InSGeP

Investigations of Slags from Next Generation Steel Making Processes



Deliverable 2.2

Data about slag produced

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Abstract

It is expected that the prevailing blast furnace - basic oxygen furnace process route will be gradually replaced in the future by a combination of direct reduction process and an electric arc furnace, a smelter, an open slag bath furnace, or a submerged arc furnace. Hydrogen plasma smelting reduction provides another potential process option for future steel production. These novel processes will produce distinct varieties of slag. Thus, significant alterations will occur in the quantities and qualities of the slag produced as a consequence of the steel industry's transformation.

Beginning with the current state of steel production, an analysis of the contemporary state of slag production forms the premise of this deliverable. The quantities of blast furnace slag, basic oxygen furnace slag, electric arc furnace slag, and ladle furnace slag, as well as their chemical composition, are described and summarized. Furthermore, Deliverable 2.2 outlines, which novel slag systems are expected. At present, there is limited knowledge regarding the precise slag-to-metal ratios, overall slag production volume, chemical and mineralogical composition, physical characteristics, technical and ecological attributes. Slag volumes and their properties are influenced by various factors (e.g., future ore and pellet availability and quality, the electrical melting process).

Deliverable 2.2



List of tables

Table 1: Typical components of BF slags and their quantities ^{6,}	4
Table 2: Typical, chemical composition of EAF slag ⁹	7
Table 3: Expected future composition of smelter slag ⁴	12
List of figures	
Figure 1: Steel and slag production in the EU between 2010 und 2019	2
Figure 2: Typical, specific slag quantities along the BF-BOF (top) and the EAF	(bottom) route
	3
Figure 3: Slag typologies and annual quantities in EU	4
Figure 4: Overview of treatment measures and flowchart for liquid BF slag 6,9.	5
Figure 5: Overview of treatment measures and flowchart for liquid BOF slag 6,9	6
Figure 6: EAF slag clustering from stainless and special steel production at Sider	
to slag, "st" to steel)	7
Figure 7: Overview of treatment measures and flowchart for liquid EAF slag ^{6,9}	8
Figure 8: Utilization of BF slag and steelmaking slag in 2021 (based on 6)	9
Figure 9: Examples of potential future steel production pathways and their by-p	roducts11

List of abbreviations and acronyms

BF blast furnace

BOF basic oxygen furnace

DRI direct reduced iron

EAF electric arc furnace

EAF C EAF slag from carbon steel production

EAF S EAF slag from stainless steel production

EU European Union

HBI hot briquetted iron

HPSR hydrogen plasma smelting reduction

LF ladle furnace

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Table of contents

A	.bstract		II
L	ist of tab	oles	IV
L	ist of fig	gures	IV
L	ist of abl	breviations and acronyms	IV
T	able of c	contents	V
1	Intro	duction	1
2	Curre	ent status of slag production	2
	2.1	Quantities and chemical composition	2
	2.1.1	Blast furnace slag	4
	2.1.2	Basic oxygen furnace slag	5
	2.1.3	EAF slag	6
	2.1.4	Ladle furnace slag	8
	2.2	Utilization of slag	9
3	Slags	s from next generation steelmaking	10
	3.1	Electric arc furnace slag using DRI / HBI	11
	3.2	Smelter slag, iBlue® and open slag bath furnace	12
	3.3	Hydrogen plasma smelting reduction slag	12
4	Conc	Plusion	14

Deliverable 2.2



1 Introduction

Next generation iron and steelmaking processes aiming to decrease CO₂ by the use of direct reduced iron (DRI) with varying reduction degrees, hot briquetted iron (HBI), liquid steel/iron melt from hydrogen plasma smelting reduction (HPSR) or by operating electrical smelters for low-grade ores will result in increase of electric arc furnace (EAF) slag and other slags with different properties. This requires the understanding of the possibility to valorize future slags in the present value chain and define innovative applications to assure a smooth transition process without disruption to the steel industry as well as other sectors (such as road construction or cement) who currently rely on slag as raw material for their processes. To understand and move forward the transition of the steel industry, InSGeP project is investigating slags resulting from next generation steelmaking in Europe. The project relies on the limited amount of currently produced slags from next generation steel production in Europe and abroad as well as on laboratory, pilot scale and industrial scale tests that will be performed based on the needs of the involved partners.

