THE APPLICATION OF QUASI-CHEMICAL APPROACH FOR THE MANAGEMENT OF THE SLAGS[1]

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Abstract

Over the last few years technologies dedicated to recycle of ladle slag have been improved. Steelmaking plants carefully evaluated the possibility to operate the recycling process in order to decrease the environmental impact. An important variation of EAF slag foaminess has been observed in plants which adopted the presented technique. The amount of the recycled material injected in the EAF is performed according to 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 goal of this work is to establish the amount of recycled material to be injected in the EAF 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. A thermodynamic model based on the quasi-chemical approach was developed to predict the amount of the slag solid fraction and its forecasting has been compared with the experimental data. 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 behaviour and permit to achieve great economic advantages.

Key words: Ladle slag; Quasi-chemical model; Foaming slag.

A APLICAÇÃO DE APROXIMAÇÃO QUASE-QUÍMICA PARA O GERENCIAMENTO DE ESCÓRIAS

Resumo

Nos últimos anos as tecnologias voltadas para a reciclagem de escória de panela se desenvolveram. Aciarias avaliaram cuidadosamente a possibilidade de operacionalizar o processo de reciclagem para reduzir o impacto ambiental. Foi observada uma importante variação da espumosidade da escória do FEA em plantas que adotaram a presente técnica. O volume de material reciclado injetado no FEA é definido com base em um balanço obtido através de um modelo termodinâmico que objetiva garantir uma formulação final da escória do FEA que possa ser classificada como rejeito não perigoso. Uma meta do presente trabalho é estabelecer o volume de material reciclado a ser injetado no FEA para melhorar a espumosidade da escória, para se conseguir um reuso completo da escória de panela e para assegurar um mix correto de espécies químicas evitando a formação de pós finos. Um modelo termodinâmico baseado na aproximação quase-química foi desenvolvido para prever o volume de fração sólida da escória e sua previsão foi comparada com os dados experimentais. Esta ferramenta pode ser proveitosa para estruturar a formulação correta da escória através da adição de material reciclado do Forno Panela para otimizar o comportamento espumoso e permitir se obter grandes vantagens econômicas.

Palavras chave: Escória de panela; Modelo quase-químico; Escória espumosa.

Introduction

Environment is becoming a key issue for the Steel Industry. Over the last few years technologies of the plant 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 $2CaO.SiO_2$ (C2S) which undergoes an allotropic solid phase transition (that occurs when the temperature go down to 500°C) from β phase to γ phase).[1] 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 (Figure 1).
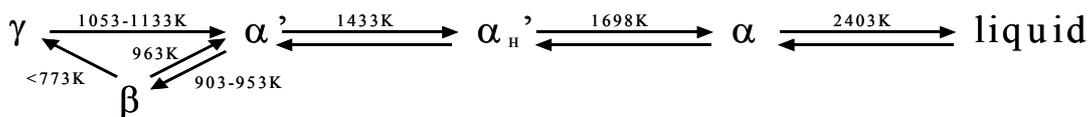
$$\gamma \xrightleftharpoons[963K]{1053-1133K} \alpha' \xrightleftharpoons{1433K} \alpha_H' \xrightleftharpoons{1698K} \alpha \xrightleftharpoons{2403K} liquid$$

$$\gamma \xleftarrow{<773K} \beta \xrightarrow{903-953K}$$

Figure 1 - Experimentally measured phase transition temperatures for $2CaO.SiO_2$ polymorphs

The conversion β-γ is accompanied by 10% volume increase (from ~56 to ~62·10^{-6} m^3/mol) and results in the matrix shattering into powder because of their different crystal structures and density.[2]

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 relation with the foaminess of EAF slag have been investigated. In agreement with the data contained in literature 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.

