REE4EU: Integrated High Temperature Electrolysis (HTE) and Ion Liquid Extraction (ILE) for a Strong and Independent European Rare Earth Elements Supply Chain

Project type:	Innovation action		
Start date of project:	01/10/2015	Duration:	48 months

D6.1 First Batch of PM derived from the HM-HTE Pilot at LCM

WP n° and title	WP6. End Product Performance Validation and LCA
Responsible Author(s)	VAC
Contributor(s)	LCM, SINTEF
Version	V_final

TABLE OF CONTENTS

TABLE OF FIGURES

LIST of TABLES

List of abbreviations and definitions

Abbreviation	Definition
B_R	Remanence of the permanent magnet (measure of the remaining magnetization when the driving magnetic field is dropped to zero)
C	Carbon
D_{50}	Mass median diameter, or diameter at which 50% of a sample's mass is comprised of small particles
Fe	Iron
H_{cJ}	Coercitivity of the permanent magnet (measure of the reverse field needed to drive the magnetization to zero after being saturated)
HD	Hydrogen decrepitation
HM	Hydrometallurgical
HTE	High temperature electrolysis
LCM	Less Common Metals
NdFeB	Neodymium-iron-boron PM
PM	Permanent magnet
PMS	Permanent magnet swarf
RE	Rare earth
REA	Rare earth alloy
REMA	Rare earth master Alloy
REO	Rare earth oxide
SEM	Scanning electron microscopy
T_a	Annealing temperature
T_s	Sintering temperature
VAC	Vacuumschmelze GmbH & Co. KG
WP	Work package
°C	Degrees Celsius

Executive Summary

The objective of this work was to validate the output from the new engineered REE4EU-pilot process by producing and testing functional permanent magnets from the obtained rare earth alloys, characterise the manufactured product and compare its properties with those of the product obtained using virgin materials (primary resources).

In this deliverable document, the results obtained when using the output material from the trials in WP4 (Pilot REE4EU HM+HTE within existing facilities of REA production from PMS) are summarized. The rare earth alloy was obtained in the high temperature electrolysis pilot cell installed at LCM's premises, using as feed material the rare earth oxide mixture derived after hydrometallurgical treatment of wastes from permanent magnet manufacture (swarf). This material was provided by partner VAC.

VAC has made a permanent magnet in his laboratory line and has determined the quality of both the rare earth master alloy input obtained in WP4 and the permanent magnet output in terms of magnetic properties and chemical composition. The results are compared to magnets from VAC's production line obtained with material derived from virgin input.

1 Introduction

During the first two and a half years of project, LCM adapted their 1 kA HTE pilot cell for the needs of the material to be treated in the REE4EU project, run several trials to obtain the REA output product, and subsequently converted it in REMA to be used by VAC in the manufacture of permanent magnets.

The input material for the HTE cell was obtained after the hydrometallurgical treatment of wastes from permanent magnet manufacture (swarf, i.e. PMS). The output material from the HTE pilot trials, i.e. REA was converted to a book-mold RE master alloy (REMA) for PM production by adjusting its chemical composition.

The material was then sent to VAC, who manufactured a PM in its laboratory line. The magnetic properties and chemical composition were compared to those obtained with PM from VAC's production line using material derived from virgin input.

2 Methodology

The ingot received from LCM was analysed in terms of PM composition and impurities, mainly Al and C, as well as its microstructure.

Then, the book-mold REMA was converted to a coarse powder by hydrogen decrepitation. Jet-milling was used in order to prepare fine powders, which were introduced in moulds for isostatic pressing and sintering under inert gas atmosphere.

The magnetic properties of the samples (density and alignment coefficient) were then determined before annealing, in order to get the optimum magnetic properties.

The whole process is shown schematically in Figure 1.

