

RECYCLING OF LF-WHITE SLAG

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Over the last few years technologies of the plants dedicated to recycle of ladle slag have been improved. The type of recycling evaluated in the present study mainly consists in the reuse of the ladle slag and refractory, injecting them into the Electric Arc Furnace. The recycling of ladle slag can permit to achieve interesting advantageous results: decreasing the amount of dumped material, the cost of EAF fluxes and improve the slag foaminess.

KEYWORDS: steel making, ecology, decarburation, recycling, slag, steel

INTRODUCTION

Environment is becoming a key issue for the Steel Industry. Over the last few years technologies of the plants dedicated to recycle of ladle slag have been improved. The most critical environmental aspect seems to be related with the formation of the powder principally due to the high content of $2\text{CaO}\cdot\text{SiO}_2$ (C2S) which undergoes an allotropic solid phase transition (that occurs when the temperature went down to 500°C) from β phase to γ phase^{1,2,3}. C2S can be present in the ladle slag in different phases: α , α_H , α' , β , γ . The phase α -C2S is stable at very high temperatures. During the cooling down of the ladle slag it changes to β -C2S at 630°C , then transforms to γ -C2S at temperatures lower than 500°C . (Fig. 1)

The conversion β - γ is accompanied by 10% volume increase (from ~ 56 to $\sim 62 \cdot 10^{-6} \text{ m}^3/\text{mol}$) and results in the matrix shattering into powder because of their different crystal structures and density¹⁷. Thus, in a lot of steelmaking plants the possibility to operate the recycling process has been carefully evaluated in order to

decrease the environmental impact and to avoid the use of dumping ground for special wastes.

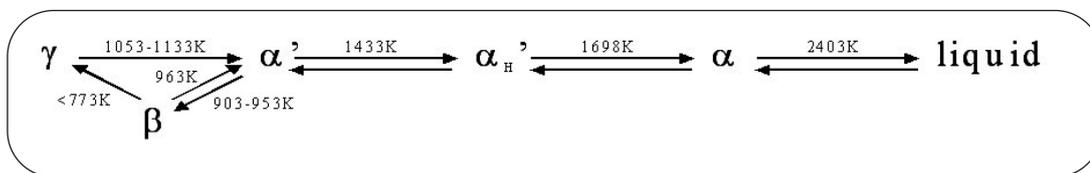
The type of recycling evaluated in the present study mainly consists in the reuse of the ladle slag and refractory, injecting them into the Electric Arc Furnace. The recycling of ladle slag can permit to achieve interesting advantageous results: decreasing the amount of dumped material, the cost of EAF fluxes and improve the slag foaminess.

Nowadays, in the northern of Italy two industrial plants have adopted the presented technique of recycling for the ladle slags. After the injection of recycled material in the EAF a significant and favorable variation of slag foaminess has been observed. The amount of the recycled material injected in the Electric Arc Furnace is performed on the basis of a balance obtained through a thermodynamic model which aims at granting a final EAF slag formulation which can be classified as non-dangerous waste.

One of the goals of the present work is to establish the amount of recycled material to be injected in the EAF in order to improve the slag foaminess, to reach a complete reuse of the ladle slag and to grant a correct mix of the chemical species avoiding the formation of fine powders.

The estimation of the physical-chemical properties of the slag and its rela-

tion with the foaminess of EAF slag have been investigated. In agreement with the data contained in literature^{4,5} the slag foaminess depends on the effective slag viscosity which is ruled by the fraction of solid phase contained in the slag. A thermodynamic model based on the quasi-chemical approach has been developed to predict the amount of the slag solid fraction and its forecasting has been compared with the experimental data obtained through chemical analysis performed through SEM-EDS facilities. This tool can be useful to structure the correct formulation of the slag through the addition of the recycled LF material in order to optimize the foaminess behavior and permit to achieve great economic advantages.



▲
Fig. 1

Experimentally measured phase transition temperatures for $2\text{CaO}\cdot\text{SiO}_2$ polymorphs.

Temperature di transizione tra le diverse fasi allotropiche di $2\text{CaO}\cdot\text{SiO}_2$, misurate sperimentalmente.

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THERMODYNAMIC MODEL

A thermodynamic model has been developed in order to calculate the solid fraction and the effective viscosity in EAF slag. The following approach is based on the quasi-chemical theory proposed by Pelton and Blander^{6,7)} which has successfully applied also for the most modern investigation about slag and fluxes behavior^{8,9,10)}. The model is applied to predict the properties of the multi-component ionic systems (CaO-MgO-Al₂O₃-SiO₂-MnO-FeO_x) containing binaries and ternaries subsystems like (CaO-MgO-Al₂O₃, CaO-Al₂O₃-SiO₂, SiO₂-MnO-FeO_x, etc.). The quasi-chemical approach represents a theoretical tool for treating the non-ideal ionic solution. The model takes into account the short order interaction among the different chemical species considering the entropy excess as a consequence of mixing. This formalism treats the pairs as fractions of the associated atoms. The name "quasi-chemical" comes from the idea on which is based the theory, because it assumes that the creation of a pair is possible between the nearest neighbor ions. The bond between two different ions is described like a chemical reaction:



