produced in several volume quantities: few kg to several 100's kg. The media sizes produced with these two processes are quite similar from few microns until 1 mm, but the microstructure and surface texture are completely different. Usually, the microstructure of fused ceramic materials has a higher bulk density and lower apparent density. For the granulated particles, the medias are sintered after shaping at a temperature below the melting point. Consequently, according to the initial raw materials particle size and sintering conditions, some residual pores well distributed can be found /remain within the microstructure.

3.1 FUSED PARTICLES

The fused particles were produced using a unique electrofusion process developed by Saint-Gobain. Raw materials (metallic oxides) are melted at very high temperature close to 2000°C.

The composition of the fused particles was developed and calculated in order to achieve a high density and heat specific value while maintaining a dark black color. The main components are SiO_2, Al_2O_3, Fe_2O_3 and MgO.

Two different types of fused particles were produced:

- **Fused particles GEN1**: in this case, conventional raw materials were used. The GEN1 was provided to the partners in the size range 0.8-1.2mm.
- **Fused particles GEN2**: made with more than 70 wt. % of recycled ceramic products (refractory waste). The particles size distribution was extended compared to the GEN1 in order to decrease the price: 0.6-1.2mm. The silica content was also increased compared to the GEN1 in order to avoid internal defects.

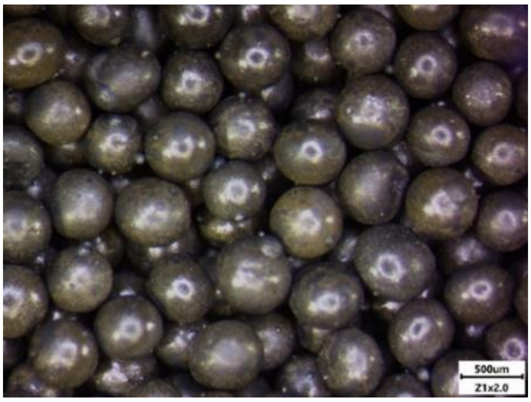

Figure 1: Fused particles GEN2 – Optical observations

3.2 GRANULATED PARTICLES

Granulated particles are made using a high shear granulation process. The raw materials used in this case are recycled iron oxides from the steel industry named as calamine or mill scale. The following simplified process flow chart was used:

- Step 1: raw materials milling and sintering additives addition,
- Step 2: high share mixing using a specific binder solution,
- Step 3: drying and sintering,
- Step 4: sorting and sieving.

After sintering, the granulated particles are mainly composed of iron oxide under the form of hematite Fe_2O_3 leading to a high thermal stability against ageing. A large particle size distribution can be produced by high shear mixing starting from 100 µm until several mm. For this project, particles with a size between 0.6 and 1.2 mm (maximum of the particle size distribution) were provided to the partners.

Four different generations of granulated particles were developed by Saint-Gobain:

- **Granulated particles GEN1**: this first generation was made with 100 % of iron oxide. Regarding the poor mechanical properties, it was decided not to send this first prototype to the rest of the partners for testing.
- **Granulated particles GEN2:** Sintering additives (metallic oxides) were used in this case in order to increase the relative density of the particles and improve the

mechanical properties. These particles were sent end of August 2021 to the different partners.

- **Granulated particles GEN3**: Increased sintering temperature and soak time, also increased additive ratio up to 5 wt.% and decrease the raw material grain size to finally further improve the mechanical properties.
- **Granulated particles GEN4**: Currently under development, aiming at further optimization of mechanical properties thanks to the addition of refractory waste.

Figure 2: Granulated particles GEN3 – Optical observations

3.3 QUANTITIES DELIVERED TO THE PARTNERS

Several quantities were provided to the partners with improved properties. The first generations were produced with pure raw materials. But once the chemical composition was selected, secondary raw materials (SRM) were introduced in the composition. The chemical composition of the developed media particularly for the granulated solution was tuned/modified according to the experience gained from the previous studies.

Table 1: Particles delivered to the European partners

Particles type	Date	Quantities delivered to the partners
Fused beads GEN1	April 2021	25 kg DLR-WF cologne 10 kg DLR-SF Almeria
Fused beads GEN2	December 2021	2 kg DECHEMA 5 kg DLR-SF Almeria 1 kg DLR-WF Cologne 5 kg CIEMAT
Granulated beads GEN2	August 2021	2 kg DECHEMA 2 kg DLR-SF Almeria 2 kg DLR-WF Cologne 2 kg CIEMAT
Granulated beads GEN3	March and May 2021	1 kg + 2 kg DECHEMA 1 kg DLR-SF Almeria 1 kg + 2 kg DLR-WF Cologne 1 kg + 2 kg CIEMAT
Granulated beads GEN4	October 2021	1 kg DECHEMA 1 kg DLR-SF Almeria 1 kg DLR-WF Cologne 1kg CIEMAT

4 NEW PARTICLES MAIN CHARACTERISTICS

The new developed particles were characterized in terms of shape, size, microstructure, color stability, softening temperature and mechanical properties. The SEM-EDX, XRD and nano indentation are not presented in this report as such data can be used for an on-going patent filling on the Saint-Gobain side.

4.1 PARTICLES DENSITY

Different types of density measurements were performed on the novel particles:

- Aerated bulk density (random loose packing) corresponds to the ratio of the mass of an untapped particle sample and its volume including the contribution of the interparticulate void volume. The measurement is done in a volumeter.
- Apparent density is measured using helium pycnometry directly on particles. It corresponds to the volumetric mass of the solid material plus the volume of the sealed pores (closed porosity).
- True/absolute density is measured on crushed particles using also helium pycnometry. The true density is based on the volume of solid material excluding the volume of the pores and voids within the particles.