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 which has successfully applied also for the most modern investigation about slag and fluxes behavior. The model is applied to predict the properties of the multi-component ionic systems (CaO-MgO-Al_2O_3-SiO_2-MnO-FeO_x) containing binaries and ternaries subsystems like (CaO-MgO-Al_2O_3, CaO-Al_2O_3-SiO_2, SiO_2-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:

$$X_{11} + X_{22} \Leftrightarrow 2X_{12} \tag{1}$$

The total number of bonds generated from a generic i atom is Z_iX_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:

$$Z_1X_1 = 2n_{11} + n_{12}$$
$$Z_2X_2 = 2n_{22} + n_{12} \tag{2}$$

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

$$Y_1 = 1 - Y_2 = \frac{Z_1X_1}{Z_1X_1 + Z_2X_2}$$

$$Y_2 = 1 - Y_1 = \frac{Z_2X_2}{Z_1X_1 + Z_2X_2} \tag{3}$$

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

$$\Delta h_m - Ts^E = \frac{Z_1X_1 + Z_2X_2}{2} \cdot \frac{X_{12}}{2} \cdot \Delta g \tag{4}$$

At first approximation, the expression for the configurational entropy of mixing can be derived from the one-dimensional Ising model:

$$T\Delta s_m^{config} = -RT(X_1 lnX_1 + X_2 lnX_2) - $$

$$- \left[\frac{RT}{2}(Z_1X_1 + Z_2X_2)\right]\left[X_{11}ln\left(\frac{X_{11}}{Y_1^2}\right) + X_{22}ln\left(\frac{X_{22}}{Y_2^2}\right) + X_{12}ln\left(\frac{X_{12}}{2Y_1Y_2}\right)\right] \tag{5}$$

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:

$$\frac{X_{1-2}^2}{X_{11}X_{22}} = 4 \cdot exp\left(-\frac{\Delta g_{12}}{RT}\right)$$

(6)

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

$$X_{12}^2(4-A) + X_{1-2} \cdot \left[2A(Y_1 + Y_2)\right] - \left(A \cdot Y_1 Y_2\right) = 0$$

(7)

where A is:

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

(8)

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

In $CaO - SiO_2 - Al_2O_3 - MgO - MnO - FeO_x$ multi-component system the formation of binary and ternary complex compounds can reasonably be expected. The possible compounds which can be formed are selected on the basis of the information contained in the related phase diagrams. In Table 1 are summarized the expected complex oxides.

Table 1 - Complex oxide considered in the thermodynamic model

Complex oxides selected			$T_{melting}$ K	$T_{melting}$ °C
3CaO.Al2O3		C3A	1913	1640
3CaO.2SiO2	Kilchoanite (Rankinite)	C3S2	1733	1460
3CaO.SiO2	Hatrurite	C3S	2403	2130
CaO.Al2O3	Grossite	CA	1881	1608
12CaO.7Al2O3	Mayenite	C12A7	1653	1380
CaO.2Al2O3		CA2	2043	1770
SiO2.CaO	Wollastonite	CS	1821	1548
2CaO.SiO2	Larnite (lime-olivine)	C2S	2463	2190
Al2O3.2SiO2	Xenolite	AS2	2153	1880
3Al2O3.2SiO2	Mullite	A3S2	2193	1920
Al2O3.SiO2	Andalusite (Kayanite, Sillmanite)	AS2	2130	1857
2MgO.SiO2	Fosterite	M2S	2161	1888
MgO.Al2O3	Spinel	MA	2408	2135
FeOx.MgO	MagnesioWustite	MW	2397	2124
MnO.Al2O3		MnA	2053	1780
2MnO.SiO2	Tephorite	Mn2S	1673	1400
2CaO.2FeOx	Srebrodolskite	C2E2	1660	1387

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:

$$\Delta G_{i,formation} = Z_i \cdot G_{i,product} - \Sigma\left(Z_j \cdot G_{reagent}\right)$$

(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:

