

Evaluation of a BOF Slag Recovery Treatment combining Experimental and Simulation Studies

Ismael Matino¹, Teresa Annunziata Branca¹, Erika Alcamisi¹, Valentina Colla¹,
Lea Romaniello²

¹ Scuola Superiore Sant'Anna, TeCIP Institute, Pisa, Italy

Corresponding autor:

Ismael Matino, Scuola Superiore Sant'Anna, TeCIP Institute, 56010 Ghezzano, Pisa,
Italy.

Email: i.matino@sssup.it

² ILVA S.p.A. , Taranto Works, Taranto, Italy

Abstract

Industrial waste and by-products can be thought as important sources to be recovered. From an environmental point of view, instead of disposal, different treatments can be considered to obtain products for new applications. The large amount of by-products and wastes produced by the steel industry justifies the efforts in management and recovery to enhance sustainability. Basic Oxygen Furnace slag is an example of steel by-product, which reuse and recycle options are supported by suitable chemical composition according to internal and external plant requirements.

The paper presents the investigation about feasibility of a possible Basic Oxygen Furnace slag recovery treatment, by combining experimental and simulation tests.

Chemical analyses have been carried out to characterize the slag, which is proposed to be firstly cooled and ground and sieved to release the slag phases with different magnetic properties. Experimental and simulation studies allow verifying slag reuse possibility and identifying the parameters that mostly affect the treatment efficiency.

The obtained final fractions appear to be possibly suitable for reuse as fertiliser and pelletization operations, with adjustments in magnetic separation operation.

Model can be used for different slag qualities and different treatments operating conditions.

Keywords

BOF Slag, Waste Management, By-Product Recovery, Process Modelling, Process Simulation

Introduction

In the last few years, the international community has become increasingly sensitive to environmental issues as well as landscape and health protection. Even more stringent legislation and the increase of landfill and disposal costs have led to employ greater efforts to improve the recycling and the reuse of waste and by-products and consequently to minimize landfills (European Commission 2008).

Regarding the steel industry, several investigations about enhancements of waste and by-products management and recycling have been carried out (Matino et al. 2014, Das et al. 2007). Different factors affect the recycling rate of by-products, such as environmental requirements, energy use and economical and technological feasibility, and for this reason process integration model can be used with the aims of improving the material and energy efficiency, together with environmental or economic

sustainability for the steel production system (Larsson et al. 2006). In effect, during ironmaking and steelmaking operations, along with hot metal and steel products, some different types of by-products are generated, i.e. slags, dusts, sludges and mill scales, where slags represent almost the 90% of the total amount. The multitude of kinds can result in various reuse options and, for this reason, over the past decades the steel industry has been committed to increase by-products recovery rate by developing innovative technologies. The recycle options are not only the external use in other industries or field of applications as construction material, road building, concrete aggregate and thermal insulation, but also the internal reuse in ironmaking and steelmaking processes as raw materials, justified by the high content of valuable elements, such as iron (World Steel Association 2010). Any of these recovery options guides to reducing landfill waste, CO₂ emissions and to the exploitation of natural resources but also to revenues, which make the by-products recycling economically sustainable (World Steel Association 2015). The innovation to traditional process technologies, demanded to the steel industry, has the objective to match the requirements of high competitiveness, due to high costs, raw material shortages, environmental issues and customer demands. The aims are the improvements of steel properties and qualities and, last but not least, the achievement of a better knowledge related to by-products.

Specific attention has to be paid on slags recycling and especially on the slags role as valuable resources, because of the large volumes (more than 400 Mt) produced worldwide (World Steel Association 2010). In effect, also focusing on the only slag as by-product a large variety can be identified and in particular Blast Furnace (BF) slag, Basic Oxygen Furnace (BOF) slag, Electric Arc Furnace (EAF) slag and Secondary

Metallurgical (SM) slag can be mentioned (The European Slag Association 2012). Some of them, such as BOF slag and EAF slag, are produced in the primary steelmaking stage, respectively from the conversion of hot metal to steel and from melting scrap operations. The addition of smelting, slagging agents and fluxes into furnaces, such as limestone, dolomite and silica sand, after removing impurities from metal baths, forms slags that protect liquid metal, maintaining the temperature value. In secondary steelmaking refining operations, other slags are generated, such as SM and Ladle Furnace (LD) slags, due to the addition of alloys and fluxes, in order to produce different steel grades.

Slags main components are silica, calcium oxide, magnesium oxide and aluminium and iron oxides and due to the high content of iron (10 – 40% in weight of metal iron, excluding iron oxides) and iron oxides, steelmaking slags can be used as a potential renewable resource. Nevertheless, different conditions during operations result in slags with different chemical compositions, mineralogy and physical properties are the discriminating factor for fate as waste or reusable product.

A deep understanding regarding the nature of slags can allow improving the recycle and the reuse with a significant reduction in the related environmental impact (Dippenaar et al. 2005). This objective justifies some innovative studies, focused on the characterization of slags. For instance, BOF slag can be used as a reactant for the CO₂ chemical absorption for carbon sequestration from the steel industry (Birat et al. 2009). On the other hand, the content of calcium silicates, carbonates, and oxides makes it suitable for agriculture purposes, in the case of proved negligible content of trace elements, such as heavy metals, which can be released and leached to surface water.

For this reason, the assessment of chemical and physical characteristics under natural and simulated conditions is the preliminary step to evaluate the potential environmental impacts associated with slag application, in agriculture such as in construction or other fields (Proctor et al. 2000). In order to assess the possible use of BOF slag in agriculture for amending purposes, the effects and possible risks by using slags in two moderately alkaline soils through a soil infiltration column test have been investigated (Pistocchi et al. 2012). Different effects as well as different soils in Europe have been analysed in order to test the use of slags. On one hand, investigations have concerned the use as liming material in the long-term field trials, for preventing acidification in Middle Europe soils. On the other hand, tests have been carried out to assess the effect of Ca contained in BOF slag for balancing negative Na effects in alkaline Mediterranean soils, characterized by seawater intrusion and irrigation with saline water (Branca et al. 2014).

Usually slag management includes different operations, such as dumping on a waterproof surface, cooling, crushing, grinding and sieving, to obtain a good magnetic separation. After tapping and discharging from the equipment, once slag is cooled and solidified under atmospheric conditions and after crushing, the metallic fraction is removed by magnetic cylinders and the nonmetallic part of slag is crushed and sieved for recycling later. Some studies have been carried out in order to reduce dust emissions coming from SM slag management, focusing on LD slag, due to instability of dicalcium silicate content, which can cause environmental impact, and to make slag suitable for further applications (Branca et al. 2009).

