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MEP 23
PROCEEDINGS





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MINING AND ENVIRONMENTAL PROTECTION

PROCEEDINGS

Editor
Prof. dr Ivica Ristović

Sokobanja

24-27th May 2023.

FOREWORD

After the consultations with business entities in the field of mining and environmental protection, faculties and scientific institutes, an initiative for organizing a scientific meeting on mining and environmental protection was taken in 1996. The Faculty of Mining and Geology in Belgrade, CENTER FOR ENVIRONMENTAL ENGINEERING, have organized the First Yugoslav Conference with International participants held from 25 to 27 April 1996. in Belgrade, Serbia. The second International Symposium was held in Belgrade from 25 to 27 May 1998. The third Symposium was held in Vrdnik from 21 to 23 May 2001. The fourth International Symposium was held in Vrdnik from 23 to 25 June 2003. Due to the large number of subjective and objective reasons organization of the symposium was discontinued in 2003. Fifth International Symposium was held in Vrdnik from 10 to 13 June 2015. The sixth International Symposium was held in Vrdnik from 21 to 24 June 2017. The seventh International Symposium was held in Vrdnik from 25 to 28 September 2019. and the eighth International Conference was held in Soko Banja from 22 to 25 September 2021.

On the basis of the conclusions made at the 8th Conference MEP 2021 and great interest of domestic and foreign scientific and professional public, the Faculty of Mining and Geology in Belgrade, in cooperation with co-organizers (Berg Faculty TU Košice, Slovakia, University of Ljubljana, Faculty of Natural Sciences and Engineering, Slovenia, Goce Delčev University in Štip, N. Macedonia, Geological Survey of Slovenia, Ljubljana, Slovenia, University in Banja Luka, Faculty of Mining, Prijedor, Republic of Srpska, Bosnia & Herzegovina and Association of Mining and Geology Engineers), shall organize the 9th International Conference Mining and Environmental Protection – MEP 2023.

The previous Symposium, were very successful and scientist and companies from many countries gathered to exchange information and research results. The objective of this Conference is to bring together engineers, scientists and managers working in mining industry, research organizations and government organizations, on development and application of best practice in mining industry in the respect of environment protection.

At the Book of Proceedings of 9th International Conference on Mining and Environmental Protection are 56 Papers. Almost half is from abroad, or their authors is from different countries. At least 166 authors and co-authors took part in the preparation of these papers. The papers were reviewed by Reviewers. Only high-quality papers were selected, from two side, one from the scientific basis and the second from point of view of applicability in resolving problems at the development of mining.

We are very grateful to the authors of the papers, who contributed to a great extent to the success of this meeting by having sent enough number of high-quality papers, and thereby made the work of the reviewers a pleasant one in respect of selecting the best quality papers. Also, we would like to thank all of the participants in the Conference, as well as the sponsors who helped and enabled us to hold such a great meeting.

Editor

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PRELIMINARY PHYSICAL-CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF FURNACE DUST SAMPLES, THE BASIS FOR THE SELECTION OF SAMPLES FOR RESEARCH WITHIN THE PROJECT EIT RAWMATERIALS DUSTREC

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Abstract: *Large amounts of EAF furnace dust are generated in Europe (1.3Mt), as well as in the world (8,764Mt). Due to the high content of Fe and Zn, whose content often reaches a total of between 50 and 60 wt.%, EAF dust has always been interesting for recycling. So far, the most commonly applied method of processing EAF dust is the pyrometallurgical Waelz kiln process of Zn extraction (85% market share). The paper presents EIT Raw Materials Project: RIS-DustRec, which aims to develop innovative technologies for the separation, reprocessing, and beneficial use of all components of EAF and CF furnace dust, to reduce the amount of toxic waste and achieve the zero-waste target in the EU. Preliminary chemical, XRD, and SEM analyses on two samples of EAF and CF furnace dust from Italy were performed and presented.*

Keywords: *EAF and CF furnance dust, recycling, sustainable green economy,*

1. INTRODUCTION

The EU, as the most technologically developed part of the world, began after the last major expansion of the Union in 2004 (the entry of Cyprus, the Czech Republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Slovenia and Slovakia) to strategically think and take care of, especially at the highest level, its further sustainable development. In this sense, initiatives were launched, strategic decisions and documents were made, studies were carried out, organizations were founded that were supposed to help solve and overcome these problems.