As slag production is an integrate part of steelmaking, the sustainable recycling or utilization of slag instead of landfilling is a major key to fulfilling circular economy goals and reduction of CO₂. Based on the currently occurring slags, Deliverable 2.2 summarizes the slag that can be expected from next generation steelmaking production.



Current status of slag production

The blast furnace - basic oxygen furnace (BF-BOF) route and the EAF route are the main approaches applied in the European Union (EU27) to produce steel. Despite differences in feedstock and process design, both process pathways produce numerous by-products such as slags, dusts, or sludge. The largest amount of by-product generated is slag. In 2022, approximately 312 million tons of granulated BF slag, 104 million tons of air-cooled BF slag, 143 million tons of BOF slag, and 68 million tons of EAF slag have been generated globally 1. According to the European Steel Technology Platform ESTEP, worldwide steel production is projected to reach its highest point at 2.8 billion tons in 2070. This would lead to an estimated total slag volume of around 1 billion tons per year if no modifications are made to process technology, slag/metal ratios, market shares, or other factors ².

The figure below (Figure 1) illustrates the slag output in the EU from 2010 to 2019, in conjunction with the corresponding steel production. On average approximately 46.9 million tons of slag were produced each year during this period ³.

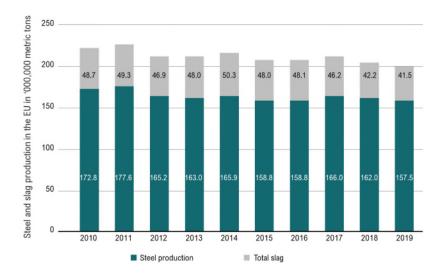


Figure 1: Steel and slag production in the EU between 2010 und 2019³

2.1 **Quantities and chemical composition**

Slags are categorized based on their origin and exhibit varying chemical and physical characteristics determined by their manufacturing process or cooling method. They are generated in varying amounts at different stages of steel production (Figure 2).

¹ Ehrenberg A.: The steel production transformation process in Europe: New slag types will substitute granulated blast furnace slag, in: ZKG Cement Lime Gypsum, Issue 6/2023, Online: www.zkg.de/en/artikel/the-steelproduction-transformation-process-in-europe-new-slag-types-will-substitute-granulated-blast-furnace-slag-4001145.html, 2023. ² European Steel Technology Platform ESTEP: Green Steel by EAF – Workshop report. Bergamo, 2019.

³ EUROFER: European Steel in Figures 2021.



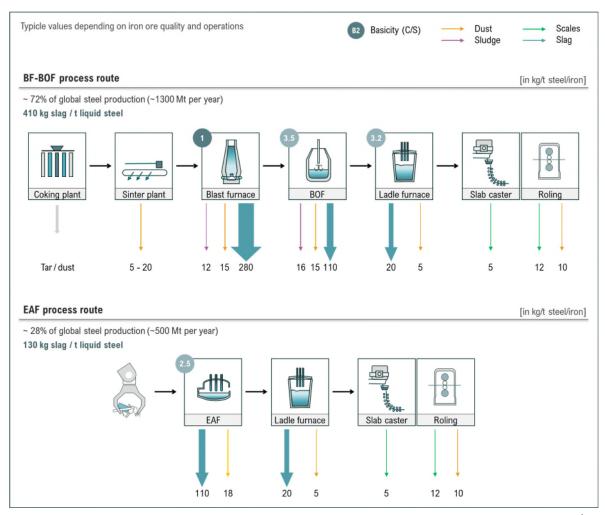


Figure 2: Typical, specific slag quantities along the BF-BOF (top) and the EAF (bottom) route⁴

In 2018, Europe generated around 25.2 million tons of BF slag and 22.6 million tons of steelmaking slag ^{5,6}.