The results are presented in the following table in comparison with the state-of the art particles (BauxLite BL 16/30).

Table 2: State-of-the-art density measurements

	Bulk density [g/cm^3]	Apparent density (particles) [g/cm^3]	Absolute density (powder) [g/cm^3]
S.O.A - BL 16 /30	**1.7**	**3.1**	**3.4**
Fused beads GEN1	**2.1**	**3.5**	**3.5**
Fused beads GEN2	**2.1**	**3.3**	**3.4**
Granulated beads GEN2	**2.8**	**4.7**	**5.1**
Granulated beads GEN3	**2.8**	**4.9**	**5.0**
Granulated beads GEN4	**2.0**	**3.6**	**3.8**

The data presented in the previous table are given for particles with a size between 0.6 to 1.2mm (0.8 -1.2 mm for fused particles GEN1). The optimized fused and granulated particles present a higher density compared to the state of the art particles in all cases.

4.2 PARTICLES MICROSTUCTURES

4.2.1 Fused particles

The fused particles present a very spherical shape with a smooth surface. The microstructure is quite dense and dendritic for both generations. Some central pores can be observed in the middle of the particles. However, the central defects were decreased from GEN1 to GEN2 thanks to the increase of the silica content.

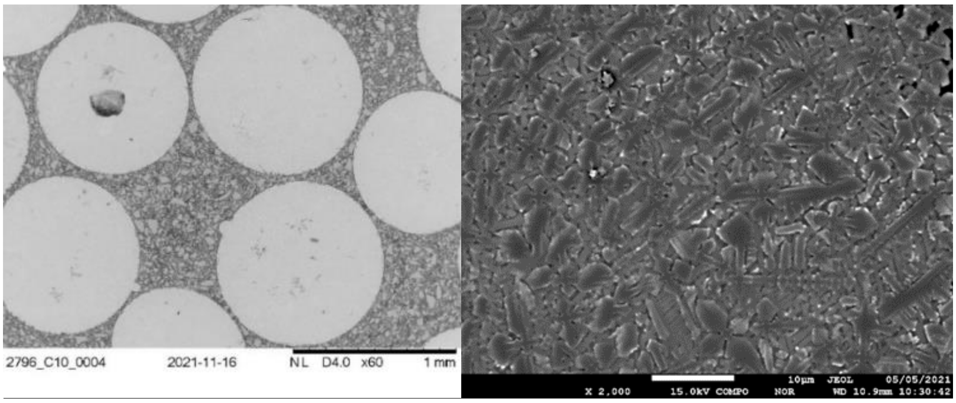

Figure 3: Fused particles GEN2 – Core microstructure.

4.2.2 Granulated particles

The granulated particles present a rough surface quite similar to the state-of-the-art particles which is probably more suitable for surface treatments compared to fused particles. Thanks to the thermal stability of the main phase, no change in color can be observed until 1000°C. The microstructure is also quite homogenous with some small pores well dispersed within the matrix.

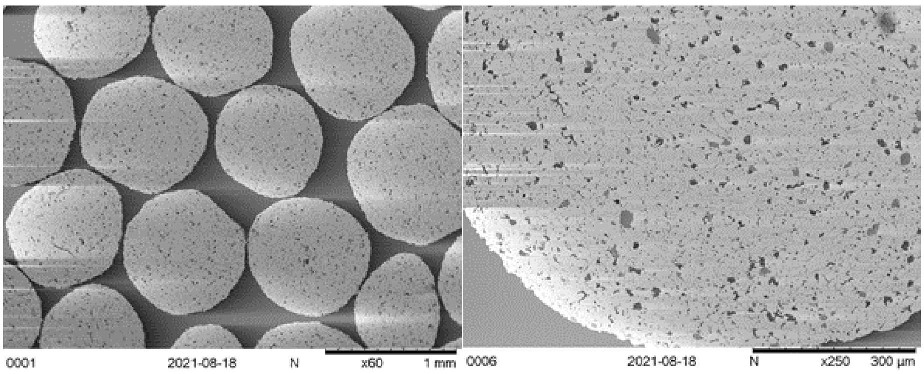

Figure 4: Granulated particles GEN3 – Core microstructure

4.3 SOFTENING TEMPERATURE

A high softening temperature is required for the mechanical endurance at operation temperature. To determine critical temperatures, the high-temperature compression behavior of single particles was tested. For this, particles were uniaxially loaded with a controlled force of 30 N and the temperature-dependent cross-head displacement was recorded for all the state-of the art and new particles as given below. Mechanical destabilization by bulk softening is indicated by an abrupt loss of applied pressure and dropping displacement curves.