For these needs, the European Union established the European Institute of Innovation and Technology (EIT) in 2008, as an EU body with a role to strengthen Europe's capacity for innovation. The EIT is an integral part of Horizon Europe, the EU Framework Program for Research and Innovation. Since 2011, the European Commission has been evaluating every 3 years a list of critical raw materials (CRM) for the EU economy as part of its Raw Materials Initiative, as well as possible solutions for the necessary critical raw materials. The EIT supports the development of dynamic, long-term thematic partnerships (Knowledge and Innovation Communities, EIT KICs) among companies, research, and higher education institutions, to tackle pressing global challenges. Since 2010, EIT has launched nine Innovation Communities. The EIT Regional Innovation Scheme (EIT RIS) was introduced in 2014 to boost the innovation performance of countries with moderate or

modest innovation scores as defined by the European Innovation Scoreboard. The RIS is steered by the EIT and implemented through the EIT's Knowledge and Innovation Communities (KICs).

Today, only a fraction of the most relevant raw materials is produced in Europe. The EU is trying to change this through a circular economy approach, through innovations in recycling, substitution, processing, mining and research. This is why the EIT RawMaterials Innovation Community was founded in 2015 to advance Europe's transition to a sustainable economy. The overarching mandate of EIT RawMaterials is to support the provision of critical raw materials for European industry by driving innovation along the raw materials value chain. EIT RawMaterials builds on the world's largest network of partners in raw materials and advanced materials, with the aim of ensuring a sustainable supply of raw materials by driving innovation, education and entrepreneurship in European industrial systems. EIT RawMaterials provides support for the European transition to a circular, green and digital economy, while at the same time strengthening its global competitiveness and securing employment. On this basis, EIT RawMaterials received a mandate from the European Commission to lead and manage the European Raw Materials Alliance (ERMA).

To successfully transition the EU towards sustainable development and a circular green economy, EIT Raw Materials announces calls for Projects that, through their implementation, should bring the EU closer to this goal. From 2015 until today, over 300 projects of this type have been implemented, approved, and financed. One of the Projects of this type that was approved (within the call KAVA 9) by EIT Raw Materials is Project: **RIS-DustRec - Zero waste reprocessing of EAF and CF dust with competence build-up.** Proposal Number: 22009, Lead Partner: Jožef Stefan Institut-Ljubljana (Slovenia).

2. PROJECT: RIS-DUSTREC-II. ZERO WASTE REPROCESSING OF EAF AND CF DUST WITH COMPETENCE BUILD-UP

Project RIS-DustRec deals with the examination, development, and determination of a whole series of innovative technologies that will lead to the acquisition of knowledge that will enable the comprehensive processing of furnace dust of electric arc furnaces (EAF) and cupola furnaces (CF). Each year about 1.3 Mt of Electric Arc Furnace (EAF) dust and around 50 kt of Cupola Furnace (CF) dusts are generated in Europe. Both materials are hazardous waste (content of Zn, Cd, Cr, Ni, Pb...) which burden metallurgical industry, but can also be an alternative source of valuable metals. About 30 steelworks in the ESEE RIS (East and South-East Europe Regional Innovation Scheme) region operate EAFs for steel scrap-based steel production. No recycling plant operates in the ESEE region, so the dust generators have additional costs of transporting the dust to the nearest Zn recovery plant. Landfilling of metallurgical dust is in many RIS countries forbidden due to the presence of toxic substances.

Nowadays, the state-of-the-art process to extract Zn from the EAF dusts is the Waelz process (with a market share of over 85%).[1] Its drawbacks are that the Waelz process leaves nearly the same amount of waste as the originally processed dusts (Waelz slag) after the Zn recovery and its process concentrates only on recovery of Zn. In Figure 1, several pyrometallurgical and hydrometallurgical processes are shown, with which EAF furnace dust has been processed and valorized with more or less success.

All these processes shown in Figure 1 are generally inefficient, expensive, and harmful to the environment, compared to the procedures that will be implemented within the Project RIS-DustRec.