Slags are commonly generated from lime and silica-based melts, making calcium oxide (CaO) and silica (SiO₂) their main components (Figure 3). Additional components include alumina (Al₂O₃) and magnesium oxide (MgO) as well as trace elements, such as iron. The iron content in BF slag is typically less than 0.5 wt. % due to its formation through a reduction process. Compared to BF slag, BOF slag and EAF furnace slag are created in an oxidizing process and consequently have iron contents that are considerably higher⁶

⁴ Provided by Primetals Technologies.

⁵ World Steel Association (Ed.): Steel Statistical Yearbook 2019 – Concise version, finalized November 2019, Brussels, Belgium.

⁶ EUROSLAG, Online: <u>www.euroslag.com</u> (accessed on 16 February 2024).



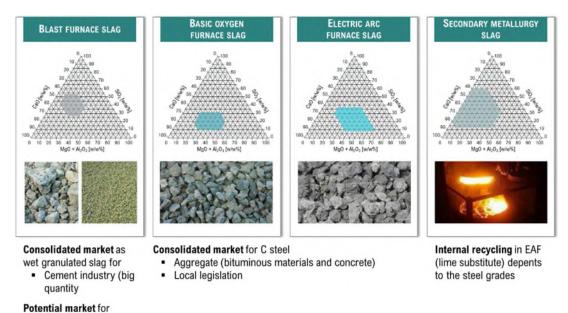


Figure 3: Slag typologies and annual quantities in EU⁷

2.1.1 Blast furnace slag

 Mortar Aggregate

The fluxes, carbon source residues, and non-metallic components of the iron ore react chemically to form liquid BF slag, which accumulates at the bottom of the BF alongside the molten metal. The less dense slag creates a layer above the molten iron and can be separated using a skimmer at temperatures around 1500 °C Error! Bookmark not defined.

The quantities of the typical components of BF slag are summarized in Table 1. The slag is predominantly composed of CaO, SiO₂, Al₂O₃, and MgO.

Table 1: Typical	components of BF	slags and their	quantities	Error! Bookmark not defined., 8

Constituent	BF slag [wt. %]
CaO	33 – 43
SiO_2	33 – 38
Al_2O_3	10 – 15
MgO	7 – 12
FeO	≤ 1.0
Fe_2O_3	0.1 - 1.0
MnO	≤ 1.0
P_2O_5	-
$\mathbf{S}_{ ext{total}}$	1 - 1.5
Cr ₂ O ₃	≤ 0.1

The quantity of slag generated is contingent upon several factors, including the gangue content of the iron ore, the ferrous burden, the presence of coke ash and ash from the injection material (e.g., coal),

⁷ Provided by Tenova.

⁸ Algermissen D.: Future slag production in a low carbon steel industry – A break in circular economy, 7th International Slag Valorization Symposium, 2021.



and the flux quantity needed to attain the desired quality of the obtained metal⁹. Typically, the amount of slag per ton of hot metal ranges from 150 to 345 kg and the basicity (B2) ranges from 0.8 to 1.0 ^{9,10}.

After the slag has been tapped from the BF, it can be treated with a variety of procedures (Figure 4). Slow cooling in pits or bottom ports results in the formation of a crystalline structure and the development of a stone-like mass. The term for this slag is air-cooled BF slag. Following the processes of crushing and sieving, this slag has a remarkable suitability as a construction aggregate. Granulated BF slag is a glassy / amorphous granular or sand-like material that is produced when BF slag is rapidly cooled, e.g. by using water. Because of its cement-like qualities, granulated BF slag is utilized as a hydraulic binder for cement, concrete, mortar, and grout. For this specific objective, it is ground; additionally, unground granulated BF slag can be utilized as an aggregate, such as in the construction of roads. BF slag can also be pelletized to make BF pellets, or it can be foamed to produce foamed BF slag. Both of these options are performed to a lesser extent.