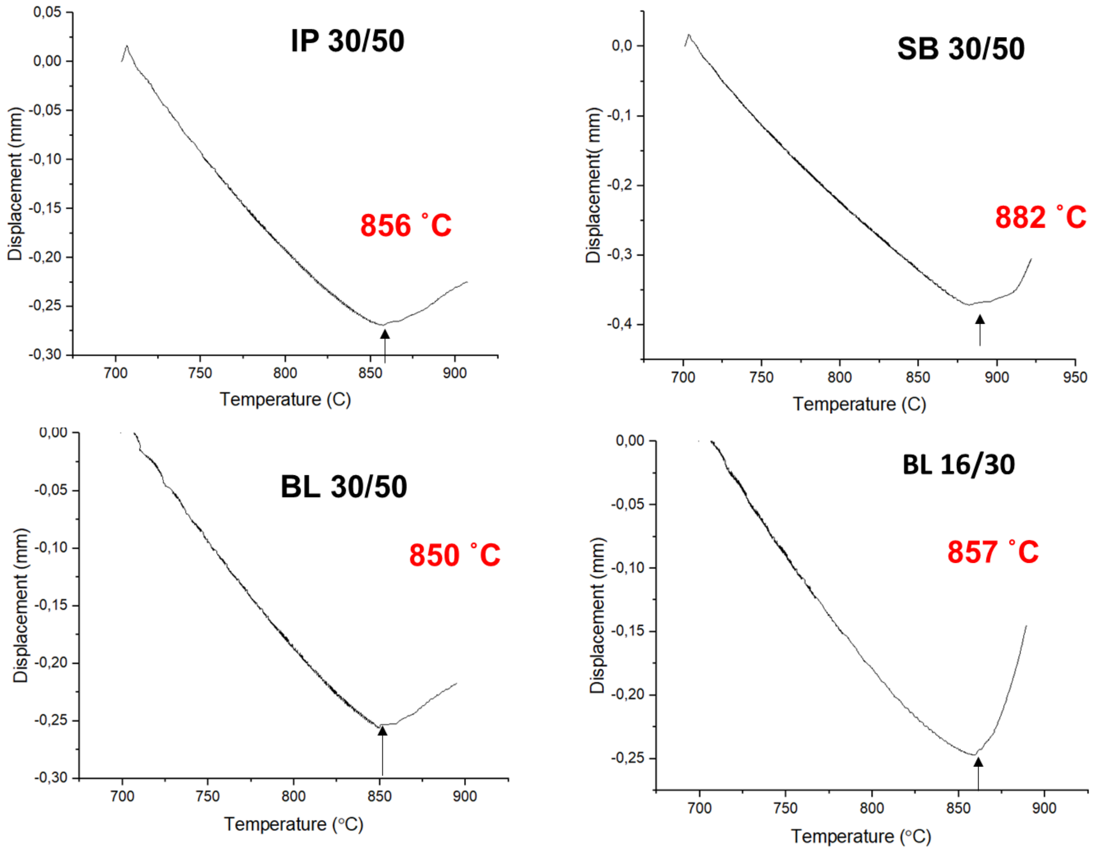

Figure 5: Softening temperature of state of art proppants

The softening temperatures measured for the state of the art were 856 ˚C, 882 ˚C, 850 ˚C and 857 ˚C for InterProp IP 30/50, Sintered Bauxite SB 30/50, BL 30/50 and BL 16/30, respectively. Considering the highest temperature achieved in the solar receiver (1000°C), those values can be considered as relatively low. In consistency with lowest glassy phase content, SB is the most promising proppant with the highest softening temperature.

The new particles exhibit a better crystallized microstructure with negligible or no amount of glassy phase, which results in higher softening temperature compared to state -of-the-art proppants close to 1100°C for fused particles GEN1 and GEN2, and between 940 to 1080°C for granulated particles.

