

Influence of the Recirculation of Various by-products Generated through Electric Arc Furnace Route on EAF Slag Quality

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The Fines2EAF project aims to increase the value of Electric Arc Furnace steelmaking residues by their internal recycling and reuse in form of cement-free briquettes. The project sustainability for a profitable fines' recirculation pass through the conservation of steel and slag quality in terms of chemistry, physics and eco friendliness. To do this, industrial trials have been conducted by the charging of self-reducing and slag-former briquettes made by primary and secondary fines materials. Several slag samples supplied from three different European EAF steel shops have been analysed. The specimens have been characterized by XRF, XRD and SEM to thoroughly define their crystallography, morphology and microstructure. The comparison with the corresponding reference samples (*i.e.*, slag produced without the fines recirculation) also allowed to highlight the differences present. Leaching tests have been conducted on reference and briquette-added slag according to EN 12457-4 standard to assess the compliant with the local environmental regulation. The obtained results highlighted that the slag obtained using cement-free briquettes made by steelmaking fines exhibits crystallographic and morphological properties very similar to the reference samples, with limited differences attributed to slag and scrap feedstock intrinsic heterogeneity. No relevant increase in the leachate concentration could be detected when compared to reference samples and the influence of raw-material fines recirculation into the EAF could be considered at worst negligible, if not positive for some elements like Ba (–22.86%), V (–13.19%) and W (–14.83%). Considering all the analyses performed, no adverse effect on slag quality could be detected.

KEY WORDS: cement-free briquettes; EAF slag; leaching behaviour; side-stream materials; LF-slag; spent refractories; recycling.

1. Introduction

The steelmaking sector is a pillar of industry and economic development on a global scale, and its proliferation is intimately linked to a growing and successful economy.^{1,2)} As a result of the increasing request of metallic materials on the global scale, the production of steel has grown continuously during the years, and with it the environmental impact of this industrial sector.³⁾ The steelmaking industry is one of the largest on the planet due to favourable material properties like strength, durability, workability, and cost.⁴⁾ Moreover, iron and steel, can be considered green materials to all intents and purposes.⁵⁾ Steel production is 15 times greater than the production of all other metallic materials.⁶⁾ While being one of the largest and most fundamental

industries on the global scale, steel production is also well renowned for its negative impact on the environment.⁷⁾

During the last few decades, the EU steelmaking industries have increased their attention to the by-products recovery and increased their quality, not only focusing on the technologies available at the time but also developing new options for future applications in order to reduce the environmental impact and promote resource savings always aiming at the zero-waste goal.⁸⁾

One way to increase the sustainability of the steel industry, not only on a European level, is the saving of primary raw materials and the costs related to the traditional disposal of the by-products of steelmaking and steel working (landfilling). This was also encouraged by the increase in landfilling costs and growing stringent regulations and initiatives in the EU for what concerns the reduction of steel industry environment impact.^{9,10)}

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The two main routes followed by the countries which are more active in protecting the environment from steel mills co-products are the development of new ways to reduce the emissions (solid, liquid, gaseous) and the valorisation of the by-products following a zero-waste philosophy.^{10,11)}

The solid wastes that are generally produced during steelmaking are composed of slag, dust, sludge, and mill scale produced among during metallurgical operations, metal working and emission reduction processes.¹²⁾ The main disposal route is landfilling but this has proved to be poorly efficient due to the growth in steel production and the subsequent increase of waste generation. In particular, steel slag represents the major solid waste produced by a steelmaking facility and it can contain quantities of heavy metals, metalloids, alkalis, and anions that can be released in the surrounding environment.⁴⁾

With the aim of maximizing the internal recovery of secondary raw materials from steelmaking wastes and saving production costs linked to the landfill disposal of waste materials, the European Union financed the Fines2EAF project through the RFCS (Research Fund for Coal and Steel) program.¹³⁾ The aim of the project is to investigate how and which by-products can be profitably recirculated inside the EAF process itself as well as evaluate the effects of internal recycling of fine residues from EAF steelmaking onto the process performances and the quality of steel and slag. This is pursued in order to increase the intrinsic value of the by-products, stimulate the efficient use of resources, and possibly generate revenues via reducing the employment of virgin raw materials in the production cycle and the landfilling operations that are normally required to dispose of the by-products. To achieve these goals the path of reinsertion in the production cycle of primary and secondary raw material fines by formulation of cement-free briquettes was selected and investigated. Briquette formulation is potentially a reuse route that permits to exploit the co-product on site, reducing costs for disposal or transport of the co-products, also reducing the indirect CO₂ connected to these operations. Moreover, no modification of the EAF plant layout would be necessary in order to exploit the by-products that can be prepared by simple presses situated in the shops. The choice of cement-free briquettes was made in order to reduce the quantity of water present in each briquette (decreasing risks of damage in the EAF), reduce the amount of SiO₂ in the slag and avoid the need for expensive modifications to the steel shops layout. In addition, cement-free briquettes do not need of long period of curing under controlled atmospheric conditions, and thus, this maximizes the payload of each briquette.

In order to evaluate the sustainability of the project, one of the most important aspects is that the recirculation of fines materials and by-products into the EAF does not compromise the quality of both steel and slag. In particular, the final properties of the slag must be kept as constant as possible in order to exploit their exceptional performances as replacement of natural stone materials without harm to human health and environment. In particular, the recirculation of fines in form of briquettes must not modify the leaching behaviour of the slag and, to a lesser extent, its chemical composition. For this reason, a survey of the effect of fines reinsertion on the slag quality is fundamental.^{14,15)}

2. Experimental Procedures

2.1. Materials and Briquettes

Along the project, several side-stream materials have

been investigated to come to the definition of suitable recipes to obtain satisfactory cement-free briquettes in term of mechanical and metallurgical properties.^{13,16–18)} The most promising formulations, in accordance with the need of the industrial partners took part in the project, were experimented through industrial trials. The most of these side-stream materials are waste or by-products obtained because of the whole steelmaking process within the steel-shop. In the case of grinding sludges, they are supplied from a third company that machines the products of shop A. An extensively characterization of the materials utilized for manufacturing the self-reducing briquettes employed in the shop A is published elsewhere.¹⁶⁾ Furthermore, the main properties of LF slag and spent refractories employed in slag-former briquettes are reported in the recent publication of Abdelrahim *et al.*¹⁸⁾ Thus, the effects of briquette recycling on steel slag have been researched conducting analyses on slag specimens obtained from three steelmaking shops which carried out the trials. Each plant adopted different strategies for the use of the briquettes to better identify if the substitution of raw materials can influence the slag behaviour.

Steel shop A is specialized in the production of special steel long products and it is an important supplier of cold finished products. Steel shop A conducted trials focused on the use of self-reducing briquettes that could, through the re-incorporation in the production cycle, increase the steel yield through reduction of by-products that have been oxidized during the production steps. In **Table 1** are reported the recipes that have been concocted to reach this objective and have been proven to possess sufficient mechanical and stability properties to allow a safe storage and handling.

In steel shop B and C, the trials have been focused on the investigation of slag forming briquettes in order to substitute virgin slag formers reducing the emissions linked to their production and the magnitude of landfilling required per steel heat. In **Table 2** are reported the various recipes that were employed. More specifically, steel shop B is specialized in concrete reinforcing steel bars production while steel shop C has the capability to cover both the production of high-quality and special steel grades for the automotive industry and its subcontractors, seamless pipes and tubes, as well as concrete reinforcing steel thanks to the two full equipped steel mills active in the same site.

2.2. Charging Profiles

Steel shop A performed a total of 12 heats in two separate trials to obtain reference specimens (without briquette

Table 2. Recipes of the slag forming briquettes tested in steel shop B and C (mass%).

