EIT Raw Materials RIS-DUSTREC: investigation and selection of furnace dust samples for valuable metals recovery

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Every year around 1.2 Mt of Electric Arc Furnace (EAF) dust and around 50 kt of Cupola Furnace (CF) dusts are generated in Europe. Both materials are classified as hazardous waste due to significant concentration of Zn, Cd, Cr, Ni and Pb, which burden the metallurgical industry, albeit their possibility to be considered as an alternative source of valuable metals. Around 30 steelworks in the East-Southeast European Regional Innovation Scheme (ESEE RIS) region exploit EAFs for scrap-based steelmaking. However, the dusts generated from the exhaust gases abatement cannot be profitably recycled due to the absence of recycling plants operating in these areas, which implies that the dust generators have additional costs due to the dust transportation to the nearest Zn recovery plant, since presence of toxic substances prohibits their landfilling.

Thanks to the extensive knowledge on the extraction of a wide range of compounds from steelmaking dusts, as well as the capacity of reutilisation of residues after extraction in the building and construction industry, the DustRec project aims at the recovery of all the economical compounds within the dusts (Zn, Pb, Cu, Fe and others) hence minimizing the final waste landfilling and generate an economically feasible process with improved environmental and societal impacts. The proposed approach includes several emerging techniques from innovative magnetic and gravity separation methods to new pyro- and hydro-metallurgical reprocessing technologies for the separated fractions. In this paper, eight different dusts from EAF and CF were collected all around the partners' countries and chemically, thermally and physically characterized in order to select the most optimal samples to be reprocessed for improved valuable extractions. Due to their high concentration of ZnO and PbO, three EAF dusts were identified as promising raw materials while two CF dusts will be employed as co-adjuvant for magnetic fraction reduction and smelting. Preliminary hints about the next reprocessing steps are also revealed.

KEYWORDS: EAF STEELMAKING, EAF DUST, CUPOLA FURNACE DUST, RECYCLING, GRAVITY AND MAGNETIC SEPARATION, CARBOTHERMIC REDUCTION SMELTING, HYDROMETALLURGY

INTRODUCTION

The Electric Arc Furnace (EAF) process is by far the most widely used process for production of carbon steel given its capacity to smelt 100 wt.% of solid charge (1) in comparison to the Basic Oxygen Furnace (BOF) which is capable to treat typically 20 wt.% of the total charge weight as cold metallic burden (2). During the melting process, in which the main fed is steel scrap, EAF dust typically accumulates at the rate of 10-20 kg per tonne of liquid steel (3). It contains Fe, Zn, and other useful metal oxides such as Pb, Mn, Ni, and Cr oxides, but also a certain amount of halides (4). The amount of elements in the dust is related to the amount of galvanized steel (Zn) or high-alloy or stainless steel (Cr, Ni) and the chemical composition can widely vary not only from day to day but also between heating batches of the same steel shop (5). During the smelting process, Zn is vaporized and leaves the metal bath as gaseous Zn. It is oxidized to ZnO during transport with the off-gas, along with other present metals (6). EAF dust is usually collected

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in bag filters in the off-gas treatment plant (7). Its disposal can be environmentally harmful if not done correctly, due to the risk of mobilization of potential toxic elements such as Zn, Cd, Cr, Ni and Pb, as well as expensive, burdening the metallurgical industry (8). In 2022 between 0.6-1.2 Mt of EAF dust (EAFD) were generated in Europe and 5.5-11 Mt globally (9–11) and this latter number is expected to increase to at least 18 million tonnes by 2050 (11,12). When considering the various treatment options for recycling EAFD, the contents of Fe and Zn are particularly striking, reaching a combined value of between 50 and 60 wt.% (13). Nevertheless, the recovery of Zn is the main motivation, since its value contributes the most to the profitability of the activity (roughly 2600 $/t) than the recovery of iron (roughly 430 $/t) (14). Thus, EAFD is currently being reprocessed only from the perspective of Zn mainly due to undeveloped technologies for the recovery of the other valuable metals within. Currently EAFD treating technologies are mostly based on pyrometallurgical methods of Zn extraction. With a market share of over 85%, the Waelz kiln process remains the predominant method for processing dust (15) although other pyrometallurgical process were developed resulting in Zn recovery in the form of ZnO, which is fed to the traditional sulphate electrolysis process or the Imperial Smelting Process (ISP) (16–18), but still struggling to achieve a full commercial competitiveness. For example, the Rotary Hearth Furnace (RHF) process is an important coal-based direct reduction method for dust recycling and has been practiced in the steel industry (19,20). The RHF direct reduction process is deemed effective in processing EAFD containing appreciable amounts of Fe, C, Zn, Pb and alkalis; high grade zinc product and Direct Reduced Iron (DRI) can be produced instead of slag and, therefore, it claimed that this process may be commercially and environmentally superior to the Waelz process. However, the RHF process was only suited for recycling EAFD with low zinc content (21) although this technology has been re-engineered to overcome some operational problems such as Zn oxide blockages at higher zinc content. Moreover, due to the large initial investment in equipment, the economic benefits of the process must be enhanced further (17). Alternatively, to RHF, the Primus® process (17,22) has been designed for reducing metal oxides using the multiple-hearth furnace technology. It is featured by unprepared and low-cost feed, rapid reduction of metal oxides due to intensive stirring and heating, high efficiency with relatively low operating temperature and excellent quality products. However, it suffers of fast corrosion due to rapid stirring and evaporation

of alkaline compounds during reduction. Meanwhile, to keep good kinetic conditions for the charged feed, the furnace has a restricted size which restrains its productivity (17,22). These drawbacks led to the shutdown of the sole European plant in 2009 (23). Other attempt to recover Zn by pyro-metallurgical process is represented by INDUTEC® process (24–26). This is based on zinc-enrichment of EAFD by means of an induction furnace. Zn and Pb are recovered by filtering the furnace flue gas with a bag filter and extracted as Crud Zinc Oxide (CZO) while the reducible oxides are recovered as molten pig iron. However, these processes are ineffective, expensive, and environmentally harmful. The technology recently developed under the EIT 2sDR project (27–29) tries to improve the process by recovering both Fe and Zn, but still fails to separate and recycle Pb and Cu, both of which are present in the average stream. Again, the process is still at the prototype scale and under analysis to assess its potential to meet requirements of present and future environmental legislation (30). In addition, alternative hydrometallurgical processes are the Zincex® (31) and the Ezinex® (25) processes. The former is based on atmospheric leaching, solvent extraction and conventional electrowinning, for the production of high purity zinc ingots (99.99 wt.%). The latter is still an electrowinning system but based on a chloride leaching able to leach materials containing oxidized zinc. Both are only operated at a pilot scale plant; thus, they do not represent a reliable solution for EAFD treating.