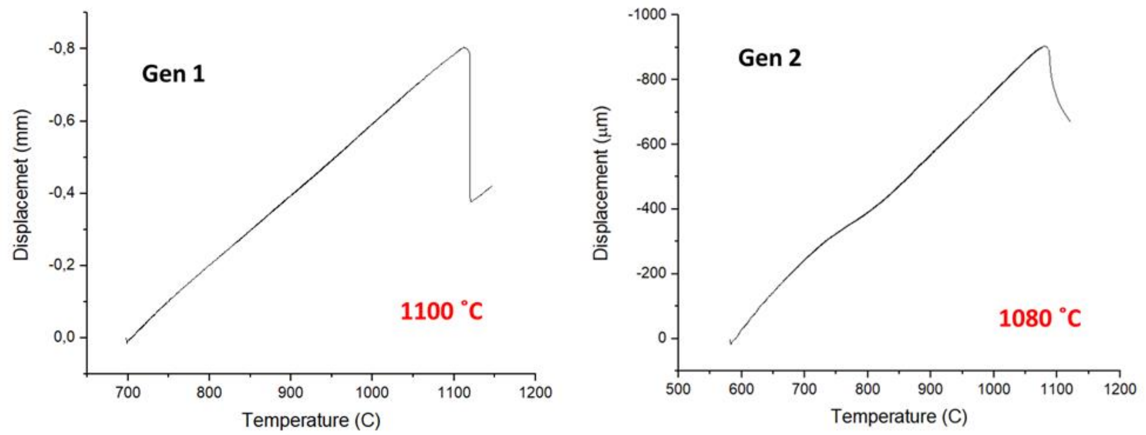

Figure 6: Softening temperature of fused particles

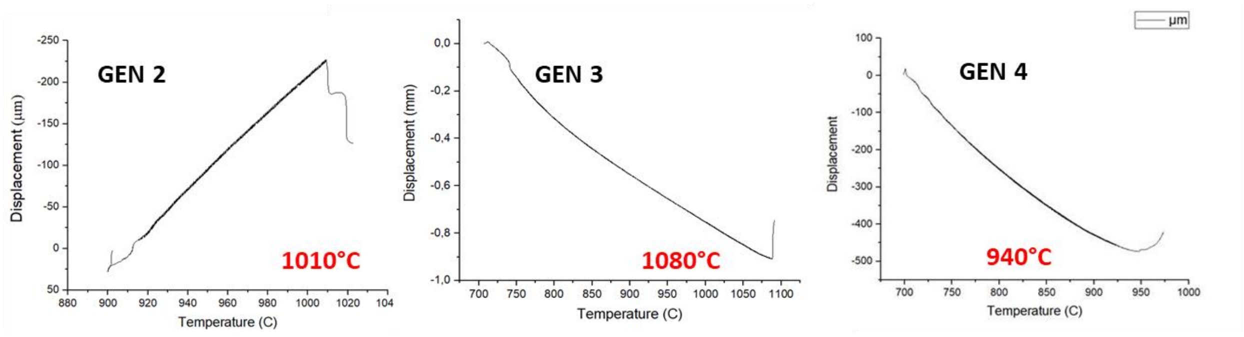

Figure 7: Softening temperature of granulated particles

4.4 COLOR STABILITY

L*a*b* color measurements were performed on particles before and after a thermal treatment at 1000°C during 24 hours. L*a*b* color space specifies color using a 3-axis system:

- The value L* represents the lightness, where L* = 0 corresponds to black and for white, L* = 100.
- The a* axis represents the green to red module with green in the negative direction and red in the positive direction.
- The b* axis represents the blue to yellow component with blue in the negative direction and yellow in the positive direction.

The L*a*b* values were then converted into RGB values using a specific application for an easier representation in this report. The particles present different colors from one grade to another one: dark grey or brown. After thermal treatment at 1000°C during 24 hours, an important modification of the color can be observed for the state of -the-art particles BL 16/30 that can be linked to a possibly change in the oxidation state of iron contained in the proppants (Fe^{3+} and Fe^{2+} states). The new particles and particularly the granulated particles show a limited change in color after thermal treatment compared to the state-of-the-art particles.

Table 3: Color stability after thermal treatment of 24h at 1000°C

Particle type	BL 16 /30	Fused particles GEN1	Fused particles GEN2	Granulated particles GEN2	Granulated particles GEN3	Granulated particles GEN4
Color						
Color after TT 1000°C / 24 h						

4.5 ISOTHERMAL AGEING TESTS AT DFI

DFI conducted short-term isothermal ageing tests to investigate the degradation of the uncoated and coated Granulated Gen 3 particles. The readers are referred to D2.1 for the results on the coated particles. The isothermal ageing tests at DFI were undertaken at 1000°C for 100 h in a muffle furnace, in which the particles were placed inside alumina crucibles, which were dried at 120°C prior to the exposure. After the exposure, the particle samples were taken out of the crucibles, mounted in plexiglass and the cross-sections were prepared using conventional metallographic methods involving the automated grinding and polishing of the samples down to 1 µm using diamond suspension. The samples were analyzed using light-optical microscopy under brightfield and polarized light as well as electron probe microanalysis (EPMA) utilized to generate high resolution back scattered electron images and elemental distribution maps.

Figure 8 depicts the macroscopic and cross-sectional light-optical microscopy images of as-received granulated Gen 3 particles. The particles had a dark gray color and the particle size ranged between 400 and 1300 µm. A two-phase microstructure can be identified from the brightfield images. Moreover, residual porosity within particles was observed to a low extent. It is worth noting that the cracks observed in the pictures most likely originate from the metallographic preparation.