Recipe	Binder	Ladle slag	Spent refractories	Starch	Fibers	Water
MH 31 R/6	Wheat starch	88.6	–	5.3	0.9	5.3
MH 31 R/4	Wheat starch	91.7	–	3.7	0.9	3.7
MH 52 B	Potato starch	69.3	20.8	3.6	0.9	5.4
MH 52 B/4	Potato starch	46.4	46.2	3.6	0.9	2.9
MI 31 R	Wheat starch	53.1	38.5	7.7	0.77	9.9
MI 52 C	Potato + wheat starch	53.4	38.7	7.8	0.2	10.1

Table 1. Recipes of the self-reducing briquettes tested in steel shop A (mass%).

Recipe	Binder	Oxycutting fines	Combustion chamber	Grinding sludges	Carbon powder	Binder	Water
CC	Sugarcane molasses	40.9	40.9	–	15.25	3.0	<3
MA	Polymeric	34.5	–	46.5	13.40	1.4	4.2

addition) and slags obtained by addition of the MA and CC recipes in the EAF. However, since steel shop A mixes the slag in the slag pit every three sequences of heats, the samples that will be further characterized by SEM and by leaching test are only two per trial, labelled B for trials and R for reference, respectively. **Table 3** summarizes all the information relative to the charging operations performed in shop A.

Steel shop B, in which slag forming briquettes were tested, produced 9 slag samples during two trials with different quantities and recipes of briquettes employed per heat as highlighted in **Table 4**. The slag is tapped into a pit, excavated and collected in containers, where finally samples were taken for investigations.

Steel shop C conducted two trials as well for a total of 29 heats and the same number of slag specimens. The effect of briquette addition was tested on the production of construction steel (C1 specimens) and high-quality steel for the automotive industry (C2 specimens). This shop also presents the peculiarity of performing a stabilization treatment on steel slag after the pouring operations in the slag pits. This leads to a generally better behaviour if compared to the other shop due to a modification of the crystallographic components of the slag generated. The charged quantities for each performed heat are summarized in **Table 5**.

2.3. Slag Characterization

The specimens obtained have been characterized by X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Scanning Electron Microscopy in Back-Scattered Electrons mode (SEM-BSE) coupled with Energy Dispersive Spectroscopy (EDS) analysis in order to gain information regarding the chemical composition, the mineralogy and the microstructure of the slag. Moreover, leaching tests have been performed to evaluate the leaching behaviour of the specimens and the effects of fines recirculation. Average chemical composition, by XRF technique, was supplied directly by the steel shops A and B and measured by the specific internal procedure. Data for steel shop C are not

available.

In order to perform XRD analysis the samples were grinded at a size below 100 µm in a 100 ml zirconia grinding jar with a total mass of 100 g zirconia balls at 250 rpm at intervals of 5 min in order to avoid powder compaction in the jar. XRD analyses were performed by means of a Rigaku SmartLab SE equipped with copper tube (Cu Kα radiation, λ= 1.54 Å) in θ-θ Bragg-Brentano configuration scanning the sample from 5 to 90°2θ at 1°/min, 0.02° step size and collecting the diffracted beam by a 1D D/TexUltra 250 detector with XRF suppressor filter. The sample was rotated at 30 rpm to minimize the texture effect. SEM analysis was performed by means of a Field Emission Gun SEM (FEG-SEM) Zeiss Sigma 300 equipped with Inca Oxford Ultim Max 65 EDS probe on slag fragment moulded in an araldite-base resin, polished and sputtered with Au to grant the conductivity necessary for imaging. The leaching behaviour was investigated following the procedures described in EN 12457-4:2002 standard on non-finely ground materials (0.063 mm < d < 10 mm). A test portion was prepared by placing 0.090 kg of slag in a 1 000 ml PE bottle with 0.900 kg of deionized water (liquid-to-solid ratio = 10 l/kg) and rotating it for 24 h at 10 rpm. After the test, the

Table 5. Charged materials for steel shop C.

Heats performed	Briquette recipe	Charged materials	Specimen ID
1st trial			
2	MI 31 R	1 000 kg dolomitic lime + 0 kg briquettes	C1-R1
4	MI 31 R	1 000 kg dolomitic lime + 500 kg briquettes	C1-B1
4	MI 31 R	800 kg dolomitic lime + 500 kg briquettes	C1-B2
4	MI 31 R	500 kg dolomitic lime + 500 kg briquettes	C1-B3
3	MI 31 R	0 kg dolomitic lime + 2.000 kg briquettes	C1-B4
2nd trial			
2	MI 52 C	1 000 kg dolomitic lime + 0 briquettes	C1-R2
4	MI 52 C	0 kg dolomitic lime + 2 000 kg briquettes	C1-B4-2
2	MI 31 R	1 000 kg dolomitic lime + 0 briquettes	C2-R
4	MI 31 R	0 kg dolomitic lime + 2 000 kg briquettes	C2-B1

Table 3. Charged materials for steel shop A.

Heats performed	Briquette recipe	Charged materials	Specimen ID
1st trial			
3	–	standard procedure	A-R1
3	CC	5 000 kg of briquettes	A-B1
2nd trial			
3	–	standard procedure	A-R2
3	MA	5 000 kg of briquettes	A-B2

Table 4. Charged materials for steel shop B.

Heats performed	Briquette recipe	Charged material	Use of the briquettes	Specimen ID
1st trial				
1	–	–	standard charge (900 kg CaO + 300 kg dololime)	B-R
1	MH 31 R/6	500 kg	as additional charge (+900 kg CaO, +300 kg dololime)	B-B1
1	MH 31 R/6	1 000 kg	as replacement of dololime (+900 kg CaO)	B-B2
1	MH 31 R/4	500 kg	partly replacement of lime (+700 kg CaO +300 kg dololime)	B-B3
1	MH 31 R/4	500 kg	partly replacement of lime and dololime (+800 kg CaO +250 kg dololime)	B-B4
2nd trial				
1	MH 52 B/4	500 kg	partly replacement of lime (+700 kg CaO +300 kg dololime)	B-B5
1	MH 52 B	500 kg	partly replacement of lime and dololime (+800 kg CaO +250 kg dololime)	B-B6
1	MH 52 B	500 kg	replacement of dololime (+900 kg CaO)	B-B7
1	MH 52 B	1 000 kg	replacement of dololime (+900 kg CaO)	B-B8

solution was vacuum filtered using 0.45 μm membrane filter and the leachate was analysed by means of the ICP-OES spectroscopic technique (Induced Coupled Plasma Optical Emission Spectrometry) in order to determine the concentration of leached elements and compare such values with the threshold values fixed by the regulations of the respective producing countries of the slag specimens. The concentration of each element in the leachate (x) were elaborated to quantify the percentage variation from reference values (R) by means of Quantile-Quantile plots method (Eq. (1)).¹⁹⁾ The shift of the distribution apex was calculated to statistically evaluate the effects of briquettes addition on the slag leaching behaviour compared to the reference slag.

$$\text{Variation \%} = \frac{x - R}{R} * 100 \dots\dots\dots (1)$$

3. Results and Discussion

The chemical composition, mineralogy and microstructure of the slag relayed by the analyses are in good agreement with the reference specimen values. In the following paragraphs the comparison among these salient parameters is presented. Every comparison must be intended between reference and briquette-added samples within the same steel shop and the same set of heats.

3.1. Chemical Composition

From a chemical point of view, the slag obtained after briquettes loading are in good agreement with the reference samples obtained following the standard production procedure (Tables 6, 7). A slight reduction in iron oxide concentration was observed for the A slag samples when CC briquettes are charged (Fig. 1(a)). The use of self-reducing briquettes seems able to reduce the oxidation of the slag, due to their reducing capability, while increasing the amount of available lime into the slag. This is reflected in the phase arrangement and morphology, as will be seen later. The same trend is visible for the most of B slag samples (Fig. 1(b)) with few exceptions (i.e., B-B4).

