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 2CaO.SiO₂ (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', γ, 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 ~62·10⁻⁶ m³/mol) and results in the matrix shattering into powder because of their different crystal structures and density\(^17\). 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\(^4,5\) 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.

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KEYWORDS: steel making, ecology, decarburation, recycling, slag, steel
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\textsuperscript{[6,7]} which has successfully applied also for the most modern investigation about slag and fluxes behavior\textsuperscript{[8,9,10]}. The model is applied to predict the properties of the multi-component ionic systems (CaO-MgO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-MnO-FeO\textsubscript{x}) containing binaries and ternaries subsystems like (CaO-MgO-Al\textsubscript{2}O\textsubscript{3}, CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}, SiO\textsubscript{2}-MnO-FeO\textsubscript{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:

\[ A_i + B_{i+1} \rightarrow 2A_{i+1} \]  

(1)

The total number of bonds generated from a generic i-atom is \( Z_{X_i} \) 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:

\[ Z_i X_i = 2m_{12} + m_{10} \]
\[ Z_i X_i = 2m_{02} + m_{01} \]  

(2)

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

\[ Y_i = \frac{Z_i X_i}{Z_i X_i + Z_i X_i} \]  

(3)

The molar enthalpy and the excess entropy of mixing are assumed to be directly related to the fraction of \( 1-2 \) pairs accord-

\[ \Delta H_{mix} - \Delta H_{mix}^0 = \frac{Z_i X_i + Z_i X_i}{2} \frac{Y_i}{2} \Delta h \]  

(4)

At first approximation, the expression for the configurational entropy of mixing can be derived from the one-dimensional Ising model\textsuperscript{[11,12,13]}:

\[ \Delta S = \frac{R}{2} \left[ (Z_i X_i + Z_i X_i) \mathrm{ln} \left( \frac{Z_i X_i}{Z_i X_i} \right) + (Z_i X_i + Z_i X_i) \mathrm{ln} \left( \frac{Z_i X_i}{Z_i X_i} \right) \right] \]  

(5)

The equilibrium of considered “quasi-chemical” reaction is calculated by minimizing (5) with respect to \( X_i \) variable. This computational derivation turns out a “quasi-chemical” equilibrium constant for the reaction:

\[ \frac{Y_i}{X_i X_{i-1}} = \exp \left( \frac{-\Delta G_{mix}}{RT} \right) \]  

(6)

In order to make (6) explicit in \( X_i \):

\[ x_1 = d + x_1 \exp \left[ \frac{-\Delta G_{mix}}{RT} \right] \]  

(7)

where \( A \) is:

\[ A = \exp \left[ \frac{-\Delta G_{mix}}{RT} \right] \]  

(8)

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

In CaO – SiO\textsubscript{2} – Al\textsubscript{2}O\textsubscript{3} – Mg\textsubscript{2}O – Mn\textsubscript{O} – FeO\textsubscript{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\textsuperscript{[13,14]}. Tab. 1 is 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:

\[ \Delta G_{mix} = \sum Z_i X_i \Delta G_{mix}^i \]  

(9)

The formation of pairs associated with the generic \( i \)-species can be obtained through:

\[ K = \exp \left( \frac{\Delta G_{mix}}{RT} \right) \]  

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

\[ K_2 = \exp \left[ \frac{\gamma \gamma_i (\xi_{A} \xi_{B} + \xi_{B} \xi_{A})}{\gamma_{\gamma} (\xi_{A} \xi_{B})} \right] \]  

(11)

where \( \xi \) represents the coordination number of the generic i-atom 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 \( \gamma \).
The activities of the ionic species \((a_i, a_j)\) are obtained relating the interaction activity coefficient \((\lambda_{i,j})\) with the molar fraction of species \((X_i)\):

\[
a_i = \lambda_{i,j} \cdot X_j
\]

The correction terms among different ions (summarized in Tab. 2) are due to the chemical interaction of mixing effect. Those terms are better considered by (13):

\[
RT \ln y_i = \sum \lambda_{i,j} X_j + \sum \lambda_{j,i} X_j + \sum \lambda_{i,j} X_j X_k
\]

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 \((Z_{i,j})\):

\[
X'_{i,j} = X_{i,j} \cdot Z_{i,j}
\]

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

\[
X'_{\text{complex}} = \frac{X_{i,j}}{X_{i,j} + X_{i,j}'}
\]

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

\[
X_{\text{bounded}} = \frac{X_{i,j}'}{1 + X_{i,j}'}
\]

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

\[
X_{\text{free}} = \frac{X_{i,j}}{1 + X_{i,j}'}
\]

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.