Regarding BOF slags, experimental studies include magnetic separator beneficiation parameters, chemical and mineralogical properties, metallurgical

properties and their optimum combination. As far as the BOF slag processing is concerned, the goal consists in achieving a product with high iron content, with the final objective of slag reuse in sintering process. The iron separation from slag allows iron recovering as a substitute for scrap, as well as making effective use of the slag for other applications, where iron would be an impurity. This is the reason why, after cooling, the steel slags are ground and the iron recovered by magnetic separation (Horii et al. 2012). The connection between iron recovery ratio and cooling conditions by applying wet magnetic separation has been investigated (Wang et al. 2012). Recently, a cleaner iron-rich product with low impurities has been obtained by coupling weak magnetic separation with selective size screening on steelmaking slag fines. This fraction could be consequently sent to different unit operations of ironmaking and steelmaking route, increasing the recycling rate of slags (Ma et al. 2014), or classified as a recyclable not hazardous waste.

This paper fits in with the BOF slag management, treatment and recovery option. The development of an Excel-based model is presented, to simulate the proposed treatment process, by combining experimental data and process modelling, providing a preliminary proof of BOF slag reuse. BOF slag supplied by ILVA Steelworks has been subjected to a treatment process including an air-cooling stage, grinding and sieving stage and a magnetic separation of the coarse fraction. The obtained magnetic fraction, mixed with the fine fraction, will be tested for the use in sinter plant while the non-magnetic fraction will be tested for the use as fertiliser.

In the first section of Material and methods, experimental studies and process modelling are presented. The developed model has been applied to one specific case study and the Results and discussion section highlights the obtained outcomes.

Finally, the Conclusion section illustrates the guidelines deduced by experimentation and simulation tests.

Materials and Methods

The investigation of BOF slag recovery requires several studies to obtain information about slag features and treatment process to recover slag fractions. The exploitation of both experimental and simulation results can be useful to achieve the objective of obtaining suitable slag fractions to be reused.

Starting from literature and heuristic information, a recovery option has been proposed, based on several slag physical treatments (Fig. 1).

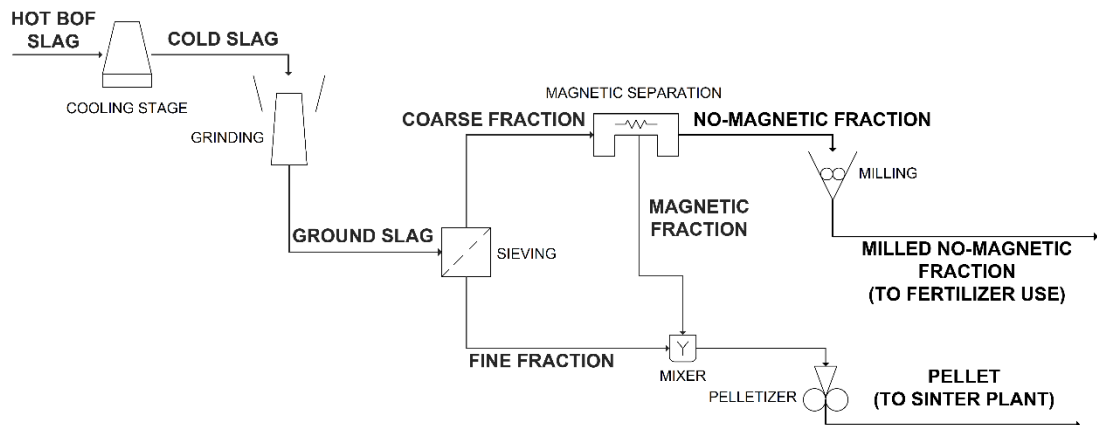


Figure1. BOF slag proposed recovery treatment.

The hot slag coming from Basic Oxygen Furnace is subjected to an initial step of cooling. Then it is ground and sieved to release the slag phases with different magnetic properties and to obtain two main fractions with suitable particle size distributions (PSD). A magnetic separation is carried out for iron removal on the coarse fraction (supposed to be richer in iron). The not-magnetic fraction is re-milled to obtain a suitable PSD for the possible reuse as fertiliser (PSD<1mm).

The paragraph describes experimental studies in order to characterize the BOF slag and preliminary laboratory tests of the proposed process. All the obtained information have been used to model the selected treatment using the approach presented in the following sections.

Simulation outputs can provide preliminary information of BOF slag reuse feasibility in terms of suitability of final slag fractions features.

Experimentation

Experimental studies are necessary to demonstrate the suitability of BOF slag as secondary raw material (e.g. as fed to sinter plant or as fertiliser) after ad hoc recovery treatment. Tests took place in Taranto ILVA plant, organized in two main tasks:

- BOF slag characterization, to obtain useful information for the next steps;
- laboratory scale tests, to deduce important guidelines for analysis and implementation of the proposed slag treatment.

BOF slag characterization

Three quality types of slag were selected in Taranto steelworks, each regarding the production of a different steel grade, and several samples for each kind of slag have been characterized.

The reference compositions related to the considered slags are highlighted in Table 1 while the sizes and appearances of two of them are shown in Fig. 2.

Table 1. Reference composition of ILVA BOF slags.

Compound	Slag I	Slag II	Slag III
	[% wt]	[% wt]	[% wt]
Fe _{tot}	22.2	17.4	23.2
CaO	40.5	46.6	42.0
SiO ₂	12.6	12.4	12.1
MnO	3.4	3.8	3.0
P ₂ O ₅	0.1	1.9	1.1
MgO	6.0	7.8	6.5
V	0.08	0.13	0.06
TiO ₂	0.7	0.7	0.6
Cr	0.19	0.17	0.12

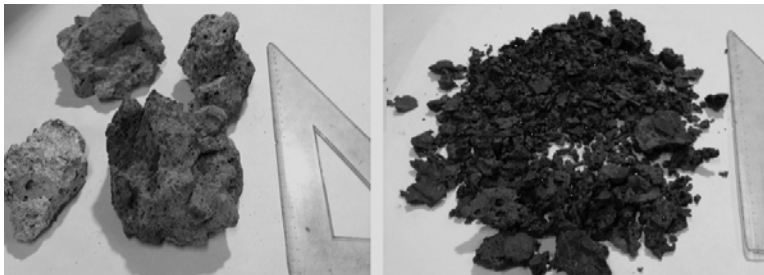


Figure 2. BOF slag types: Slag I (left) and Slag III (right).

Chemical compositions were obtained by internal X-Ray Fluorescence Spectroscopy analyses (XRF). The choice of testing several samples is justified by the necessity to identify the variability ranges of chemical elements (Table 2).

Table 2. Range of composition of ILVA BOF slags.

