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Fabrication of improved ferrite loose powder with target values: remanence Br> 2.0 kG; coercivity jHc> 4.0 kOe

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06	31/05/2023	Alberto Bollero (IMDEA)	Revision and validation

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LIST OF ACRONYMS

Abbreviation	Unit	Meaning
Br	G and emu/g	Remanence
jHc	Oe	Coercivity
Sr	-	Strontium
XRD	-	X-Ray Diffraction
SEM	-	Scanning electron microscopy
VSM	-	Vibrational sample magnetometer
TEM	-	Transmission Electron microscopy

SUMMARY

Deliverable goal is to create better Strontium Ferrite Powder based on an increase in coercivity and remanence with no use of critical raw materials (e.g. lanthanum and cobalt, as it is the case for high-quality commercial Sr-ferrite). Two strategies were therefore taken into consideration: ferrite powder for compounding/injection molding and for sintering. The production process involves mixing of raw materials (iron oxide, strontium carbonate and additives) with water to form a slurry, which is then pumped in the high temperature ovens. The powder is then cooled, transported to the milling equipment and delivered to other PASSENGER partners for further characterizations and testing. Table 1 summarizes the deliverable goals and the achieved values for the two applications.

Table 1. Achieved magnetic values compared to deliverable target

		Target values	Ferrite for compounding	Ferrite for sintering
Remanence [kG]	Br	2.0	2.576	2.795
Coercivity [kOe]	jHc	4.0	5.360	5.699

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1. INTRODUCTION

The aim of the deliverable is the production of ferrite loose powder with remanence of Br > 2.0 kG and a coercivity of jHc > 4.0 kOe. Regarding practical applications, one of ferrite's key limitations is the tendency for coercivity to decline with operating temperature (e.g., motor performance in cold weather), which may lead to a serious demagnetization risk of the magnets during operation. The main objective is therefore to create a ferrite powder with improved magnetic characteristics while maintaining an increased coercivity to compensate for temperature-related losses. ILPEA's approach to achieve the deliverable is to modify both powders formulations and process parameters in order to improve magnetic performance in close collaboration with IMDEA (application of the self-developed flash-milling method and use of specific additives) and also with MBN (up-scaling of laboratory methods), JSI (advanced characterization techniques) and TUDA (assessment of magnetic properties with temperature). Given that the production parameters (in particular the raw materials cost and temperatures) do not surpass those commonly employed in the routine manufacture of Sr-ferrite, ILPEA's techniques are also feasible from an economic perspective.

IMDEA, JSI, TUDA and MBN have collaborated with ILPEA for the achievement of the deliverable.

2. METHODOLOGY

2.1. FLASH-MILLING METHOD

IMDEA has applied its self-developed flash-milling method and a novel approach consisting on the pre-addition of Fe_2O_3 powder to the Sr-ferrite produced by ILPEA for successful development of coercivity, while maintaining a well-balanced vale or magnetization based on the chosen milling time [1,2]. Both approaches have gone through an optimization process of the heat treatment (including both temperature and duration).

The resulting samples have been characterized at IMDEA by XRD, SEM and VSM (the latter for magnetic characterization at room temperature). TEM characterization has been carried out by JSI. TUDA has been responsible of making the magnetic characterization at different temperatures.

The list of samples provided by ILPEA and processed by IMDEA is detailed in the following. The different names refer to different aim (final magnet fabrication) and to different commercial grades (all of them with nominal composition $SrFe_{12}O_{19}$, and with different grades).

- *P02Sr* *[Aim: injected magnets]*
- *P11* *[Aim: injected magnets]*
- *P21B* *[Aim: injected magnets]*

- *P07-UE* *[Aim: sintered magnets]*
- *P07-QME* *[Aim: sintered magnets]*
- *P07-PSG* *[Aim: sintered magnets]*
- *P07 PSG 2M* *[Aim: sintered magnets]*

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2.2. SR-FERRITE FABRICATION

The industrial production process flow followed by ILPEA can be outlined as follows:

Mixing of raw materials (Iron Oxide, Strontium Carbonate and additives) with water to form a slurry (Fig. 1).