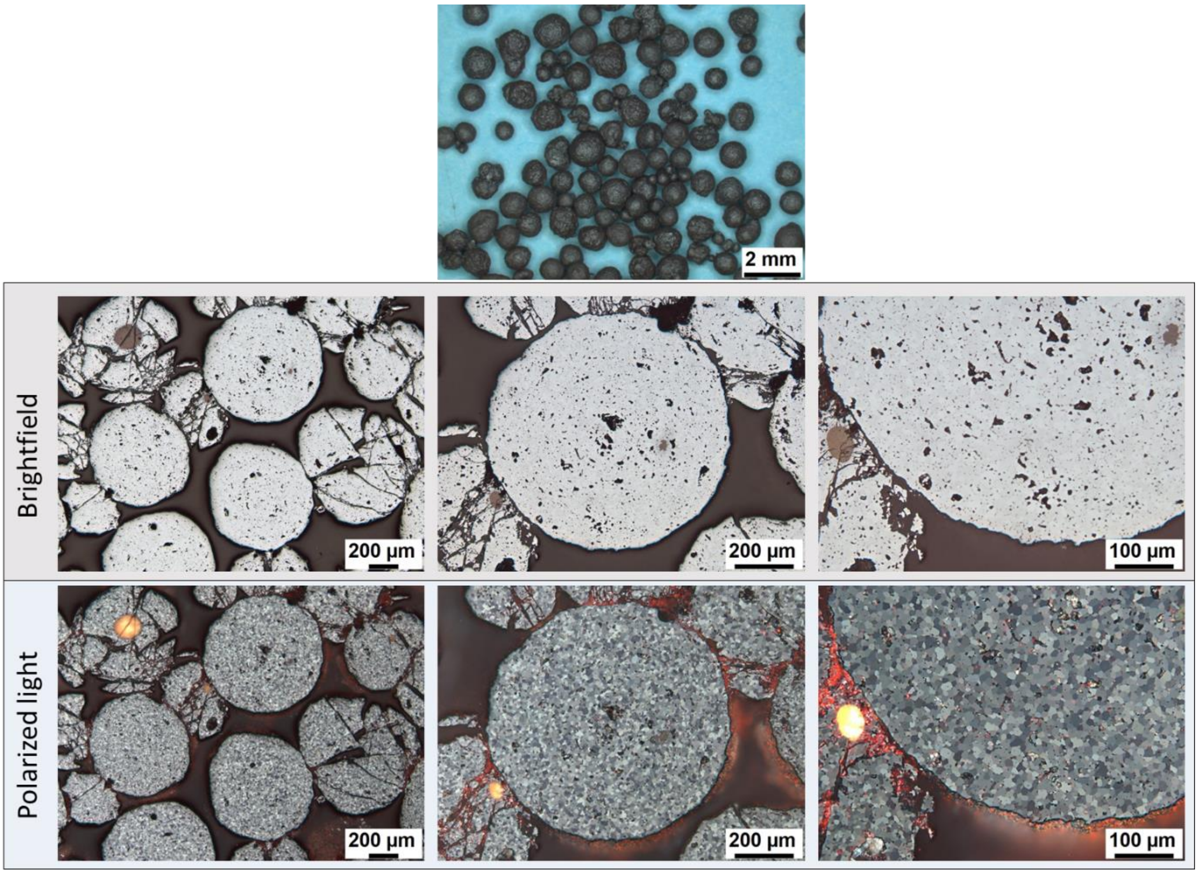

Figure 8: Macroscopic and cross-sectional light-optical microscopy (brightfield and polarized light) images (with increasing magnification from left to right) of as-received granulated Gen 3 particles. Please note that, the cracks might originate from the sample preparation.

Figure 99 shows the cross-sectional back scattered (BSE) images and elemental distribution maps of the as-received granulated Gen 3 particles acquired by EPMA. Evidently, the two-phase microstructure consists of an iron oxide matrix (Fe_2O_3, confirmed by XRD analysis, not shown here) and finely dispersed particles of a second oxide phase, which was Al- and Si-rich (see Al and Si maps in Figure 9). The C-rich regions probably originated from the residual porosity being filled by the carbon-containing components used for the metallographic sample preparation such as the SiC paper.

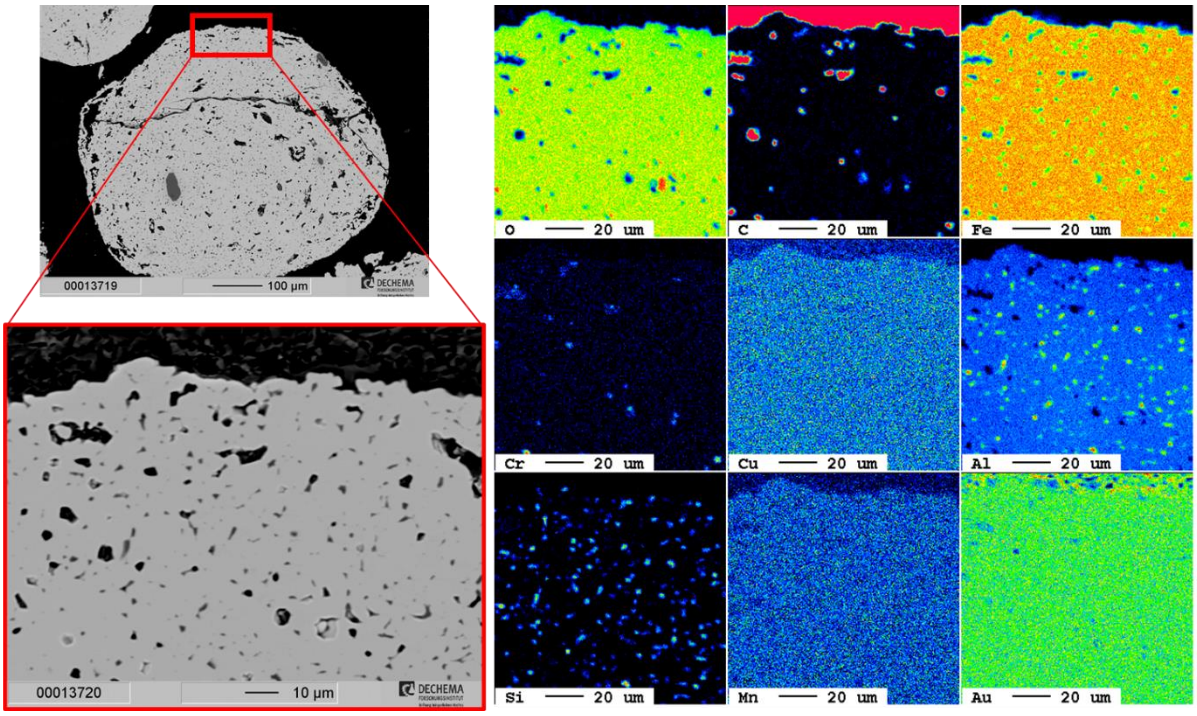

Figure 9: Cross-sectional back scattered electron images (top: lower magnification, bottom: region marked with the red rectangle within the top image with a higher magnification) and elemental distribution maps acquired by EPMA belonging to the bottom image of the as-received granulated Gen 3 particles. Please note that, the cross-sections were sputtered with Au for electrical conductivity.

Figure 10 illustrates the macroscopic and cross-sectional light-optical microscopy images of granulated Gen 3 particles after isothermal ageing at 1000°C for 100 h. The macroscopic images showed that the dark gray color of the particles was maintained after isothermal ageing tests, indicating a stable absorptivity during short-term ageing. The cross-sectional images exhibited the retainment of the two-phase microstructure. A coarsening of the precipitate phase was not observed. Hence it can be stated that the granulated Gen 3 particles show a high microstructural stability during short-term isothermal ageing tests. It is worth noting that, the dark colored (or bright in the polarized light images) impurity at the center of the particles might be originated from the sample preparation.