Compound	min	max	average
	[% wt]	[% wt]	[% wt]
Fe _{tot}	16.9	40.5	26.0

CaO	32.1	51.3	43.2
SiO ₂	4.7	19.1	12.5
MnO	1.5	10.6	3.0
P ₂ O ₅	0.02	2.8	1.6
MgO	4.8	14.9	9.0

The amount of microcompounds and heavy metals was obtained by EPA 3051A 2007 testing methods. Analyses results showed amounts of total chromium in the range 1-1.7 mgkg⁻¹ and of vanadium between 0.7-1.5 mgkg⁻¹. Furthermore, UNI EN ISO 12457:2004 leaching tests on slags, previously ground, gave negligible heavy metals elution:

- total chromium = 12 µg l⁻¹;
- vanadium < 0.10 µg l⁻¹.

In addition, the BOF slag mineralogy has been investigated. Analyses have been carried out through X-Ray Diffraction equipment (XRD), in laboratories not ILVA-owned, obtaining chemical compositions reported in Table 3.

Additional semi-quantitative and qualitative investigations, such as Scanning Electron Microscopy analyses (SEM), have been carried out to extrapolate information about the oxides distribution on black (e.g. iron compounds) and white phases (e.g. larnite).

Table 3. Mineralogical composition of ILVA BOF slags.

Compound	min [% wt]	max [% wt]	average [% wt]
Larnite	55	55	65
Srebodolskite	25	15	20
Wüstite	<5	5	5
Magnesiowüstite	5	5	5
Magnetite	10	-	5
Free Lime	-	10	-
Periclase	5	10	-

Fig. 3 shows an example of SEM analysis results, confirming that the BOF slag is polyphasic and composed of complex oxides similar to the calcium silicate. The area fraction of white phase is about 22 %.

The range of composition in weight percentage of elements is reported in Table 4 for the Slag I.

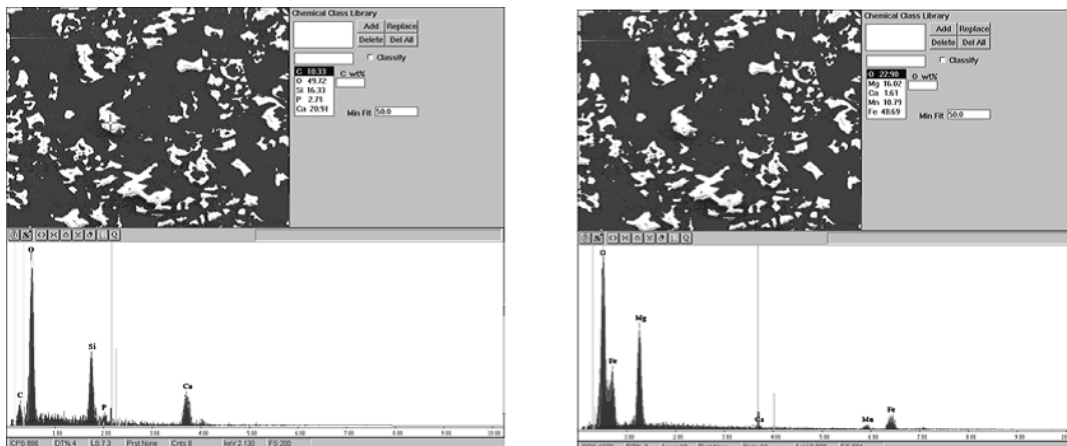


Figure 3. SEM analyses of BOF slag I: white phase (left) and black phase (right).

Table 4. Average composition of white (wp) and black (bp) phases of ILVA BOF Slag I.

Element	wp		bp	
	min	max	min	min
	[% wt]	[% wt]	[% wt]	[% wt]
C	6.7	10.7	-	-
O	38.4	49.7	21.7	22.9
Si	14.7	16.5	-	-
P	2.7	3.6	-	-
Ca	20.9	27.6	1.6	2.9
Mg	-	-	12.7	16.3
Mn	-	-	8.3	10.8
Fe	0	11.5	48.7	54.4

Slag grain sizedistribution has been examined by physical analyses (ISO 4701:2008).

The chemical characterization demonstrates that calcium and iron are the main slag components. Other interesting compounds such as phosphorous oxides make BOF slag potentially suitable as secondary raw material (e.g. fertiliser).

Adhoc physical treatments can be required to separate slag in its two main fractions, the iron-rich one, to be fed in sinter plant, and the calcium-and-phosphorous-rich, to be used as fertiliser. Heavy metals content is negligible as well as the leaching behaviour.

Laboratory scale test

Preliminary laboratory scale tests have been carried out to confirm the suitability of the proposed procedure to separate solid slag into two main fractions, one richer and one poorer in iron. The tests have been carried out on different slag qualities.

The BOF slag have been sampled after an air-cooling stage of 24 hours at atmospheric temperature and pressure. The samples have been aged for some days and then subjected to milling and sieving processes.

The grinding step has been executed in a lab jaw crusher equipment, resulting in two main fractions, one coarse (PSD >1mm) and one finer (PSD <1 mm). In this lab tests, the slag appeared brittle with negligible ductile metallic iron.

Each obtained fraction has been treated by manual magnetic separation, using a neodymium magnet upon a thin layer of slag.

The two parts coming from the finer fraction have been analysed but presented similar iron content. This could be justified by not suitability of manual magnetic

separation, as the iron particles are bonded to the fine grains of slag.

On the other hand, the analyses of the two parts of coarse fraction confirmed that the magnetic part is richer in iron. The non-magnetic matter has a composition similar to the initial one, as shown in Table 5 for the Slag I. In this case, the larger grain size facilitates the manual magnetic separation.

Table 5. Iron and phosphorous content before and after magnetic separation of Slag I.

Compound	Slag I (before magnetic separation) [% wt]	No-magnetic fraction (after magnetic separation) [% wt]
Fe(0)	0.6	0.3
Fe ²⁺ oxide	22.3	21.3
Fe ³⁺ oxide	7.6	7.5
P ₂ O ₅	0.9	0.9

Nevertheless, different techniques of magnetic separation are supposed to be more suitable to achieve higher efficiency.

In the final step of these lab tests, the two finer fractions (PSD < 1mm, without magnetic separation) and the magnetic part of coarse slag have been mixed in order to evaluate the possibility of pelletizing. The remaining non-magnetic coarse slag needs to be tested to prove the suitability for the possible reuse as fertiliser.

Model Development

Heuristic models have been developed in order to represent in detail the pre-tested slag treatment, allowing evaluating the process behaviour in different operating scenarios. In this way, useful guidelines have been obtained about hypothetical treatment improvements, to obtain slag features that better match with reuse

suitability.

The model can be used to simulate different case studies, varying BOF slag qualities (chemical and mineralogical composition, particle size distribution, etc.) and operating conditions of treatment units, as simultaneous, auxiliary and complementary support for lab tests instead of executing plant on-line applications.

The outputs, i.e. slag fractions characteristics, can be analysed in order to evaluate possible reuse feasibility as raw materials in other contexts.