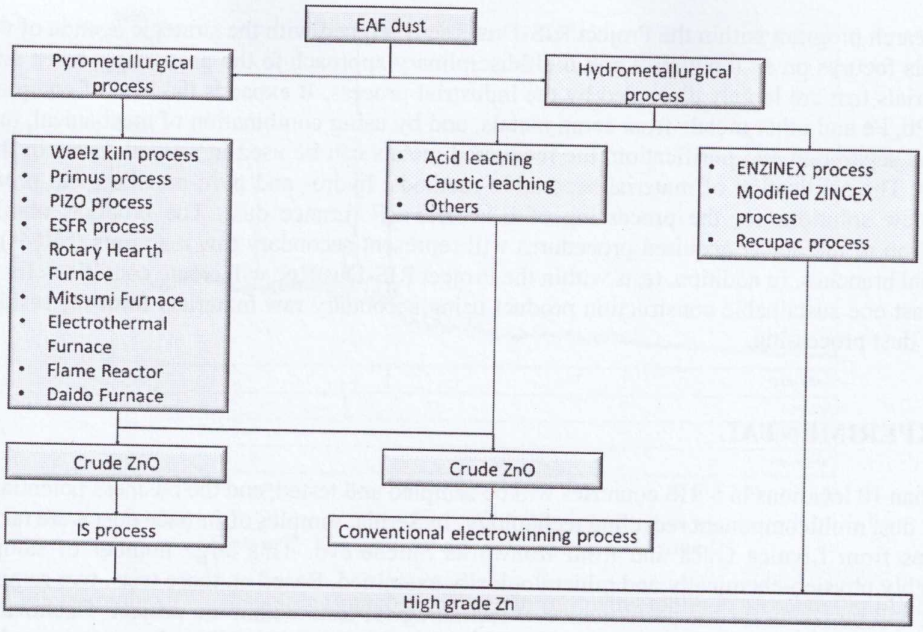


Figure 1. *Processes used so far for the processing of EAF furnace dust. %).[1]*

The physico-chemical characteristics of EAF and CF dusts can vary extensively regarding the content of different metals depending strongly on the type of scrap fed into the furnace. [2,3,4] The average chemical composition of EAF dust from the Slovenian steel producer. is shown in Table 1. This steel plant produces about 10.000 tons of furnace dust per year.

Table 1. *Chemical composition of electric arc furnace dust sample from a Slovenian steel producer*

Comp.	Fe	Cr	Cu	Mo	Ni	Pb	Zn	Al	Mn	Mg	S	Si
Content, %	26.5	1.67	0.31	0.07	0.26	1.67	24.1	0.51	2.04	2.75	0.51	0.52

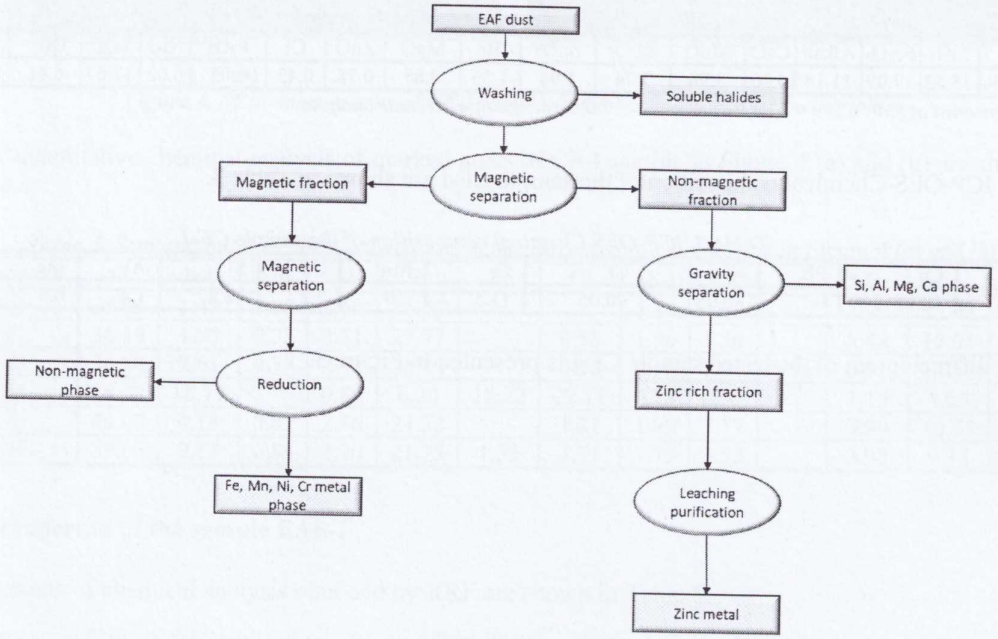


Figure 2. *Purification of separation products and obtaining starting products for various industrial branches Project RIS-DustRec*