In the same vision, the dust produced by the abatement of the exhaust gases collected at the top of Cupola Furnaces (CF) represents a collateral source of raw materials. The CF is the most predominant melting furnace for cast iron. It produces about 60% of the liquid iron used worldwide for cast iron (32). The cupola furnace is charged mainly with ferrous scraps mixed with pig iron and coke and it generates dust in amounts between 4 and 15 kg per tonne of molten cast iron depending on the charging materials and operating conditions (33,34). The CF dust (CFD) depends, in its chemical composition, on the type of charge material. It can contain Zn when the charging material for cupola contains a lot of galvanized steel that is predominately found in automotive scraps. In that case most of Zn evaporates and is sucked out with other gases and fumes. It is reported that Zn content in the cupola dust can reach up to 20 wt.% (33,34). According to other literature data on CFD, ZnO content ranges between 0 and 65 wt.%, and Fe oxides extends between 5 and 20 wt.% (35). Recycling of CFD, in contrast to

EAFD, has less literature data. Thus, the research dealt with recycling or, at least, characterizing of CFD is sparse (36). It is reported that huge amounts of CFD are landfilled annually (37), although it can contain some environmentally potential toxic elements, e.g. Cr, Pb, and Cd (34). Thus, its recycling in a valuable way is auspicious.

Summarizing, the efficient recovery of valuable components from EAFD and CFD is a matter of salience and, at the same time, represents an immense resource, especially for those metals categorized as critical (38). Thus, in the view of reducing the amounts of toxic and hazardous wastes and pursue the European zero-waste philosophy, the DustRec project aims to develop and integrate innovative technologies for the separation, reprocessing and beneficial use of all the components within the EAFD and CFD.
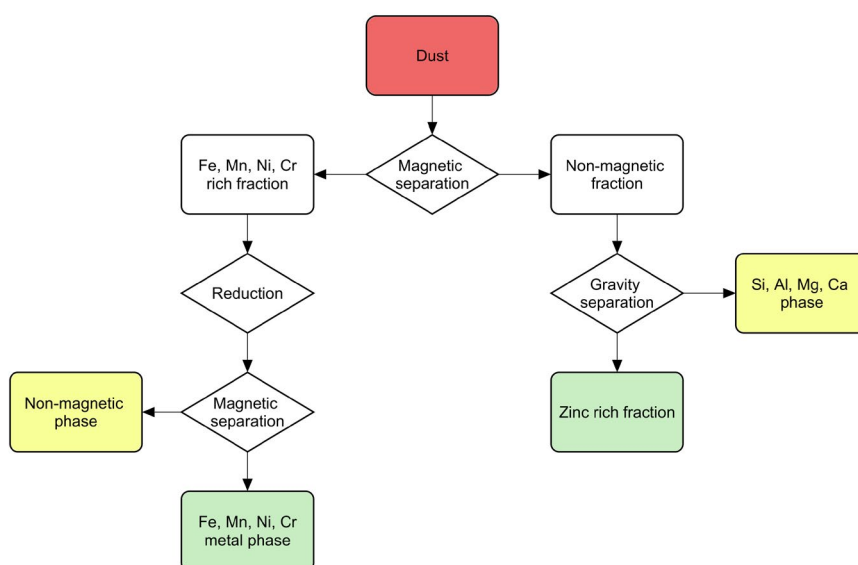
THE DUSTREC PROJECT

Specifically, the project aims to reprocess all technically and economically feasible elements within the EAFD and CFD with minimal waste generation. Several objectives are to be achieved, such as maximizing the extraction of ferrous and non-ferrous fraction with the purpose of recirculate back elements needed in respective metallurgy, i.e., for recycling in the steel making industry (Fe, Mn, Cr, Ni and Mo) and other industries (Cu, Pb, Al). Besides that, the recycling and beneficial use of the processed residues in construction

industry is foreseen. Furthermore, the project seeks:

(i) to establish an effective self-sustaining network of the EAFD/CFD value chain stakeholders from the knowledge triangle (industry, academia and research institutes) in the ESEE region, interested in processing metallurgical dusts with near-zero waste vision;

(ii) to assess data from previous research as well as historical technological data on EAFD and CFD in the ESEE region, especially from the point of their heterogeneity (dust from different producers, scrap metal inputs, countries etc.) and geographic distribution;

(iii) to demonstrate that the developed Best Available Technology (BAT) for halides washing and magnetic-gravity separation is feasible for effective separation of material flows from selected dust sources;

(iv) to evaluate the potential of this technology for the other EAFD and CFD in the region;

(v) to evaluate the residues after recyclable material flows separation for applications in the building composites.

Fig. 1a depicts the general concept of the DustRec project highlighting that the core for the successful achievement of the several goals is the reliable fulfilling of magnetic and gravimetric separation of selected dusts in order to produce two main streams: a magnetic fraction and a non-magnetic non-ferrous fraction. Fig. 1b shows the main processes are applied to the separated fraction in order to maximise the recovery yield of all the valuable elements in the dusts.
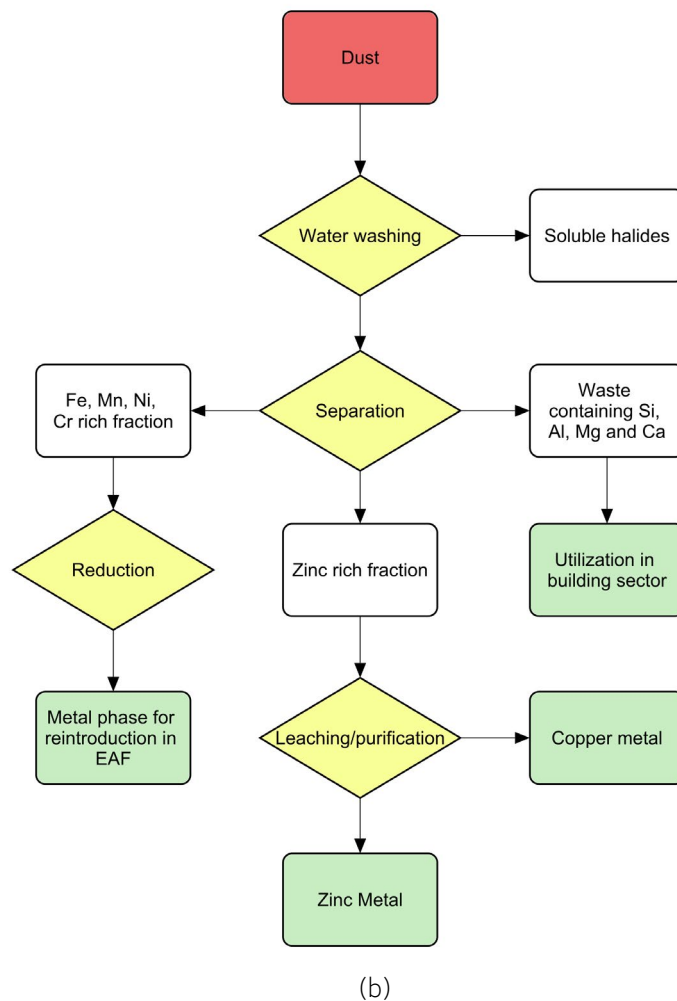

