THE BEHAVIOUR OF THE SECONDARY METALLURGY SLAG INTO THE EAF. HOW TO CREATE A GOOD FOAMY SLAG WITH THE APPROPRIATE BASICITY USING A MIX OF LIME AND RECYCLED LADLE SLAG AS EAF SLAG FORMER[1]

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Abstract
Several steel plants, in Italy and in the rest of Europe, recycle with different methods and techniques the slag proceeding from the secondary metallurgy as slag former for their Electric Arc Furnaces. In this paper the excellent results of this non-standard practice are analysed and related to the characteristics of the EAF-slag resulting from this recycling. An interesting effect has been found on the characteristics of foaming velocity, slag basicity and slag density. Slag foaming studies were conducted in the laboratories of UNSW (Sydney,Australia) using the high temperature visualization facility. The studies have established the differences in the slag foaming phenomenon between the electric arc furnace slag formed with usual components (lime, dololime, etc.) and the slag formed with the non-standard mix (lime and recycled ladle slag). Using a model of isothermal solubility, developed by Politecnico di Milano University (Italy), the other EAF slag properties, in particular the density and the basicity, are correlated to the saturation of silicates, aluminates and other complex components of the secondary metallurgy slag into the EAF slag. The results of these studies confirm that this particular type of ladle slag recycling is viable, as it does not affect the EAF foaming properties, and in some cases it is even more favourable than the standard practice.
Key words: EAF slag; Ladle slag; Recycling; Powder injection; Foamy slag.

O COMPORTAMENTO DA ESCÓRIA DE METALURGIA SECUNDÁRIA NO FEA. COMO CRIAR UMA BOA ESCÓRIA ESPUMANTE COM A BASICIDADE ADEQUADA USANDO UMA MISTURA DE CAL E ESCÓRIA DE PANELA RECICLADA COMO FORMADORA DE ESCÓRIA DE FEA

Resumo
Várias usinas siderúrgicas, na Itália e no resto da Europa, reciclam com diferentes métodos e técnicas a escória proveniente da metalurgia secundária como formadora de escória nos seus Fornos Elétricos a Arco. Neste trabalho os excelentes resultados desta prática não padrão são analisados e relacionados às características da escória de FEA resultante dessa reciclagem. Um efeito interessante foi observado nas características de velocidade de espumação, basicidade da escória e densidade da escória. Estudos de escória espumante foram realizados nos laboratórios da UNSW (Sidnei, Austrália) usando as facilidades de visualização de alta temperatura. Os estudos estabeleceram as diferenças no fenômeno de espumação da escória entre a escória de FEA formada com componentes usuais (cal, cal dolomítica etc.) e a escória formada com a mistura não padrão (cal e escória de panela reciclada). Usando um modelo de solubilidade isotérmica, desenvolvido pela Universidade Politecnico di Milano (Itália), as outras propriedades da escória de FEA, particularmente a densidade e a basicidade, são correlacionadas à saturação de silicatos, aluminatos e outros componentes complexos da escória de metalurgia secundária na escória de FEA. Os resultados desses estudos confirmam que este tipo particular de reciclagem de escória de panela é viável, pois não afeta as propriedades de espumação do FEA, e, em alguns casos, é até mais favorável que a prática padrão.
Palavras chave: Escória de FEA; Escória de panela; Reciclagem; Injeção de finos; Escória espumante.

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INTRODUCTION

The Environment is becoming more and more a key issue for the Steel Industry. In particular areas where the increasing variable cost of production and the cost of men work are reducing the profit on the final product, the additional cost of residues dumping can reduce to zero the result of the steel plant. In Italy the production of steel using Electric Arc Furnaces generates more than two million tons of slag and various types of other residues per year.
The recycling of these by-products permits to achieve two important goals: minimizing the exploitation of natural resources and reducing the amount of waste material.
In Italy, the first Industrial Plant for recycling electric arc furnace and ladle furnace by-products has operating since January 2001 at Ferriere Nord works in Osoppo (Italy) - on industrial scale since January 2003. The Plant convert ladle slag – also called "white slag" – and spent refractory into a final powder mix that can be injected in the Electric Arc Furnace through specially designed injectors. The industrial application has shown the sustainability of this recycling procedure, cost and process-wise. Important benefits, moreover the reduced cost for slag disposal, is coming from the reduced amount of lime to add to the Electric Arc Furnace, about 35% less.
The application of this recycling process provides major advantages, such as the lower amount of lime required for the formation of the EAF slag. But this is not the only existing benefit.
The foaming properties of the slag are thus increased, and so the electrical energy efficiency is increased, as the arc can be better covered during flat bath operation.
Nevertheless, the increase of tenor of MgO in the EAF slag is in favour of a lower consumption of the EAF refractory bricks, an additional benefit to be considered. [ref. 14]
Some phonometric analysis of noise level in the EAF are conducted during the standard practice and during the recycling practice.
These analyses were executed between the end of melting phase and refining phase.The Figure 1 shows the noise analysis during a heat without recycling material. [ref. 13]