The developed Excel-based model includes sub-models related to the main stages of the proposed BOF slag treatment, as follows:

- cooling stage;
- grinding and sieving;
- magnetic separation.

Literature and real data obtained in the preliminary experimentation and lab tests are the required information for tuning and validation steps, which the models are based on.

Cooling Stage Sub-Model

BOF slags coming from the process are very hot ($T \approx 1600^\circ\text{C}$). A cooling stage is essential before any hypothetical treatment to avoid equipment damages.

The developed cooling sub-models is able to estimate the final slag temperature, taking into account each involved phenomena, in order to monitor time temperature and heat losses on the basis of the cooling time. Slag has been discretised in layers with computed temperatures.

Useful guidelines on energy contributions can be obtained, aimed at the

investigation on the eventual possibility of recovery.

The simplified Newton's law of cooling (Eq. 1) and the Fourier equation for conductivity (Eq. 2) are the foundations of the model (O' Sullivan 1990). The Newton's law is expressed as follows:

$$\frac{dT(t)}{dt} = -h(T(t) - T_a) \quad (1)$$

where h is the heat transfer coefficient in s^{-1} , $T(t)$ the temperature of the slag surface at the time t in K and T_a the temperature of environment in K.

In the Fourier equation:

$$\frac{dT}{dt} = \frac{k}{c \cdot \rho} \cdot \frac{d^2T}{dx^2} \quad (2)$$

T represents the temperature of the conductive layers of the slag in K unit, t the time in s, k the slag thermal conductivity in $J m^{-1} K^{-1} s^{-1}$, c the slag specific heat in $J kg^{-1} K^{-1}$, ρ the slag density in $kg m^{-3}$ and x the thickness of conductive layers in m.

The solution of Newton's law, related to the convection and radiation, can be expressed with respect to the temperature as in (Eq. 3):

$$T(t) = T_a + (T_{t-1} - T_a) \cdot e^{-ht} \quad (3)$$

where $T(t)$ is the temperature of the slag surface at the time t in K, T_{t-1} the temperature of the slag surface at the time $t-1$ in K, T_a the temperature of environment in K, h the heat transfer coefficient in s^{-1} and t the time in s.

On the other hand, hereinafter the discretized solution of Fourier equation in (Eq. 4) linked to the conduction:

$$T_{i,j} = T(x_i, t_j) = T_{i,j-1} + \frac{k}{c \cdot \rho} \cdot \frac{\Delta t^2}{\Delta x^2} \cdot (T_{i+1,j-1} - 2T_{i,j-1} + T_{i-1,j-1}) \quad (4)$$

where $T_{i,j}$ is the temperature in the layer i and at the time j in K, $T_{i,j-1}$ the temperature in the layer i at time $j-1$ in K, $T_{i+1,j-1}$ the temperature in the layer $i+1$ at

time $j-1$ in K, $T_{i-1,j-1}$ the temperature in the layer $i-1$ at time $j-1$ in K, k the slag thermal conductivity in $\text{J m}^{-1} \text{K}^{-1} \text{s}^{-1}$, c the slag specific heat in $\text{J kg}^{-1} \text{K}^{-1}$, ρ the slag density in kg m^{-3} , Δt the magnitude of discretized time period in s and Δx the thickness of each conductive layer in internal fraction of slag in m.

The model is iterative: at each time step, the temperature of the external layer is computed (Eq. 3) by the evaluation of global heat transfer coefficient (Eq. 7) coming from the calculation of the convective/conductive (Eq. 5) and radiant heat transfer coefficients (Eq. 6):

$$h_{\text{conv}/\text{cond}} = \frac{k \cdot S}{F_{\text{ext}} \cdot c \cdot \delta} \quad (5)$$

where $h_{\text{conv}/\text{cond}}$ is the convective-conductive heat transfer coefficient in s^{-1} , k the air thermal conductivity in $\text{J m}^{-1} \text{K}^{-1} \text{s}^{-1}$, S the external area of slag heap in m^2 , F_{ext} the mass of slag external radiant layer in kg, c the slag specific heat in $\text{J kg}^{-1} \text{K}^{-1}$ and δ the thickness of the conductive layer in external fraction of slag in m;

$$h_{\text{rad}_i} = \frac{S}{F_{\text{ext}} \cdot c} \cdot \varepsilon \cdot \sigma \cdot \left(\left(\frac{T_{i-1} + T_i}{2} \right)^2 + T_a^2 \right) \cdot \left(\frac{T_{i-1} + T_i}{2} + T_a \right) \quad (6)$$

where h_{rad} is the radiative heat transfer coefficient in s^{-1} , S the external area of slag heap in m^2 , F_{ext} the mass of slag external radiant layer in kg, c the slag specific heat in $\text{J kg}^{-1} \text{K}^{-1}$, ε the slag emissivity, σ the Stefan-Boltzmann constant in $\text{W m}^{-2} \text{K}^{-4}$, T_{i-1} the temperature of the slag surface at time t_{i-1} in K, T_i the temperature of the slag surface at time t_i in K and T_a the temperature of environment in K;

$$h = h_{\text{rad}} + h_{\text{conv}/\text{cond}} \quad (7)$$

where h is the global heat transfer coefficient in s^{-1} , h_{rad} the radiative heat transfer coefficient in s^{-1} and $h_{\text{conv}/\text{cond}}$ the convective-conductive heat transfer coefficient in s^{-1} .

On the other hand, the model estimates conductive heat transfer coefficient and the

temperature value of each internal conductive layer of the BOF slag on the basis of Fourier equation (Eq. 4).

To summarize, the global mass of residue is preliminary divided in several layers. Then, given an initial hot slag temperature, atmospheric temperature and a user specified cooling time, the model gives the external slag temperature and the internal core ones as outputs. Heat losses are also estimated by the model, as in Table 6.

The height of slag heap is an approximate value but fundamental for the cooling model, which main sheet is shown in Fig.4.

Table 6. Input and Output of Cooling Stage Model.

