Deliverable D3.7

Results of recovered materials harnessing in other fields

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Feasible Recovery of critical raw materials through a new circular Ecosystem for a Li-Ion Battery cross-value chain in Europe

WP3 - Recycling technologies and materials re-using for Li-batteries

D3.7 Results of recovered materials harnessing in other fields

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FREE4LIB

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Versions

DATE	VERSION	AUTHOR	COMMENT
10-06-2024	1	TORRECID	first draft of the document
12-06-2024	2	TORRECID	Comments from WP3
17-06-2024	3	CARTIF	Version reviewed
18-06-2024	4	CSIC	Version reviewed

Contents

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List of Abbreviations

ACRONYMS	DESCRIPTION
KPI	Key Performance Indicator
GHG	Greenhouse Gas
ICP	Inductively Coupled Plasma Spectroscopy
XRD	X-ray diffraction
SEM-EDAX	Scanning electronic microscope-elemental analysis

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1. Executive summary

This deliverable presents results of revalorization of valuable precursors and black mass within alternative material. FREE4LIB address use in other fields to minimize risks in case black mass were not useful for active materials. The use of black mass and precursor recovery in other sectors is of high interest reducing the dependency on metal oxides from outside EU.

2. Introduction

FREE4LIB aims to develop at TRL 5-6 technologies to achieve 6 new sustainable and efficient processes to recycle end-of-life (EOL) LIBs (dismantling, pre-treatment and 4 materials recovery processes) delivering very innovative recycling solutions to reach highly efficient materials recovery (metal oxides, metals and polymers) improving the supply of secondary resources at EU level. FREE4LIB also will deliver technologies to improve 3 processes aiming at metals and polymers re-using and electrode synthesis on the same value chain as secondary raw materials for re-manufacturing greener batteries, and it will study options to harness non-reusable elements in other fields FREE4LIB will also deliver a methodology based on the Battery Passport principles to improve processes traceability.

Within scope of the project, the WP3 focuses on development of material technology for recovery of valuable materials and their valorisation within the battery value chain. WP3 has focused mainly on recovery within active materials like NMC622 and LMNO. Task 3.9 studies the viability of recycled cobalt, nickel and manganese in alternative industries.

Task 3.9 studies the viability of recycled cobalt, nickel, manganese in alternative industries. Ceramic sector is an important industry at European level, including ceramic tiles, tableware, sanitaryware pigment production and frit production. Within Ceramic sector metal oxides are used on different applications like ceramic pigments for tile, glass, table ware decoration, for frits used in enamelling steel for household appliances, protective coatings. The use of revalorized sources for metal oxides like NiO, MnO2 and CoO will reduce dependency from outside EU as well as reduce GHG emissions allocated to transport. In addition, as social aspect, the reduction of CoO from mining will impact also on the current situation of CoO mining related to childhood use in industrial mining. This deliverable 3.7 will summarize main results towards the validation in use of recycled materials for alternative resources.

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3. Objectives

The specific objectives of the deliverable 3.7 is to present results on evaluation of the black mass and recycled materials as alternative source for metal oxides in ceramic materials, specifically ceramic pigments and frits for enamels. Ceramic sector uses different raw materials for their production.

Ceramic pigments are inorganic structures based on spinels ($CoAl2O4$), ferrites ($FeNiMnCrO$, $NiFeO3$), cassiterite ($SnCaSbO2$), or vanadates ($BiVO4$) that use metal oxides such as CoO, $Fe2O3$, $MnO2$, NiO and CuO. Ceramic pigments are widely used in ceramics, the glass and in plastic industries.

In the ceramic sector, frits are basic materials for the manufacture of enamels, as well as for digital application with application temperatures between 1,140 and 1,180 °C on ceramic substrate. Frits are used in other fields such as glass decoration and sheet metal enameling, with working temperatures of 700 and 820 °C. Ceramic frits are glass-based systems based on oxides such as SiO2, Al2O3, Li2O, Na2O, K2O, CaO, MgO, TiO2, ZrO2, BaO, CeO2, Bi2O3, V2O5, ZnO or B2O3 and in the case of enamel frits, adding CoO, NiO and MnO2 as adhesion promoters. Frits are obtained by mixing raw materials and melting between 1,200 and 1,500 ° C.