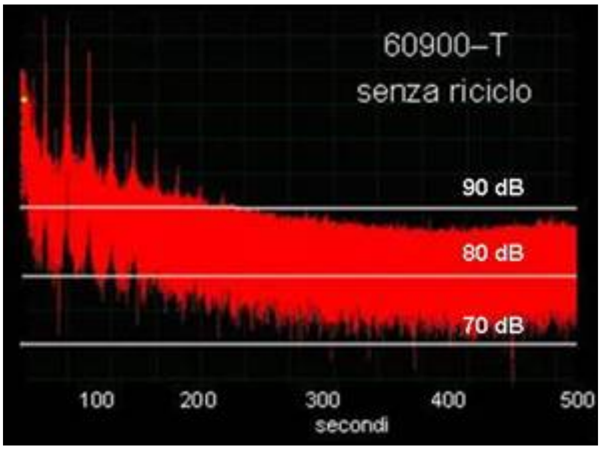

Figure 1: Phonometric analysis of noise level during standard practice in the EAF

In the end of melting period the noise is higher than the one that is produced during the decarburization period. This indicates that in first measurement stage the slag doesn't foam yet. The slag starts foaming after around 180-200 sec.
The Figure 2 shows the noise analysis during a heat with recycling material. The noise level is lower than the previous case and the transitory doesn't occur. This indicate that the foam with recycling material grows earlier and with higher volume.

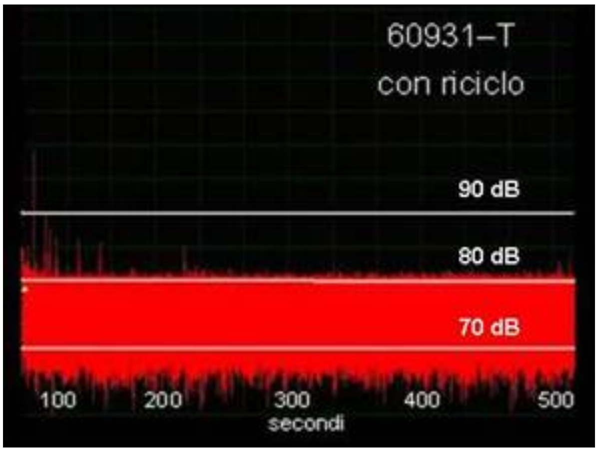

Figure 2: Phonometric analysis of noise level during a heat with injection of recycling material

SLAG FOAMING

Some important benefits can be obtained in the EAF through the foaming slag practice. Slag is foamed to improve the heat transfer from the arc to the metallic bath, and to protect the refractory bricks from the arc radiation improving the efficiency of the furnace.
A good foam must have some physical and chemical characteristics.

Physical characteristics for a good foaming slag:

The formation and stability of foams are influenced by surface tension and viscosity. Foaming characteristics improved with decreasing surface tension, increasing viscosity of slag. However the presence of second phase particles improves the foaming behavior. The second phase particles serve as gas nucleation sites, which lead to a high amount of favourable small gas bubbles and promote a better stability.
According to this theory, the ISD diagram shows that the “optimum” foaming slag is saturated with C2S and Magnesio-wustite solid solution. [ref. 1]

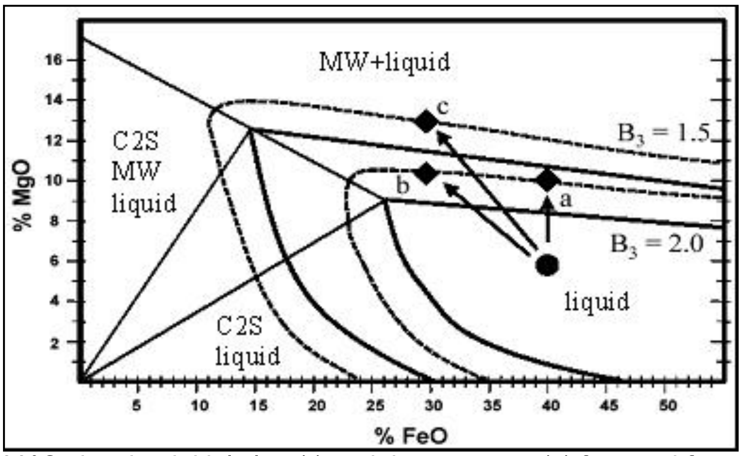

Figure 3: ISD at 1600°C showing initial slag (•) and three targets (♦) for good foaming slags with (a) at 40 %FeO and (b) at 30 %FeO relative to the curve for B3=2.0 and (c) with 30%FeO for B3=1.5.