The total number of bonds generated from a generic *i*-atom is $Z_i X_i$, where Z_i represents nearest neighbor coordination number of the generic *i*-atom or molecule and X_i represents the molar fraction of generic *i*-atoms or molecules. Thus, the mass balance equation can be written as:

$$\begin{aligned} Z_1 X_1 &= 2n_{11} + n_{12} \\ Z_2 X_2 &= 2n_{22} + n_{12} \end{aligned} \quad (2)$$

It is possible to define an equivalent fraction of bonds emanating from a single chemical species through:

$$Y_i = 1 - Y_j = \frac{Z_j X_j}{Z_i X_i + Z_j X_j} \quad (3)$$

The molar enthalpy and the excess entropy of mixing are assumed to be directly related to the fraction of 1-2 pairs according to:

$$\Delta h_m - T \Delta s^E = \frac{Z_1 X_1 + Z_2 X_2}{2} \cdot \frac{X_{12}}{2} \cdot \Delta g \quad (4)$$

At first approximation, the expression for the configurational entropy of mixing can be derived from the one-dimensional Ising model^{11,12)}:

$$\begin{aligned} T \Delta S_m^{config} &= -RT(X_1 \ln X_1 + X_2 \ln X_2) - \\ & - \left[\frac{RT}{2} (Z_1 X_1 + Z_2 X_2) \right] \left[X_{11} \ln \left(\frac{X_{11}}{Y_1^2} \right) + X_{22} \ln \left(\frac{X_{22}}{Y_2^2} \right) + X_{12} \ln \left(\frac{X_{12}}{2Y_1 Y_2} \right) \right] \end{aligned} \quad (5)$$

The equilibrium of considered "quasi-chemical" reaction is calculated by minimizing (5) with respect to X_{12} variable. This computational derivation turns out a "quasi-chemical" equilibrium constant for the reaction:

$$\frac{X_{12}^2}{X_{11} X_{22}} = 4 \cdot \exp \left(- \frac{\Delta g_{12}}{RT} \right) \quad (6)$$

In order to make (6) explicit in X_{12} :

$$X_{12}^2 (4 - A) + X_{12} \cdot [2A(Y_1 + Y_2)] - (A \cdot Y_1 Y_2) = 0 \quad (7)$$

where A is:

$$A = \left[4 \cdot \exp \left(- \frac{\Delta g}{RT} \right) \right] \quad (8)$$

the solution of equation (7) gives the amount of mixed bonds present within the considered solution.

In CaO - SiO₂ - Al₂O₃ - MgO - MnO - FeO_x multi-component system the formation of binary and ternary complex compounds can reasonably be expected. The possible compounds

Complex oxides selected			T _{melting} K	T _{melting} °C
3CaO·Al ₂ O ₃		C3A	1913	1640
3CaO·2SiO ₂	Kilchoanite (Rankinite)	C3S2	1733	1460
3CaO·SiO ₂	Hatrunite	C3S	2403	2130
CaO·Al ₂ O ₃	Grossite	CA	1881	1608
12CaO·7Al ₂ O ₃	Mayenite	C12A7	1653	1380
CaO·2Al ₂ O ₃	Wollastonite	CA2	2043	1770
SiO ₂ ·CaO	Larnite (lime-olivine)	CS	1821	1548
2CaO·SiO ₂	Xenolite	C2S	2463	2190
Al ₂ O ₃ ·2SiO ₂	Mullite	AS2	2153	1880
3Al ₂ O ₃ ·2SiO ₂	Andalusite (Kayanite, Sillmanite)	A3S2	2193	1920
Al ₂ O ₃ ·SiO ₂		AS2	2130	1857
2MgO·SiO ₂	Fosterite	M2S	2161	1888
MgO·Al ₂ O ₃	Spinello	MA	2408	2135
FeO _x ·MgO	MagnesioWustite	MW	2397	2124
MnO·Al ₂ O ₃		MnA	2053	1780
2MnO·SiO ₂	Tephorite	Mn2S	1673	1400
2CaO·2FeO _x	Srebrodolskite	C2E2	1660	1387

▲
Tab. 1

Complex oxide considered in the thermodynamic model.

Ossidi complessi considerati nel modello termodinamico.

which can be formed are selected on the basis of the information contained in the related phase diagrams^{13,14)}. In Tab. 1 are summarized the expected complex oxides.

On the basis of the formation of pairs by short order interaction it is possible to describe the formation of complex oxide like a chemical reaction. The driving force for a reaction can be obtained by taking into account the free energy change for the chemical reaction considered:

$$\Delta G_{i,formation} = Z_i \cdot \bar{G}_{i,product} - \sum (Z_j \cdot \bar{G}_{j,reactant}) \quad (9)$$

On the basis of the value of the Gibbs free energy associated with the generic species, the equilibrium constant value K for the formation of pairs associated with the generic *i*-species can be obtained through:

$$K = \exp \left(\frac{\Delta G_{i,formation}}{RT} \right) \quad (10)$$

Within compounds formed by the coupling among ionic species characterized by different stoichiometric ratios the mixing effect among different pairs and the solubility constant of the reaction must be corrected by a factor dependent on ion molar fraction and ion valence number:

$$K_{\phi} = 4 \cdot K \cdot \left\{ \gamma_i \left[\frac{\xi_i X_i}{\xi_i X_i + \xi_j X_j} \right]^{(\xi_{i,j})} \cdot \gamma_j \left[\frac{\xi_j X_j}{\xi_i X_i + \xi_j X_j} \right]^{(\xi_{j,i})} \right\} \quad (11)$$

where ξ_i represents the coordination number of the generic *i*-cation within the oxide complex. The terms within the square brackets include the probability that the cations composing the complex oxides can meet themselves to form the complex molecules multiplied by the correspondent activity coefficients γ_i (11).