Figure 1. Mixers used for raw materials dispersion in water at ILPEA

After powder mixing with water, the slurry is pumped in the cylindrical oven (Fig. 2). In the first part of the cylindrical ovens (colder zone) water evaporates, while in the second part of the oven the sintering process takes place (hotter zone). Powder is then cooled to ambient temperature and transported to the milling equipment.

Water removal through evaporation and sintering of powder in high temperature cylindrical oven at temperatures up to 1300 °C. By-products consist of evaporated water and CO_2 from the process that is removed from the oven.

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Figure 2. High temperature cylindrical oven at ILPEA

Milling is carried out in a closed environment to avoid pollution in the environment caused by small particles powder. An air flow transports the powders in the milling systems (Fig. 3) using a selection grid to sort out the particles size. The powder is than stored in big bags with weight controlled by an electronic balance.

Figure 3. Milling systems at ILPEA

3. RESULTS

PASSENGER has focused on the development two different materials, based on two major ferrite applications: injection molding/compounding and sintering.

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3.1. APPLICATION OF IMDEA'S FLASH-MILLING METHOD

IMDEA has combined two self-developed and novel approaches: flash-milling in combination with the pre-addition of additive (in particular Fe_2O_3). Figure 4 shows results for one of the ferrite powders (named P02Sr, intended for injection molding/compounding) produced by ILPEA and processed at IMDEA.

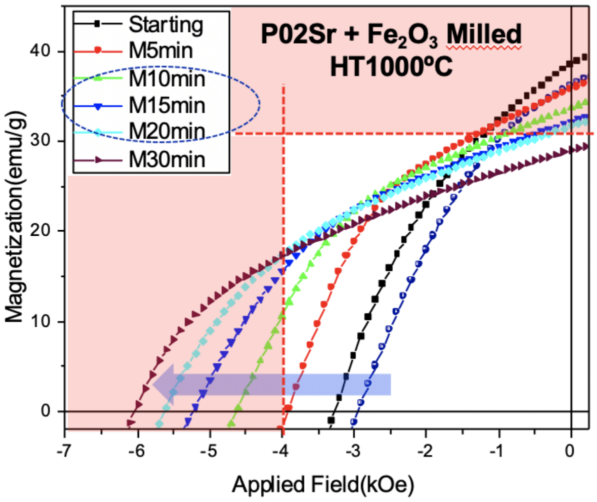

Figure 4. Room temperature VSM hysteresis loops (second quadrant is shown) measured at IMDEA for Sr-ferrite powder named P02Sr by ILPEA at production. The process comprised: pre-addition of additive + flash- milling for different duration (in minutes) and heat treatment (1000ºC in air). Red shadowed areas show the threshold for coercivity (>4.0 kOe) and remanence (>2.0 kG, equivalent to 31 emu/g) based on goals contained in the deliverable. Results from processing related to milling times of 10-20 min fulfilled the objectives of the deliverable.

The effect of flash-milling application on reducing particle size in short milling times is obvious from images shown in Fig. 5.

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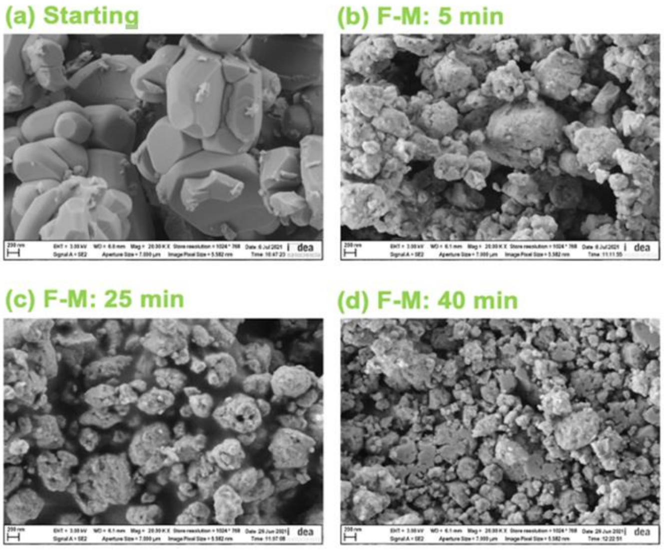

Figure 5. SEM images (IMDEA) for (a) precursor powder (Grade: P02Sr) provided by ILPEA, (b), (c) and (d) Powder flash-milled at IMDEA after 5 min, 25 min and 40 min, respectively.