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

\[
\eta = \eta_0 \left(1 - 1.35 \cdot \phi \right) \gamma_{\text{mol}}
\]

### 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 slag.

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<tr>
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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 (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.

<table>
<thead>
<tr>
<th>LF slag</th>
<th>%</th>
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<tbody>
<tr>
<td>CaO</td>
<td>42%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>21%</td>
</tr>
<tr>
<td>MgO</td>
<td>6%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12%</td>
</tr>
<tr>
<td>MnO</td>
<td>4%</td>
</tr>
<tr>
<td>FeOx</td>
<td>1%</td>
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<tr>
<td>Other oxides</td>
<td>6%</td>
</tr>
<tr>
<td>IB2</td>
<td>2.00</td>
</tr>
<tr>
<td>IB3</td>
<td>1.27</td>
</tr>
<tr>
<td>IB4</td>
<td>1.45</td>
</tr>
</tbody>
</table>

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 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 sucked 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 looses their power.

The injection of solid particles results in three consequences:

- a mass effect lowering the FeOx 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.
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·SiO₂ 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 FeOₓ concentration. On the other hand, cellular microstructure was found in the slag observed with recycling. This difference is a possible consequence of the lower FeOₓ concentration and of the larger amount of nucleation centres 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. 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.

<table>
<thead>
<tr>
<th></th>
<th>% MgO</th>
<th>% Al₂O₃</th>
<th>% SiO₂</th>
<th>% CaO</th>
<th>% MnO</th>
<th>% FeOₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without recycle</td>
<td>2.64%</td>
<td>10.09%</td>
<td>18.94%</td>
<td>32.01%</td>
<td>4.60%</td>
<td>31.72%</td>
</tr>
<tr>
<td>With recycle</td>
<td>3.94%</td>
<td>9.18%</td>
<td>17.13%</td>
<td>36.91%</td>
<td>5.34%</td>
<td>27.51%</td>
</tr>
</tbody>
</table>

**Table 5**

Average chemical composition of EAF slag.

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 FeOₓ 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).
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. Pretorius\textsuperscript{4}) 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 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
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 trap a larger quantity of small CO bubbles.

**CONCLUSIONS**

In order to optimize slag foami-ness 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 foami-ness. Thus, metallurgical and economic advantages could be summarized in:

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

<table>
<thead>
<tr>
<th>Complex oxides</th>
<th>Model expected</th>
<th>Really found</th>
<th>Model expected</th>
<th>Really found</th>
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<tr>
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<td>yes</td>
<td>yes</td>
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**LIST OF SYMBOLS**

- $X_i$: bond fraction between cation pair in solution
- $X_i$ 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
- $(X'_{i,j,l})$: relative linked pairs in complex oxides
- $(X'_{i,j,f})$: relative free fraction ions
- $(X_{i,j,l})$: linked ionic fraction in complex oxides
- $(X_{i,j,f})$: 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
- $\Delta G$: variation of the Gibbs free energy [J]
- $S^G$: Entropy excess give by mixing [J]
- $\Delta hm$: variation of molar enthalpy [J]
- $\Delta g_{m}$: variation of mixing energy on the system [J]
- $T$: temperature [K]
- $R$: universal constant of gas [R=8.314 kJmol-1K-1]
- $\xi$: valence number of generic i ion
- $a_{ij}$: activity of i,j atom
- $n$: viscosity of slag [Pas]
- $n_{eff}$: effective viscosity of slag [Pas]
- $\theta$: solid fraction in slag
- $Z_{i,j}$: stoichiometric factor
La scoria bianca coinvolta nel processo di affinazione del forno siviera può subire un processo di trasformazione allotropica del $2\text{CaO}.\text{SiO}_2$ (Figura 1) al diminuire della temperatura. Questo fenomeno porta ad una progressiva polverizzazione della scoria che ne imporrrebbe 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 deferritizzazione 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 processo 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 nelle 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 fono-metriche (Figura 7) realizzate all’interno del forno per valutare la stabilità della scoria schiumosa indicano un migliore schiumeggiamento in presenza di riciclo, probabilmente legato 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.