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

(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 to be corrected by a factor dependent on ion molar fraction and ion valence number:

$$K_Q = 4 \cdot K \cdot \left\{ \gamma_i \left[\frac{\xi_i X_i}{\xi_i X_i + \xi_j X_j} \right]^{(\xi_{tot-i})} \cdot \gamma_j \left[\frac{\xi_j X_j}{\xi_i X_i + \xi_j X_j} \right]^{(\xi_{tot-j})} \right\}$$

(11)

where ξ_i represents the coordination number of the generic i-cation within the oxide complex (i.e. for Ca is 2, for Al is 3 and for Si is 4), while ξ_{tot-i} represents the total number of the generic i-cation in the considered oxide complex, i.e. in $3CaO.Al_2O_3$ the ξ_i for Ca is 3 while for Al_2O_3 is 2. 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 ($\varepsilon_{i,j}$) with the molar fraction of species (X_i):

$$a_i = \varepsilon_{i,j} \cdot X_j$$

(12)

The correction terms among different ions (summarized in Table 2) are due to the chemical interaction of mixing effect.[3]

Table 2 - Table of the interaction coefficients between ions species

	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	-127,61	-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	

Those terms are better considered by:

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

(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 ($X'_{i,j}$) is obtained multiplying, for

each chemical formation reaction, the ionic fraction ($X_{i,j}$) by the stoichiometric factor ($Z_{i,j}$):

$$X_i^{'} = X_{ij} \cdot Z_i \qquad (14)$$

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

$$X_{bounded,i}^{'} = \frac{X_i}{X_i^{'}} \qquad (15)$$

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:

$$X_{bounded,i} = \frac{X_{free,i}^{'}}{\sum_i X_{bounded,i}^{'}} \qquad (16)$$

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

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

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 (Table 2) the total liquid and solid slag fraction are calculated (Table 3).

Table 3 - Example of ionic fraction in the complex oxides for a (30% CaO, 15% SiO$_2$, 5% MgO, 11% Al$_2$O$_3$, 5% MnO, 29% FeOx, other oxides residual) slag at the temperature of 1.677°C

Complex oxides			Oxide complex fraction
3CaO.Al2O3		C3A	0,04%
3CaO.2SiO2	Kilchoanite (Rankinite)	C3S2	0,51%
3CaO.SiO2	Hatrurite	C3S	0,31%
CaO.Al2O3	Grossite	CA	0,00%
12CaO.7Al2O3	Mayenite	C12A7	7,03%
CaO.2Al2O3		CA2	0,03%
SiO2.CaO	Wollastonite	CS	0,06%
2CaO.SiO2	Larnite (lime-olivine)	C2S	0,35%
Al2O3.2SiO2	Xenolite	AS2	0,00%
3Al2O3.2SiO2	Mullite	A3S2	0,00%
Al2O3.SiO2	Andalusite (Kayanite, Sillmanite)	AS2	0,00%
2MgO.SiO2	Fosterite	M2S	0,05%
MgO.Al2O3	Spinel	MA	0,07%
FeOx.MgO	MagnesioWustite	MW	23,81%
MnO.Al2O3		MnA	0,06%
2MnO.SiO2	Tephorite	Mn2S	0,93%
2CaO.2FeOx	Srebrodolskite	C2E2	0,00%

The solid fraction calculated is utilized to estimate the effective viscosity slag according to the well known relation:[4]

$$\eta_e = \eta \left(1 - 1.35 \cdot \vartheta\right)^{-5/2} \qquad (18)$$

Experimental investigations and discussion

The experimental investigation has been done at Stefana SpA steel plant. This location has been selected because there is one of the two existing and working white-slag recycling plants. The tests were carried out during 52 heats 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 heat carried out with and without white slag recycling. Thus, in order to realize this comparison a half of heats was carried out with injection of recycling 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 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 Table 4.

Table 4 - White slag average chemical composition

LF slag	%
CaO	42%
SiO_2	21%
MgO	6%
Al_2O_3	12%
MnO	4%
FeOx	1%
Other oxides	6%
IB2	2
IB4	1,45

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 iron particles are take out from the ladle slag. Then the slag grain size was checked.