(a)

(b)

Fig.1 - General concept of DustRec project (a) and detailed separation, reprocessing and beneficial use process steps for EAFD recycling (b).

As a part of the process-flow, the separation of the original dusts will produce an Fe, Mn, Ni and Cr rich fraction mainly contained as metal oxides. Through a pyrometallurgical process of carbothermal reduction, the magnetic fraction will be converted into an iron-based alloy that will be returned to the originating steelmaking processes because of its high value, cost reduction, and with lower consumption of primary scraps with lower carbon footprint and increased steel quality (no recirculation of copper). On the other hand, the non-magnetic fraction will be treated mainly through hydrometallurgical processes. Metal extraction technological maturity level is still low for specific elements; i.e., between TRL 3 and 5 for Zn and other elements' extraction (39), while reached consolidated level for Pb recycling (TRL 7) (40).

From the concept above, the implementation of such a multi-step process needs to be demonstrated on a large variety of dusts. Since scrap iron used in production differs both in composition and coating, the obtained dust contains different elemental and mineralogical compositions, as well as different grain size. All this has an impact on the reprocessing capability and the financial profitability of reprocessing. Screening of the selected dusts depending on the processes and production parameters will be carried out in order to define reliable parameters for further reprocessing. This activity will also help to create a value chain with the common goal of determining the prospects of the different EAFD and CFD in the ESEE region. Thus, in this paper several EAFD and CFD sources are evaluated in order to select the best samples to be reprocessed for improved valuables extraction.

MATERIALS AND METHODS
With the aim to evaluate homogeneity and characteristics of samples from selected producers of EAF and CF dusts in the ESEE region, eight different dust samples were collected. Tab. 1 summarises their provenience and main characteristics. For all the samples, general chemical composition was determined through Wavelength Dispersion X-Ray Fluorescence (WD-XRF) by Bruker S8

Tiger spectrometer after calcining the sample at 850 °C in air and preparing a pearl by the coadjutant of lithium tetraboride. Carbon and sulphur concentration were measured through Bruker G4 ICARUSC elemental analyser. Most significant elements concentration (Zn, Cu, Pb, Ni, Cr, Fe, Mn, Ca, Si, Al, Mg and S) was determined through Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) after digesting the samples according to ISO 26845/EPA6010D methods. Crystallographic analysis and minerals identification were performed by means of a Rigaku SmartLab SE diffractometer, in θ-θ Bragg-Brentano configuration, scanning the samples from 5 to 80 ° 2θ at 2 °/min, with a step size of 0.02° 2θ and a fixed divergent slit of 0.5°. To reduce the preferred orientation effect, the samples were rotated at 60 rpm. A copper tube (Cu Kα radiation, λ = 1.54 Å) excited at 40 kV and 40 mA was used to generate X-ray. Diffracted X-ray was collected through 1D D/teX Ultra 250 detector with fluorescence suppressor filter. The morphology and the semi-quantitative chemical analysis were done by a Zeiss Sigma 300 Field Emission Gun Electronic Scanning Microscope (FEG-SEM) equipped with an Oxford Xmax Ultim 65 Energy-Dispersive X-Ray Spectroscopy (EDS) probe.

On the selected samples, further investigations were conducted. In particular, other elements (Ag, Au, Co, Cl, F, Mo) were measured by ICP-OES at the same conditions as above. The granulometric distribution is obtained through optical granulometry by means of a Malvern Morphology 4 granulometer. The lens used were 25X and 50X, in order to identify particles with a minimum diameter of 2.65 and 1.34 μm, respectively. 250.000 particles were analysed in each test.

Heat treatments for measurement of moisture, loss on ignition and carbonates content were performed according to the standards:

• EN 14346:2006: Characterization of waste — Calculation of dry matter by determination of dry residue or water content
• EN 15169:2007: Characterization of waste — Determination of loss on ignition in waste, sludge and sediments
• EN 459-2:2021: Building lime – Test methods

For each temperature test, absolute mass variation was expressed as equation [1]

$$mass\ loss[\%] = \frac{m_i - m_f}{m_i - m_c} \qquad [1]$$

where m_i is the initial mass of the sample, m_f is the mass of the sample after heat treatment and mc is the mass of the empty crucible.

Water content measurement was performed ad 105 °C dwelling the samples overnight in the furnace, loss on ignition (LOI) was measured at 550 °C dwelling the samples for 2 hours, carbonates concentration was measured at 1050 °C dwelling the samples for 2 hours.

Dry mass and water content was express as indicated in the EN 14346 standard as equations [2] and [3]

$$m_{DR} = \frac{m_c - m_a}{m_b - m_a} \cdot 100 \qquad [2]$$

$$m_W = 100 - m_{DR} \qquad [3]$$

where m_{DR} is the dry residue of the sample, m_c is the mass of the crucible containing the dried sample, m_b is the mass of the crucible containing the undried sample, m_a is the mass of the empty crucible and m_W is the water content of the sample.

LOI, associated to the hydroxide within the samples, was expressed as indicated in the EN 15169 standard (equation [4])

$$m_{LOI} = \left(\frac{m_b - m_c}{m_d - m_a} \cdot 100 - (100 - m_{DR}) \right) \cdot \frac{100}{m_{DR}} \qquad [4]$$

where m_{LOI} is the loss on ignition of the sample, m_c is the mass of the crucible containing the ignited sample, m_b is the mass of the crucible containing the undried sample, m_a is the mass of the empty crucible.