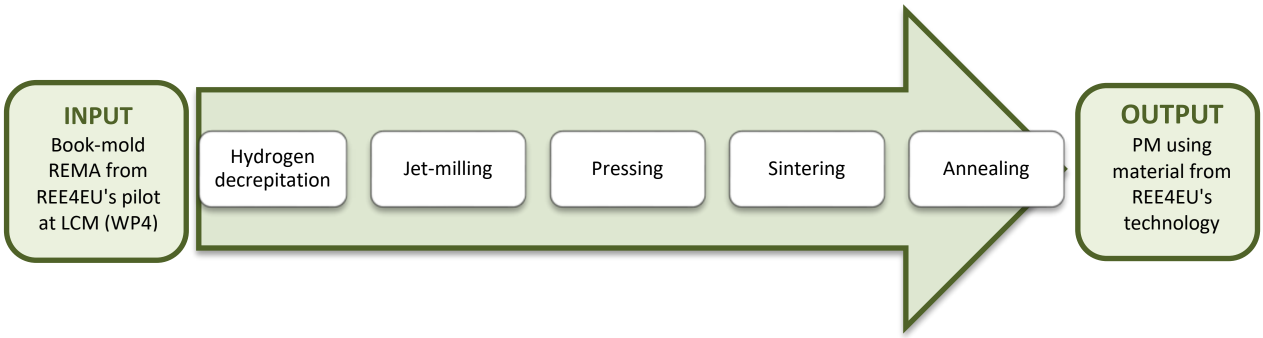


Figure 1. Schematics of the different steps followed in the manufacture of sintered NdFeB PM in the REE4EU project.

3 Results

3.1 Chemical Analysis of the REMA

The REA obtained in the HTE pilot at LCM was re-melted and adjusted in chemical composition to a suitable REMA to be used by VAC. A picture of the ingot is shown in Figure 2.

Chemical analysis of the book-mold REMA is shown in Table 1. All elements, especially the C content, were within the materials specification. The presence and quantity of C is important, because it forms non-magnetic Nd-carbides, which reduce the remanence of the magnet, B_R, significantly.

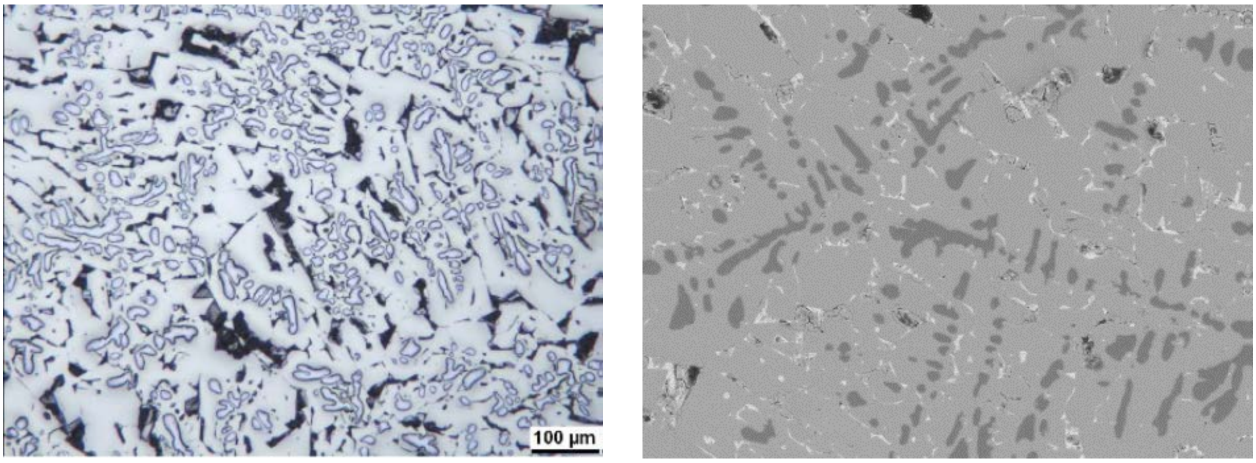
Figure 2. 4.5 kg book-mold REMA received at VAC.

Table 1. Chemical composition of the REMA from Figure 2 provided by LCM. Analysis performed at both LCM and VAC premises, and compared to the required specifications.