The advantage of making a pre-addition of additive (Fe_2O_3) prior milling is illustrated in Fig. 6. The beneficial effect is the possibility of reducing further the milling time (decreased processing time) and the possibility of achieving higher coercivity values in such a reduced processing time.

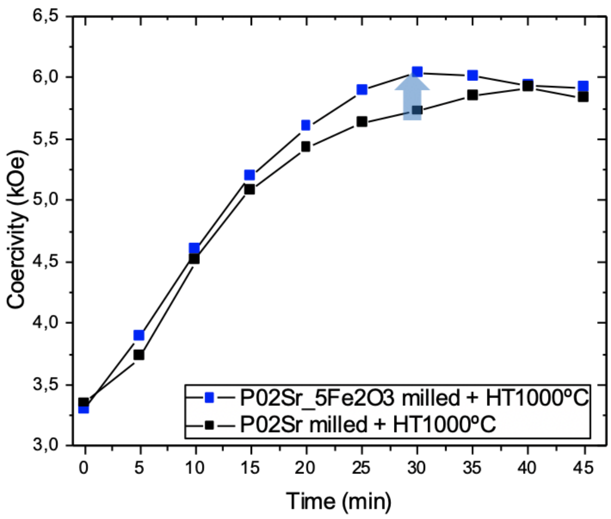

Figure 6. Comparison of the evolution of the coercivity with increasing milling time in the range 5-45 min, after heat treatment (1000ºC) for two different materials: Sr-ferrite ($P0_2Sr$) powder produced by ILPEA (black symbols) and this same ferrite with a pre-addition of 5 wt.% Fe_2O_3 powder (blue symbols).

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In order to demonstrate the functionality of this improved ferrite at high and low temperatures, TUDA carried out measurements on the samples produced by IMDEA. Based on these results (Fig. 7), we can confirm that the objective of developing a Sr-ferrite permanent magnet material with excellent magnetic properties at high and low temperatures (the latter being critical for hard ferrites) has been successfully managed. This has been possible by application of IMDEA's flash-milling and, further improved, through the use of additives and with no use of any critical raw materials (e.g. La and Co as typically used in commercial ferrites to achieve this objective). The large improvement (two-fold increase in coercivity) is obvious when comparing coercivity evolution for the P02Sr ferrite powder processed by IMDEA and the initial commercial ferrite powder (ILPEA's P02Sr).