ID	Variables	Unit	Type
F	Inlet mass	kg	IN
T _{in}	Initial slag temperature	°C	IN
T _a	Atmospheric temperature	°C	IN
h	Height of slag heap	m	IN
t	Cooling time	min	IN
PM	Slag mean molar weight	g mol ⁻¹	REF
rho	Slag density	kg m ⁻³	REF
ε	Slag emissivity		REF
c	Slag specific heat	J mol ⁻¹ K ⁻¹	REF
k _{slag}	Slag conductivity	J mol ⁻¹ K ⁻¹ s ⁻¹	REF
K	Air thermal conductivity	J mol ⁻¹ K ⁻¹ s ⁻¹	REF
σ	Stefan-Boltzmann constant	W m ⁻² K ⁻⁴	REF
δ	Thickness of the conductive layer in external fraction of slag	m	REF
s	Thickness of each conductive layer in internal fraction of slag	m	REF
T _{core}	Final temperature of core slag	°C	OUT
T _{ext}	Final temperature of external slag	°C	OUT
Q _{loss}	Heat Losses	GJ	OUT

INPUT VARIABLES				CALCULATED VARIABLES			
F	kg	2000000,00	Slag mass	Tin	K	1873,15	Initial slag temperature
Tin	°C	1600,00	Initial slag temperature	Ta	K	298,15	Ambient temperature
Ta	°C	25,00	Ambient temperature	V	m ³	606,06	Slag Volume
h	m	2,00	Height of slag heap	L	m	17,41	Length of slag heap
t	min	1440,00	Cooling time	S	m ²	442,29	External area of slag heap
				t	s	86400,00	Cooling time
REFERENCE AND AUXILIARY DATA				c	J/(kg*K)	328,02	Slag specific heat
				Vrad	m ³	43,46	Volume of the external radiant layer of the slag
PM	g/mol	1,82E+02	Mean molar weight of slag	Fext	kg	143407,88	Mass of the external radiant layer of the slag
rho	kg/m ³	3,30E+03	Slag density	n	-	9,00	Maximum number of conductive layers in internal part of slag
ε	-	7,50E-01	Slag emissivity				
c	J/(mol*K)	5,97E+01	Slag specific heat				
kslag	J/(m*K*s)	1,50E+00	Slag conductivity	OUTPUT VARIABLES			
K	J/(m*K*s)	1,00E-02	Air thermal conductivity				
σ	W/(m ² *K ⁴)	5,68E-08	Stefan-Boltzmann constant	Tcore	°C	920,24	Final temperature of core slag
δ	m	5,00E-03	Thickness of the conductive layer in external fraction of slag	Text	°C	25,00	Final temperature of external slag
s	m	0,10	Thickness of each conductive layer in internal fraction of slag	Qloss	GJ	488,07	Heat Losses

Figure4. Main sheet of Cooling stage model.

Grinding and Sieving Sub-Model

The BOF slag reuse requires a grinding and sieving step. Also for this step, a sub-model has been developed, according to real (e.g. SEM, XRD and XRF analyses as in *BOF slag characterization*) and literature data related to minerals and oxides, which concentrations have to be specified as inputs: larnite, srebrodolskite, wuestite, magnetite, magnesiowuestite, periclase, Fe(0), Cr₂O₃, MnO₂, P₂O₅, TiO₂, K₂O and PbO.

In the case of not-normalized analyses data, the model starts an internal computation of normalization. The initial particle size distribution of the slag is one of the required fundamental information for the correct operation of the model (Table 7).

Table 7. Input of Grinding and sieving model.

ID	Variables	Unit	Type
F	Inlet mass	kg	IN
-	Slag composition	% wt	IN
PSD	Particle Size Distribution	% wt	IN
-	Grinding grade efficiency		AUX
-	Distribution efficiency		AUX

The main sheet of the proposed model is shown in Fig.5.

A heuristic approach for the grindability of a specific mineral has been considered: particle size and grinding grade and distribution efficiencies are specified and fixed, based on collected tenacity and hardness (Mohs scale) values and work index of each slag compounds (Mindat, Mineral Data Publishing 2001-2005, Tsakalis).

A global overview for the model operating principle can be described as follows: starting from an initial slag composition and PSD, the model uses fixed grinding grade and distribution efficiencies respectively to reduce the BOF slag size by specific factors, allocating each fraction in the relative partition of the new particle size distribution.

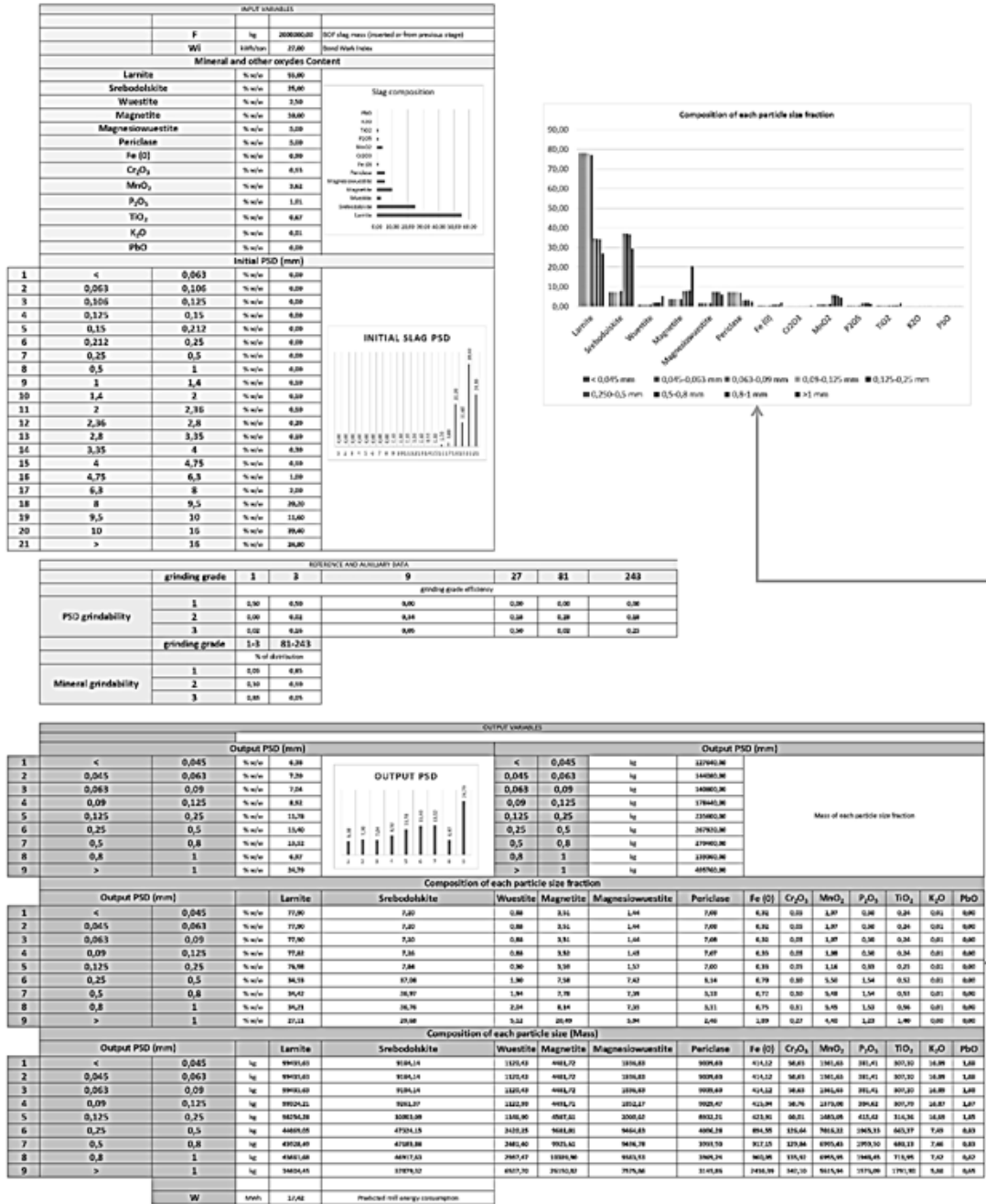


Figure 5. Main sheet of Grinding and sieving model.