In this case, this effect seems more related to a dilution effect promoted by the recirculation of LF slag and refractories, that notoriously are free of oxidized iron. Still in B samples, the SiO₂ and CaO concentration appears slightly higher than the reference. This is again associated to the recirculation of LF slag and spent refractories into the EAF that allows a higher availability of SiO₂ and CaO. To better visualize this effect, the LF fraction of the briquettes share ratio to the slag-former materials addition was calculated (Eq. (2)) and presented in Fig. 2. Unfortunately, the analysis was possible only for shop B slag samples, since for shop A samples briquette share ration could not be calculated due to a lack of the virgin raw materials amount used for the trial

Table 6. Comparison among the average chemical composition of the 12 heats (one is missing) performed in steel shop A (mass%).

Heat	SiO ₂	FeO	Al ₂ O ₃	CaO	MgO	MnO	Cr ₂ O ₃	P ₂ O ₅	V ₂ O ₅	K ₂ O	Na ₂ O	Other ¹	Slag sample
1st trial													
1	7.41	42.33	5.76	25.37	4.91	5.40	2.47	0.30	0.22	0.00	0.07	5.76	
2	9.11	39.27	5.93	25.63	5.34	6.43	2.54	0.37	0.26	0.00	0.08	5.04	A-R1
3	8.07	38.33	7.37	26.35	5.50	6.93	2.43	0.31	0.22	0.00	0.06	4.43	
4	6.45	40.22	4.97	29.43	5.13	5.98	1.70	0.30	0.22	0.00	0.05	5.55	
5	10.90	34.29	4.90	30.08	5.05	6.21	1.73	0.31	0.23	0.01	0.06	6.23	A-B1
6	10.17	28.30	6.47	35.79	5.60	6.94	1.89	0.44	0.18	0.00	0.06	4.16	
2nd trial													
7	7.71	44.84	4.63	19.67	6.12	7.95	3.37	0.29	0.28	0.01	0.10	5.03	
8	7.94	43.73	5.68	19.47	6.26	8.06	3.14	0.28	0.26	0.00	0.10	5.08	A-R2
9	6.81	46.41	4.60	19.80	6.13	7.87	3.02	0.27	0.28	0.00	0.10	4.71	
10	7.23	44.85	5.28	19.55	6.57	8.39	3.34	0.26	0.29	0.00	0.10	4.14	A-B2
11	6.20	48.58	4.16	18.46	6.18	7.81	2.83	0.23	0.29	0.00	0.09	5.17	

¹TiO₂, SO₃, SrO, ZrO₂, BaO, NiO, CuO, ZnO, PbO, HfO₂

Table 7. Comparison among the average chemical composition of the 9 heats performed in steel shop B (mass%).

Heat	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	Mn ₃ O ₄	Cr ₂ O ₃	P ₂ O ₅	V ₂ O ₅	K ₂ O	Na ₂ O	Other ¹	Slag sample
1st trial													
1	13.11	41.40	13.44	21.11	5.87	5.16	3.01	0.35	0.12	0.03	0.22	1.20	B-R
2	17.98	36.24	12.81	23.55	5.39	4.55	2.04	0.30	0.09	0.06	0.30	1.24	B-B1
3	17.25	34.64	15.05	24.16	5.41	4.71	1.97	0.29	0.12	0.04	0.24	1.29	B-B2
4	12.46	47.05	13.39	20.45	5.76	4.82	1.94	0.30	0.08	0.03	0.16	1.08	B-B3
5	16.54	37.69	12.16	22.78	5.68	4.92	2.25	0.30	0.09	0.05	0.26	0.92	B-B4
2nd trial													
6	16.36	37.91	13.01	24.59	5.21	4.96	2.51	0.56	0.15	0.07	0.36	1.23	B-B5
7	13.8	42.65	10.35	23.81	7.24	5.50	2.59	0.28	0.19	0.03	0.23	0.99	B-B6
8	16.69	36.47	13.04	24.98	6.09	5.65	2.50	0.43	0.14	0.04	0.21	1.17	B-B7
9	15.93	41.17	13.32	23.42	5.53	4.92	2.18	0.38	0.13	0.04	0.23	1.24	B-B8

¹TiO₂, SO₃, SrO, ZrO₂, BaO, NiO, CuO, ZnO, PbO, HfO₂

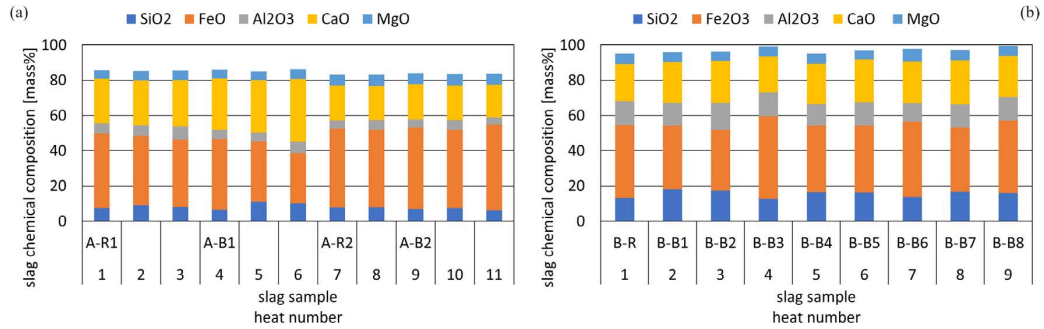


Fig. 1. Major oxide comparison between reference and briquetted slag samples for steel shop A (a) and B (b) (mass%). (Online version in color.)

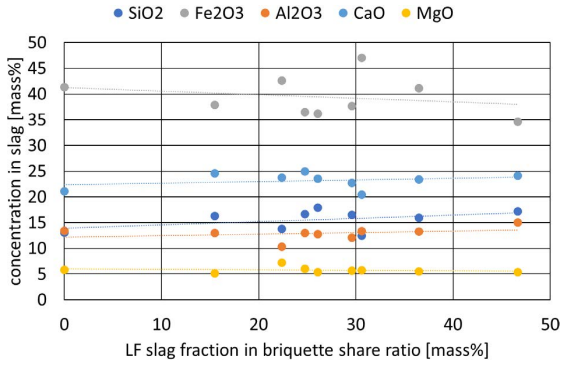


Fig. 2. Qualitative effect of LF slag fraction on the average chemical composition of shop B slag (mass%). (Online version in color.)

Table 8. SEM-EDS general chemical composition of steel shop A slag surface (mass%).

Slag sample	Mg	Al	Si	Ca	Ti	V	Cr	Mn	Fe
1st trial									
A-R1	3.93	3.48	3.03	17.79	0.16	0.16	4.61	8.68	58.06
A-B1	5.71	8.47	5.42	29.69	0.39	0.10	2.93	9.17	38.12
2nd trial									
A-R2	3.73	8.04	7.13	21.66	0.43	–	2.02	6.9	50.1
A-B2	3.83	6.73	5.99	19.54	0.45	–	2.68	7.39	53.38

Table 9. SEM-EDS general chemical composition of steel shop B slag surface (mass%).