The activities of the ionic species (a_i, a_j) are obtained relating the interaction activity coefficient (ξ_{ij}) with the molar fraction of species (X_i):

$$a_i = \xi_{i,j} \cdot X_j \quad (12)$$

The correction terms among different ions (summarized in Tab. 2) are due to the chemical interaction of mixing effect.

Those terms are better considered by¹⁵⁾:

$$RT \ln \gamma_i = \sum_j \alpha_{ij} X_j^2 + \sum_k \sum_x (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) \cdot X_j \cdot X_k \quad (13)$$

The total amount of complex oxides is given by a mass balance. The quantity of ionic fraction involved in the formation of a complex oxide ($X_{(i)}$) is obtained multiplying, for each chemical formation reaction, the ionic fraction ($X_{(ij)}$) by the stoichiometric factor ($Z_{(ij)}$):

$$X'_i = X_{ij} \cdot Z_i \quad (14)$$

Relative linked pairs in complex oxides ($X'_{bounded,i}$) is given by free and bounded ionic fraction ratio featuring the solution:

$$X'_{bounded,i} = \frac{X_i}{X'_i} \quad (15)$$

The bounded ionic fraction in complex oxides ($X_{bounded,i}$) is obtained by ratio between relative free fraction ions ($X'_{free,i}$) and totally relative bounded fraction ions:

$$X_{bounded,i} = \frac{X'_{free,i}}{\sum_i X'_{bounded,i}} \quad (16)$$

And the free ionic fraction in complex oxides is given by a mass balance:

$$X_{free,i} = \frac{X_i}{(1 + \sum X_{bounded,i})} \quad (17)$$

Summing the results given by the reaction (7) - for all the considered complex oxides-it is possible to compute the total amount of complex species in the slag.

Through the comparison of the process temperature with the melting temperature for each complex oxide (Tab. 2) the total liquid and solid slag fraction are calculated (Tab. 3).

The solid fraction calculated is utilized to estimate the effective viscosity slag according to the well known relation⁹⁾:

$$\eta_e = \eta(1 - 1.35 \cdot \theta)^{-5/2} \quad (18)$$

EXPERIMENTAL INVESTIGATIONS AND DISCUSSION

The experimental investigation has been done at Stefana SpA steel plant. This location has been selected because in it there is one of the two existing and working white-slag recycling plants. The tests

were carried out during 52 taps similar in terms of work process, scrap, and kind of steel produced and they consisted in two different fundamental steps: characterization of EAF slag and measurement of the noise within EAF which is function of the slag performances. The main goal of the investigation is to perform a comparison among EAF slag foaminess proprieties in tap carried out with and without white slag recycling. Thus, in order to realize this comparison a half of taps was carried out with injection of recycled

Complex oxides			Oxide complex fraction
3CaO.Al ₂ O ₃		C3A	0,04%
3CaO.2SiO ₂	Kilchoanite (Rankinite)	C3S2	0,51%
3CaO.SiO ₂	Hatrurite	C3S	0,31%
CaO.Al ₂ O ₃	Grossite	CA	0,00%
12CaO.7Al ₂ O ₃	Mayenite	C12A7	7,03%
CaO.2Al ₂ O ₃		CA2	0,03%
SiO ₂ .CaO	Wollastonite	CS	0,06%
2CaO.SiO ₂	Larnite (lime-olivine)	C2S	0,35%
Al ₂ O ₃ .2SiO ₂	Xenolite	AS2	0,00%
3Al ₂ O ₃ .2SiO ₂	Mullite Andalusite	A3S2	0,00%
Al ₂ O ₃ .SiO ₂	(Kyanite, Sillmanite)	AS2	0,00%
2MgO.SiO ₂	Fosterite	M2S	0,05%
MgO.Al ₂ O ₃	Spinello	MA	0,07%
FeO _x .MgO	MagnesioWustite	MW	23,81%
MnO.Al ₂ O ₃		MnA	0,06%
2MnO.SiO ₂	Tephorite	Mn2S	0,93%
2CaO.2FeO _x	Srebrodolskite	C2E2	0,00%

▲ Tab. 3

Example of computed fraction of complex oxides for a (30% CaO, 15% SiO₂, 5% MgO, 11% Al₂O₃, 5% MnO, 29% FeO_x, other oxides residual) slag at the temperature of 1677°C
Esempio della frazione di ossidi complessi calcolati per la scoria (30% CaO, 15% SiO₂, 5% MgO, 11% Al₂O₃, 5% MnO, 29% FeO_x, altri residui ossidi) alla temperatura di 1677°C.