The research program within the Project RIS-DustRec is aligned with the strategic agenda of the EIT Raw Materials focuses on an innovative and multidisciplinary approach to the processing, reuse and recycling of materials that are largely discarded by the industrial process. It expands the idea of complete recovery of Zn, Pb, Fe and other metals from scrap metals, and by using combination of mechanical, magnetic and chemical separation and purification, the recovered metals can be used in several forms in their specific markets. The application of material separation methods, hydro- and pyro-metallurgical processing will create new solutions for the processing of EAF and CF furnace dust. The products obtained by the application of the newly acquired procedures will represent secondary raw materials (SRMs) for various industrial branches. In addition, tests within the Project RIS-DustRec will create conditions for the creation of at least one sustainable construction product using secondary raw materials from the residues of EAF and CF dust processing.

3.0 EXPERIMENTAL

More than 10 locations in 5 RIS countries will be sampled and tested, and the business potential of the EAF and CF dust multicomponent recycling technology. In Serbia, samples of furnace dust were taken from two locations from Livnica Guča and from Ironworks Smederevo. This large number of samples will be thoroughly physico-chemically and mineralogically examined. Based on these tests, two samples of about 700 kg will be taken, for the performance of technological tests within the project. Chemical, XRD, and SEM analyses were performed on EAF and CF furnace dust samples. All analyses were performed at the Politecnico di Milano in the Department of Mechanical Engineering. The paper presents the results of the characterization of two samples of furnace dust from Italy:

- Sample Cupola Furnace dust (CF-I)
- Sample EAF dust (EAF-I)
- Sample EAF dust (EAF-Slo)

3.1. Properties of the sample CF-I

The results of chemical analysis obtained by XRF are shown in Table 2.

Table 2. *Chemical composition of the sample CF-I*

Comp.	SiO_2	Fe_2O_3	Alkali	CaO	MnO	Al_2O_3	SnO_2	Br	MgO	ZnO	Cl	P_2O_5	NiO	LOI[1]	OH^{-2}	C_{tot}[3]	S[3]
Content, %	35.52	19.09	11.14	4.46	3.98	2.74	1.94	1.35	0.85	0.78	0.43	0.05	0.02	17.67	6.41	10.80	0.46

[1] determined at 850 °C; [2] LOI-C_{tot}-S; [3] determined by elementar analysis

The ICP-OES Chemical composition of the sample CF-I are shown in Table 3.

Table 3. *ICP-OES Chemical composition of the sample CF-I*

Zn	Cu	Pb	Ni	Cr	Fe	Mn	Ca	Si	Al	Mg	S
0.6	<0.05	0.1	<0.05	<0.05	11.5	3.0	3.1	16.8	1.4	0.5	0.5

The diffractogram of the tested sample CF-I is presented in Figure 3.

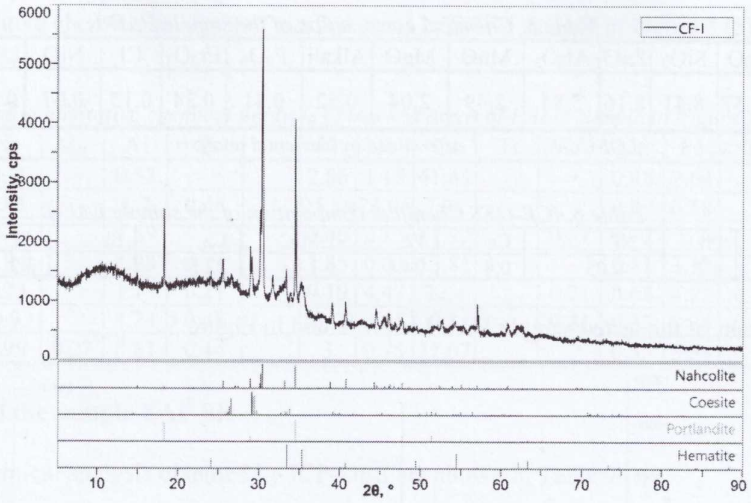
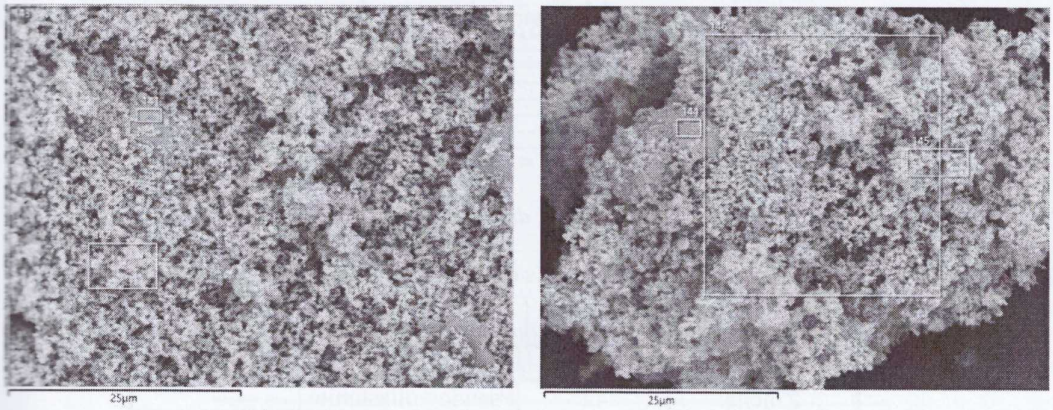