Slag sample	Mg	Al	Si	Ca	Ti	Cr	Mn	Fe	Ba
1st trial									
B-R	3.90	11.32	11.78	19.82	0.53	3.59	5.44	43.30	0.36
B-B1	4.64	11.41	14.11	23.09	0.50	2.28	3.97	40.00	–
B-B2	4.82	14.28	17.21	27.85	0.80	2.28	5.88	26.90	–
B-B3	4.26	17.05	13.43	28.04	0.88	2.79	6.22	26.50	0.80
B-B4	4.75	12.27	15.19	24.94	0.47	2.32	4.94	35.00	–
2nd trial									
B-B5	6.40	13.66	13.63	31.00	0.75	4.15	7.35	22.95	–
B-B6	3.77	10.91	16.12	29.77	0.43	0.36	4.73	33.89	–
B-B7	5.17	12.86	15.49	34.6	0.72	2.32	6.55	22.31	–
B-B8	3.23	10.62	10.65	22.54	0.37	2.25	4.99	45.35	–

Table 10. SEM-EDS general chemical composition of steel shop C slag surface (mass%).

Slag sample	Mg	Al	Si	Ca	Ti	V	Cr	Mn	Fe
1st trial									
C1-R1	3.36	7.63	22.39	21.36	0.47	–	2.89	5.92	36.00
C1-B1	4.04	6.06	19.98	32.83	0.47	0.17	2.11	6.40	28.25
C1-B2	4.83	7.40	20.75	28.33	0.45	–	2.94	6.44	29.00
C1-B3	4.03	6.90	29.03	25.24	0.49	0.22	3.04	6.68	24.13
C1-B4	4.13	8.86	24.00	26.60	0.59	0.20	3.05	7.40	25.00
2nd trial									
C1-R2	3.11	7.90	21.37	21.91	0.59	0.08	4.82	7.40	32.84
C1-B4-2	3.41	5.14	19.28	30.17	0.41	0.10	1.56	8.58	31.29
C2-R	4.01	5.65	19.70	29.29	0.26	0.11	2.17	7.18	31.49
C2-B1	2.62	10.91	24.01	21.24	0.73	0.10	2.54	6.00	31.93

tests, while the natural chemical composition of the shop C samples is unforecastable modified by the quartz addition during slag tapping.

$$LF_{\text{fraction}} = \frac{LF_{\text{fraction}} \text{ [mass\%]} \cdot \text{Briquette amount [kg]}}{\text{slag former materials [kg]}} / 100 \quad \dots (2)$$

From Fig. 2, it is possible to see that the amount of LF slag circulated as briquettes in the EAF of the steel shop B contributes to a decrease in iron oxide and a parallel increase in CaO, SiO₂ and Al₂O₃, too. MgO concentration remained quite constant, and this is another significant aspect because the right saturation in MgO is fundamental to avoid fast refractory corrosion.²⁰⁾

The same conclusions can be stated by observing the general chemical composition of the slag surface analysed by SEM-EDS (Tables 8–10).

However, SEM-EDS analysis better highlight the reduction in FeO concentration in the slag B samples than the

XRF analysis. A similar behaviour is depicted also for the slag sample belonging to steel shop C. For instance, due to the same type of slag-former briquettes, the slag produced in the shop C is characterized by higher CaO than the reference samples. In detail, the reduction in iron oxide concentration for sample A-B1 was of roughly 35 mass% in face of an increase of CaO and SiO₂ of 65 and 75 mass%, respectively. For samples B, the reduction in iron oxide was averagely of 25 mass% in face of an increase of CaO and SiO₂ of 40 and 20 mass% respectively, while for sample C, the saving in iron oxides accounts averagely for 18 mass% in face of a rise of lime of 23 mass%. In this latter case, SiO₂ concen-

tration remained practically constant due to the stabilization treatment performed by quartz addition before slag tapping.

3.2. Mineralogical Composition

XRD spectra of both 1st and 2nd trial for slag samples from shop A are reported in **Fig. 3(a)**, together the 1st trial slag samples belonging to steel shops B and C (Figs. 3(b) and 3(d), respectively). From the graphs some small relative oscillations in the intensity of the peaks can be visible, but the main crystalline compounds characterizing both the slag group remained the same. Also, the proportion within the crystalline phases remains in the same range from sample to sample. Similar results were obtained also for the samples of 2nd trials among the three groups. The crystallographic composition of the different slag groups reflects their chemical composition. Slags from shop A are characterized by wustite, larnite and brownmillerite, and to a lesser extent of chromite, being characterized by high binary basicity index

(from 2.5 to 3.5) and significant iron oxide fraction.^{21,22} This is also confirmed by the SEM analysis presented in the next paragraph. Samples B are mainly formed by akermanite-gehlenite, kirschsteinite and wustite. Significant amount of chromite is detected, while larnite is practically absent (Fig. 3(b)). This is in agreement with the less basicity of these slag (averagely 1.5) if compared to slag A.^{23,24} For the C group, the samples analysed by XRD showed good agreement in their respective subgroups and among their totality. The core phases are the same for all the samples and are: wustite, chromite (in its various forms), kirschsteinite-monticellite (in solid solution), anorthite and quartz that has not melted completely (Fig. 3(d)). Kirschsteinite and anorthite are promoted by the low basicity if compared with traditional EAF slag. This is due to the addition of quartz carried out outside the EAF and before the slag tapping in the yard.^{25,26} The difference between spectra is generally not very pronounced and can be attributed to the different