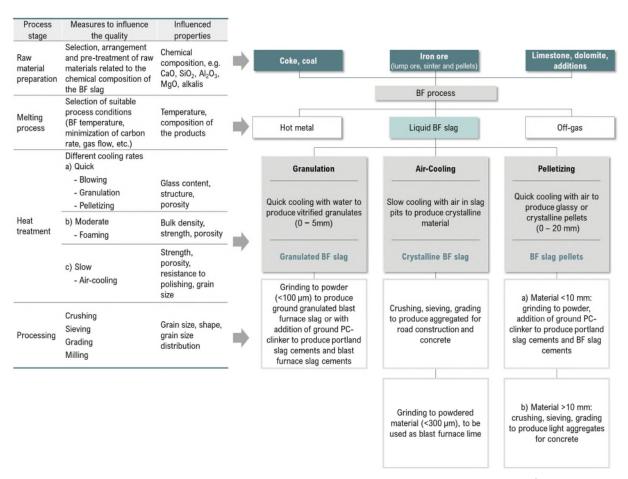


Figure 4: Overview of treatment measures and flowchart for liquid BF slag.⁹

2.1.2 Basic oxygen furnace slag

After the reactions in the BOF are finished, liquid slag floats on top of the molten crude steel that has accumulated on the bottom of the furnace. Subsequently, the slag and crude steel are removed at temperatures above $1600\,^{\circ}$ C in separate ladles or pots. The slag rate for the BOF process varies between

⁹ Joint Research Centre, Institute for Prospective Technological Studies Remus R., Roudier S.; Delgado Sancho L. et al.: Best Available Techniques (BAT) Reference Document for Iron and Steel Production. 2013.

¹⁰ Feedback from stakeholders.

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85 and 165 kg/t of liquid steel. The slag has a basicity (B2) between 2.5 and 3.0 and an approximate iron content of 21% Error! Bookmark not defined.,10.

The molten slag is poured into slag pots and later into slag pits, where it undergoes controlled air-cooling, resulting in the formation of crystalline slag. The slag can be subjected to various processes, including weathering, pulverizing, and sieving, in order to achieve the desired technical properties for a particular application (Figure 5).

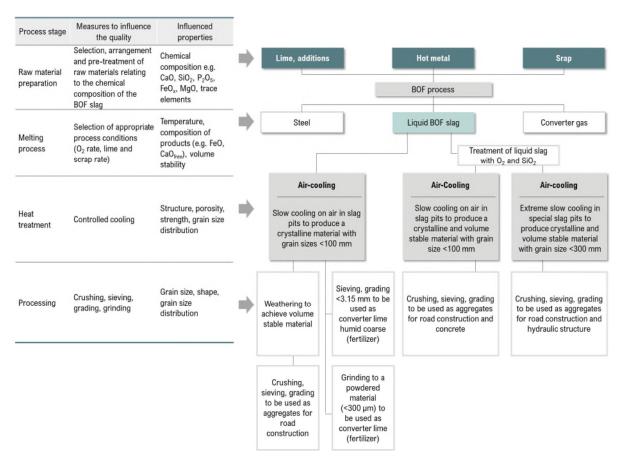


Figure 5: Overview of treatment measures and flowchart for liquid BOF slag Error! Bookmark not defined., 9

Compared to natural rocks (e.g. basalt), BOF slag has a high level of strength (as measured by its impact and pulverizing values) and enhanced skid resistance, which makes it an ideal aggregate for road constructions and surface layers requiring high slip resistance Error! Bookmark not defined. Due to the high basicity of those slag, the volume stability must be taken into account.

2.1.3 EAF slag

EAF slag is generated during the melting process in an EAF and consists of fluxes, non-metallic scrap components and steel incompatible elements. Due to its lower density in comparison to the steel, the slag swims above the steel bath. Depending on the desired steel grade (carbon steel or stainless/highalloy steel), there is a differentiation between EAF slag from carbon steel production (EAF C) and EAF slag from stainless steel production (EAF S). Table 2 summarizes the typical chemical components of EAF slag.



Table 2: Typical, chemical composition of EAF slag ⁹

Constituent	EAF C slag [wt. %]	EAF S [wt. %]
CaO	15 – 64	17 – 68
$\overline{ m SiO_2}$	4 – 26	2 - 42
Al_2O_3	1 – 16.5	<0.1 – 30
MgO	0.5 - 15.5	1.5 – 25
FeO	10 - 63	<0.1 -39
MnO	0.5 - 19.5	<0.1 – 21
P_2O_5	<0.01 - 2	-
Cr ₂ O ₃	<0.1 – 11	<0.1 – 22

Figure 6 illustrates the grouping of EAF slags resulting from the production of special steel and stainless steel at Sidenor.