Carbonates content was expressed as indicated in the EN 459-2 standard as reported in equation [5]

$$m_C = \left(\left(\frac{m_{11} - m_{12}}{m_{11}} \cdot 100\right) - \left(\frac{m_b - m_c}{m_d - m_a} \cdot 100\right)\right)$$
$$\cdot \frac{100}{100 - \left(\frac{m_b - m_c}{m_d - m_a} \cdot 100\right)}$$

[5]

where m_{11} is the mass of the sample before ignition at 1050 °C, m_{12} is the mass of the sample after ignition at 1050 °C, m_c, m_b, md and ma are the masses referred to the LOI determination.

Heat treated samples were analysed again by XRD in the same conditions as as-received samples.

Thermogravimetry-differential scanning calorimetry (TG-DSC) simultaneous thermal analysis was performed on 25 mg of sample in a NETZSCH STA 449F3 Jupiter machine, imposing and heating ramp of 30 °C/min from room temperature to 1200 °C under argon atmosphere and using Al2O3 pans of 90 µl.

Tab.1 - Provenience and main characteristics of investigated dusts.

TYPE	COUNTRY	SAMPLE ID	APPEARANCE
AOD dust	Slovenia	AOD-SLO	Brown fine powder
CF dust	Italy	CF-ITA	Light brown fine powder
CF dust	Serbia	CF-SRB-I	Dark black fine spiky powder
CF dust	Serbia	CF-SRB-II	Light black crumbly powder
EAF dust	Italy	EAF-ITA	Brown coarse powder
EAF dust	Poland	EAF-POL	Brown fine powder
EAF dust	Slovenia	EAF-SLO-I	Brown fine powder
EAF dust	Slovenia	EAF-SLO-II	Brown fine powder

RESULTS AND DISCUSSION
Preliminary characterization
The visual appearance of some of the dusts and their morphology observed by high magnification SEM images is reported in Fig. 2. EAF dusts have the typical appearance and morphology of this kind of by-product, characterized by light brown fine and silky appearance with a spherical morphology and a particle size ranging from 0.5 to 3 µm clustered in larger agglomerates of approximately 5 to 10 µm (41,42). Argon oxygen decarburation (AOD) dust is very similar to EAF dust while the CF dusts vary a lot along the three samples collected from the three foundries. For instance, the sample CF-SRB-I is characterized by dark black colour while the morphology of the particles is blocky-shaped with a particle size ranging from 50 to 100 µm whereas the sample CF-SRB-II appears more likely to a Blast Furnace Sludge either from morphological and chemo-mineralogical points of view (43–45). Completely different from the previous CF samples is CF-ITA dust both from colour and mineralogy: it is indeed light brown with very silky texture and it is mainly constituted by nahcolite and coesite.
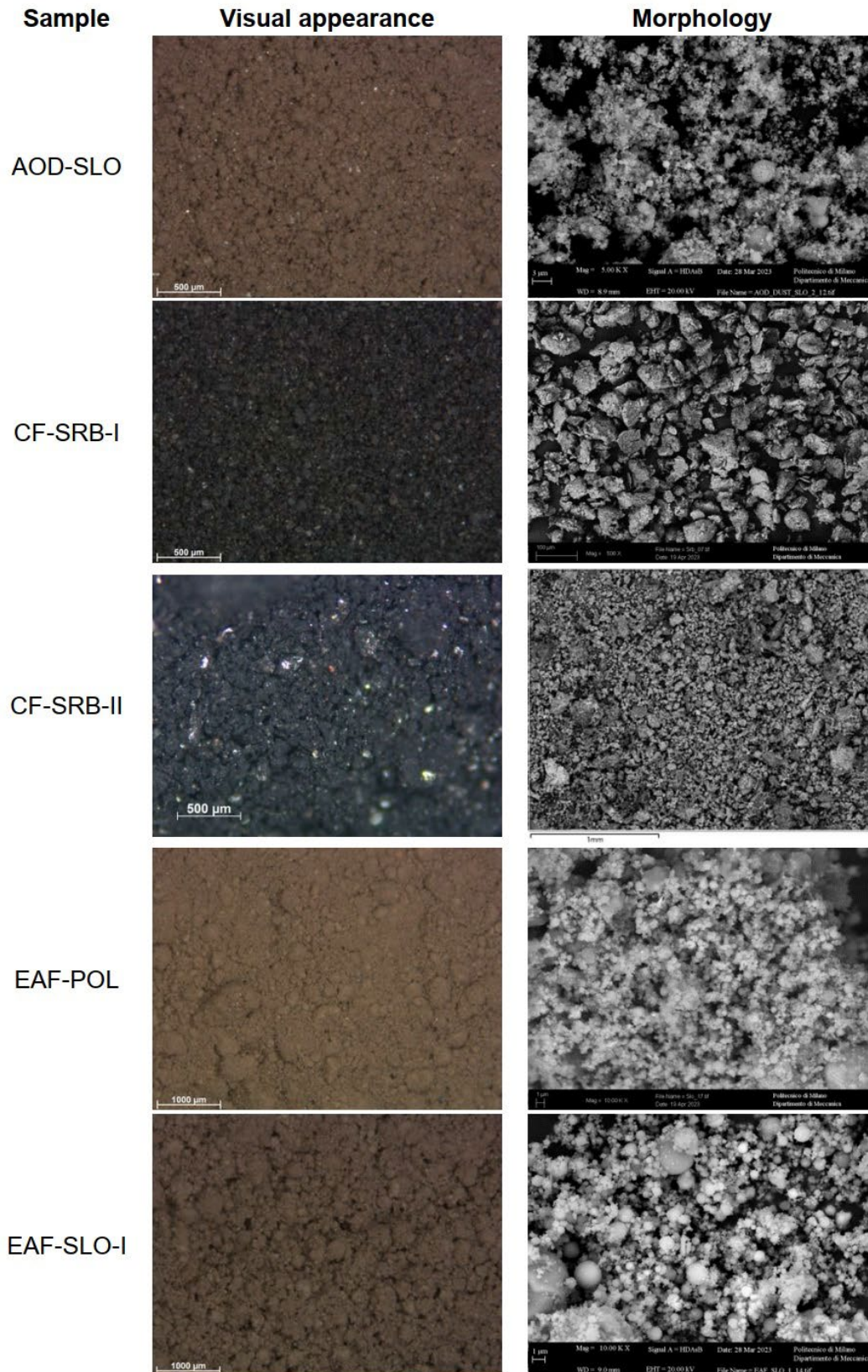
Fig.2 - Visual appearance and morphology of some of the investigated dusts.