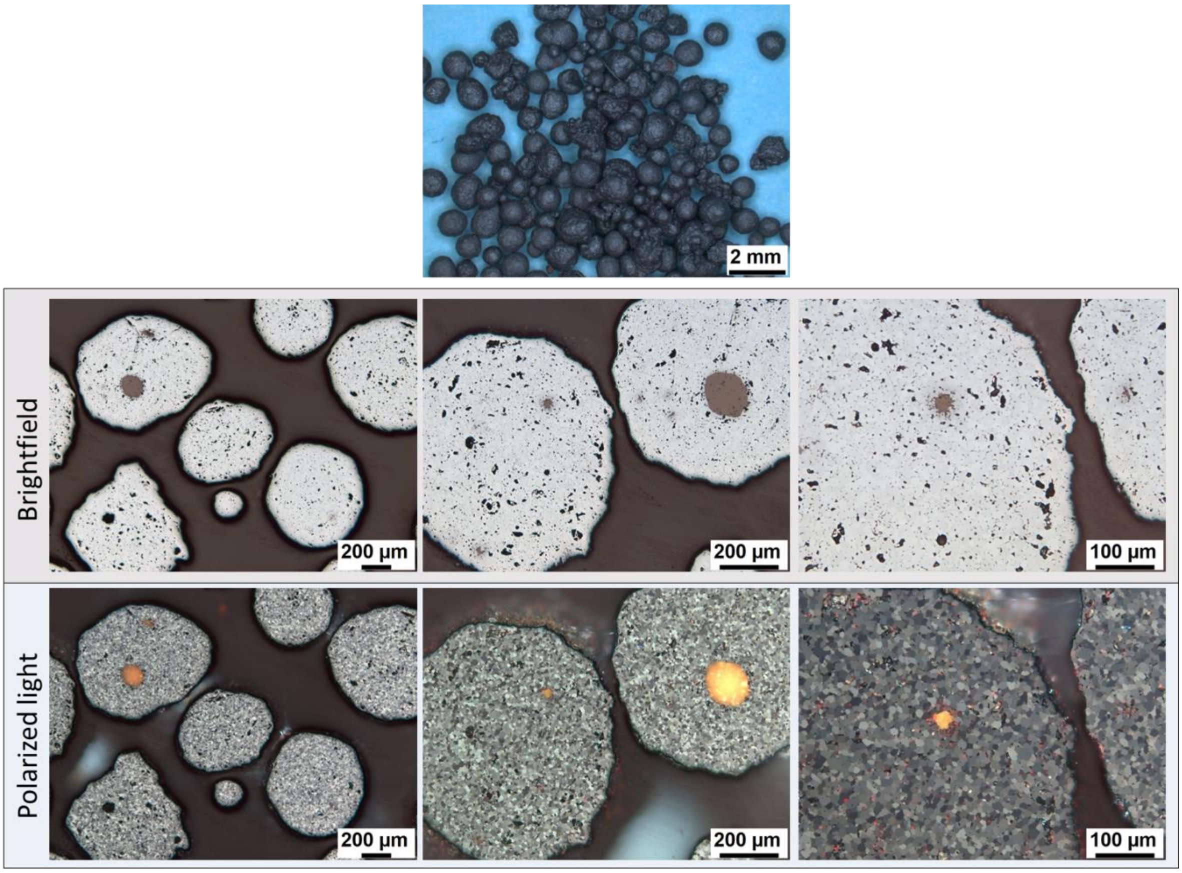

Figure 10: Macroscopic and cross-sectional light-optical microscopy (brightfield and polarized light) images (with increasing magnification from left to right) of the granulated Gen 3 particles after isothermal exposure at 1000°C for 100 h.

The cross-sectional BSE images and elemental distribution maps of granulated Gen 3 particles after isothermal ageing at 1000°C for 100 h are shown in Figure 1111. Strictly analyzing the selected particle, a lesser amount of residual porosity was observed. The two-phase microstructure was clearly retained, as the matrix phase consisted of hematite and the precipitate phase was enriched in Al and Si. The presence of the precipitate phase at the surface was more pronounced compared to the as-received particles. Nevertheless, the microstructure and the chemical composition of the particles barely showed any changes. Thus, the high microstructural stability of the particles during short term ageing can be confirmed via the EPMA analysis.