By pneumatic transportation the powder is driven into the EAF via special powder

injectors - the KT Powder Injectors by TENOVA. 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 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 looses their power.

The injection of solid particles results in three consequence:

- 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 grater amount of little bubbles;
- a growing effect acting on the particles, improving the kinetic bubble nucleation, thus increasing the foam slag formations.

EAF slag

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

EAF slag, due the presence of P_2O_5 that stabilizes $2CaO.SiO_2$, during its cooling does not form powder, thus assuming the form of little chips.[5]

The chips embedded in a conductive thermoplastic resin were polished and then examined. In Figure 2 it is possible to observe the slag morphology. The image shows a slag sampled at the end of a heat 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 without recycling. This difference is a possible consequence of the lower FeO_x concentration and of the larger amount of nucleation points in the slag. In fact the injection of cold powdered material in 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.
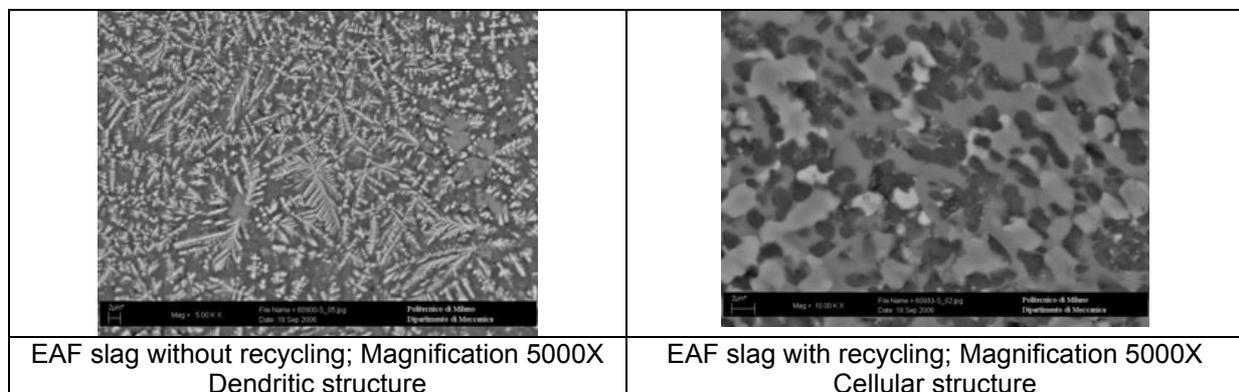

| EAF slag without recycling; Magnification 5000X Dendritic structure | EAF slag with recycling; Magnification 5000X Cellular structure |

Figure 2 - EAF slag morphology

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

Table 5 - Average chemical composition of EAF slag

	% MgO	%Al2O3	%SiO2	%CaO	%MnO	%FeOxx
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%

It is possible to observe that in EAF slag without 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 the chemical composition in EAF.
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 Figure 3).
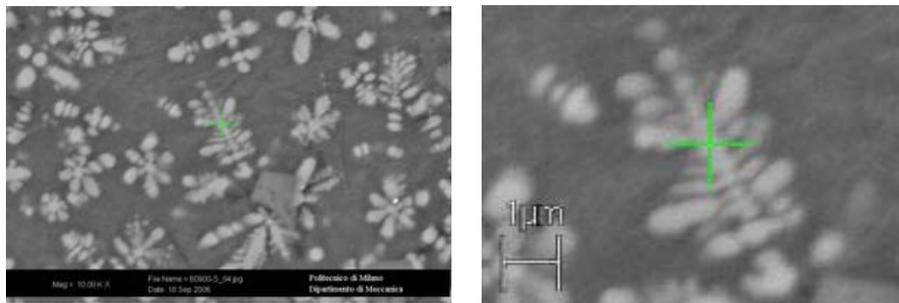

Figure 3 - EAF slag (without white recycle material), zoom on Magnesio.Wustite (MgO.FeOx) phase particle

Subsequently the measured data of chemical composition were compared with theoretical complex oxide composition.
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. Pretorius 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 foaminess slag. 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 two "typical heats" 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.