	Ca ²⁺	Mg ²⁺	Al ³⁺	Mn ²⁺	Si ⁴⁺	P ⁵⁺	Fe ²⁺	Fe ³⁺
Ca ²⁺		-100,42	-154,81	-92,05	-133,89	-251,04	-31,38	-95,81
Mg ²⁺	-100,42		-71,13	61,92	-66,94	-37,66	33,47	-2,93
Al ³⁺	-154,81	-71,13		-83,68	-127,61	-261,5	-41	-161,08
Mn ²⁺	-92,05	61,92	-83,68		-75,31	-84,94	7,11	-56,48
Si ⁴⁺	-133,89	-66,94	-27,61	-75,31		83,68	-41,84	32,64
P ⁵⁺	-251,04	-37,66	-261,5	-84,94	83,68		-31,38	14,64
Fe ²⁺	-31,38	33,47	-41	7,11	-41,84	-31,38		-18,66
Fe ³⁺	-95,81	-2,93	-161,08	-56,48	32,64	14,64	-18,66	

▲ Tab. 2

Table of the interaction coefficients between ions species.

Tabella dei coefficienti di interazione utilizzata per il calcolo delle attività delle specie ioniche.



▲
Fig. 2
Powdered white slag.
Scoria bianca polverizzata.

material and the other one half was performed through a traditional route does not involving slag recycling. The described procedure was used for sampling both furnace slags (EAF and LF) in order to define the properties of recycling material and the effect due to its injection in the EAF furnace.

Slag sampling was performed at the ending of EAF refining period during temperature measurements. The slag detached from the temperature bolt was taken. Such a procedure implies two advantages. The rapid cooling due to the little slag mass attached on the temperature bolt avoids excessive atmospheric slag contaminations. Moreover, the slag sampling during temperature measurement allows to obtain a precise reference about the bath and the slag temperature.

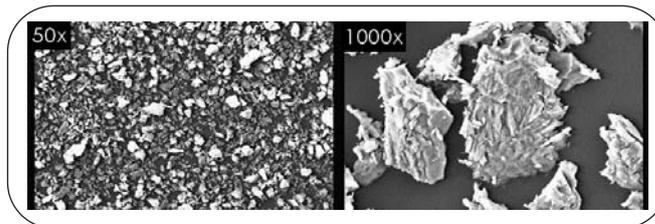
The samples were subsequently analyzed in the laboratory of Politecnico di Milano by a scanning electron microscope (SEM Zeiss EVO 50) equipped by a (EDS) probe. Chemical composition and morphological tests were performed.

LF (white) slag

From a chemical point of view, the injection of slag recycled from EAF (Fig. 2) increases the amount of the CaO and MgO already present within EAF favoring slag saturation with respect to these chemical species. 30 samples of injected white slags were analyzed and their average chemical composition is summarized in Tab. 4.

LF slag	%
CaO	42%
SiO ₂	21%
MgO	6%
Al ₂ O ₃	12%
MnO	4%
FeO _x	1%
Other oxides	6%
IB2	2,00
IB3	1,27
IB4	1,45

▲
Tab. 4
White slag average chemical composition.
Composizione chimica media della scoria bianca.



▲
Fig. 3
Samples prepared for powder X-ray diffraction (XRD) analysis.
Campioni di scoria preparati per la diffrazione a raggi X.

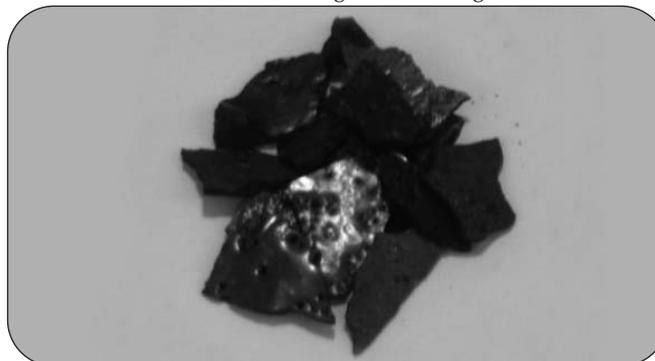
The recycle of LF slag influences also the physical characteristics of the foam. The excess of CaO and MgO promotes the formation of "second phase particles" (complex oxides) that are solid at the process temperatures. Those particles act like a sort of "foaminess modulator".

Before injection in EAF the ladle slag is purified from iron particles and its grain size was checked (Fig. 3).

By pneumatic transportation the powder is driven into the EAF via special powder injectors - the KT Powder Injectors by TENOVA¹⁶. The peculiar characteristics of the cooling system of these injecting lances permits their installation submerged into the slag line with maximum operational safety (this was tested on more than 250 lances operating worldwide for different types of injections, included Stefana SpA lances). The efficiency of powder injection into the slag is certainly nearly 100%, as the tip of the lance is right into the slag line. Actually, if the powder mix had been injected with a normal pipe out of the slag line, the EAF Dedusting System would have immediately suck the very fines particles, due to the delta pressure difference imposed between EAF and fumes duct. The use of a correct injector is one of the key success for this recycling process, because the injecting system has to assure the transfer to the slag of the whole amount of recycled slag, otherwise the computation performed for the designing of the desired slag loses their power.