	Nd	Pr	Dy	B	Al	C
Spec.	28,7 ± 0,5	< 0,5	2,8 ± 0,3	0,91 ± 0,02	0,20 ± 0,03	< 0,020
LCM	28,6	< 0,1	2,8	0,91	0,18	
VAC	29,0	< 0,1	2,9	0,91	0,18	0,017

3.2 Microstructure

Book-mold REMA ingots are cooled slower during the casting process than strip cast alloys and therefore contain some amounts of free Fe. This can be seen in the micrographs shown in Figure 3.



A) B)

Figure 3. Microstructure of the book-mold REMA ingot. A) light microscopy; B) SEM image.

Inspection of the micrograph from Figure 3 showed ca. 10% of free-Fe in the REMA (see Figure 4). This was confirmed by magnetic measurements.

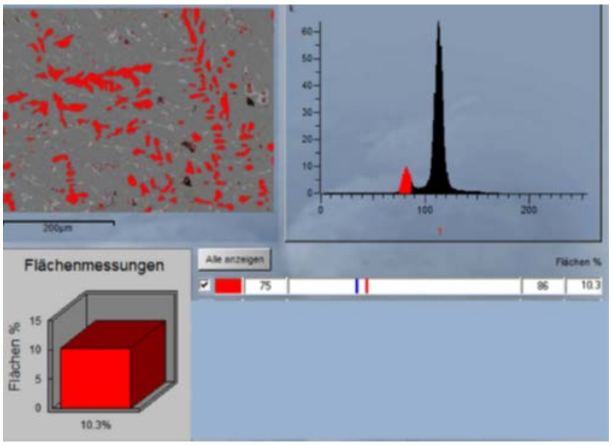
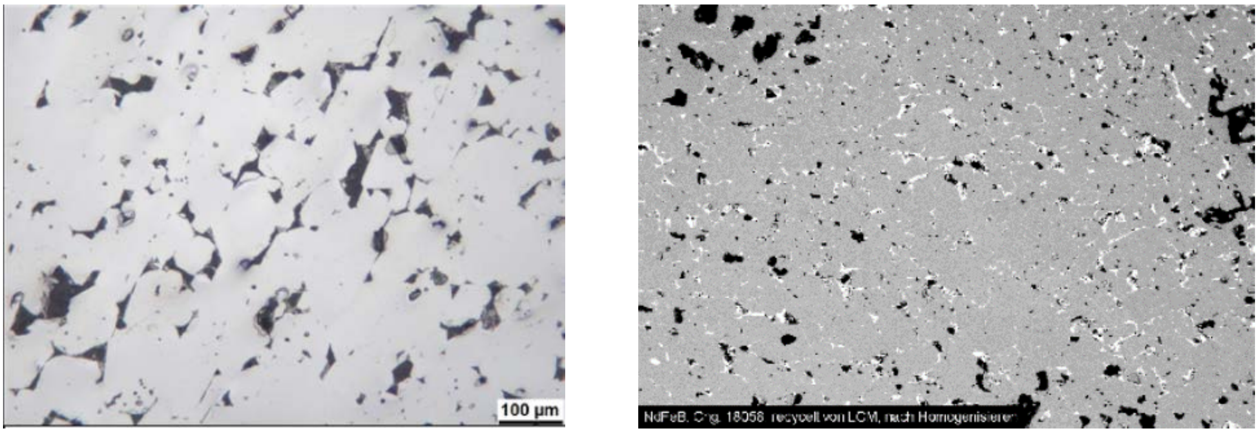


Figure 4. Metallographic determination of free Fe (marked in red).

A long time annealing treatment was carried out in order to dissolve the free Fe. After the treatment, less than 1% free Fe was found to be present in the sample. (see Figure 5).



A) B)

Figure 5. Microstructure of the book-mold REMA ingot after long duration annealing. A) light microscopy; B) SEM.

3.3 Coarse Powder Preparation

A coarse powder was prepared from the long-duration annealed book-mold REMA block (see Figure 6).