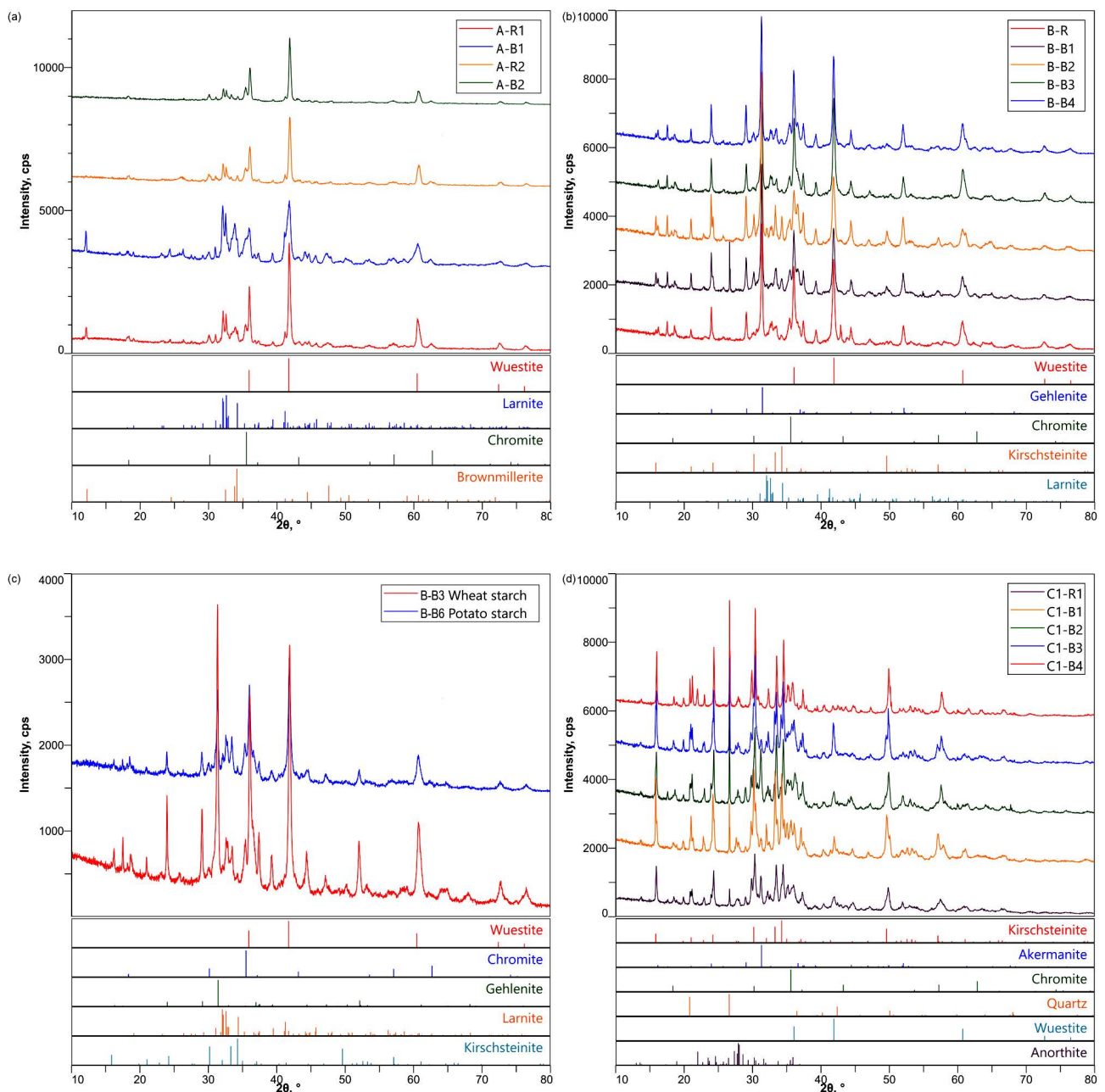


Fig. 3. Examples of XRD spectra: (a) comparison between reference and briquette-added samples for shop A for both the trials; (b) comparison of 1st trial slag samples from steel shop B; (c) comparison of two B slag samples with wheat-starch briquettes and potato-starch briquettes (d) comparison of 1st trial slag samples from steel C. (Online version in color.)

conditions experienced during the heats and mainly due to the quartz correction.

Since in plant B and C two different starches have been used as binder, a comparison between slag obtained by the use of potato and wheat starch was carried out (Fig. 3(c)). The results show no influence of the starch source on the slag quality, as these are organic compounds, consisting of various hydrocarbons, they evaporate immediately during the melting process in the EAF. Indeed, the same crystalline phases were identified in both wheat and potato-starch briquettes slags although their amount differs due to the difference in chemical composition of the charge (scraps, flux and briquettes itself). This is also true for the slag sample produced by shop A where the two recipes used molasses (A-B1) and polymeric binder (A-B2), respectively (Fig. 3(a)).

3.3. Morphological and Microstructural Characterization

For what concerns the microstructural and morphological analyses performed by SEM, no significant difference has been highlighted between slag samples after briquettes addition and the respective reference sample, as well as can be seen by some sample images in Fig. 4. An important result obtained by all the analyses performed is that no difference between the samples can be directly associated to the quantity of briquettes that were added during steel production. This entails that from the constitutive aspect of the slag specimens examined, the briquettes act as virgin raw materials would. Compared to the XRD analysis shown above, the microstructural investigation is in good agreement about the phases' arrangement. In addition, it helps to identify minor crystalline compounds that are below the detection limit of the XRD, like perovskite in A and B slag.

3.4. Leaching Behaviour

To inspect if the fines recirculation is also neutral on the environmental properties of the slag, leaching tests have been performed. The results obtained for each steel shop are reported in Table 11.

For all specimens, in addition to the released compounds, pH measurement and electrical conductivity are also reported even if not explicitly required by national legislations. It is quite evident that the release behaviour of slag obtained from shop C are quite different in magnitude

compared to the other two even if most of the specimens come from the re-bar steel line of production. This is not due to the use of the briquettes or any internal variable of the process but to the stabilization treatment, as described before. Deliberately, the local maximum admissible concentrations are not reported for privacy reasons. However, typical leaching limits in force in some EU countries can be found in.^{23,27-29)} The results are referred only on Ba, Cr, F, Mo, V and W, which are the six elements known in literature for causing problems and, in this case, are also present in relevant concentrations.²³⁾ Their concentration in the leachate, the electrical conductivity (EC) and the pH of the leachate, have been represented in some graphs where on y-axis is reported the leached values from

Table 11. Leaching test results for specimens from shop A, B, C according to BS EN 12457-4:2002. All data in ppm_{DM} (mg/kg_{DM}), where DM = dry matter.

Slag sample	Heat number	Parameter	pH	EC	Ba	Cr _{TOT}	F ⁻	Mo	V	W
		Unit	-	μS/cm	ppm _{DM}	ppm _{DM}	ppm _{DM}	ppm _{DM}	ppm _{DM}	ppm _{DM}
1st trial										
A-R1	1		11.67	1 106	5.8	<0.5	9.4	1.5	<0.5	-
A-B1	1		11.19	337	2.0	<0.5	10.8	0.9	1.9	-
B-R	1		11.28	445	13.8	<0.5	10.0	0.5	1.4	1.8
B-B1	1		11.08	293	7.1	<0.5	10.7	0.5	0.9	2.3
B-B2	1		11.14	353	11.2	<0.5	10.8	0.3	0.5	3.0
B-B3	1		11.36	426	7.3	<0.5	9.8	<0.5	0.8	1.1
B-B4	1		11.26	399	7.7	<0.5	10.6	0.6	1.0	3.7
C1-R1	1		11.22	329	1.0	<0.5	9.7	<0.5	0.7	0.9
	2		11.04	226	1.1	<0.5	11.5	<0.5	<0.5	1.2
C1-B1	3		11.33	430	1.2	<0.5	15.9	<0.5	<0.5	1.0
	4		11.02	238	1.1	<0.5	9.5	<0.5	0.8	0.9
C1-B2	1		11.05	254	0.7	<0.5	10.7	<0.5	0.6	0.9
	2		11.38	500	1.0	<0.5	12.2	<0.5	<0.5	0.6
C1-B3	1		11.23	302	0.8	<0.5	10.9	<0.5	<0.5	1.1
	3		11.17	301	0.7	<0.5	11.5	<0.5	<0.5	0.5
C1-B4	1		10.43	76	<0.5	<0.5	9.3	<0.5	<0.5	0.5
	2		11.53	560	1.3	<0.5	14.1	<0.5	<0.5	0.7
	3		10.92	205	5.3	<0.5	9.8	<0.5	0.5	1.0
2nd trial										
A-R2	1		11.61	755	1.2	2.6	12.1	0.5	1.3	-
A-B2	1		11.52	594	1.0	0.7	11.6	<0.5	1.4	-
B-B5	1		11.40	542	6.2	0.6	11.7	0.6	1.1	3.6
B-B6	1		11.50	642	7.2	<0.5	11.1	0.7	1.6	2.5
B-B7	1		11.34	420	6.7	<0.5	12.2	<0.5	1.3	1.4
B-B8	1		11.31	409	4.8	<0.5	11.6	<0.5	1.3	1.4
C1-R2	1		11.04	203	2.4	<0.5	13.2	<0.5	<0.5	1.0
	2		11.36	430	1.0	<0.5	12.8	0.5	0.8	1.2
C1-B4-2	1		10.94	191	1.3	<0.5	11.7	<0.5	<0.5	1.0
	4		10.93	180	0.7	<0.5	11.6	<0.5	<0.5	0.5
C2-R	1		11.40	449	1.0	<0.5	13.3	1.1	0.8	0.8
	2		11.19	331	1.3	<0.5	11.2	0.6	0.7	2.0
C2-B1	1		11.29	431	1.1	<0.5	11.0	<0.5	<0.5	2.0
	4		11.18	320	2.7	<0.5	11.2	1.1	0.5	2.6