The injection of solid particles results in three consequences:

- a mass effect lowering the FeO_x concentration and increasing the attitude to the formation of solid particles with consequent increase of the foam stability;
- a stabilizing effect - particles act like nucleation centers for complex oxides and for gas bubbles, thus giving a more stable emulsion with a greater amount of little bubbles;
- a growing effect acting on the particles, improving the kinetic bubble nucleation, thus increasing the foam slag formations.



▲
Fig. 4
EAF slag chips.
Scaglie della scoria proveniente dal forno elettrico ad arco.

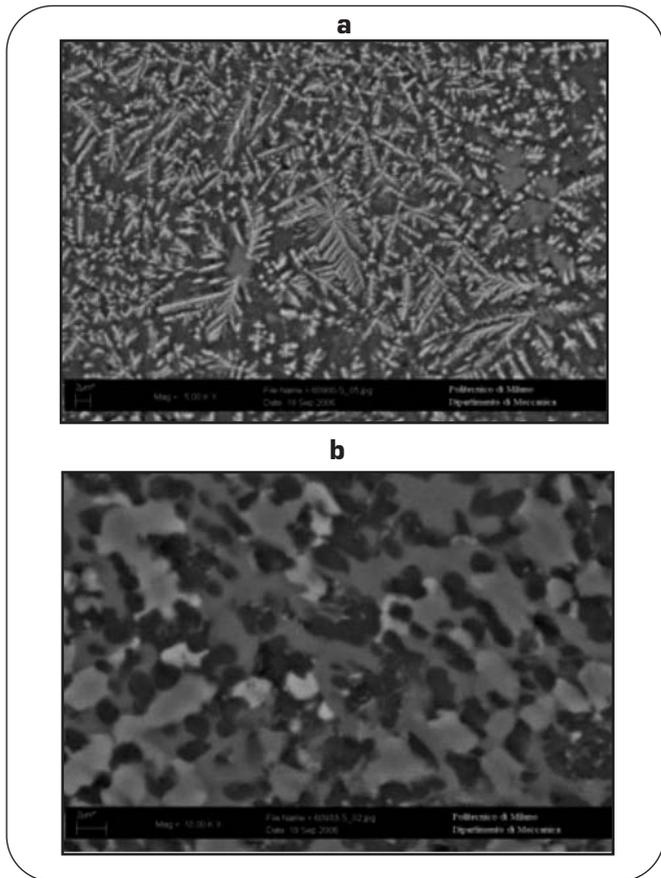


Fig. 5

EAF slag morphology with and without recycling of white slag.

Morfologia delle scorie osservate a partire da campioni prelevati nel forno elettrico ad arco in presenza ed assenza di riciclo della scoria bianca.

EAF slag

In order to compare EAF slag obtained in different taps with and without white slag recycling, morphological and chemical analysis were carried out on those materials.

EAF slag, due to the small amount of $2CaO \cdot SiO_2$ found in it, during its cooling does not form powder, thus assuming the form of little chips (Fig. 4).

The chips embedded in a conductive thermoplastic resin were polished and then examined. In Fig. 5 it is possible to observe the slag morphology. The image shows a slag sampled at the end of a tap led up after injection of white slag. The image shows a dendritic structure probably generated by a rapid cooling and by the high FeO_x concentration. On the other hand, cellular microstructure was found in the slag observed with recycling. This difference is a possible consequence of the lower FeO_x concentration and of the larger amount of nucleation centres in the slag. In fact the injection of cold powdered material in

	% MgO	% Al_2O_3	% SiO_2	% CaO	% MnO	% FeO_x
Without recycle	2,64%	10,09%	18,94%	32,01%	4,60%	31,72%
With recycle	3,94%	9,18%	17,13%	36,91%	5,34%	27,51%

Tab. 5

Average chemical composition of EAF slag.

Composizione chimica media della scoria del forno elettrico ad arco.

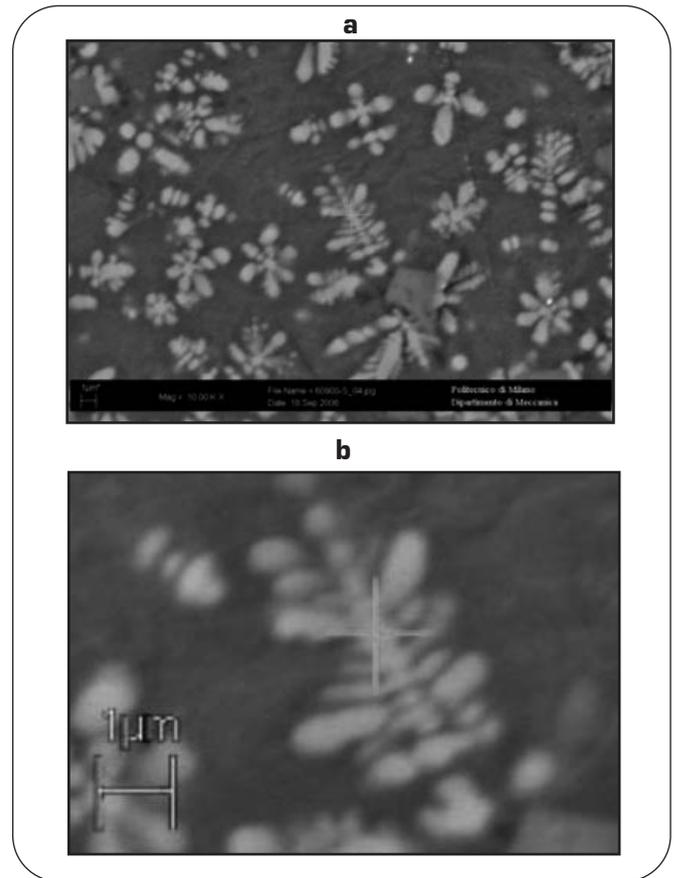


Fig. 6

EAF slag (without white recycled material), zoom on Magnesia.Wustite ($MgO \cdot FeO_x$) phase particle.