4. Experimental works in recovery of materials

Within Free4lib diverse recycled materials were supplied by partners CISC and Cartif. These materials were characterized by Torrecid to check viability and later on test in different matrixes. Table 1 shows the materials received and viability.

Table 1 Type of recycled material received.

SAMPLE	MATERIALS	COMMENTS
BM01	Mixture of NI, Mn,Co, C by hydrometallurgical process	High C amount
BM02	Mixture of NI, Mn,Co, C by hydrometallurgical pricess	High C amount
BM01-LC	Lithium carbonate by hydrometallurgical process	Good for frits. Low amount received, used in active materials LNMO

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PRE04	Mixture of NI, Mn, by hydrometallurgical process	Good for frits Low amount received, used in active materials LNMO
CP021	Mixture of Ni, Mn:Co. Li, Al, Cu by ultrasound delamination process	Tested

BM01 and BM02 showed a high carbon content as shown below in figure 1. Graphite showed a high thermal resistance. To reduce the carbon content materials were thermal treated up to 1000 °C. at 1000 °C, carbon content was reduced from 80 to 24 %.

This material was considered not useful for reuse in frits or pigments.

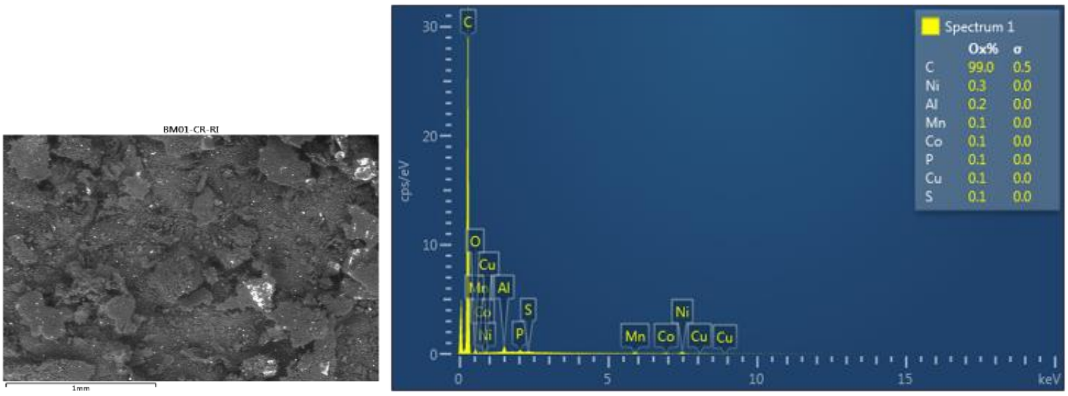

Figure 1 Microstructure and SEM-EDAX of BM01.

Li_2CO_3 showed a great purity and is feasible for use in frits. Due to low availability at the moment no trail could be done.

CP021 black mass received from CARTIF was considered feasible to be used as Ni, Mn and Co source in either frits or pigments. Figure 2 shows the SEM-EDAX analysis made by Torrecid. Figure 3 shows the XRD of CP021.

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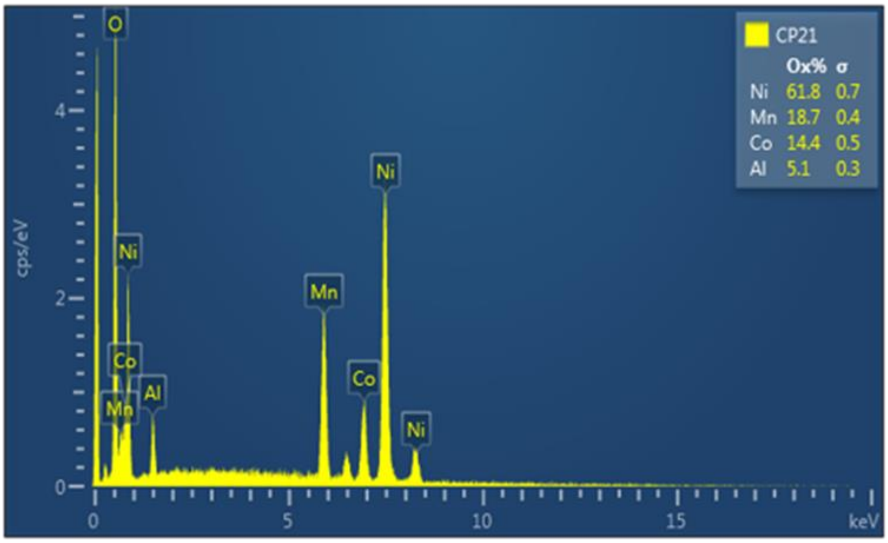