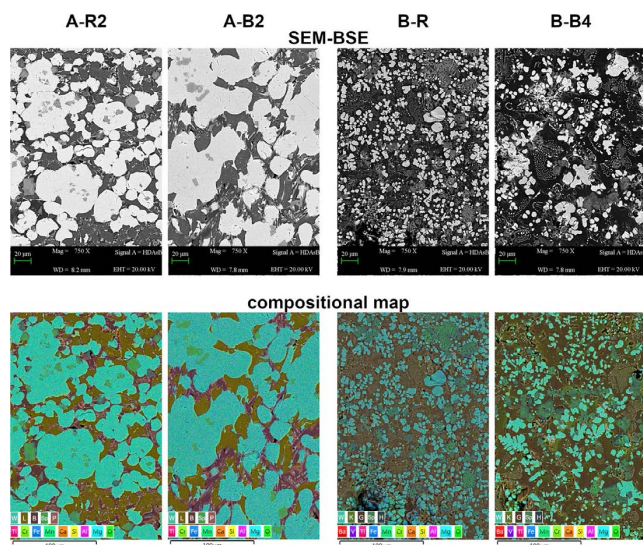


Fig. 4. Example of SEM analysis on two slag samples after briquettes addition and their comparison with the relative reference sample (W = wustite, B = brownmillerite, G = gehlenite-akermanite, H = hercynite, K = kirschsteinite, L = larnite, P = perovskite, Sp = spinel (chromite)). (Online version in color.)

briquettes-added slag sample and on the x-axis the leached values of the reference ones (Fig. 5).

Examining the graphs, it can be evaluated that for Ba leaching, the briquettes-added samples leachate generally lower concentration and no samples were over the specific threshold values. Cr behaved as well in a favourable manner

and only two specimens had releases above their limit. F is the only parameter that seems to have gotten slightly worse and only samples from shop B are above threshold. For Mo no clear effect could be detected and only a small number of specimens were above the limitations. V has generally a favourable behaviour, like Ba, with only few specimens

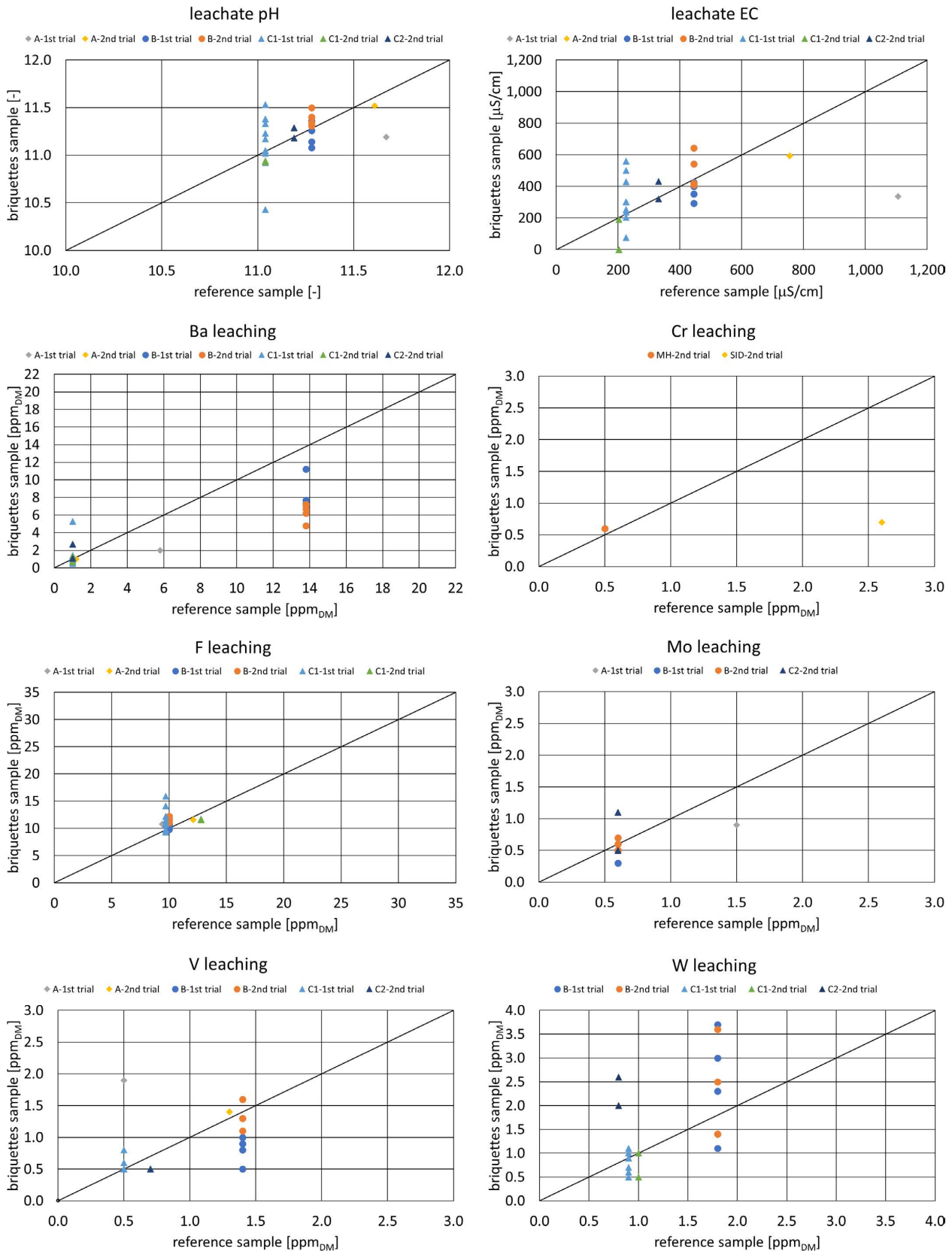


Fig. 5. Leaching behaviour comparison between briquettes-added slag and the respective references. (Online version in color.)

that present leached concentration increased compared to the reference. For W there is a relative high scattering of the data, and no trend can be visualized and hence no com-

ments on the slag behaviour can be done considering only these graphs. pH and EC both present a balanced behaviour around the bisectrix and no critical effect seems to take