In this diagram the better foaming slag is between the continues line and dotted line. In this region of diagram the slag is not fully liquid and is not crusty and there are the second phase particles suspended in the slag. In fact this region corresponds to the saturation of CaO and MgO. This signifies that the presence of C2S ($2CaO.SiO_2$) suspended in the slag offers an advantage to foaming.

Chemical characteristics for a good foaming slag:

The formation and the stability of a foam is influenced by the chemical composition of the slag.
The presence of high percentage of FeO in the slag promotes the reaction with the carbon in accordance with the reaction:

$$FeO + C = Fe + CO$$

In these experiments the quantity of FeO influences the foaming behavior because is the only source of oxygen for the reaction.
Silica favours the foaming slag stability. The presence of silica lowers the surface tension and promotes the formation of small bubbles of CO.
On the contrary, sulphur suppresses the slag foaming. Sulphur tends to increase the size of CO bubbles and make worse the stability. [ref. 6, 10 and 11]

Influence of Recycling material:

From a chemical point of view, the injection of recycling material increases the amount of the already present di-calcium silicate of EAF slag favouring the saturation respect to C2S. The injection of recycling material influences also the physical characteristics of foam. In fact the dicalcium silicate is normally present at EAF slag temperature as "second phase particles". The addition of other particles coming from the recycled mix has three consequences: a mass effect (lowering FeO, and increasing slag width), the increase of MgO (present in the mix) and the increase of the CO nucleation sites, which leads to a high amount of favourable small gas bubbles in the foamy slag.
In order to understand the behaviour of EAF slag with recycling materials some experiments have been conducted in the laboratories of UNSW using slag samples with recycling materials and without recycling materials.

Figure 4: horizontal tube furnace [ref.11]

EXPERIMENTS

In this project, the foaming behaviour of slag with recycling material is investigated in a horizontal tube furnace. The sessile drop technique is used for slag foaming experiments. The purpose is to compare the effect of the recycled ladle slag materials during slag-carbon interaction.

Samples slag description:

Two types of EAF slag samples are used in the experiments:

- The first type is the sample with recycled ladle slag

Table 1: characteristics of heat with recycling material

Heat	Ton.	Lime (kg)	Ladle Slag (kg)	Carbon (kg)	Oxygen (Nm3)	temperature (°C)
A	131	2885	2460	521	3561	1570
B	121	2887	2395	160	4370	1575
C	148	2972	2404	149	4912	1580
D	130	2895	2414	198	3361	1570
E	128	2889	2407	194	3061	1585

- The second type is without recycled ladle slag

Table 2: characteristics of heat without recycling material

Heat	Ton.	Lime (kg)	Ladle Slag (kg)	Carbon (kg)	Oxygen (Nm3)	temperature (°C)
F	129	3432	0	322	3207	1575
G	128	3538	0	231	3316	1575
H	127	3540	0	234	3055	1580
I	130	2982	0	254	3196	1610
L	134	3000	0	584	3457	1580

.
In the follow table are reported the chemical analysis of every slag sample:

Table 3: chemical analysis of slag samples

Heat	FeO	Fetot	CaO	SiO2	MgO	Al2O3	MnO	S	P2O5	Cr2O3	TiO2	Total
A	43,14	33,44	23,79	14,92	2,14	6,25	5,34	0,11	0,60	0,52	0,36	**97,16**
B	33,97	26,34	31,11	16,47	2,27	6,19	5,37	0,08	0,82	0,78	0,38	**97,45**
C	37,16	28,80	28,69	15,34	3,24	7,23	3,74	0,10	0,72	0,75	0,38	**97,35**
D	36,09	27,98	28,40	16,66	2,70	6,71	5,02	0,08	0,72	0,59	0,38	**97,38**
E	32,25	25,00	30,89	17,39	2,44	6,89	5,93	0,08	0,65	0,56	0,41	**97,50**
F	24,40	18,92	33,13	20,36	2,79	8,49	6,41	0,06	0,96	0,66	0,49	**97,74**
G	24,39	18,90	34,32	18,90	3,17	8,80	6,01	0,04	1,10	0,54	0,48	**97,74**
H	27,34	21,19	32,87	18,01	2,56	8,40	6,14	0,05	1,20	0,61	0,47	**97,65**
I	27,84	21,58	28,55	19,40	3,11	10,27	6,29	0,04	0,92	0,65	0,56	**97,64**
L	35,79	27,75	23,80	18,24	2,32	9,60	5,90	0,06	0,53	0,63	0,51	**97,39**

The experiment sample consist of a coal substrate and a slag sample. The slag sample is powderized and placed over the substrate sample.