Figure 2 SEM-EDAX of CP021

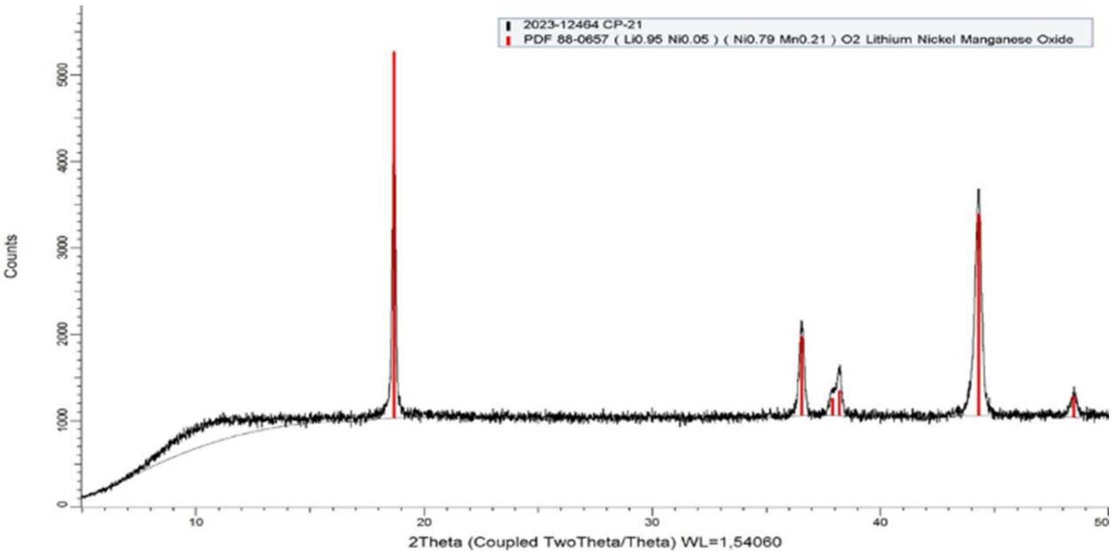

Figure 3 XRD of CP021

This data was consistent with the data from CARTIF by ICP displayed in next table 2 Lithium is not measured by SEM-EDAX.

Table 2 ICP for CP021

ICP	%
Ni	39,87

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Mn	8,71
Co	6,54
Li	6,95
Al	0,21
Fe	0

4.1 Use of recycled materials in ceramic pigments

Ceramic pigments are prepared by solid state synthesis. Raw materials are mixed, milled and sintered between 1200 and 1300 ºC. Ceramic pigments are used in ceramic glazes, for ink jet inks in ceramics and glass as well as in plastic. As inorganic structures, the hue or colour can be adjusted by modifying metal oxide ratio. In addition, advantage of ceramic pigments is the stability against small impurities.

Two inorganic structures were selected as inorganic matrixes to incorporate recycled materials:

- Blue pigment Cobalt spinel Al_2O_3 Co_3O_4
- Black pigment black ferrite: Cr_2O_3 Co_3O_4 Fe_2O_3 Mn_3O_4 NiO

Figure 4 shows the application colour for each pigment used in a ceramic glaze at 4 %. On each image left is standard size and right reduced to 400 nm for use in digital decoration.

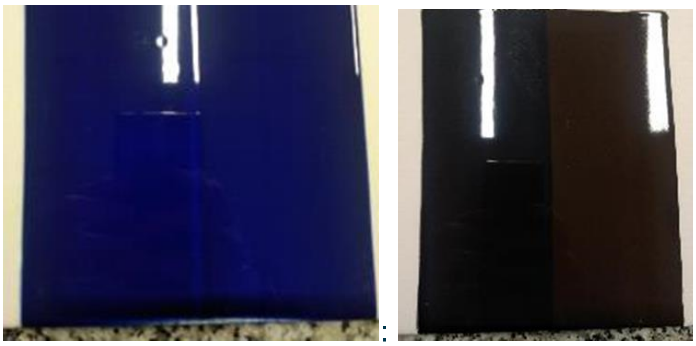

Figure 4 Color development of pigments

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Figures 5 and 6 below show the XRD pattern of the pigments.