Figure 3. *XRD powder diffractogram of CF-I sample*

Thw SEM micrographs of CF-I sample (punctual spectra in following table) is presented in Figure 4.



(a) (b)

Figure 4. *SEM micrographs of CF-I sample (punctual spectra in following table)*

Semi-quantitative chemical analysis of marked areas of CF-I sample in Figure 4 (a) and (b) are shown in Table 4.

Table 4. *Semi-quantitative chemical analysis of marked areas of CF-I sample in Figure 4 (a) and (b)*

Spectrum #	O	Na	Mg	Al	Si	S	Cl	K	Ca	Cr	Mn	Fe	Zn	Sn
141	38.06	1.48	0.80	3.60	31.82			3.17	4.68		3.99	12.04	0.36	
142	36.19	1.95	0.72	2.51	27.77		0.38	1.96	5.30		5.43	17.01	0.79	
143	36.80	2.61	0.77	2.48	28.40		0.52	2.16	5.95	0.16	5.91	13.57	0.68	
144	24.27	18.77		0.89	6.20	18.22	22.71	0.78	0.93		1.15	4.65		1.41
145	44.07	4.18	0.82	2.56	24.22		1.21	1.99	3.77		3.99	10.35	0.49	2.35
146	39.65	9.13	0.84	2.20	21.73	1.55	3.71	1.79	3.52		3.98	9.35	0.34	2.22

3.2. Properties of the sample EAF-I

The results of chemical analysis obtained by XRF are shown in Table 5.

The ICP-OES Chemical composition of the sample EAF-I are shown in Table 6.

Table 5. *Chemical composition of the sample EAF-I*

Comp.	Fe_2O_3	CaO	SiO_2	ZnO	Al_2O_3	MnO	MgO	Alkali	P_2O_5	Er_2O_3	Cl	NiO	LOI[1]	OH-[2]	C_{tot}[3]	S[3]
Content, %	39.55	31.57	8.41	8.16	5.84	2.49	2.04	0.52	0.41	0.24	0.15	0.07	0.55	0.22	0.21	0.12

[1] *determined at 850 °C;* [2] *LOI-C_{tot}-S;* [3] *determined by elemental analysis*

Table 6. *ICP-OES Chemical composition of the sample EAF-I*

Zn	Cu	Pb	Ni	Cr	Fe	Mn	Ca	Si	Al	Mg	S
6.2	0.3	0.2	<0.05	0.4	24.8	1.8	22.5	1.1	3.2	1.0	0.2

The diffractogram of the tested sample EAF-I is presented in Figure 5.