The average chemical composition (expressed as oxide) and the significant elements concentration of the eight dusts collected are reported in Tab. 2 and Tab. 3. EAFD have an overall chemical composition very similar to literature reported one. On the other hand, AODD and CFD differ from the typical range measure by other researchers. For instance, CFD are very poor in Zn (< 6 wt.%) and other high value elements (Cu, Ni, Pb) undermining the profitability of their recycling while AODD can be interesting from the perspective of Cr and Ni recovery. However, their processing may lead to the production of large amount of sterile material, being they formed by significant concentration of hardly reducible and leachable metal oxides, like alkali, Al_2O_3, CaO, MgO and SiO_2. Thus, from the perspective of maximization of extraction yield and remunerability of the whole multi-step process, the EAFD coming from Poland and Slovenia were selected as suitable raw material for demonstrating the feasibility of the multi-disciplinary approach. They indeed possess the highest Zn concentration among all samples (11-25 wt.%), significant Pb concentration (max 2.3 wt.%) and good magnetic fraction (Fe+Mn+Cr) concentration (22-40 wt.%).

Tab.2 - WD-XRF chemical composition of investigated dusts (% by weight).

	AOD-SLO	CF-ITA	CF-SRB-I	CF-SRB-II	EAF-ITA	EAF-POL	EAF-SLO-I	EAF-SLO-II
Al_2O_3	-	2.74	13.93	3.30	5.86	0.22	-	0.28
Alkali	1.66	11.14	2.06	0.95	0.52	7.74	1.38	3.04
Br	-	1.35	-	-	-	-	-	-
CaO	20.58	4.46	2.77	3.31	31.64	5.35	2.64	6.36
Cl	0.11	0.43	-	-	0.15	2.17	-	0.43
Cr_2O_3	13.29	0.00	-	-	-	3.83	11.06	7.17
CuO	0.60	-	-	-	-	0.42	0.35	0.49
Fe_2O_3	31.50	19.09	4.78	26.35	39.64	32.64	54.69	45.44
MgO	11.93	0.85	1.32	0.89	2.05	3.55	2.52	7.89
MnO	11.02	3.98	0.04	0.16	2.50	2.61	2.17	5.18
MoO_3	0.53	-	-	-	-	-	0.38	0.20
NiO	3.01	0.02	-	-	0.07	0.80	0.58	1.85
P_2O_5	-	0.05	-	-	0.41	-	-	-
PbO	0.28	-		0.69	-	1.29	0.20	0.52
SiO_2	3.50	35.52	43.22	8.48	8.43	3.23	3.27	3.75
SnO_2	-	1.94	-	-	-	-	-	-
TiO_2	-	-	0.53	0.11	-	-	-	-
ZnO	1.99	0.78	-	5.65	8.18	30.28	19.33	14.83
LOI 850 °C	0.00	17.67	31.35	50.12	0.55	5.86	1.43	2.55
OH-	0.00	6.41	15.30	4.33	0.22	3.28	0.00	0.33
C_{tot}	0.89	10.80	15.15	44.11	0.21	2.13	2.05	2.22
S	0.44	0.46	0.90	1.68	0.12	0.45	0.18	0.41

Tab.3 - ICP-OES elements concentration of investigated dusts (% by weight).

	AOD-SLO	CF-ITA	CF-SRB-I	CF-SRB-II	EAF-ITA	EAF-POL	EAF-SLO-I	EAF-SLO-II
Al	0.3	1.4	7.5	3.4	3.2	0.5	0.3	0.4
Ca	15.3	3.1	1.9	2.3	22.5	4.0	2.1	4.8
Cr	2.4	<0.05	<0.05	<0.5	0.4	0.6	1.8	1.4
Cu	0.4	<0.05	<0.05	<0.05	0.3	0.3	0.2	0.4
Fe	16.0	11.5	3.0	21.2	24.8	20.5	33.0	29.0
Mg	6.5	0.5	0.8	<0.5	1.0	2.0	1.3	4.3
Mn	7.0	3.0	<0.05	0.2	1.8	1.8	1.4	3.6
Ni	1.6	<0.05	<0.05	<0.05	<0.05	0.4	0.3	1.2
Pb	0.3	0.1	<0.05	0.9	0.2	2.3	0.2	0.6
S	0.6	0.5	0.6	2.0	0.2	0.6	0.2	0.4
Si	2.2	16.8	19.6	2.0	1.1	1.8	2.0	2.5
Zn	1.4	0.6	<0.05	5.5	6.2	25.5	15.0	11.2

Advanced characterization

The selected three samples, i.e. EAF-POL, EAF-SLO-I and EAF-SLO-II were characterized mainly by spinel ferrite (MFe_2O_4) and zincite (ZnO) besides minority phases (Fig. 3, Fig. 4). This composition is typical for this kind of by-products (46). It is worthy to mention that the Slovenian samples should require less effort during preparatory washing step thanks to the low halides concentration in comparison to the Polish sample (Tab. 4).

Tab.4 - Elements concentration by further ICP-OES analysis (wt.%).

	Ag	Au	Cl-	Co	F-	Mo
EAF-POL	< 0.005	< 0.005	3.24	0.008	0.05	0.035
EAF-SLO-I	< 0.005	< 0.005	0.14	0.005	0.05	0.21
EAF-SLO-II	< 0.005	< 0.005	0.8	0.027	0.08	0.12

The further ICP-OES analysis performed on those selected samples reveals non negligible concentration of Mo and Co that can be recovered in the separated magnetic fraction while highlight the absence of noble metals. Since it is difficult to discern between franklinite ($ZnFe_2O_4$) and magnetite ($FeFe_2O_4$) by only XRD analysis being both the spinel isostructural (47), some heat treatments were performed to better characterize the dusts mineralogy while determining moisture, LOI and carbonates fraction. The content of moisture and volatising compounds in the two Slovenian samples were very low, hardly exceeding the 0.1 wt.% for the former and the 1 wt.% for the latter. Polish dust was still characterized by low moisture content, but it showed a volatilization of about 4 wt.% when exposed to 550 °C (Tab. 5). Since this samples has the highest chlorine concentration (confirmed by both the WD-XRF and ICP-OES techniques), it is reasonable that such a mass loss is related to chlorides partial decomposition, especially halite (NaCl) when simultaneously present with sylvite (KCl) (48,49). This is further confirmed by the variation in mass curve (TG) and its derivate (dTG) in TG-DSC analysis (Fig. 5). Similar behaviour was identified by Chen et al. (48). When exposed at higher temperature (1050 °C) only the sample EAF-SLO-I did not exhibit a significant mass variation, while EAF-SLO-II and EAF-POL samples lose 9.8 and 15.7 wt.%, respectively. Such a mass loss can be associated to the volatilization of more stable chlorides (i.e., KCl). Indeed, sylvite tends to reacts with some oxides within the dust and volatilize sharply between 800 °C to 950 °C, basically evaporating at 950 °C