The composition of each fraction is provided, as shown in Figure 5. The model gives also an estimation of mill energy consumption based on Bond's law of comminution(Saeidi et al. 2013, Venkateswaran 2007):

$$W = 10W_i \cdot \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right) \quad (8)$$

where W is the predicted mill energy consumption in kWh ton⁻¹, W_i the work index in kWh ton⁻¹, P_{80} the 80% passing size in μm of product and F_{80} the 80% passing size in μm of feed.

The outputs of the model are listed in the Table 8.

Table 8. Output of Grinding and sieving model.

Variables	Unit
Output PSD (fraction)	% wt
Output PSD (mass)	kg
Composition of each particle size fraction	% wt
Mass of each particle size fraction	kg

Magnetic Separation Sub-Model

Magnetic separation is the final treatment stage to separate from BOF slag a magnetic and iron rich fraction, potentially suitable for sintering process, and a non-magnetic fraction.

Fig. 6 highlights the third sub-model related to this treatment.

As in the previous grinding and sieving model, the composition of BOF slag in terms of common minerals and oxides are input for the model.

Literature information about magnetic properties of slag compounds have been used to estimate separation efficiencies between magnetic and non-magnetic fractions(Mindat, Mineral Data Publishing 2001-2005).

Model outputs, shown in Table 9 together with inputs, are the amount and mass compositions of magnetic and non-magnetic fractions from fixed efficiencies.

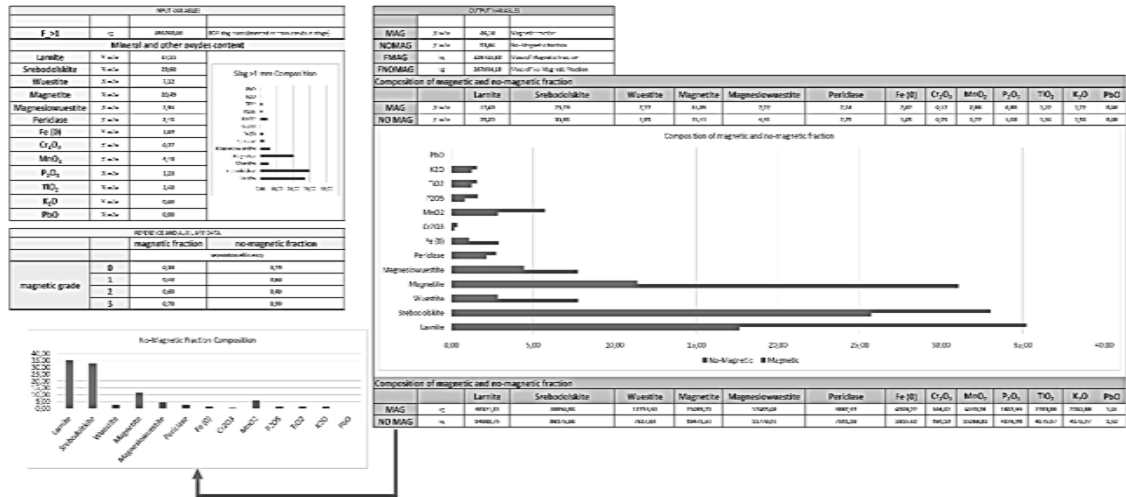


Figure 6. Main sheet of Magnetic separation model.

Table 9. Input and Output of Magnetic Separation model.

ID	Variables	Unit	Type
F	Inlet mass	kg	IN
-	Slag composition	% wt	IN
-	Magnetic separation efficiency	-	AUX
MAG	Magnetic fraction	% wt	OUT
NOMAG	Non-Magnetic fraction	% wt	OUT
FMAG	Magnetic fraction mass	kg	OUT
FNOMAG	Non-Magnetic fraction mass	kg	OUT
-	Composition of magnetic fraction	% wt	OUT
-	Composition of magnetic fraction (mass)	kg	OUT
-	Composition of non-magnetic fraction	% wt	OUT
-	Composition of non-magnetic fraction (mass)	kg	OUT

Results and discussion

Case Studies simulation

The developed models are useful to analyse the proposed treatment behaviour with different quality of BOF slag or under different operating conditions in order to obtain final slag features to reinforce/attenuate the hypothesis of the internal or external reuse and recycle.

Each described sub-model of the whole treatment process has been tested for one case study, presented hereinafter regarding one kind of BOF slag quality: initial models outputs were found to be similar with data from preliminary lab tests.

The initial composition and particle size distribution of the considered BOF slag are shown respectively in Figure 7 and in Table 10. Figure 7 highlights model normalization on input data.

In Table 11 the inserted values for the inputs are listed.

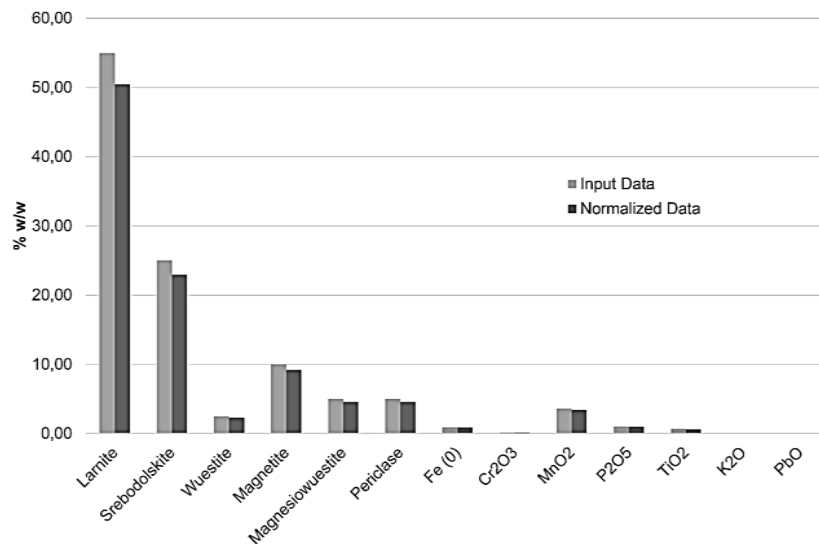


Figure 7. BOF slag initial composition.