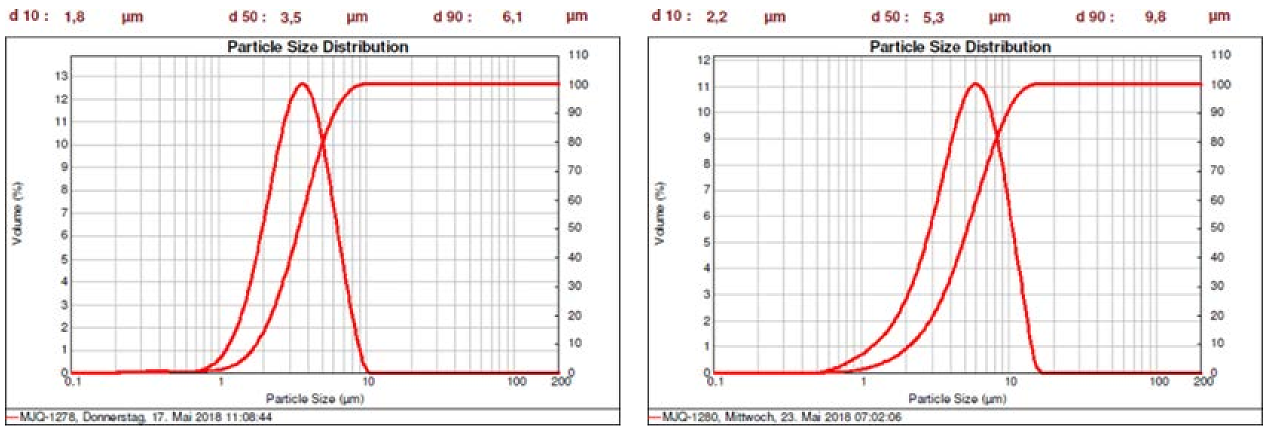
The block was placed in a vessel, which was evacuated. Then H_2 was introduced and the block was cracked by hydrogen decrepitation. The H_2 was partly removed by heating the powder to 500 °C under vacuum. Finally, the powder was cooled to room temperature and was ready for the next step, i.e. jet milling.

Figure 6. Coarse powder obtained after HD treatment of the long-duration annealed book-mold REMA block.

3.4 Fine Powder Preparation

A laboratory scale jet mill was used to prepare two batches of fine powders. Both batches showed D_{50} values of 3,5 and 5,3 µm, which are optimum values for best magnetic properties.

The particle size distributions are shown in Figure 7. Narrow distributions were found with no oversized particles similar to other powders from mass production at VAC.



A) B)

Figure 7. Particle size distributions of two batches of fine powders. A) D_{50} = 3,5 µm; B) D_{50} = 5,3 µm.

3.5 Pressing and Sintering of Small Magnet Blocks

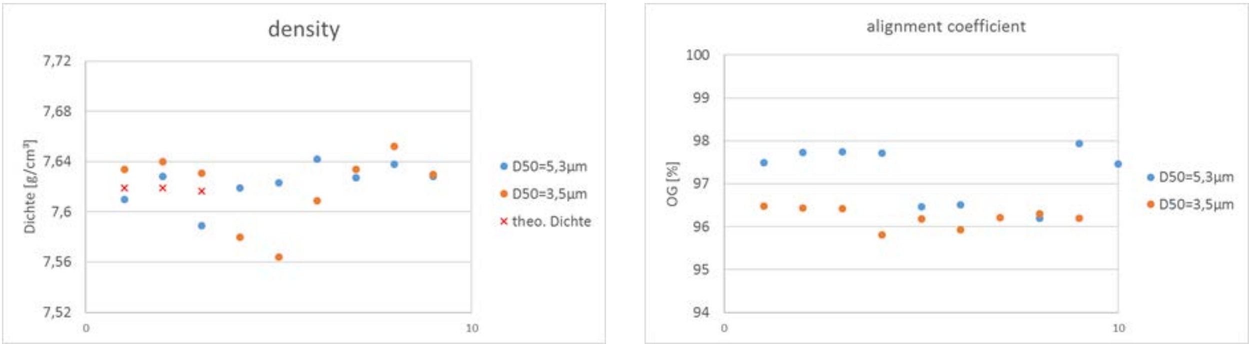
The fine powder was filled into rubber bags under inert gas atmosphere, aligned in a magnetic field and then isostatically pressed in order to fix the magnetic orientation.