(50). This is again confirmed by the huge mass variation registered during TG-DSC tests for both the samples. This behaviour is in good agreement with the chemical composition and the increasing magnitude of mass loss registered is proportional to the concentration of chlorine and alkalis of the three samples (Tab. 2, Tab. 4).
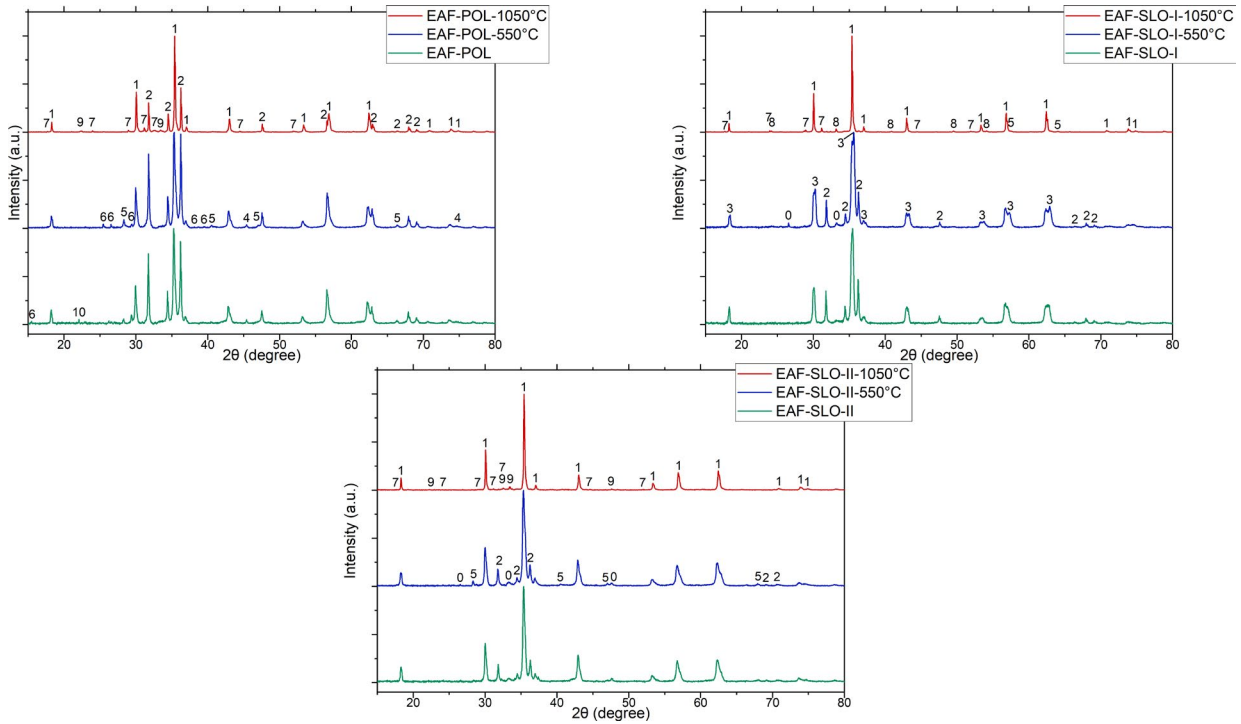

Fig.3 - XRD pattern of as-received and heat treated selected dusts (0: celite ($3CaO \cdot Al_2O_3$); 1: franklinite ($ZnFe_2O_4$); 2: zincite (ZnO); 3: magnetite ($FeFe_2O_4$); 4: halite (NaCl); 5: silvite (KCl); 6: asisite ($Pb_7SiO_8Cl_2$); 7: hardystonite ($Ca_2ZnSi_2O_7$);8: hematite (Fe_2O_3); 9: merwinite ($Ca_3Mg(SiO_4)_3$); 10: quartz (SiO_2)
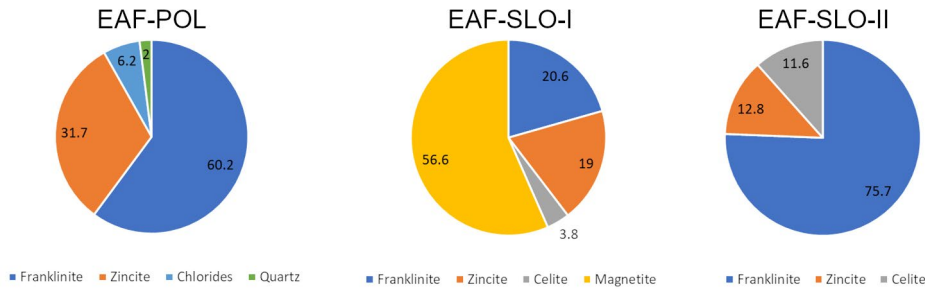

Fig.4 - Quantitative analysis by Rietveld method for the three selected EAF dusts.

The consequence of heat treatment is also evident from a mineralogical point of view. If no salient differences can be highlight between as-received and 550 °C treated samples, at 1050 °C important changes in mineralogy are detected. In particular, in all the samples the formation of hardystonite ($Ca_2ZnSi_2O_7$), slag phase (merwinite) and an increase in peaks intensity of franklinite are observed. The former phase is formed by the reaction between zincite and silicates while franklinite is probably formed due to the reaction around 800-1000 °C (51,52) between zincite and oxidized magnetite to hematite (53,54) but direct reaction between magnetite and zincite can occur even at lower temperature (52). About this last aspect, the heat treatment allowed to well discern between magnetite and franklinite in EAF-SLO-I sample, proving that in the as-received material, both form of spinel are coexisting. Indeed, beside the split shape of the peaks belonging to these phases, after the exposure to 1050 °C a part of magnetite resulted in unreacted fraction of hematite while another part participate after oxidation to hematite in franklinite formation. In the other two samples, since this behaviour was not highlighted, it is reasonable to assume