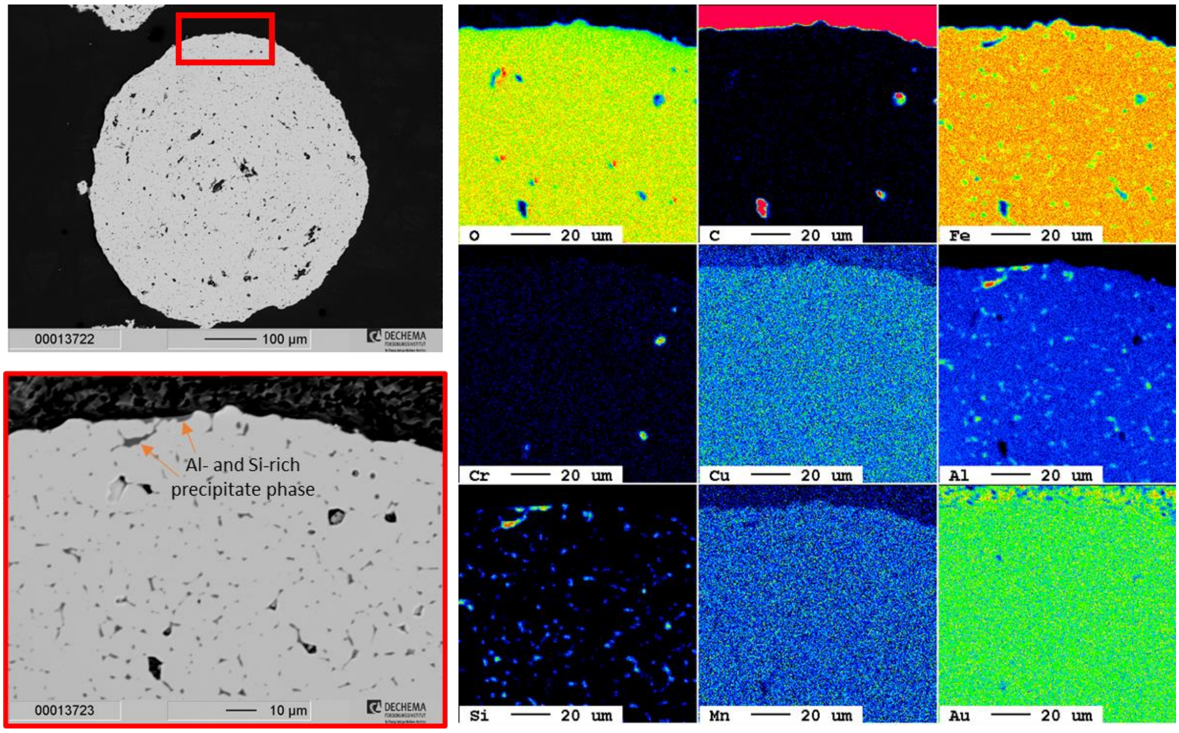

Figure 11: Cross-sectional back scattered electron images (top: lower magnification, bottom: region marked with the red rectangle within the top image with a higher magnification) and elemental distribution maps acquired by EPMA belonging to the bottom image of the granulated Gen 3 particles after isothermal ageing for 100 h at 1000°C. Please note that, the cross-sections were sputtered with Au for electrical conductivity.

DFI will conduct high temperature XRD-analysis to investigate possible in-situ phase changes occurring in coated and uncoated granulated Gen 3 particles. Furthermore, thermocyclic exposure tests with 1 h dwell at 1000°C and cooling down to room temperature are planned. Under service conditions particles experience temperature changes. While being heated up at the absorber, they cool down during the heat transfer to the heat exchanger tubes. Such temperature changes can lead to build-up of thermally induced stresses due to the mismatch of thermal expansion coefficients between the two phases for the uncoated particles as well as the mismatch between the coating and the substrate for the coated particles. The build-up of tensile or compressive stresses depending on the mismatch can lead to buckling or crack formation and eventually induce loss of functionality by mechanical failure. DFI will simulate such temperature changes in a highly accelerated way, as the particles will be cooled down to room temperature, which will likely induce a significantly high extent of thermally induced stresses in the particles.

4.6 MECHANICAL PROPERTIES

The breaking force was measured on the particles after sieving between 0.8 mm and 1 mm. The particles were crushed between two tungsten carbide plates and the breaking force was measured and recorded for each particle (20 particles analyzed).

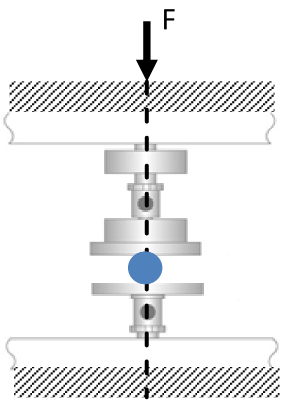

Figure 12: Compression test

The results are presented in the Table 4. From one generation to another one, the mechanical properties were improved gradually. And for the new developed particles, the highest mechanical properties were achieved for the granulated particles GEN4. The mechanical properties achieved are in same range compared to the state-of-the-art BL 16/30.

Table 4: Compression test results

Average on 20 particles 0.8-1mm	Proppants BL 16/30	Fused particles GEN1	Fused particles GEN2	Granulated particles GEN2	Granulated particles GEN3	Granulated particles GEN4
Breaking force [N]	142.4±33.3	63.2 ± 10.6	97.9±24.5	70.3±25.0	86.9±27.6	148.2±31.1

4.7 SOLAR ABSORPTANCE

Figure 13 shows a comparison of the measured absorptance spectra of the different particle types examined so far. The absorptance spectra have been weighted with the direct solar irradiance spectrum at Air Mass 1.5 according to ASTM G173. The solar-weighted absorptance for each particle type is displayed in Table 5. Figure 13 show superior absorptance of the novel particles, especially the Fused Gen 1 and Gen 2 (>97% for GEN2), but also the Granulated Gen2, in comparison with the state-of-the-art proppants.