As observed, the stainless steel slags form a distinct group due to their low content of iron and silicon oxides but higher chromium oxide content. This latter characteristic complicates their revalorization, posing a challenge in the transition towards zero waste for steel mills manufacturing these types of steels.

The remaining groups belong to slags from the production of special steel. The slags resulting from the manufacturing of steels with specifications for phosphorous and/or copper, and steels without specific requirements, show notable differences. When low phosphorous is specified, an increase in CaO and phosphorus oxide content is noticeable to achieve low phosphorous levels in the steel. On the other hand, when low copper levels are required along with a low phosphorous content, the use of clean scrap is mandated, resulting in a low initial phosphorous content. In this case, there is no significant increase in phosphorus oxide content in the slag. In instances where there are no specifications regarding tramp elements, it can be observed that iron and silicon oxide levels are slightly higher due to reduced lime usage and possibly an increased oxidation level in the furnace for part of the production.

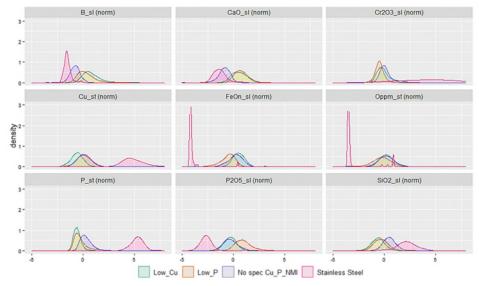


Figure 6: EAF slag clustering from stainless and special steel production at Sidenor ("sl" refers to slag, "st" to steel) 11

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¹¹ Provided by Sidenor.

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Usually, the amount of slag per ton of steel ranges from 100 to 180 kg ¹². The liquid slag is tapped at temperatures of approximately 1600 °C and then progressively air-cooled to form a crystalline structure (Figure 7).

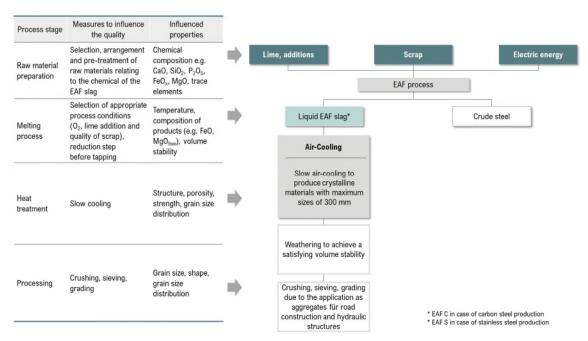


Figure 7: Overview of treatment measures and flowchart for liquid EAF slag Error! Bookmark not defined., 9

EAF slag is a durable, compact, non-porous aggregate with high resistance to polishing and a strong affinity to bitumen. Its resistance to deformation (rutting), safe, and lasting properties make it a perfect material for asphalt and road surface treatments. Error! Bookmark not defined.

2.1.4 Ladle furnace slag

Ladle furnace (LF) slag is created during secondary metallurgical processes used to manufacture and refine crude steel. Secondary metallurgical slags are typically high in CaO concentration and low in oxidation levels Error! Bookmark not defined. Each ton of refined steel yields between 30 and 80 kg of LF slag ¹². Its characteristics and heterogeneity pose challenges to its recycling and valorization and is therefore subject of several studies and research ^{13, 14, 15, 16, 17} since the composition strongly depends on the LF process (i.e., changing sequences and quantities of refining / alloying agents).

¹² Piemonti A.; Conforti A.; Cominoli L. et al.: Exploring the Potential for Steel Slags Valorisation in an Industrial Symbiosis Perspective at Meso-scale Level, in: Waste and Biomass Valorization (2023) 14:3355–3375, 2022.