that the most of spinel phase was in the form of franklinite and its increased amount is due to Fe oxidation as present as impurities or solid solution into its lattice. The solid-state reactions of zincite with the other dusts compounds leads to an obvious reduction of ZnO peaks intensity, that for some samples is practically no more identifiable.
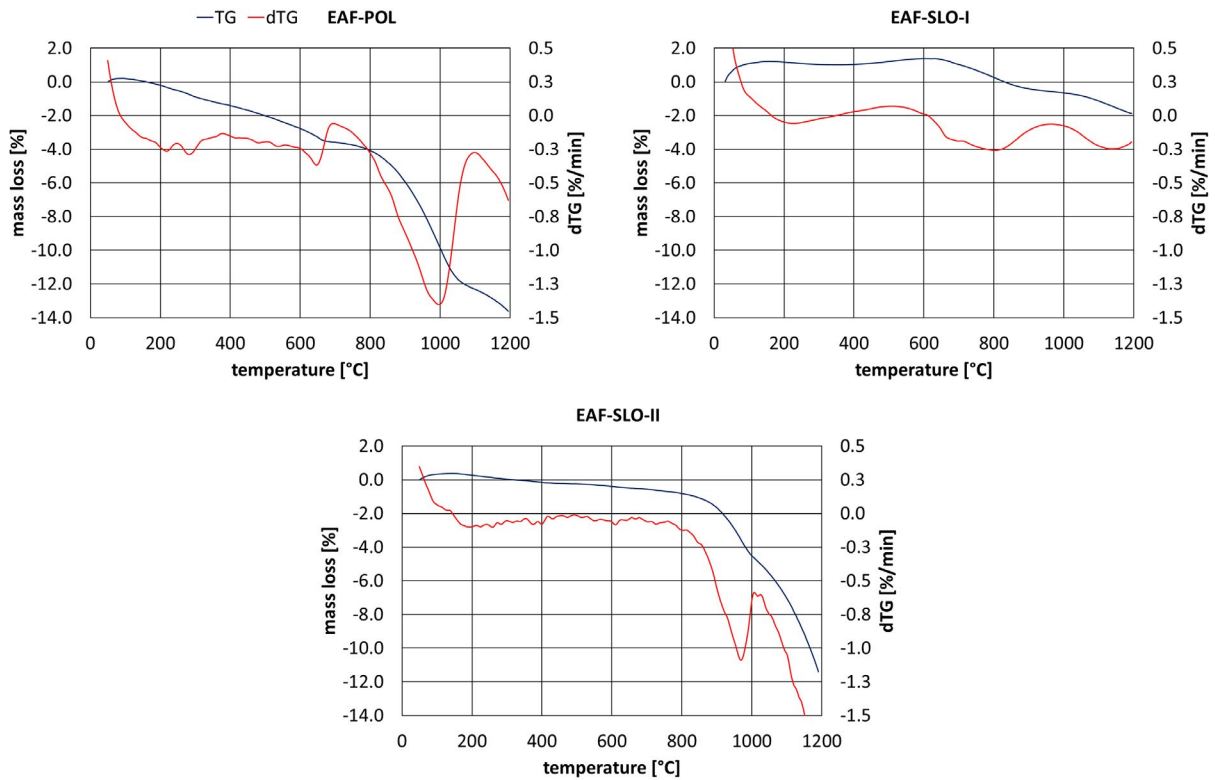

Fig.5 - TG-DSC results for the three selected dusts (Ar atmosphere).

Tab.5 - Mass loss measured after heat treatment on the selected EAF dusts.

Test tem-perature [°C]	EAF-POL		EAF-SLO-I		EAF-SLO-II	
	Absolute mass loss [%]	Dry mass loss [%]	Absolute mass loss [%]	Dry mass loss [%]	Absolute mass loss [%]	Dry mass loss [%]
105	0.061	0.061	0.111	0.111	0.081	0.081
550	4.097	4.039	1.033	0.923	1.368	1.287
1050	15.742	12.164	1.622	0.594	9.795	8.571

Because of the separation step is the core of the entire valorisation process, particle size distribution is mandatory information which must be known in order to optimize the parameters (feed grain size range, solids load in wet separation as well as in dry separation, flow rate, magnetic force applied). Fig. 6 reports the number Particle Size Distribution (PSD) of the three selected dusts, confirming the fineness of the investigated powders but also their tendency to naturally aggregate in coarser clusters. Nevertheless, nearly 90% of the analysed particles under the optical granulometer have an equivalent diameter lower than 8 µm and 50% vary between 3.1 and 3.3 µm.
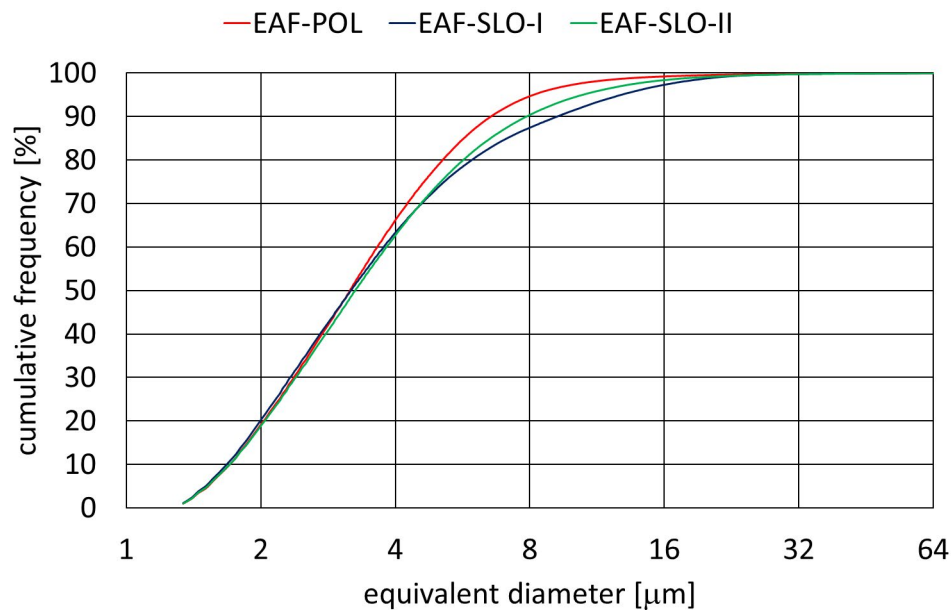
Fig.6 - Cumulative particle size distribution (in number) for the three selected dusts (measured at 50X magnification).

Further steps of processing

As the project is still ongoing and entering its second year of activities, the selection of raw materials to be processed along the several steps is just the beginning. Here in the following a brief description of the further activities expected to be fulfilled in the 2024 are summarized.