Particolare di una dendrite di Magnesia.Wustite osservata nella scoria del forno elettrico ad arco.

EAF causes the formation of a large number of nucleation sites on which CO bubble and complex oxides could be adsorbed and where they can grow.

Through SEM-EDS probe, chemical analysis of slag samples were performed. For each tap five measurements were done and the average measured values were assumed to be characteristic of EAF slag composition. In Tab. 5 the average chemical composition for all the sampled slags is summarized.

It is possible to observe that in EAF slag with recycling, not only MgO and CaO (main basic oxide) content grew but also FeO_x concentration significantly decreased. In this condition the basic refractories in EAF can be preserved and a lower Fe quantity in bath can become oxide, thus giving rise to important economic savings.

Thermodynamic model validation

The model forecasts the formation of complex oxides and identifies if they are present as solid or liquid phases as a function of the temperature and of the chemical composition in EAF introduced into the model as input data. In order to validate the thermodynamic model a chemical analysis on several little spots was realized. The analysis goal was to detect the complex oxides really grown in the slag and to compare this result with the computed results. Each revealed different phase in EAF slag was analyzed by SEM-EDS probe (an example is show in Fig. 6).

Chemical particle analysis					
MgO	Al ₂ O ₃	SiO ₂	CaO	MnO	FeO _x
9,07%	3,49%	8,09%	11,21%	9,26%	58,87%
Composition rate calculated					
$\frac{\text{CaO}}{\text{CaO} + \text{SiO}_2}$					
58,09					
Theoretical complex oxide composition					
FeO _x .MgO	MW	magnesiowustite	%FeO _x	%MgO	
			82	18	

▲
Tab. 6

Example of complex oxide analysis.

Esempio di analisi degli ossidi complessi.

Subsequently the measured data of chemical composition were compared with theoretical complex oxide composition (an example is reported in Tab. 6). Proceeding in this way it has been possible to determine which complex oxide has really grown during the metallurgical process. Comparing the complex oxide melting temperature with the one measured during the process permits to approximate the solid fraction in slag. Thus, according to E. Pretorius⁹⁾ it is possible to calculate the slag viscosity and then to define an index related to slag foaminess.

In the same way, considering in input also LF slag parameters, the model can calculate the influence given by injection of recycled material on the EAF slag foaminess. So a software able to produce reliable projection has been developed in order to optimize the slag foaminess and to give the amount of flux and LF white slag that must be charged in EAF to reach an optimal EAF slag composition.

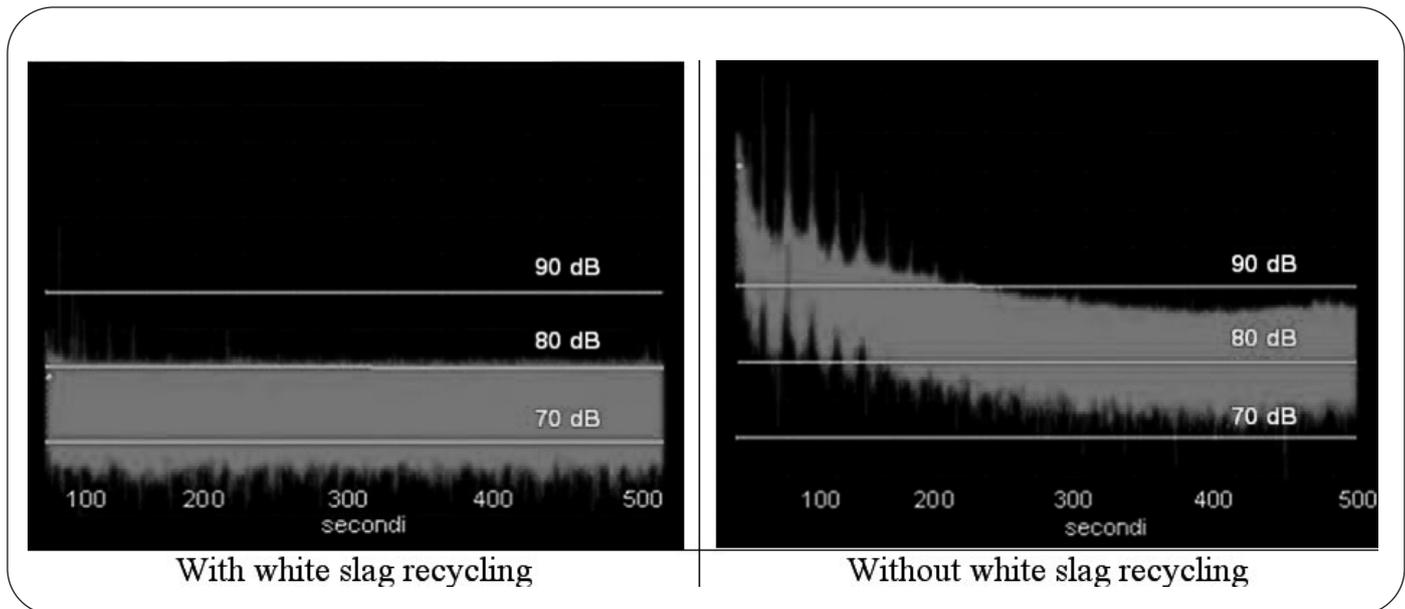
In Tab. 7 two "typical taps" carried out with and without the recycling of white slag has been performed in order to validate the model. The computational results seem to fit well with reality.