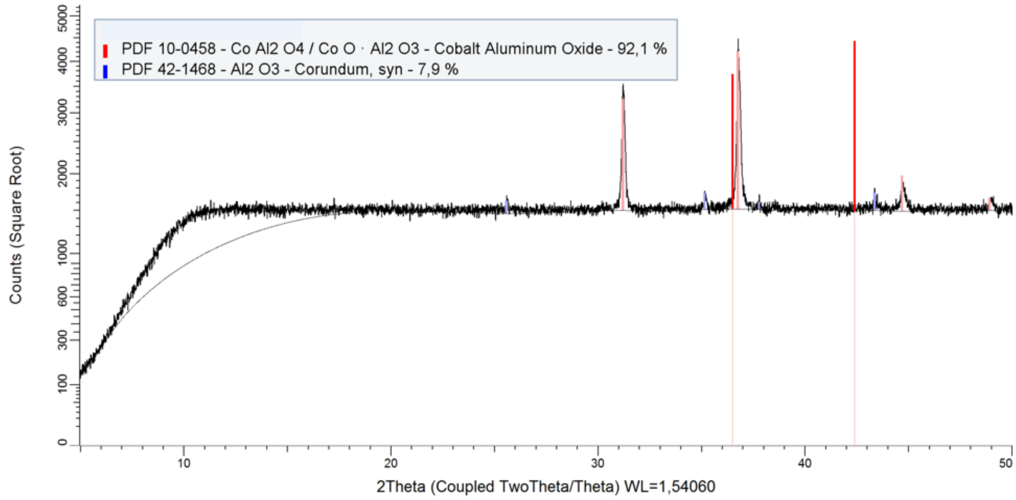

Figure 5 XRD of Blue pigment.

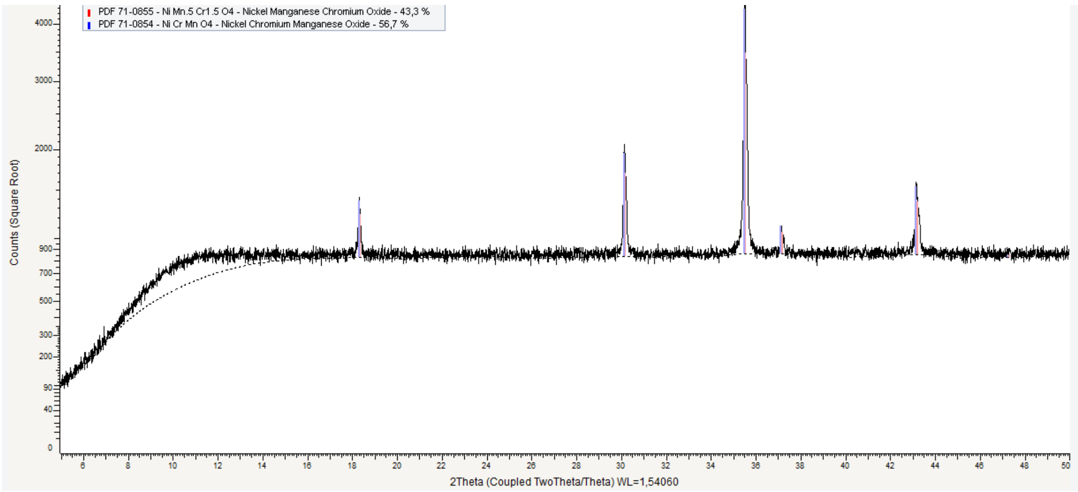

Figure 6 XRD of Ferrite black pigment

Next figure 7 shows pigment size used in glazes measured by laser scattering.