¹³ Montenegro-Cooper J. M.; Celemín-Matachana M.; Cañizal, J. et al.: Study of the expansive behavior of ladle furnace slag and its mixture with low quality natural soils. Construction and Building Materials. 203(2019) 201-209

¹⁴ Adesanya E.; Sreenivasan, H.; Kantola, A. M. et al.: Ladle slag cement – Characterization of hydration and conversion. Construction and Building Materials. 193 (2018) 128-134

¹⁵ Bocci, E.: Use of ladle furnace slag as filler in hot asphalt mixtures. Construction and Building Materials.161 (2018), 156-164

¹⁶ Skaf M.; Ortega-López V.; Fuente-Alonso J. A. et al.: Ladle furnace slag in asphalt mixes. Construction and Building Materials. 122 (2016) 488-495

¹⁷ Radenovic A; Malina J. and Sofilic T.: Characterization of Ladle Furnace Slag from Carbon Steel Production as a Potential Adsorbent, Advances in Materials Science and Engineering, Volume 2013, 2013.

Deliverable 2.2



2.2 Utilization of slag

Slag is not considered a waste material but rather a valuable resource in the iron and steel industry. According to their chemical features, slags can be used in various fields of applications and sectors such as:

- Construction material: Especially ground granulated BF slag is often used as a cementitious material in the production of concrete ^{18, 19, 20}. It enhances the durability and strength of concrete structures while it decreases the carbon footprint of the final cement.
- Road construction: Slag can be used as a base or fill material in road construction, providing a cost-effective and environmentally friendly alternative ^{21, 22, 23}.
- Agricultural sector: Some types of slag can be processed and used as a fertilizer, liming material and as soil amendment, contributing to soil improvement ^{24, 25, 26}.
- Other applications (e.g. internal recycling, hydraulic engineering) Error! Bookmark not defined., 23

Figure 8 depicts the utilization of slag from the iron and steel industry in 2021. A total of 29.4 Mio tons of slag were recycled, including 19.9 tons of BF slag and 9.8 Mio tons of steelmaking slag (BOF slag, EAF slag and secondary metallurgical slag). Error! Bookmark not defined.



Figure 8: Utilization of BF slag and steelmaking slag in 2021 (based on Euroslag Error! Bookmark not defined.)

The classification and handling of slag has become a key topic for the iron and steel industry in recent years and regional differences exist in terms of valorization depending on the respective legislation and

¹⁸ Surovstov M.M.; Novoselova Y.N. and Slobozhankina, L.R.: On use of blast-furnace granulated ground slag in construction. IOP Conf. Series: Mater. Sci. Eng. 451, (2018); p. 012013.

¹⁹ Parron-Rubio M.E.; Perez-Garcia, F.; Gonzalez-Herrera A. et al.: Concrete properties comparison when substituting a 25% cement with slag from different provenances. Materials 11, 1029 (2018).

²⁰ Parron-Rubio M.E.; Perez-Garcia F.; Gonzalez-Herrera A. et al.: Slag substitution as a cementing material in concrete: mechanical, physical and environmental properties. Materials 12, 2845 (2019).

²¹ Sorlini S.; Sanzeni A. and Rondi L.: Reuse of steel slag in bituminous paving mixtures. J. Hazard. Mater. 209–210, 84–91 (2012).

²² Handley P. and Basuyau V.: Legal and environmental bottelnecks and opportunities for slag-based products valorisation, 6th International Slag Valorisation Symposium, 2019.

²³ Bollen J.; Hanrot D.; Deruwe A. et al.: Slags valorisation in the EU: Tapping the full potential, 6th International Slag Valorisation Symposium, 2019.

²⁴ Branca T.A.; Fornai B.; Colla V. et al.: Application of basic oxygen furnace (BOFS) in agriculture: a study on the economic viability and effects on the soil. Environ. Eng. Manage. J. 18(6), 1231–1244 (2019).

²⁵ Branca T.A.; Pistocchi C.; Colla V. et al.: Investigation of (BOF) Converter slag use for agriculture in Europe. Metall. Res. Technol. 111, 155–167 (2014).