Five different sintering temperatures, T_s, between 1040 and 1080 °C were chosen in order to find the optimum value. If the sintering temperature is too low, the resulting block is not fully dense, and pores exist thus reducing the B_R. If the sintering temperature is too high, the grains in the magnet grow rapidly and the coercivity, H_{cJ}, is reduced.

For the further investigations the blocks obtained with sintering temperature of 1040 °C for D_{50} = 3,5 µm powders and 1070 °C for D_{50} = 5,3 µm were used. The obtained magnets (shown in Figure 8) had no pores and the grains did not grow significantly.

Figure 8. Examples of sintered PM obtained in the REE4EU project.

The density and the alignment coefficient (average misalignment angle of the grains with respect to the easy axis values) obtained for the two samples of magnets are shown in Figure 8. The magnets are fully dense, with density values higher than 7,6 g cm^{-3} and the alignment is always higher than 96 %. The "coarser" powder has a slightly better alignment than the "finer" powder.



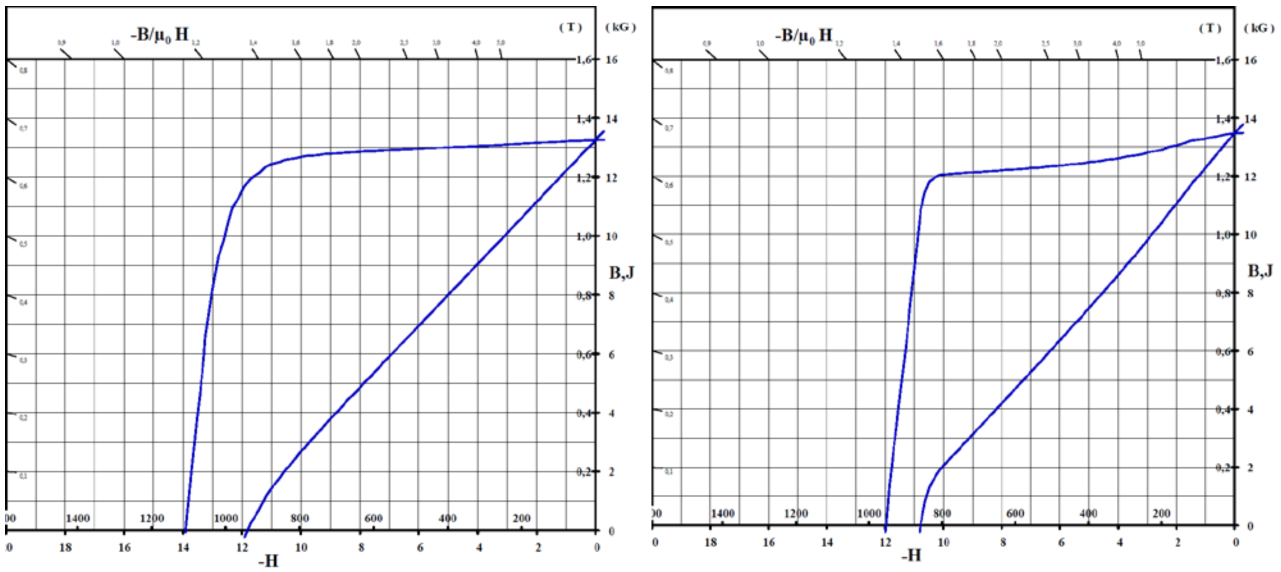
A) B)

Figure 9. Density and alignment coefficient values obtained for the two samples shown in Figure 8 (10 measurements each). The red cross density values in A) (x) referred to the theoretical desired density value.