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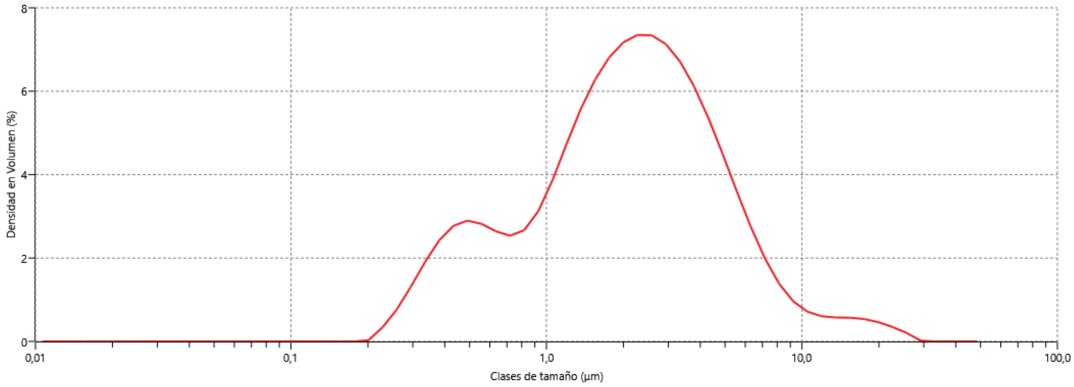

Figure 7 Pigment size (microns).

CP021 was tested in black ceramic pigment due to analysis. Material was tested at two levels, whole replacement of NiO and partial resulting in 25 and 10% use of black mass. The remaining oxides were adjusted to match composition. N14NMC-A 25 % and N14NMCB 10 % replacement.

Pigment was prepared by dry milling of black mass and raw materials and sintering at 1,250 °C for 15 hours. After calcination powder was milled to 5 microns and used in ceramic glaze compositions. To assess validation, two glazes were used, single firing wall tile glaze and floor tile glaze adding 4 % pigment in the glaze. The glaze was applied on ceramic biscuit and fired between 1,120 and 1,180 °C.

The resulting glaze was analysed for defects that could arise from the presence of lithium as well as color yield. Novel pigments were characterized by XRD and colorimetric values Figure 8 and 9 below shows the XRD of novel pigments.

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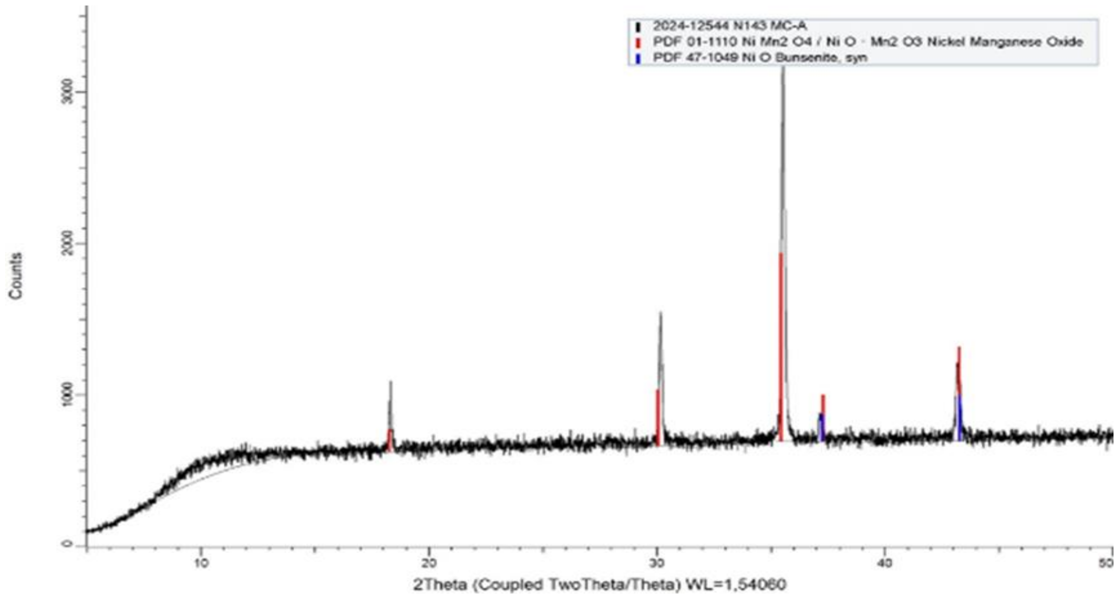