²⁶ Pistocchi C.; Ragaglini G.; Colla V.; Branca T.A.; Tozzini C.; Romaniello L.: Exchangeable Sodium Percentage decrease in saline sodic soil after Basic Oxygen Furnace Slag application in a lysimeter trial. Journal of environmental management, 203, 896-906 (2017).

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market situations ^{27, 28}. However, provided their technical suitability, environmental compatibility and regular quality assurance, slags can be processed into viable products.

Additional comprehensive details regarding the jurisdictions, in which slags are applicable and the corresponding legal frameworks in specific countries, are available in Deliverable 2.3 "Compilation of regulatory information about slag use in Europe".

3 Slags from next generation steelmaking

In the future, the BF-BOF process route is expected to be replaced by a combination of DR process (based on natural gas and later on green hydrogen) with an EAF, a smelter, an open slag bath furnace, or a submerged arc furnace. HPSR is an additional viable process option for future steel production. These new process routes will generate new types of slag. Although the solid-state DR process itself does not produce any slag, the melting unit (EAF, smelter, open slag bath furnace or submerged arc furnace) and HPSR will result in new differing types of slag.

The graphics below (Figure 9) depicts two potential future steel production routes (DR in combination with smelter route for low grade iron ore and DR in combination with EAF for high grade iron ore) and their by-products.

Currently, the particular slag/metal ratios, total quantity of slag generated, chemical and mineralogical composition, and physical properties of the new slags, as well as their technical and ecological features, are unknown.

The availability and quality of ore and pellets in the future, the electrical melting process, the DRI/scrap ratio, the slag adjustment in accordance with metallurgical and cementitious requirements, the possibility of a separate slag treatment to lower the high iron oxide and heavy metal content, and the liquid slag cooling process will affect volumes and properties. ¹

²⁷ Endemann G.: KrWG, AwSV und MantelIV: Auswirkungen auf die Stahlindustrie und ihre Nebenprodukte, Schlacken aus der Metallurgie, Band 2 (M. Heußen and H. Motz (eds.)), TK Thomé-Kozmiensky, Neuruppin (2012), pp. 21–31.

²⁸ Algermissen D.: Development of New Products from BOF-Slag, Mineralische Nebenprodukte und Abfälle (S. Thiel et al. (eds.)), Thomé-Kozmiensky Verlag GmbH, Neuruppin (2018), pp. 298–309.



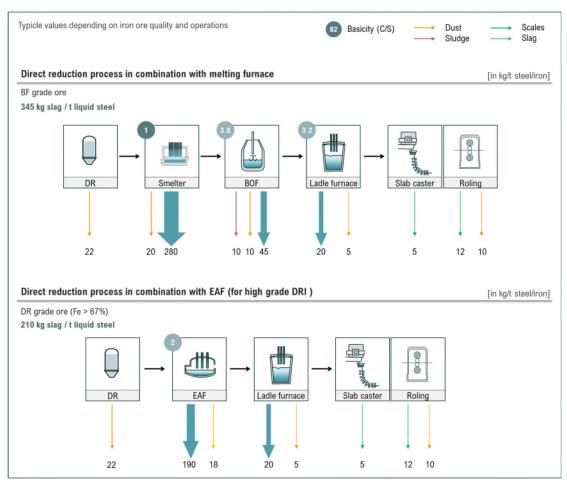


Figure 9: Examples of potential future steel production pathways and their by-products²⁹

While smelter/submerged arc furnace slag is intended to be comparable to BF slag, the new EAF slag will be closer to today's scrap-based EAF slag. However, the heavy metal content will be decreased, but still significantly greater than BF slag. As the exact slag/metal ratios, resulting slag volumes, chemical and mineralogical compositions, and physical properties of the new slags are not yet clear, their cementitious and environmental qualities remain unclear as well. ¹

3.1 Electric arc furnace slag using DRI / HBI

In general, increasing the amounts of DRI/HBI (and in general the deterioration in the quality of the metal charge, including scrap) in the electrical steel route will lead to several changes in the EAF process, including the increase in black-slag production. This slag will have a different chemistry than slag produced by scrap-based processes. By using HBI in ever greater quantities it is expected to have more acidic components (to be compensated with more lime and/ or dolomite) and in greater quantities.