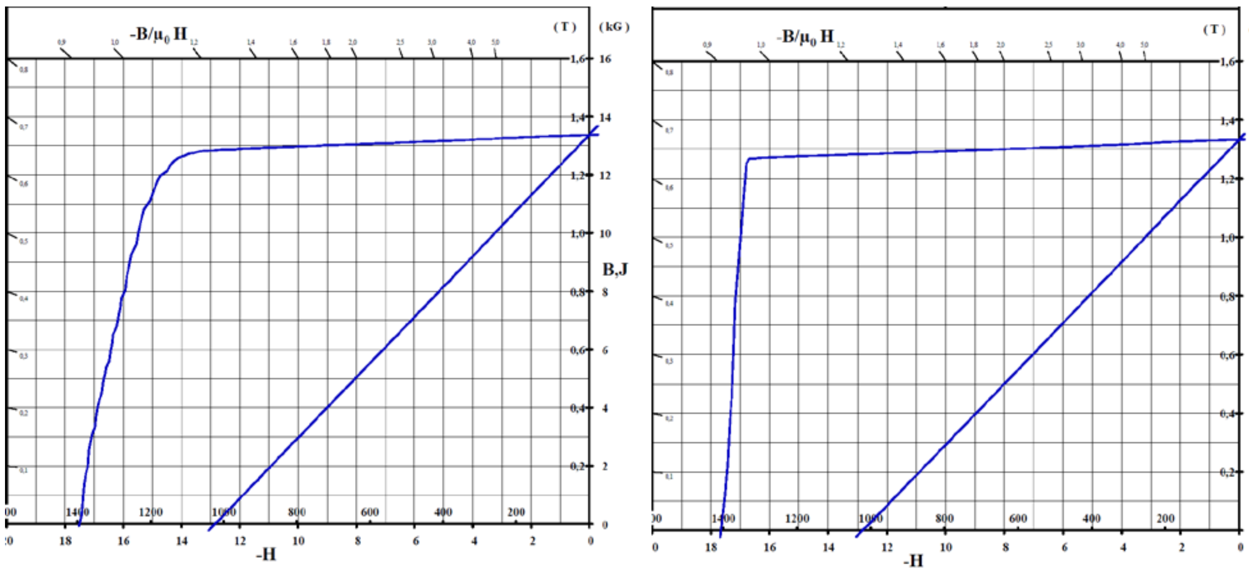
3.6 Annealing

NdFeB based magnets require an annealing treatment at temperatures, T_a, between 500 and 540 °C in order to obtain the optimum magnetic properties, i.e. optimum H_{cJ} and squareness of the demagnetization J(H)-curve.

Some demagnetization curves obtained using the different powders at different sintering and annealing temperatures are shown in Figure 10.



A) B)



C) D)

Figure 10. Demagnetization J(H)-curves obtained with the different samples. A) D_{50} = 5,3 µm, T_s = 1070 °C and T_a = 500 °C; B) D_{50} = 5,3 µm, T_s = 1070 °C and T_a = 540 °C; C) D_{50} = 3,5 µm, T_s = 1040 °C and T_a = 500 °C; and D) D_{50} = 3,5 µm, T_s = 1040 °C and T_a = 540 °C.

The values of remanence, B_R, and coercitivity, H_{cJ}, can be obtained from the demagnetization curves, as shown in Figure 11.

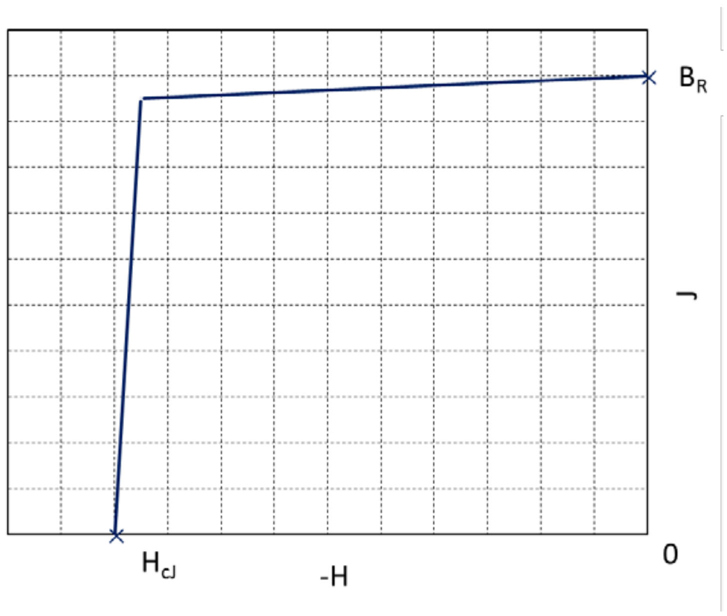


Figure 11. Example of determination of the remanence, B_R, and coercitivity, H_{cJ}, from a demagnetization J(H) curve.