Figure 8 XRD of pigment with 25 % of us of black mass CP021

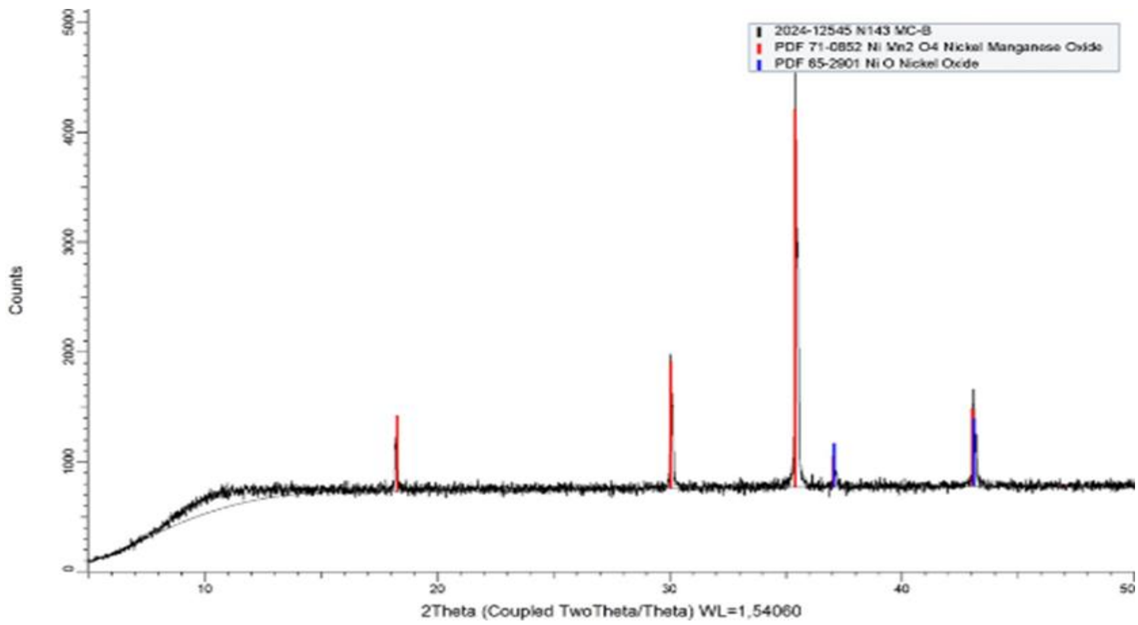

Figure 9 XRD of pigment with 10 % of CP021

Figure 10 shows the application in wall tiles glaze.

Figure 10 pigments in tile glaze (std-25 %replacement-10 % replacement)

Table 3 shows Lab color hues for 4 % in ceramic glaze for wall and floor tiles as example after dispersion of pigments in glaze, and firing of the glaze. Hue variation (DE) versus standard is below 3, therefore CP021 can be used for ceramic pigments.

Table 3. Colorimetric values for use of novel pigments

Wall tile - 2% SCI	L	a	b				
N143STD	26,58	0,90	0,30	DL	Da	DB	DE
N14NMC-A 25 %	26,67	0,78	0,19	0,09	-0,12	-0,11	0,19
N14NMC-B 10 %	26,71	0,76	0,11	0,13	-0,14	-0,19	0,27

Gres 4% SCI	L	a	b				
N143STD	36,13	0,27	-1,75	DL	Da	DB	DE
N14NMC-A 25 %	37,10	0,14	-1,95	0,97	-0,13	-0,2	1,00
N14NMC-B 10 %	37,00	0,12	-2,07	0,87	-0,15	-0,32	0,94

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From the provided values in Table 3 in terms or colorimetric properties it can be concluded that novel pigments developed with incorporation of black mass are suitable. No defects were observed on the surface of the glaze due to pigments. The low amount of impurities of Al, Cu and Li does not affect the pigments.