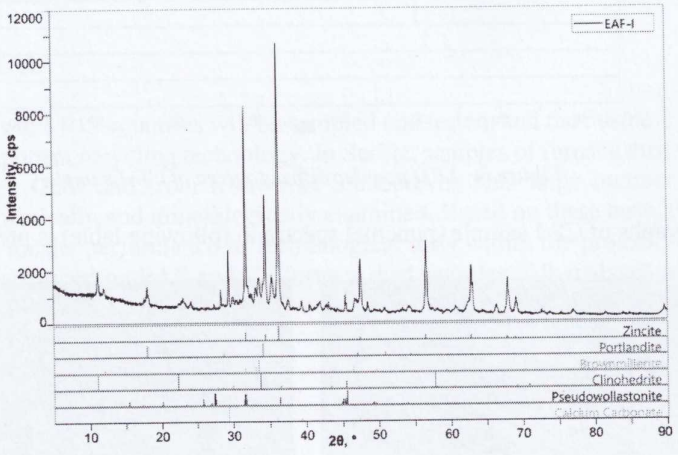


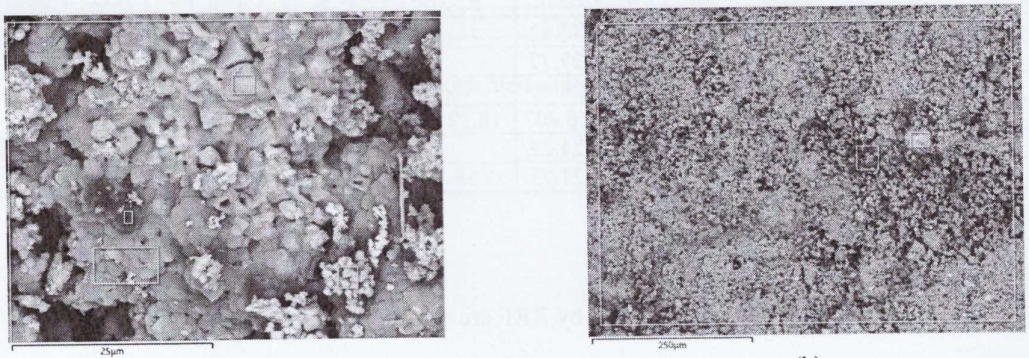
Figure 5. *XRD powder diffractogram of EAF-I sample*

Table 7 shows the Rietveld mineralogical analysis of the EAF-I sample.

Table 7. *Rietveld analysis of EAF-I sample (goodness of refinement: Rwp = 6.40%; S = 1.3168)*

Mineral	Content, %	Mineral	Content, %
Zincite	42	Pseudowollastonite	7
Portlandite	2.8	Calcium Carbonate	10.0
Brownmillerite	17		
Clinohedrite	11		
Magnetite	10.4	/	/

The SEM micrographs of EAF-I sample (punctual spectra in following table) is presented in Figure 6.



(a) (b)

Figure 6. *SEM micrographs of EAF-I sample (punctual spectra in following table)*

The semi-quantitative chemical analysis of marked areas of EAF-I sample in Figure 3 (a) and (b) shown in Table 8.

Table 8. Semi-quantitative chemical analysis of marked areas of EAF-I sample in Figure 3 (a) and (b)

Spectr. #	O	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Cu	Zn	Pb
1	26.51	1.9		0.58			2.86	1.15	41.41			0.48	2.64		21.98	0.48
2	8.23	7.41		1.7	0.43		25.16	23.05	7.94			0.89	6.18		19	
3	10.33	4.8		1.49			4.66	2.15	11.22		0.31	0.72	5.7		58.63	
4	21.92	6.84		1.28			1.85	0.63	13.81			0.81	3.12		49.75	
5	15.6	8.23		1.19	0.21		9.19	4.47	22.4		0.21	0.68	4.71	0.38	32.73	
6	12.18	10.93		1.24	0.48		10.99	4.05	9.3		0.21	0.83	6.24	0.41	41.38	1.76
7	32.09	2.99	0.27	0.81	0.44		3	0.75	37.07			0.55	3.54		18.49	

3.3. Properties of the sample EAF-Slo

The results of chemical analysis obtained by ICP-OES are shown in Table 9.

Table 9. ICP-OES Chemical composition of the sample EAF-Slo

Zn	Cu	Pb	Ni	Cr	Fe	Mn	Ca	Si	Al	Mg	S
11.2	0.4	0.6	1.2	1.4	29.0	3.6	4.8	2.5	0.4	4.3	0.4

The diffractogram of the tested sample EAF-Slo is presented in Figure 7.