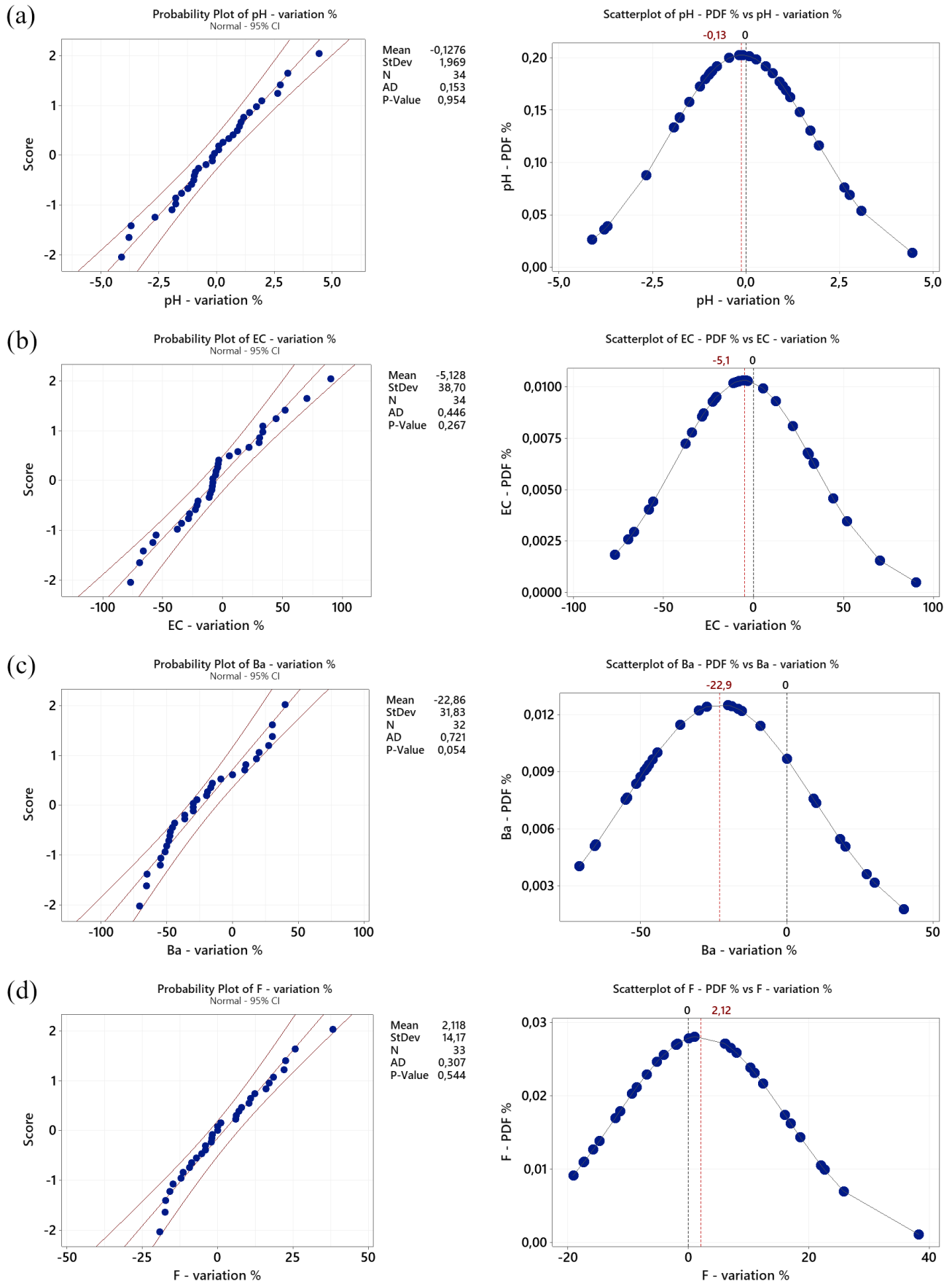


Fig. 6. Q-Q probability plot (on the left) and normal distribution (on the right) for (a) pH, (b) EC, (c) Ba, (d) F, (e) Mo, (f) V, (g) W. (Online version in color.)

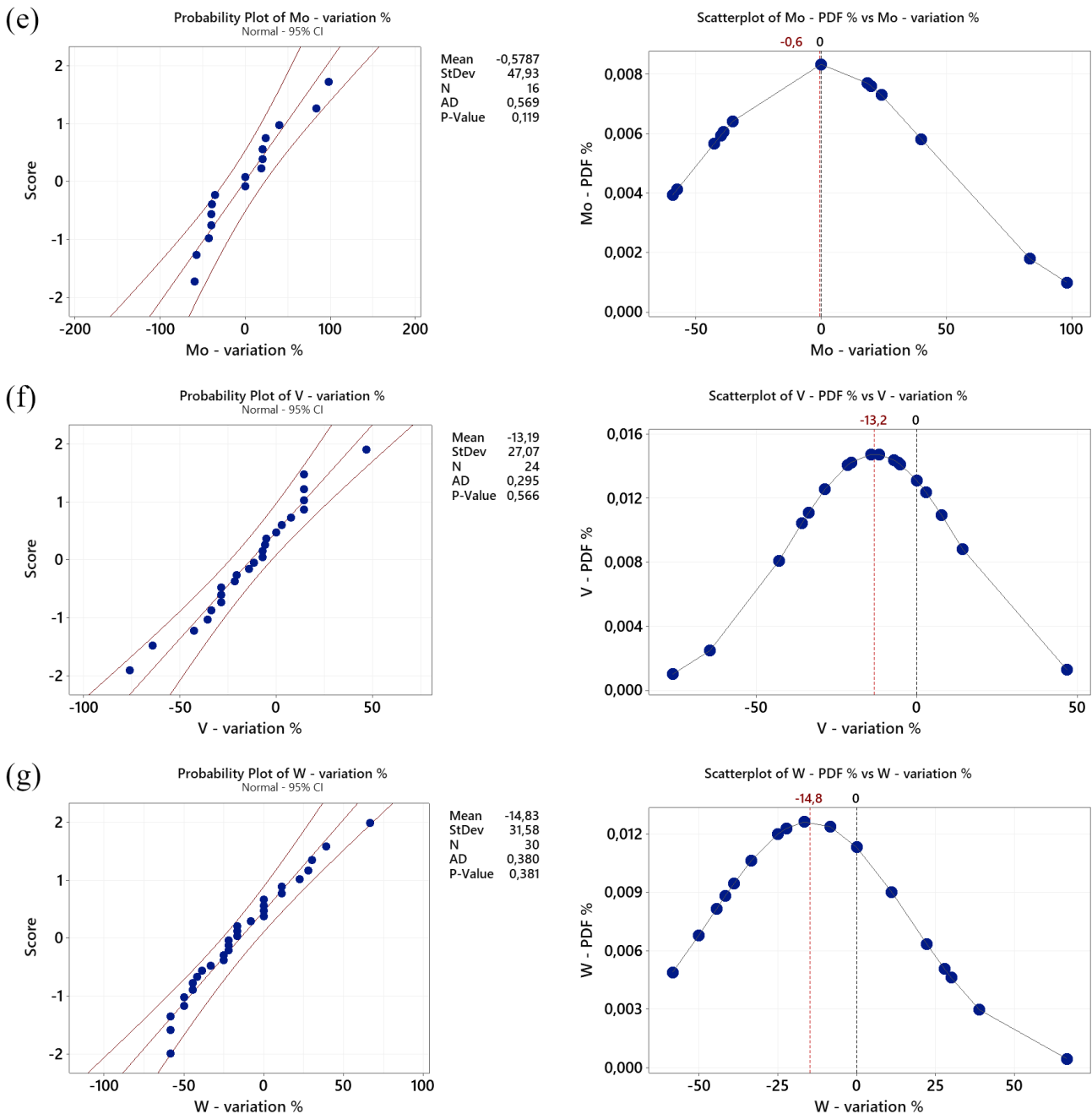


Fig. 6. Q-Q probability plot (on the left) and normal distribution (on the right) for (a) pH, (b) EC, (c) Ba, (d) F, (e) Mo, (f) V, (g) W. Continued. (Online version in color.)

place.

In order to have a clearer interpretation of the effects caused by the use of briquettes during the steelmaking activities, the relative difference in element concentration, compared to the reference ones, has been considered (Eq. (1)). More specifically, the comparison procedure took into account the following parameters and chemical elements: pH, EC, Ba, W, V and F. Other element such as Cr have a high number of values below the limit of detection (LOD) of the ICP-OES, for both reference and briquette-containing slag specimens. Therefore, creating a probability distribution for such data would lead to many null values that could pollute and greatly alter the resulting set. For this reason, data with an abundance of values below the LOD were not considered.

The overall data obtained appear to follow a normal distribution. To verify this assumption, Q-Q plot were generated to visibly assess whether a set follows a normal distribution. Outliers' data have been neglected due to their anomalous

nature compared to the other values obtained and their potential polluting effect on the probability distributions of the relative variation percentages. The Q-Q plots reported in Fig. 6 show that for all the investigated parameters, the data effectively distribute like a Gaussian. Normality test performed according to Anderson-Darling method^{30,31} confirmed this assumption, since a p-value higher than 5% was obtained for all the parameters. Thus, all the data sets can be effectively considered normal distributed, even with some differences. For instance, pH, F, V and W adhere better to a Gaussian distribution (high p-value) than EC, Mo and Ba (low p-value).