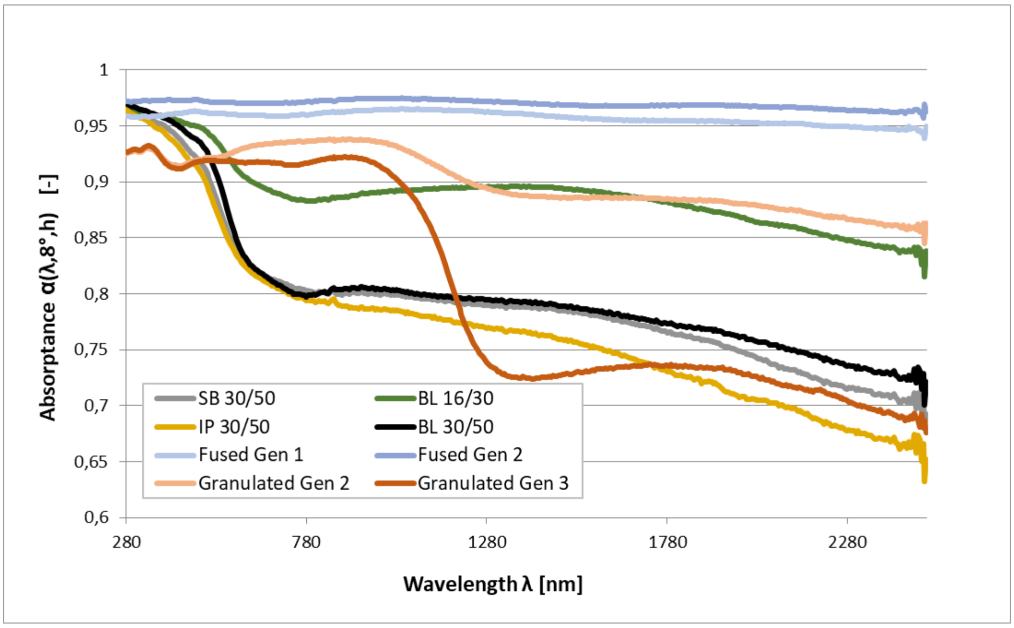

Figure 13 : Absorptance spectra : SOA particles versus new particles

	Solar absorptance α [-]
SB 30/50	0.835
BL/16/30	0.901
BL 30/50	0.837
IP 30/50	0.834
Fused particles GEN1	0.963
Fused particles GEN2	0.972
Granulated particles GEN2	0.922
Granulated particles GEN3	0.882

Table 5 : Solar-weighted absorptance for each particle type

To measure the effect of thermal ageing, some samples of state-of -the art and novel material were exposed in alumina crucibles in muffle furnaces to the constant temperature of 1000°C during 0, 500, 100, 1500, 2000 and 4000 hours. Results indicate reduced ageing for fused particles and no degradation effect on granulated particles compared to the state-of -the art even after 4000 hours.

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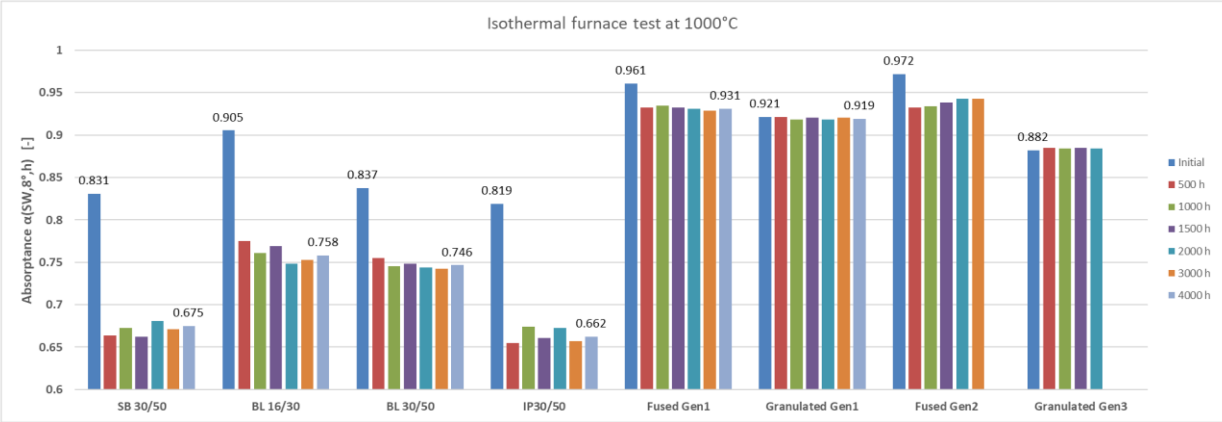

Figure 14: Ageing at constant temperature of 1000°C

5 FINAL CONCLUSIONS

Two types of particles made with through different platforms were developed and tested in this project: granulated and fused particles. Different generations of these new particles were proposed to the partners with improved properties compared to the state-of-the-art.

Fused particles achieve excellent solar absorptance beyond 97% and good optical durability even after 4000 hours. The softening temperature measured is above 1000°C which is higher than the working temperature of the solar receiver. But their cost is higher than the state-of-the art particles and their mechanical properties also need to be improved.

Granulated particles exhibit high optical performance. Their optical durability, softening temperature and density are also higher than the state-of-the-art particles. We can notice no modification of the optical absorptance even after 4000 hours at the temperature of 1000°C. In addition, the mechanical properties were clearly improved for the GEN 4: the breaking force obtained is comparable to the state-of-the art particles.

The main characteristics of the two solutions proposed by Saint-Gobain are detailed in *Table 6*.

Table 6: Particle candidates – main characteristics

"granulated particles"	"fused particles"
Main phase: Fe_2O_3 (hematite) Porous and homogenous microstructure High thermal stability of the main phase Rough surface Lower price compared to the fused particles	Complex chemical composition: SiO_2, MgO, Al_2O_3, Fe_2O_3 Dense and dendritic microstructure with some central defects Dark color and good thermal stability Smooth surface