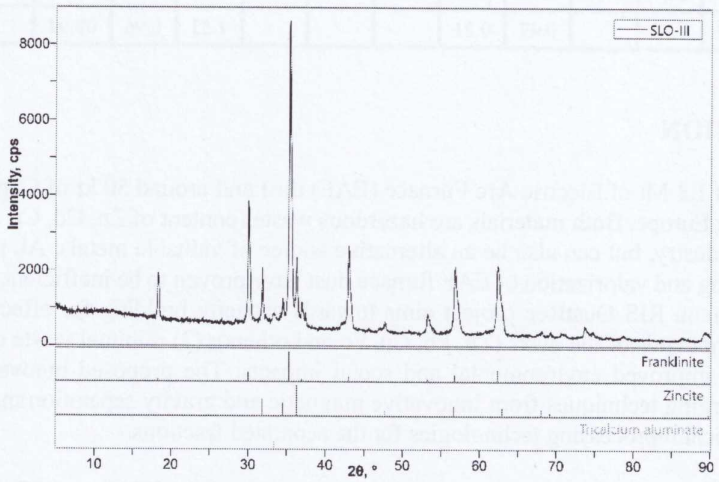


Figure 7. XRD diffractogram of EAF-Slo sample

The rietveld analysis of EAF-Slo sample are shown in Table 10.

Table 10. Rietveld analysis of EAF-Slo sample (goodness of refinement: Rwp = 7.24%; S = 1.3975)

Mineral	Content, %
Franklinite	75.7
Zincite	12.8
Tricalcium aluminate	11.6

The SEM micrographs of EAF-Slo sample (punctual spectra in following table) is presented in Figure 8.

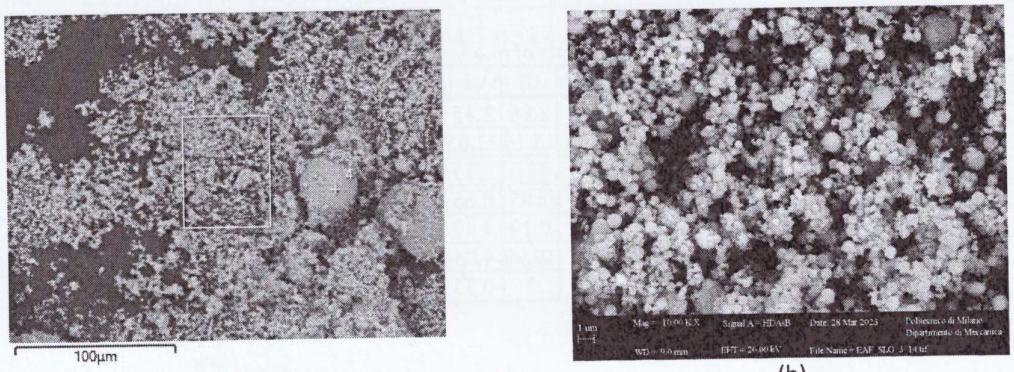


Figure 8. *SEM micrographs of EAF-Slo sample (punctual spectra in following table)*

Semi-quantitative chemical analysis of marked areas of EAF-Slo sample in Figure 9 (a) are shown in Table 11.

Table 11. *Semi-quantitative chemical analysis of marked areas of EAF-Slo sample in Figure 9 (a)*

Spectr. #	O	Na	Mg	Al	Si	Cl	K	Ca	Cr	Mn	Fe	Ni	Cu	Zn	Pb
3	24.25	3.57	5.61	0.70	1.85	0.92	0.81	2.87	4.62	4.77	30.39	1.16	0.90	16.33	1.26
4	25.02			0.47	0.21				1.51	0.96	68.94			2.89	

4. CONCLUSION

Each year about 1.3 Mt of Electric Arc Furnace (EAF) dust and around 50 kt of Cupola Furnace (CF) dusts are generated in Europe. Both materials are hazardous waste (content of Zn, Cd, Cr, Ni, Pb...) which burden metallurgical industry, but can also be an alternative source of valuable metals. All processes applied so far for the processing and valorization of EAF furnace dust have proven to be inefficient, expensive and harmful to the environment. RIS DustRec project aims towards capacity building for effective (1) recovery of all economical compounds of the dusts (Zn, Pb, Cu, Fe and others); (2) minimal waste discharge; (3) economic feasibility with improved environmental and social impacts. The proposed innovative approach involves combining emerging techniques from innovative magnetic and gravity separation methods to new pyro and hydrometallurgical reprocessing technologies for the separated fractions.

Preliminary chemical, XRD, and SEM analyses on two samples of EAF and CF furnace dust from Italy were performed and presented. When complete detailed analyzes are performed on all samples from all 10 locations of furnace dust, it will be possible to select two furnace dust samples on which complete technological tests will be performed as foreseen by the plan and program of the RIS-DustRec-II Project.

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