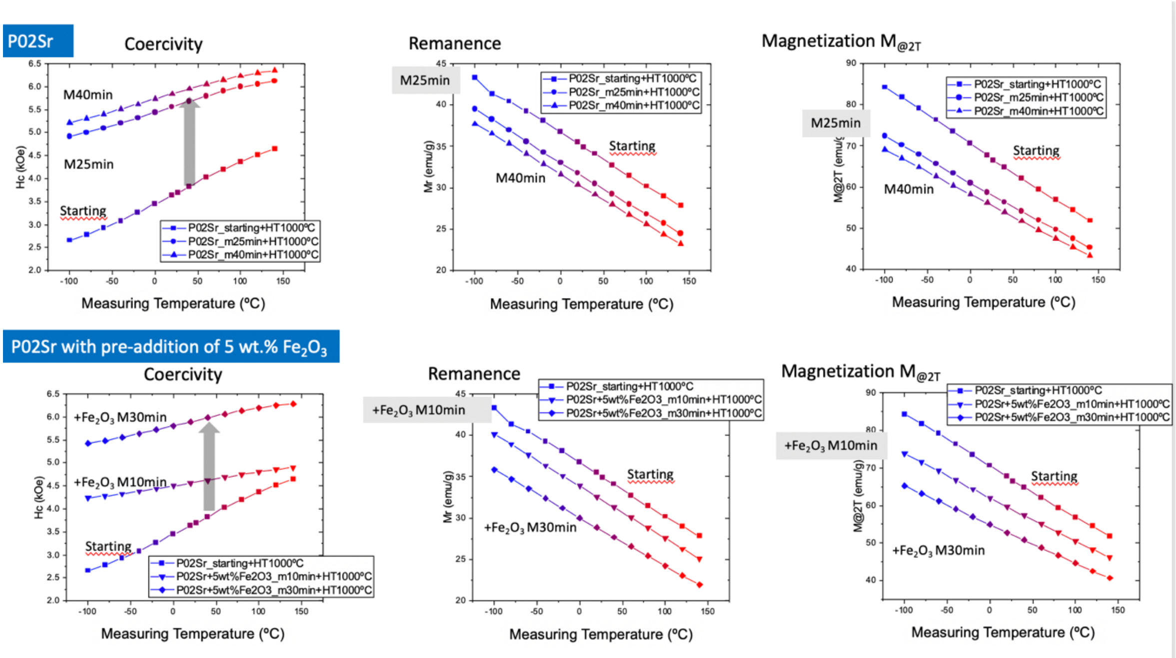

Figure 7. Evolution of coercivity, remanence and maximum magnetization as a function of the measurement temperature for the precursor (starting) and same material + Fe_2O_3 pre-addition.

3.2. ILPEA'S FERRITE FOR INJECTION MOLDING/COMPOUNDING IN PASSENGER

The next open question might be how well results obtained in the lab by IMDEA can be moved to industrial production to achieve the objectives considered in this deliverable. Figure 8 shows that ILPEA has successfully managed the achievement of the target values (remanence and coercivity) following achievements discussed in previous sections.

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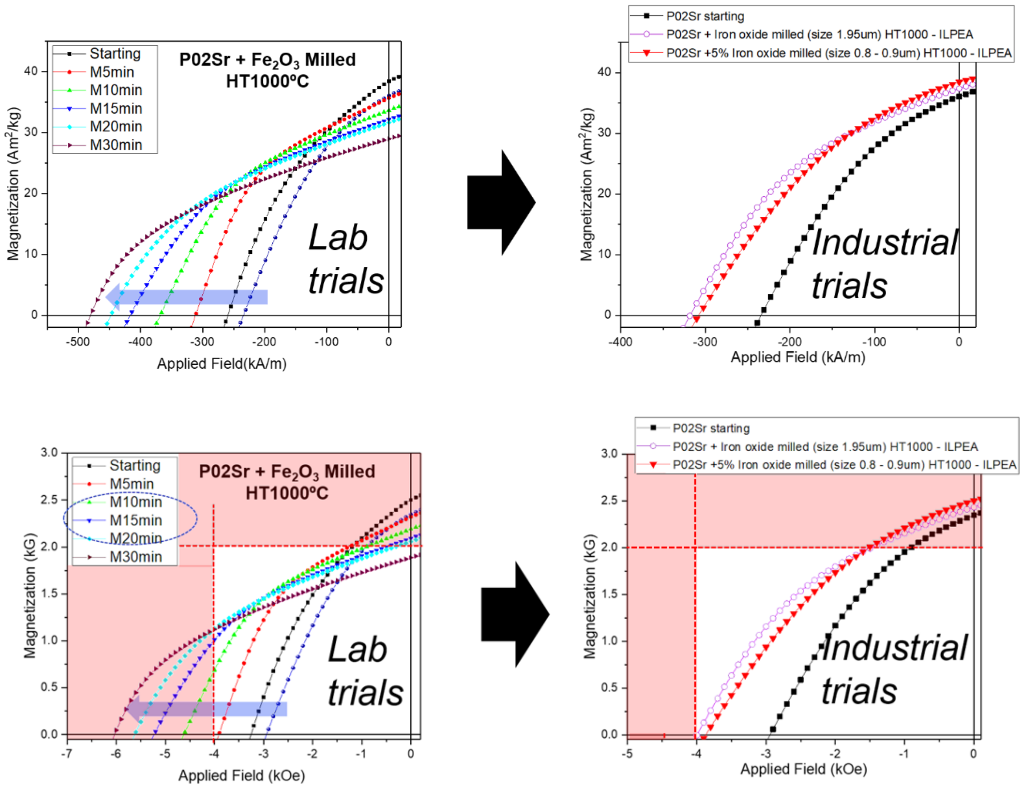

Figure 8. Comparison of the second quadrant of the hysteresis loops for IMDEA's lab trials (left-hand side) and ILPEA's industrial trials (right-hand side) on the ferrite named "P02Sr". Shaded areas show those successful results fulfilling deliverable D1.3 in both cases.