4.2 Use of recycled materials in frits

Ceramic frits are produced by melting at 1400-1500 °C mixture of oxides. Once molten materials are water quenched. Frits are main components in glazes, enamels used in ceramics, glass and metal enamel. Specifically, FREE4LIB has focused on ceramic frits for metal enameling since these frits have metals like Fe_2O_3, NiO, MnO_2 and CoO to improve adhesion on steel alloys. These materials can be used to include recycled materials in their compositions.

Two types of frits were selected initially NiO bearing and NiO free to have options depending on type of material. Table 4 shows analysis of two types of frits.

Table 4 Composition of frits

	FR4EFV1	FR4EFV2
SiO_2	52	68
Al_2O_3	1	5
B_2O_3	17	6
CaO + MgO+ BaO	5	2
TiO_2+ZrO_2	9	4
Na_2O+ Li_2O+K_2O	13	12
MnO_2	1	1
CuO	0	
CoO	1	2
NiO	2	

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The figure 11 shows the aspect of DC01EK steel enameled with both frits. On the left NiO bearing frit FR4EFV1, right FR4EFV2. The steel was coated by a wet milled composition made up of frit, clay and additives. The steel plate was coated by spraying and fired at 810' °C for 5 min.

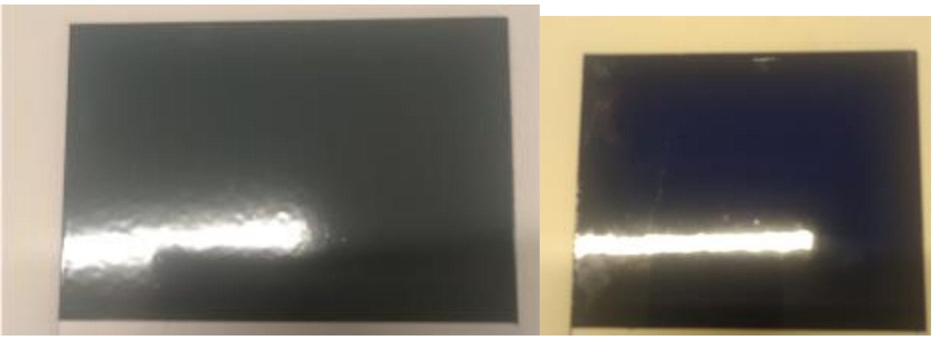

Figure 11 Enameled steel with frits (NIO bearing left).

Melting properties of the frits in terms of characteristic points were determined by hot stage microscope, being shown un table 5

Table 5 Characteristic points of frits

	FR4EFV1	FR4EFV2
Sintering point	640	646
Softening point	694	706
Sphere point	756	831
1/2 sphere point	792	878
1/3 shpere -flow point	828	920

In the case of frit, FR4EFV1 was used as matrix based on the analysis of the black mass, replacing metals by black mass CP021. Composition was adjusted replacing NiO by the CP021 and adjusting the composition of remaining metals. Two tests were made, 100% replacement of NiO and 50% of replacement.

The frit was molten at 1300 °C, water quenched and enamel was prepared with specific additives by wet milling. The enamel was applied by spraying on DC01EK steel and fired at 810 °C. Figure 12 shows ceramic performance on

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DC01EK fired at 810ºC for the standard enamel and the modified enamel with CP021. Adhesion was tested and novel frits perform good.

Figure 12 Left Steel enameled with std frit and novel frits std (left) 50% 100% replacement-Right adhesion test

Melting properties of the frit in terms of characteristic points was determined for the highest addition by hoy stage microscope, showing results in table 6. Variations are not significant.

Table 6 Characteristic points for frits with recycled material

	FR4EFV1 reference	FR4EFV1 with CP021 100 %
Sintering point	640	640
Softening point	694	685
Sphere point	756	746
1/2 sphere point	792	790
1/3 sphere -flow point	828	820

From the application of the enamels, and the properties of the frits in table 5 it can be concluded that the use of black mass is feasible, does not affect the performance.

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5. Conclusions

FREE4LIB has shown viability of use of recycled materials in hosts like ceramic pigments and ceramic frits. Both matrixes can use the material without effect of low impurities like Al and Cu. Results of the T3.9 and work in WP3 will feed WP4 for upscaling of the application. These results are in line with objective ST02 "Develop until TRL3-4 innovative technologies for recovered materials re-using and explore options to harness non reusable elements in other fields", validating the use of recycled materials in other fields.

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