Table 10. BOF slag initial PSD.

mm	mm	% wt
<	0.063	0.00
0.063	0.106	0.00
0.106	0.125	0.00
0.125	0.15	0.00
0.15	0.212	0.00
0.212	0.25	0.00
0.25	0.5	0.00
0.5	1	0.00
1	1.4	0.10
1.4	2	0.10
2	2.36	0.10
2.36	2.8	0.20
2.8	3.35	0.10
3.35	4	0.30
4	4.75	0.10
4.75	6.3	1
6.3	8	2
8	9.5	20.20
9.5	10	11.60
10	16	39.40
>	16	24.80

Table 11. Model global input.

Input Data	Unit	Value
Mass of the slag to be treated	t	2000
Initial slag temperature	°C	1600
Atmospheric temperature	°C	25
Initial slag PSD	% wt	Table 10
Slag composition	%wt	Figure 7

For the first stage a cooling time of 24 hours at atmospheric temperature and pressure has been considered, obtaining an external BOF temperature of 25°C, according to real data. The model provides also a temperature value of about 920° C for the internal core of the slag and heat losses of about 488 GJ: possibilities for

energy recovery can be evaluated.

The results obtained after grinding and sieving steps are shown in Table 12 and Figure 8, respectively the PSD of treated slag after grinding and the composition of each particle size fraction.

Table 12. BOF slag final PSD.

mm	mm	% wt
<	0.045	6.38
0.045	0.063	7.20
0.063	0.09	7.04
0.09	0.125	8.92
0.125	0.25	11.78
0.25	0.5	13.40
0.5	0.8	13.52
0.8	1	6.97
>	1	24.79

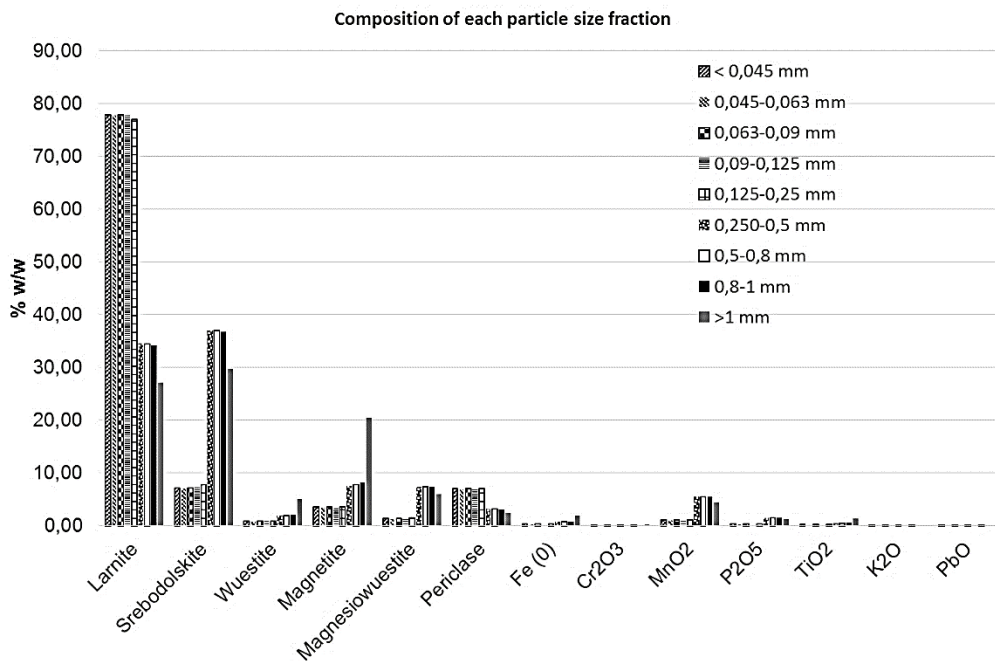


Figure 8. Composition of each particle size fraction of slag after grinding and sieving.

It is clear that fractions with PSD lower than 0.25 mm are richer in calcium compounds and poorer in ferrous compounds if compared with the other bigger fractions, richer in phosphorus. An estimated mill energy of about 17,5 MWh are necessary to grind the considered mass of slag.

According to the proposed global treatment, only the coarse fraction is fed to the magnetic separation.

The sub-model for this step divides the coarse slag in the following fractions:

- 46 % wt. of magnetic fraction;
- 54 % wt. of non-magnetic fraction.

The Figure 9 compares the composition of the two obtained fractions: as expected the non-magnetic portion appears suitable as fertiliser because of its higher content in calcium and phosphorus. On the other hand, the magnetic coarse fraction is richer in ferrous compounds and so hypothetically suitable to be fed in sinter plant.

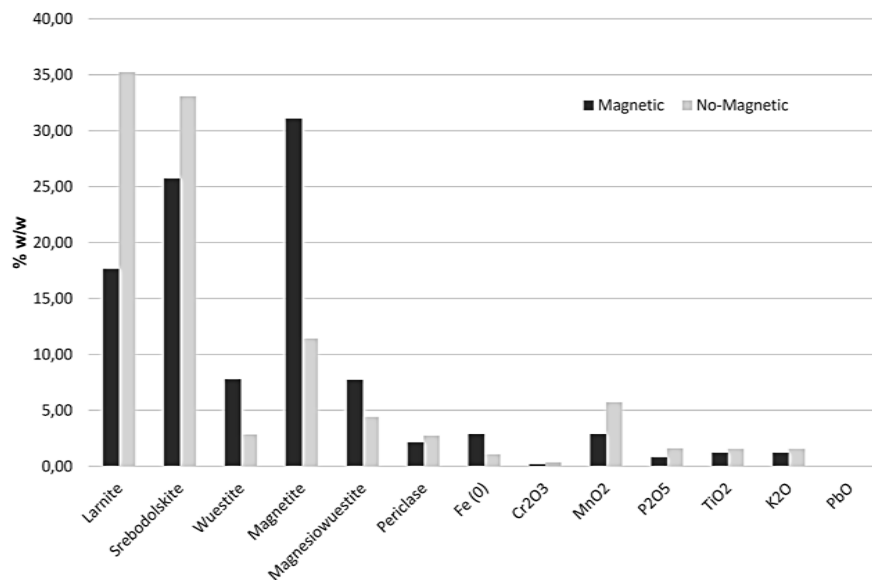


Figure 9. Composition of magnetic and non-magnetic coarse fraction of BOF slag.

Feed to pelletizing unit is finally obtained by mixing the magnetic fraction obtained in this step with the previous separated fine portion of the BOF slag, with an evaluated composition shown in Figure 10. The content in larnite (calcium compound) is not negligible and for this reason, a better separation could result in a higher amount of slag to be reused as fertiliser and in a fraction with higher iron content, more suitable for the sinter plant.