A critical issue arises with the specification for phosphorus, a requirement that many of the steels must also meet. This compels the use of HBI with the lowest possible phosphorus content. The utilization of high phosphorus HBI would necessitate a conscientious adjustment of timings, processes, and facilities to accommodate higher lime consumption, leading to an increased volume of generated EAF slag. It is important to note the economic impact of this outcome, simply due to the extended melting time or, in other words, the loss of productivity.

²⁹ Provided by Primetals Technologies.

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3.2 Smelter slag, iBlue® and open slag bath furnace

There is currently no smelter in operation to produce iron, but the slag is projected to be equivalent in basicity to BF slag. Furthermore, a generation of 200 kg to 300 kg smelter slag per ton of hot metal is expected, whereby the quantity varies depending on the quality of iron ore used. The expected composition (based on thermodynamic calculations) is summarized in Table 3.

Table 3: Expected future composition of smelter slag ⁴

	1 0
Constituent	Smelter slag [wt. %]
CaO	42.03 %
MgO	7.00 %
Al_2O_3	10.50 %
SiO_2	38.29 %
MnO	0.05 %
P_2O_5	0.03 %
S	0.22 %
TiO ₂	0.34 %
Na ₂ O	0.01 %
-K ₂ O	0.42 %
FeO	1.00 %
Basicity	
B2	~1.1

For the smelter slag, a utilization in the cement industry or at least for construction should be possible. It is planned to operate the smelter's slag basicity in a way to get a substitute for the replaced BF slag. The target is to make it saleable to the cement industry.

The iBlue® process (combination of the ENERGIRON®'s DR process with an EAF) will result in an unchanged production of BF-like slag in terms of quantities and qualities. The target of iBlue® is to obtain a slag with the same chemical composition as BF slag. This new slag could be, potentially, utilized in cement production substituting BF slag. ³⁰

Also, in case of open slag bath furnace, the target is to obtain a slag similar to BF slag to be valorized in the cement industry. Therefore, the slag and the open slag bath furnace process are managed to obtain a slag output just like this.

3.3 Hydrogen plasma smelting reduction slag

At the moment, first test trails at the HPSR plant are being conducted by K1-MET and voestalpine (projects SuSteel³¹ and SuSteel follow-up³²). Here the target is to become aware about the process limitations and to achieve reproduceable results. At this stage of the process development, the slag chemistry is not the focus of the research activities. Nevertheless, most of the tests are operated with a slag basicity of about 1.2. In future, it is planned to run several test trails with higher slag basicity to get aware about the changes in dephosphorisation rate due to the increase of the slag basicity.

³⁰ Tenova: Online: tenova.com (accessed on 05 February 2024).

³¹ <u>SuSteel: K1-Met Metallurgisches Kompetenzzentrum</u>

³² Sus-F: K1-Met Metallurgisches Kompetenzzentrum

Project coordinator: FEhS Germany Deliverable 2.2



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4 Conclusion

In an integrated steel mill, nowadays about 410 kg/t of steel slags are produced. This is mainly BF slag (around 150 to 345 kg/t) and BOF slag (around 85 and 165 kg/t). Due to the transformation of the iron and steel industry and the associated implementation of new technologies or technology combinations, the slag amount won't be reduced significantly; however, their composition and properties will change.

For the smelter slag with an assumed basicity of about 1.0 and the open slag bath furnace slag, the recycling in the cement industry seems realistic like it is currently done with BF slag. Regarding the EAF process, the increasing amounts of DRI/HBI will result in several changes in the process as well as an increase in slag production. For HPSR slag, a usage in road construction and a partial usage in the cement industry could be possible due to the low heavy metal content.

Even though there is only limited information about the new slags, their characteristics, and total volume, it is evident that landfill should be prohibited, and sustainability should remain a main driver in shaping the future of steelmaking slags.

InSGeP

Investigations of Slag from Next Generation Steel Making Processes

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PROJECT DURATION | 48 months

TOPIC | RFCS-02-2022-RPJ

BUDGET | 4.5 M€

COORDINATOR | FEhS

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