Phonometric measure

In order to evaluate the efficiency of EAF slag foaminess with and without white slag recycling the noise produced during the process was measured. As a consequence of the covering offered from the slag foam on the electric arc, process noise is reduced when slag foam increases. 32 taps were undergone the measurement procedure; 16 of those taps have been carried out with injection of recycled material. A digital phonometer Brüel & Kjær Mediator 2238 was used. Thanks to an AO 0408 wire it was linked with an acquisition system National Instruments, NI AT-MIO-16E-1. The signal was continuously acquired and recorded and the signal was analysed with Misure 5 software. In order to reduce the measurement errors the phonometer was fitted on a tripod and located inside the dog house (about 4 meters close to the furnace side) in a covered location so that the temperature (45°C), the depression wind and the dust could not damage the instrument. In order to capture all the significant noise the acquisition frequency was selected to be 5000 Hz. Because of the instrumental limits the maximum acquisition time was limited to 500s. The foaminess of the slag developing on the flat bath was considered and the measurement allows to observe carefully the changing for the slag foaminess.

On the basis of Fig. 7 it is possible to infer that when the recycled material is injected in the furnace, the EAF slag foaminess improves. In fact, the average noise is higher when recycled material is not injected (Tab. 8).

At the end of the scrap melting step the noise is higher than the one measured during the refining step. Transitory indicates that in the first measurement stage the slag does not foam yet; the slag starts foaming after



▲
Fig. 7

Spectrum of noise phonometric analysis in refining step with and without white slag recycling.

Spettro dell'analisi del rumore d'arco rilevato all'interno del forno in presenza ed in assenza di riciclo.

Complex oxides			Tap without recycle		Tap with recycle	
			Model expected	Really found	Model expected	Really found
3CaO.Al ₂ O ₃		C3A	yes	yes	yes	yes
3CaO.2SiO ₂	Kilchoanite (Rankinite)	C3S2	yes	yes	yes	yes
3CaO.SiO ₂	Hatrurite	C3S	yes	no	yes	yes
CaO.Al ₂ O ₃	Grossite	CA				
12CaO.7Al ₂ O ₃	Mayenite	C12A7	yes	yes	yes	yes
CaO.2Al ₂ O ₃	Wollastonite	CA2				
SiO ₂ .CaO	Larnite (lime-olivine)	CS				
2CaO.SiO ₂	Xenolite	C2S	yes	yes	yes	yes
Al ₂ O ₃ .2SiO ₂	Mullite	AS2				
3Al ₂ O ₃ .2SiO ₂	Andalusite (Kyanite, Sillmanite)	A3S2				
Al ₂ O ₃ .SiO ₂		AS2				
2MgO.SiO ₂	Fosterite	M2S				
MgO.Al ₂ O ₃	Spinello	MA				
FeO.MgO	MagnesioWustite	MW	yes	yes	yes	yes
MnO.Al ₂ O ₃		MnA				
2MnO.SiO ₂	Tephorite	Mn2S	yes	no	yes	yes
2CaO.2FeO _x	Srebrodolskite	C2E2				

trap a larger quantity of small CO bubbles.

CONCLUSIONS

In order to optimize slag foaminess a thermodynamic model based on "quasi-chemical" approach has been revealed to be efficient in order to optimize:

- slag chemical composition
- complex oxide formation in slag
- slag solid fraction
- optimal amount of flux in charge
- optimal amount of recycle material to inject.

On the basis of phonometric measurement the white slag recycle through injection in EAF has been revealed to improve EAF slag foaminess. Thus, metallurgical and economic advantages could be summarized in:

- better slag foaminess
- lower refractories consumption
- higher heat transfer to steel bath (with savings of electrical energy cost)
- savings in white slag dumping cost

▲
Tab. 7

Comparison between the expected and observed complex oxides present in EAF slag.

Confronto tra gli ossidi complessi teoricamente previsti e quelli osservati nella scoria del forno elettrico.

	With white slag recycle	Without white slag recycle	Difference
Average noise (dB)	73	82	82
Asymptotic noise (dB)	65	72	72

▲
Tab. 8

Noise level during refining step.

Rumore misurato durante lo studio di affinazione.

about 180-200 s. When recycling took place it was not possible to observe the transitory decreasing of noise and the average value of the noise intensity was significantly more contained. This indicates that through the injection of recycled material foam grows earlier and with higher volume.