P41B is an improved strontium ferrite loose powder made by ILPEA based on previous results (P02Sr followed by a next generation named P21B) to advance even further towards an improvement of the quality (important for integration of the final magnets in PASSENGER's products). Figure 9 shows images of different ferrite batches produced at industrial scale by ILPEA in PASSENGER.

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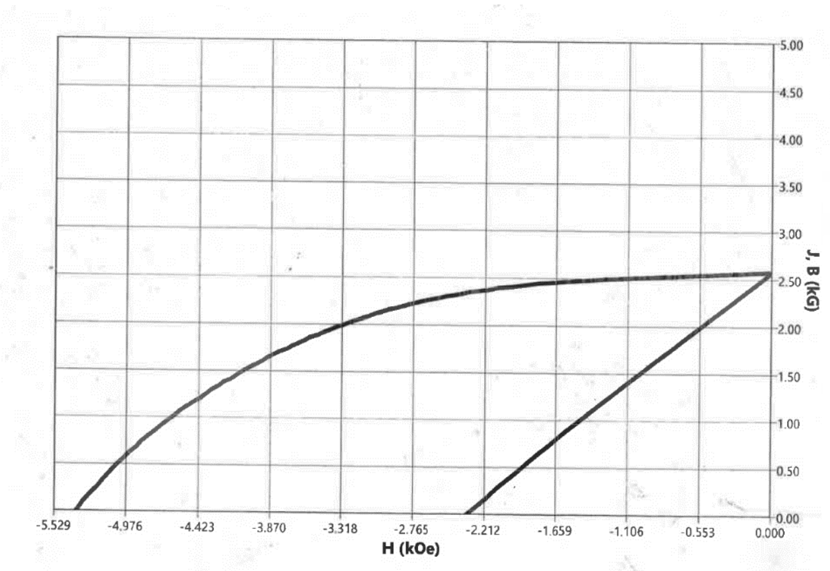
Figure 9. Improved Sr-ferrite materials produced by ILPEA in the framework of PASSENGER, achieving a production of 4 tones already at this stage (M24) in the project.

The powder was enclosed in a polymeric matrix and calendered in order to study its properties. It was characterized with hysteresisgraph measurement by ILPEA (Fig. 10), finding values of Br = 2.576 kG and jHc = 5.360 kOe that meet the deliverable targets.



Temperature	20.0 °C
Br	(2.576 ± 0.026) kG
HcB	(2.346 ± 0.035) kOe
HcJ	(5.360 ± 0.080) kOe
BHmax	(1.562 ± 0.031) MG·Oe
BA	(1.289 ± 0.013) kG
HA	(1.212 ± 0.018) kOe
Hknee	(2.441 ± 0.037) kOe

Figure 10. Hysteresisgraph curve and values for P41B.

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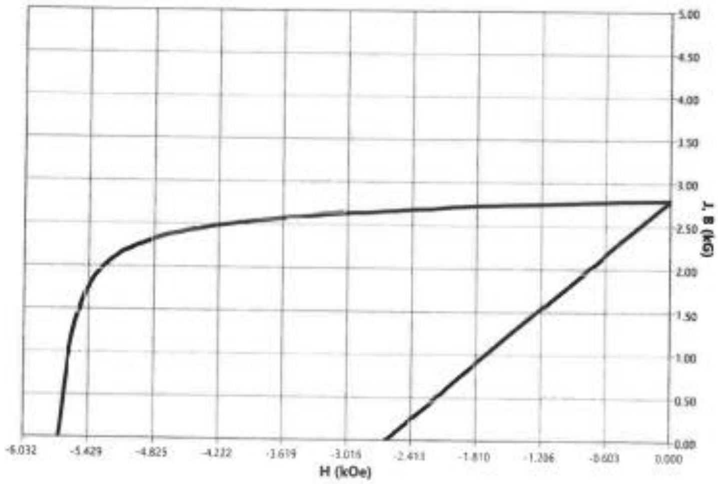
3.3. ILPEA'S FERRITE FOR SINTERING IN PASSENGER