The probability distribution function (PDF) obtained helps visualize that the use of additional briquettes does not lead to a considerable variation in pH (Fig. 6(a)) and a slight decrease in EC (Fig. 6(b)) compared to the reference values. For pH, the average variation is slightly less than zero (-0.127%), however the margin is so low that for all intents and purposes no positive or negative effect could be consid-

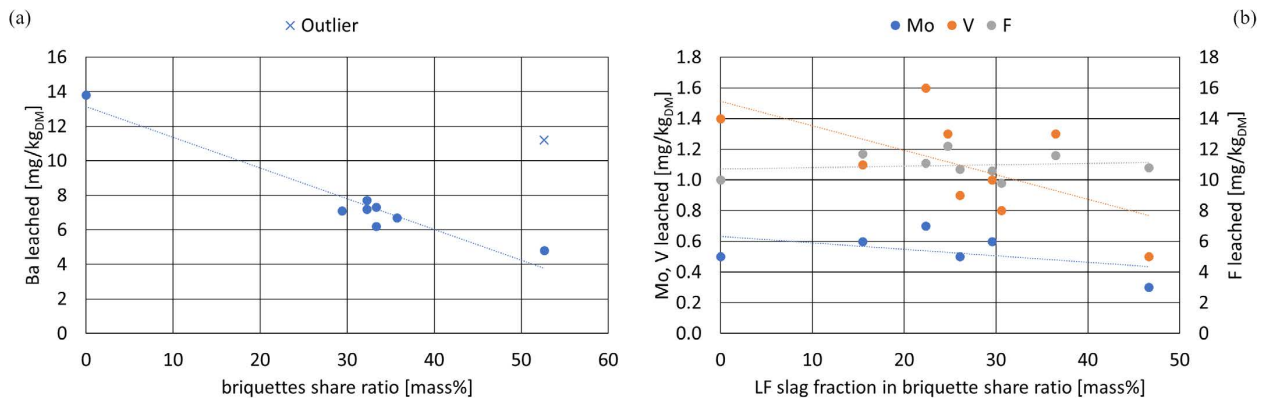


Fig. 7. Relationship between briquettes share ratio on Ba leaching (a) and LF slag fraction in briquettes share ratio on F, Mo and V leaching (b) for sample from shop B. (Online version in color.)

ered. For conductivity, an average reduction of -5.13% is obtained and can be considered as a positive effect.

For what concerns the barium leaching (Fig. 6(c)), the probability density highlights a positive effect of briquettes addition to the leaching of barium. For instance, the average value (-22.86%), and consequently the apex of the PDF, are shifted toward negative values of relative variation percentage. Therefore, the probability of having higher Ba leaching for briquettes-added slag samples is lower than the one of reference slag samples. This effect appears to be much more significant on Ba rather than on pH, confirming the qualitative observation made during the discussion of Fig. 5. The direct influence of briquettes loading on Ba leaching was directly investigated for shop B samples, by comparing the briquette share ratio (*i.e.*, the ratio between briquettes charged and raw materials charged) and the leachate concentration itself. As can be seen in Fig. 7, as the briquette share increases, the leached Ba tends to decrease. This is probably due to a diluting effect that briquettes operate into the slag. Since the primary source of Ba is the scrap painting, the addition of higher fraction of briquettes as slag former contributes to dilute the BaO oxide concentration and hence, its leaching.

The probability distribution of F (Fig. 6(d)) is slightly translated toward the positive value with an average of $+2.12\%$. However, this positive increase is very limited and will reasonably slightly affect the overall behaviour of F leaching; especially since the allowable emission threshold is quite far from any leaching values observed during the trials. Overall, the effect of the briquette usage with respect to F release could be considered practically unvaried.

Despite of the low number of data relate to Mo leaching, the data distribution can be considered normal (Fig. 6(e)). The effect of briquettes addition to the EAF charge appears to be favourable for slightly reducing the leachability of this element. For instance, the mean of the distribution is minimally shifted towards negative values (-0.6%) thus implying a null or slightly beneficial contribution of briquettes addition to Mo leaching remediation. In addition, the statistical distribution of the available data helps resolve the interpretation of qualitative behaviour reported in Fig. 5.

Vanadium leaching (Fig. 6(f)) seems to be influenced in a similar way compared to Ba since a considerable translation of the values toward the negative values (-13.19%) is present. The overall employment of briquettes seems to yield favourable results and confirm the qualitative trend observed in Fig. 5.

Analogously to Ba, the leaching of F, Mo and V was correlated to the briquettes charged into the EAF. In particular, the LF fraction of the briquette share ratio seems able to explain the observed statistical trend of the three above elements. In detail, V and Mo leaching can be reduced by the recirculation of LF slag since the secondary metallurgy slag are free of oxidized metals, being the treatment at the LF

performed in non-oxidizing conditions. On the other hand, F leaching could be slightly increased if during the LF treatment, slag flux based on CaF_2 is used. These hypotheses, even if qualitatively, seem to be confirmed by the trend depicted in Fig. 7(b).

Tungsten leaching (Fig. 6(g)), however, seems to be less influenced by the briquette use than Ba and V. It is still present a considerable translation of the PDF values toward the negative values (-11.13%) that entails how the effect of the briquettes could be considered overall positive for the leaching behaviour for this element, too.

4. Conclusions

In this paper, the effect of fines recirculation in form of briquettes on the quality of slag was evaluated. Several slags were sampled from three different EAF steel shop and characterized from the chemical, crystallographic and microstructural point of view. Leaching behaviour was also investigated and the results compared with slag samples produced following the standard smelting procedure.

The examined specimens are characterized by the same chemical, crystallographic, and morphological properties of the reference ones. Briquette addition seems to not cause significant negative effects on the steelmaking processes. Furthermore, the results highlighted a neutral or a slightly positive effect has been obtained after the addition of various degrees of charged materials and briquette typology.

The occasional increase in the leaching behaviour of some specific elements and the slight differences in XRD spectra or chemical compositions can be attributed to the heterogeneous nature of the slag and can be considered as aleatory.

The statistical analysis has highlighted how briquette use has, at best, a quite positive effect for the leaching behaviour of Ba, V and W, which concentration in leachate decreased of -22.86% , -13.12% and -14.83% , respectively. For some other parameters (pH, EC, Mo) there is a slightly beneficial or neutral effect, whereas F leaching is worsened ($+2.12\%$) by briquettes addition.

In addition to the previous considerations, thanks to internal evaluations at the three steel shops participating in the trials, the benefits of substitution of virgin raw materials by internal side-stream materials briquettes was determined. For instance, a comparison of total CO_2 emission from production (indirect) to use (direct) of the different slag forming materials shows an unambiguous advantage for the cement-free residues briquettes even though the typical operation profile of 1 000 kg/charge of dolomitic lime must be substituted with 2 000 kg/charge of slag forming briquettes. This substitution offers the opportunity to strongly reduce the CO_2 emissions by more than 90% and even by more than 50% compared to cement bonded briquettes. In a similar way, by evaluating the Fe balance between input (scraps, hot

heel, self-reducing briquettes) and output (tapped steel, hot heel, Fe in slag and dusts) from the EAF, a recovery rate of iron of 62% can be stated when self-reducing briquettes are employed in comparison to the standard operating practice.

Finally, no significant influence on furnace operation and product quality was observed by the three industrial partners while performing the trial heats.

Author Contributions

Conceptualization, D.Mu., C.S., L.F.A., T.E., T.G. and S.S.; methodology, D.M., M.Q., C.M.; formal analysis, D.M., M.Q.; investigation, D.M., M.Q.; data curation, D.M., D.Mu., C.S., L.F.A., T.G., S.S.; writing—original draft preparation, D.M., M.Q.; supervision, C.M.; project administration, C.M., T.E.; funding acquisition, C.M., T.E. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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