Moreover, as already observed the asymptotic noise (average of the minimum noise measured) in case of recycling is 7dB lower than without it. So recycling of white slag not only promotes a better slag growth but also stabilizes it. Moreover, due to the greater amount of nucleation centres the slag structure is expected to be composed by a more viscous frame which has the attitude to

LIST OF SYMBOLS

X_{ii}	bond fraction between cation pair in solution
X_{ij}	mixed bond fraction between different ions in solution
Y_i	equivalent fraction of bond for ion pair
Z_i	nearest neighbor coordination number of i atoms
$X_{i,j}$	molar fraction of i,j atom
$(X'_{i,j})$	quantity of ionic fraction involved in the formation of a complex oxide
$(X'_{linked,i})$	relative linked pairs in complex oxides
$(X'_{free,i})$	relative free fraction ions
$(X_{linked,i})$	linked ionic fraction in complex oxides
$(X_{free,i})$	free ionic fraction in complex oxides
n_{ii}	number of simple bond in one mole of solution
n_{ij}	number of mixed bond in one mole of solution
ΔG	variation of the Gibbs free energy [J]
S^E	Excess entropy give by mixing [J]
Δh_m	variation of molar enthalpy [J]
Δg_m	variation of mixing energy on the system [J]
T	temperature [K]
R	universal constant of gas [R=8.314 kJ/mol-1K-1]
ξ_i	valence number of generic i ion
$a_{i,j}$	activity of i,j atom
η	viscosity of slag [Pas]
η_{eff}	effective viscosity of slag [Pas]
θ	solid fraction in slag
$Z_{i,j}$	stoichiometric factor

ABSTRACT

RICICLAGGIO DELLA SCORIA BIANCA DEL FORNO SIVIERA ALL'INTERNO DEL FORNO ELETTRICO AD ARCO

Parole chiave: siderurgia, ecologia, decarburazione, riciclaggio, scorie, acciaio

Le scorie bianche coinvolte nel processo di affinazione del forno siviera possono subire un processo di trasformazione allotropica del $2\text{CaO}\cdot\text{SiO}_2$ (Figura 1) al diminuire della temperatura. Questo fenomeno porta ad una progressiva polverizzazione della scoria che ne imporrebbe lo smaltimento in discarica. Le scorie bianche, oggetto dello studio, si presentavano in forma di scaglie finemente suddivise (Figura 3) e sono state sottoposte ad analisi chimica volta a determinarne i principali componenti, che sono stati poi considerati all'interno del modello termodinamico strutturato secondo l'approccio quasi-chimico (Tabella 1).

Nel modello termodinamico, che è stato utilizzato, l'interazione tra le specie ioniche considerate è stata realizzata attraverso l'applicazione di opportuni coefficienti di interazioni applicati per il calcolo delle attività (Tabella 2). Nella tabella 3 è indicato un esempio del risultato delle specie chimiche calcolate per una scoria caratteristica della marcia del forno elettrico. Durante l'osservazione sperimentale di 32 marce fusorie, in 16 di queste colate sono state riciclate scorie bianche caratterizzate dalla composizione chimica media mostrata in tabella 4; tali scorie sono state iniettate dopo opportuno processo di deferrizzazione all'interno del forno elettrico, portando a scorie caratterizzate dalla composizione chimica media mostrata in tabella 5, dove si può osservare la differenza rispetto a scorie che non hanno subito il pro-

cesso di iniezione della scoria bianca riciclata. Già a partire dall'aspetto della microstruttura delle scorie prodotte in presenza ed in assenza di riciclo, si nota chiaramente come nelle prime si sia sviluppata una struttura a fasi globulari, mentre nella seconda è presente una significativa struttura dendritica (Figura 5). Le strutture dendritiche sono costituite da magnesiowustite (Figura 6). Le strutture osservate indicano chiaramente che la scoria formatasi durante il riciclo ha presentato durante l'esercizio una maggiore frazione solida, probabilmente associata a due fattori: l'introduzione di fasi altofondenti presenti nella scoria bianca e un effetto di calmieramento della temperatura svolto dalle fasi fredde riciclate ed iniettate nel forno. La presenza di una maggiore frazione solida, formatasi in forza della composizione chimica raggiunta a seguito del riciclo, sembra confermata dai risultati del modello di calcolo che, oltre a mostrare un'ottima concordanza con le misure sperimentali, confermano un arricchimento dei costituenti strutturali in grado di portare alla formazione di una maggiore frazione solida (Tabella 6, Tabella 7). Le misure fonometriche (Figura 7) realizzate all'interno del forno per valutare la stabilità della scoria schiumosa indicano un migliore schiumeggiamento in presenza di riciclo, probabilmente legato proprio alla formazione di una maggiore quantità di particelle solide in grado di aumentare la viscosità della scoria, intrappolare le bolle di monossido di carbonio e quindi provocare la formazione dell'emulsione in modo più rapido, limitando il transitorio di rigonfiamento.

Quindi, il riciclo della scoria del forno siviera pare essere vantaggioso sia per la diminuzione dell'impatto ambientale, legato all'eliminazione dello smaltimento in discarica, sia per il miglioramento della stabilità della scoria schiumosa.