The J(H)-curves obtained indicated that the particle size of the powder, the sintering and the annealing temperatures selected all have a strong influence on the H_{cJ} values and on the squareness of the J(H)-curve. The best results were achieved for the finest powder, using lower sintering and higher annealing temperatures (Figure 10D). In this case, the values of B_R and H_{cJ}, obtained were 1,32 T and 1402 kA m^{-1}, respectively.

3.7 Comparison with Mass Production

VAC produced magnets from book-mold alloys with the same chemical composition as the laboratory magnets. The production route is very similar to the laboratory production. Such magnets from mass production showed magnetic properties as in Figure 12. The magnetic properties of these magnets were typically: B_R = 1,34 T and H_{cJ} = 1378 kA m^{-1}.

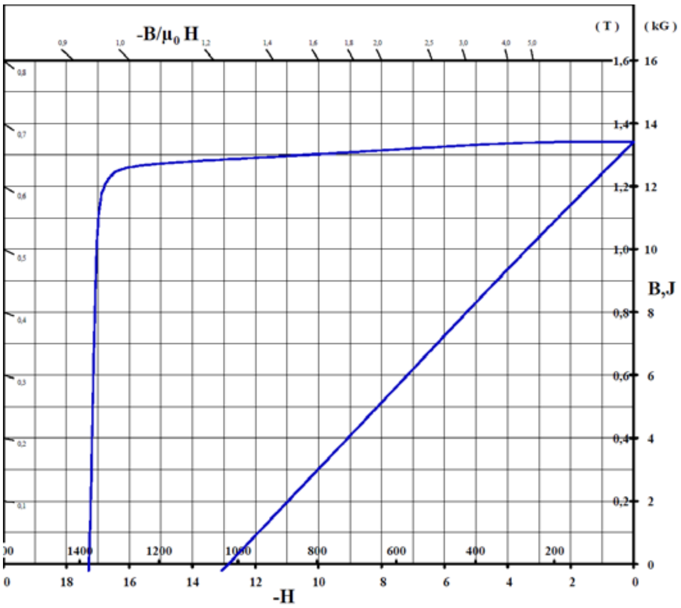


Figure 12. Demagnetization J(H)-curve of magnets from VAC mass production made from book-mold alloys with similar composition as the magnets obtained with the REE4EU's technology.

4 Conclusions

VAC has made a permanent magnet in its laboratory line using a book-mold REMA produced using the REA obtained in the HTE pilot cell installed at LCM's premises (WP4). The feed material in the HTE process was a REO mixture derived after hydrometallurgical treatment of wastes from permanent magnet manufacture, i.e. PMS. This material was provided by VAC.

The quality of both the REMA input obtained in WP4 and the permanent magnet output in terms of magnetic properties and chemical composition was checked.

Demagnetization curves were obtained using REMA powders of different particle size, as well as different sintering and annealing temperatures. The best results were obtained from powders with a particle size D_{50} equal to 3,5 µm, Ts = 1040 °C and Ta = 540 °C. In this case, the values of remanence, B_R, and coercitivity, H_{cJ}, obtained were of 1,32 T and 1402 kA m^{-1}, respectively.

The results obtained showed that the permanent magnets prepared from the book-mold REMA processed in the HM-HTE pilot at LCM have the same properties as magnets from mass production at VAC using virgin material.

That means that the REE4EU technology is suited for obtaining REA for PM production using PM-wastes, thus demonstrating a closed-loop recycling scheme for permanent magnets in Europe, using less steps than conventional state of art methods.

Acknowledgements

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 680507