Investigation on an additional magnetic separation including slag finer fraction can be investigated to increase the separation between ferrous and non-ferrous compounds before the final mixing stage.

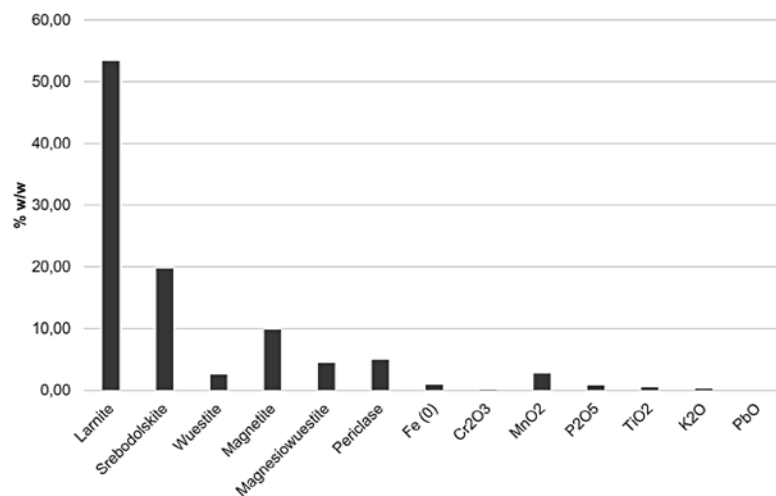


Figure 9. Composition of slag fraction to pelletize.

The simulation results reinforce the hypothesis of the possibilities of treated slag reuse as fertiliser and suggest some treatment modifications to improve the

separation efficiency between magnetic and non-magnetic materials.

Conclusion

A BOF slag recovery option has been investigated by combining experimental data collection and process simulation. The presented Excel-based model represents each stage of the selected BOF slag treatment process, according to ILVA tests. Model, such as each contained sub-model, can be used to test treatment behaviour with different slag qualities and treatments operating conditions. Simulation results are similar to experimental and lab test data for the analysed case study.

The obtained final fractions have features that fit with requirements for reuse as fertiliser and pellettization operations, with adjustments in magnetic separation operation.

Results show a preliminary proof of possibility for BOF slag reuse, encouraging for further studies and investigations.

Acknowledgments

The work described in the present paper has been developed within the projects entitled "Efficient use of resources in steel plants through process integration" (Contract No. RFSR-CT-2012-00039) and "Removal of Phosphorus from BOF-slag" (RFSR-CT-2013-0032) and that have received funding from the Research Fund for Coal and Steel of the European Union. The sole responsibility of the issues treated in the present paper lies with the authors; the Commission is not responsible for any use that may be made of the information contained therein.

References

Birat, J.-P. (2009) Steel and CO₂–the ULCOS program, CCS and mineral carbonation using steelmaking slag. Proceedings of the 1st International Slag Valorization Symposium, pp. 6-7.

Branca, T.A., Colla, V., Valentini, R. (2009) A way to reduce environmental impact of ladle furnace slag, *Ironmaking & Steelmaking*, 36, 597-602.

Branca, T.A., Pistocchi, C., Colla, V., Ragaglini, G., Amato, A., Tozzini, C., Mudersbach, D., Morillon, A., Rex, M., Romaniello, L. (2014) Investigation of (BOF) Converter slag use for agriculture in Europe, *Metallurgical Research & Technology*, 111, 155-167.

Das, B., Prakash, S., Reddy, P., Misra, V. (2007) An overview of utilization of slag and sludge from steel industries, *Resources, conservation and recycling*, 50, 40-57.

Dippenaar, R. (2005) Industrial uses of slag (the use and re-use of iron and steelmaking slags), *Ironmaking & Steelmaking*, 32, 35-46.

E. Commission, Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain directives (Waste framework directive, R1 formula in footnote of attachment II): <http://eur-lex.europa.eu/LexUriServ.do>, (2008).

Jankovic, A., Dundar, H., Mehta, R. (2010) Relationships between comminution

energy and product size for a magnetite ore, *Journal of the South African Institute of Mining & Metallurgy*, 110.3, 141.

Larsson, M., Wang, C., Dahl, J., Wedholm, A., Samuelsson, C., Magnusson, M., Lampinen, H.O, Su, F., Grip, C.E. (2006) Improved energy and material efficiency using new tools for global optimisation of residue material flows, *International journal of green energy*, 3, 127-137.

Ma, N., Houser, J.B. (2014) Recycling of steelmaking slag fines by weak magnetic separation coupled with selective particle size screening, *Journal of Cleaner Production*, 82, 221-231.

Matino, I., Alcamisi, E., Porzio, G.F., Colla, V., Romaniello, L. (2014) Modelling of oily millscale and sludge treatment process for improved by-product recovery and waste minimization in steel industry, in: 1st International Process Integration Forum for the Steel Industry, Swerea MEFOS, 2014.

Mindat:<http://www.mindat.org/>

Mineral Data Publishing v.1,v.1.2 (2001-2005).

O'Sullivan, C.T. (1990) Newton's law of cooling - A critical assessment, *American Journal of Physics*, 58, 956.

Pistocchi, C., Ragolini, G., Branca, T.A., Bonari, E., Colla, V. (2012) Use of BOF steel slag in agriculture: column test evaluation of effects on alkaline soils and drainage water. Proceedings of the 7th Conference on Sustainable Development of Energy, Water and Environment System, Faculty of Mechanical Engineering and Naval Architecture.

Proctor, D., Fehling, K., Shay, E., Wittenborn, J., Green, J., Avent, C., Bigham, R., Connolly, M., Lee, B., Shepker, T. (2000) Physical and chemical characteristics of blast furnace, basic oxygen furnace, and electric arc furnace steel industry slags, *Environmental Science & Technology*, 34, 1576-1582.

Saeidi, N., Azizi, D., Noaparast, M., Aslani, S., Ramadi, R. (2013) A developed approach based on grinding time to determine ore comminution properties, *Journal of Mining and Environment*, 4.2, 105-112.

The European Slag Association (2012), Position Paper on the Status of Ferrous Slag, complying with the Waste Framework Directive (Articles 5/6).

Tsakalakis, K. G., Bond work index tables (w_i) from various sources.

Venkateswaran, D., Sharma, D., Muhmood, L., Vitta, S. (2007) Treatment and characterisation of electric arc furnace (EAF) slag for its effective utilisation in cementitious products.

Wang, D., Jiang, M., Liu, C., Min, Y., Cui, Y., Liu, J., Zhang, Y. (2012) Enrichment of Fe-Containing Phases and Recovery of Iron and Its Oxides by Magnetic Separation from BOF Slags, steel research international, 83, 189-196.

World Steel Association (2010), Steel Industry By-Products - Project group report 2007-2009.

World Steel Association: <https://www.worldsteel.org/>