Table 6 - Complex oxide actually computed and theoretically expected in EAF slag

Complex oxide			heat without recycle		heat with recycle	
			Model expected	Really found	Model expected	Really found
3CaO.Al2O3		C3A	yes	yes	yes	yes
3CaO.2SiO2	Kilchoanite (Rankinite)	C3S2	yes	yes	yes	yes
3CaO.SiO2	Hatrurite	C3S	yes	no	yes	yes
CaO.Al2O3	Grossite	CA				
12CaO.7Al2O3	Mayenite	C12A7	yes	yes	yes	yes
CaO.2Al2O3		CA2				
SiO2.CaO	Wollastonite	CS				
2CaO.SiO2	Larnite (lime-olivine)	C2S	yes	yes	yes	yes
Al2O3.2SiO2	Xenolite	AS2				
3Al2O3.2SiO2	Mullite	A3S2				
Al2O3.SiO2	Andalusite (Kayanite, Sillmanite)	AS2				
2MgO.SiO2	Fosterite	M2S				
MgO.Al2O3	Spinel	MA				
FeOx.MgO	MagnesioWustite	MW	yes	yes	yes	yes
MnO.Al2O3		MnA				
2MnO.SiO2	Tephorite	Mn2S	yes	no	yes	yes
2CaO.2FeOx	Srebrodolskite	C2E2				

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 heats were undergone the measurement procedure; 16 of those heats 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.
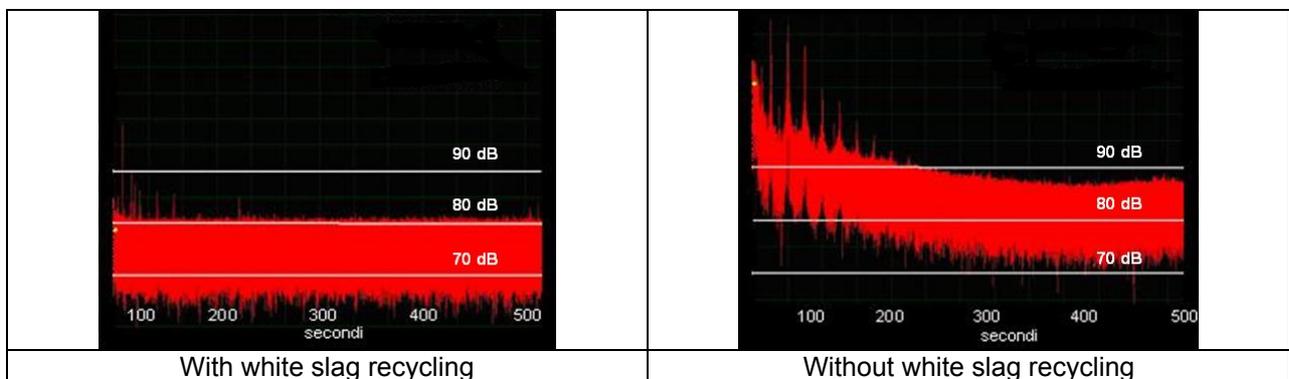

With white slag recycling	Without white slag recycling

Figure 4 - Spectrum of noise phonometric analysis in refining step with and without white slag recycle

On the basis of Figure 4 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 (Table 7).

Table 7 - Refining step noise

	With white slag recycle	Without white slag recycle	Difference
Average noise (dB)	73	82	-9
Asymptotic noise (dB)	65	72	-7

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 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 points the slag structure is expected to be composed by a more viscous frame which has the attitude to 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 damping cost

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 kJmol^{-1}K^{-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

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