Testing the best available technology (BAT) for gravity and magnetic separation

Separation represents the crucial step on the entire workflow to obtain the two fractions from which valuables must be extracted. Several separation methods, like magnetic and gravity separation, are available and already tested at laboratory scale on primary mineral raw materials, quartz sands, boron minerals, phosphates at ITNMS and TH-ReMining institutes. However, these techniques were never tested on EAFD so far. Moreover, the real challenge to overcome is application of these methods to large scale sample, i.e., semi-industrial one. Non-magnetic fraction will be separated using gravity and centrifuge force. These investigations will be obtained by using shaking table, hydrocyclones, multi-gravity and centrifugal separators – Sharples P600 Pennwalt Decanter Centrifuge. Sharples P600 Pennwalt Decanter Centrifuge separates the particles using centrifugal force, which at max 6000 RPM reaches a force value of about 3,100 G. The magnetic fraction can

be obtained by using magnetic separator with permanent magnet "Dings" with magnetic induction B=0.1 T, and high-gradient magnetic separator (HGMS) Sala Magnetics model 10-15-20, with an electromagnet capable to apply a magnetic field between 0.1-2 T. HGMS Sala can work in discontinuous and continuous mode of operation.

Reduction and utilization of the magnetic fraction

In the perspective of the large iron oxide fraction recovery, carbon-thermal reduction of the Fe-, Mn-, Ni-, Cr-rich magnetic fraction will be applied with the aim to transform it into an iron-based alloy to recover Fe, Mn, Cr, Ni (Mo and Co) and separate the resulting slag for civil engineering application purposes. Carbothermic Reduction (CTR) is an alternative to pyrometallurgical technique to pursue the reduction of metallic oxides through the use of a carbon source where it is not gaseous CO but elemental C that fulfil the process reacting directly with the oxygen of the oxides (55). CRT is possible only when the intimate contact between carbon and oxides is ensured and for this reason the separated magnetic fraction will be mixed with a suitable biochar and then agglomerated in form of a self-reducing briquette (44,56). Different biochars obtained by the pyrolysis of wooden matrices and characterized by a different ratio between total, volatile and fixed carbon will be used (57,58). Furthermore, in the attempt to maximise

the recovery of less attractive steel- and iron-making dusts, samples CF-SRB-I and CF-SRB-II will be employed as basicity corrector and reductant, respectively, exploiting their unique concentration of Al_2O_3, SiO_2 and C among the eight investigated powders (43,45,59,60). Smelting experiments will be carried out at laboratory scale and resulting iron-based alloy will be characterized to find the right market placing and pricing.

Removal of halides and hydrometallurgical separation of metals

The non-magnetic fraction will be reprocessed for the recovery of Pb, Cu and Zn through hydrometallurgy process. First of all, halides will be removed from the separated fraction. This will be done by washing the material with hot water. Eventually a second washing step using sodium carbonate solution will be tested under different conditions (61). Processes will be carried out in 0.7 L autoclave at elevated temperature 100-210 °C with the overpressure of 16 bar resulting only from increased vapour pressure. Leaching of the Zn-rich fraction will be carried out with sulfuric acid to selectively dissolve zinc. Since small amounts of iron affect the further purification step, different bases ($Ca(OH)_2$, NaOH, NH_3) will be tested to precipitate iron, since the results may vary depending on the base, concentration and pH. Cementation with zinc powder will be used in the next step for reduction and further removal and recovery of copper from the solution. The zinc powder used for reduction will be recovered along with the zinc extracted from the treated and separated EAFD. The remaining zinc solution must be purified to the point where electrolytic recovery or precipitation produces a pure zinc product. For the purification solvent extraction with D2EHPA will be performed and obtained eluate will be then used in electrowinning. Different concentrations of used reagents will be investigated to achieve optimal capacity for the zinc and to avoid extracting residual impurities.

After the leaching, the residues may contain up to several percent lead in form of insoluble lead sulphate. The selective lixiviant for lead sulphate will be triethylenetetramine solution in water, which is highly selective towards lead sulphate and can extract entire lead into solution (62). The feasibility of proposed technology has been already

demonstrated at precommercial scale (TRL 7) when treating battery paste from lead-acid batteries (63). The key advantages of this technology are almost effluent free operation, possibility to recycle leaching amine solution after a set of purification and regeneration operations, beneficial production of lead carbonate which may be sold to lead smelters. The research within this task will deal with evaluation of basic process parameters affecting lead sulphate extraction i.e., amine concentration, solid-to-liquid ratio, temperature, and time. Similarly, precipitation trials will be done to test best available conditions for lead carbonate production including time and volumetric gas flow rates. Finally, purification of amine solution will be tested to regenerate triethylenetetramine solution for reuse in the next leaching stage.

Utilization of non-metallic residues in construction

Although the entire process is theoretically a waste-free technological route, a certain amount of waste are foreseen for both the pyro- and hydro-metallurgical recovery. Thus, as a final processing step, the evaluation of such a residue in the perspective of their use in the building and construction sector will be carried out. A detailed characterization will include determination of their mineralogical, chemical, physical and environmental parameters (i.e., the residues might contain leachable potential toxic elements). A set of composites for geotechnical works (64) and cementitious products (65) (e.g. green concretes with manufactured aggregates and supplementary cementitious materials) will be designed, produced and tested on the laboratory level and on small testbeds. Due to fine grained nature, the residues shall be mixed with proper additive, either waste-based or natural, in order to ensure sufficient mechanical stability and compaction. Durability and other aspects of technical functionality, as well as environmental performance will be assessed. A tutorial and guideline on recycling of such residues in building composite will be prepared. Depending on the intended use and properties of the new building composites, possible certification schemes under EU Regulation No. 305/2011 (the Construction Products Regulation) will be presented in order to show the possibility for future market penetration.

CONCLUSION

Within the DustRec project, a novel, integrated and multidisciplinary pathway for EAFD and CFD recycling is proposed. Different sources for EAFD and CFD were selected in the ESEE region and several samples were collected and investigated. The extensive physical and chemical analysis of such dusts made possible the selection of three promising matrices of EAFD which undergo several treatment steps (separation, carbothermic reduction and leaching extraction) to maximise the recovery of all the valuables contained within, trying to overcome the limits of the currently marketed processes for EAFD recovery. Although CFD are presented as a promising further resource for recovery critical metals

(Zn, Cu, Pb), the analysis carried out in this work highlight their low attractiveness from this perspective if they are to be used as a sole raw material. However, they seem promising to integrate as a feeding material based on EAFD, especially if used as a blend conditioner during carbothermic reduction and smelting.

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