The ferrite named P07PSG2M is a strontium ferrite loose powder for sintering applications, which has been also developed in the framework of PASSENGER. The sintered powder was characterized by ILPEA with hysteresisgraph measurement (Fig. 11), finding values of Br = 2.795 kG and jHc = 5.699 kOe that meet the deliverable targets. This last ferrite produced by ILPEA has also managed to meet the goal for coercivity considered in another deliverable: D 1.4 (intended for M30).



Temperature	20.0 °C
Br	(2.795 ± 0.028) kG
HcB	(2.658 ± 0.040) kOe
HcJ	(5.699 ± 0.085) kOe
BHmax	(1.881 ± 0.038) MG·Oe
BA	(1.391 ± 0.014) kG
HA	(1.352 ± 0.020) kOe
Hknee	(4.036 ± 0.061) kOe

Figure 11. Hysteresisgraph curve and values for P07PSG2M.

P07PSG2M was additionally characterized by IMDEA using VSM (Fig. 12). The analysis with a different technique confirmed the aforementioned properties.

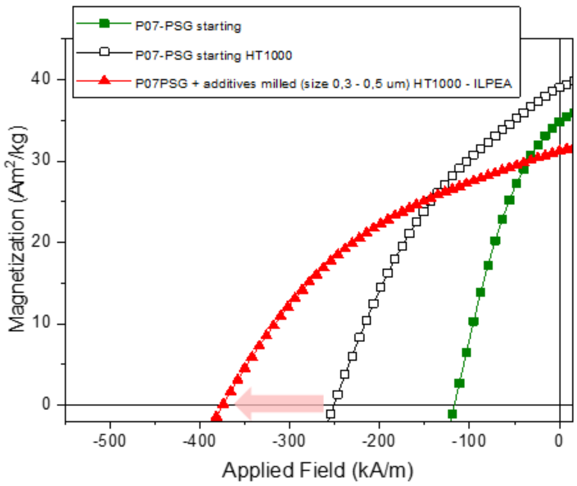


Figure 12. VSM curve for P07PSG2M.

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4. CONCLUSIONS

The target values specified for the D1.3 are:

- Remanence Br=2.0 kG

- Coercivity jHc=4.0 kOe

After improving both ferrite formulations and production process parameters based on the collaborative work carried out with IMDEA (laboratory scale production through an innovative method), JSI, MBN and TUDA in the framework of the PASSENGER project. ILPEA has been able to produce loose powders with the following properties:

- P41B for compounding/injection molding with Remanence Br =2.576 kG and Coercivity jHc=5.360 kOe
- P07PSG2M for sintering with Remanence Br =2.795 kG and Coercivity jHc=5.699 kOe

The second material not only fulfil the objectives considered in Deliverable 1.3 but also the coercivity target (jHc > 5.5 kOe) fixed in Deliverable 1.4 (intended for M30). Remarkably, a production scale at ILPEA of 4 tons of the improved ferrite material -to share among the partners to continue working in WP2 and WP3- illustrates a successful up-scaling of improved strontium ferrite in PASSENGER.

Moreover, ALL the raw materials here used have their origin in Europe (Spain and Germany) with the production of the improved ferrite guaranteed also in Europe (in Italy by ILPEA).

P41 ferrite family (and possibly a next generation as well) will be tested by BARLOG and KOLEKTOR for preparation of ferrite/polymer compounds to be used in WP2 and afterwards in WP3 in the integration in products considered in PASSENGER.

5. REFERENCES

[1] A.Bollero *et al.*, ACS Sustainable Chem. Eng. 5, 3243 (2017).

[2] A. Bollero *et al.*, PCT/EP2018/063222: “Ferrite type materials and process for the production thereof”.

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