Preparation of substrate:
The substrates used in the slag foaming experiments, were prepared from the metallurgical coke. Each sample was ground to a fine powder with particle size <10µm, using a Rocklabs rotation grinder fed with compressed air. The grinding container and ball were cleaned with ethanol before every use to prevent

contamination of samples. 1 gram of coke powder was then placed in a die cylinder and uni-axially pressed at 7 tonnes for 1 min [using the Enerpac 10 tonne press]. The compacted, circular substrate of diameter 15 mm and thickness 3-4 mm was then removed from the die and placed on the alumina stage. No binder was used in compacting the materials to avoid contamination.

Preparation of slag sample:
The EAF slag sample was ground in a fine powder using a Rocklabs rotation grinder. A quantity of 0,1 g of powder slag is placed over the compacted coke substrate.
The foaming experiments were conducted in a laboratory scale horizontal tube furnace using the sessile drop method. A schematic diagram of the experimental set-up is shown in Figure 4.

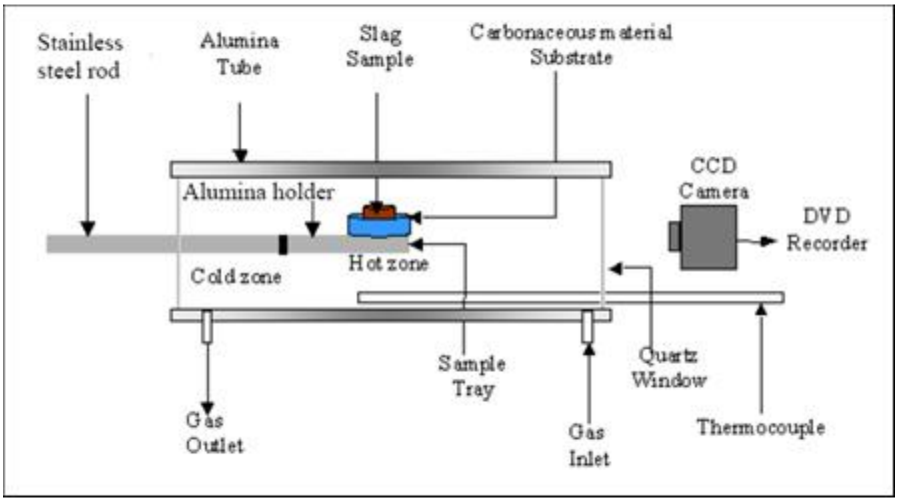

Figure 5: schematic diagram of the horizontal tube furnace [ref. 12]

At the start of the experiment, the sample is placed on an alumina holder, in the cold zone of the furnace. When the required experimental temperature is attained (1550°C), the sample and holder are advanced to the hot zone using graphite sample rod, in preparation for the slag-carbon interaction study. The experimental temperature is controlled using the digital temperature indicator on the furnace. At the gas inlet, argon is introduced into the furnace, carrying the CO/CO2 off-gas to the gas outlet. A high quality, high resolution CCD camera fitted with IRIS lens is used to capture live, the “in-situ” foaming phenomena in the furnace. A DVD-TV system is used to record the entire foaming process, and the recorded images are then transferred onto a computer. Slag foaming is characterized by direct continuous measurement of foaming height as a function of time. The volume of the molten slag droplet will be measured using the image analysis software based on digital integration and used in computer programming. In this way it is possible to calculate the volume ratio as:

$$volume\ ratio = {}^{V_t}\!/_{V_0}$$

Where V_0 is the starting volume value of the bubble and V_t the actual volume value of the bubble.

RESULTS

The experimental results are confirmed the general principles of foaming practice: the graphs of Figures 7, 9 and 10 confirm that the %FeO influences, during the experiments, the reaction with carbon. Higher %FeO increase the foam volume because FeO is the only source of oxygen for the formation of CO bubbles. For this reason some comparison are shown at same %FeO.

The graph of Figure 6 shows the volume ratio (V_t/V_0) as time function (sec) for the sample with recycling material and this one without.

The diagram shows that the slags with recycling material have a higher volume ratio and higher stability: the volume ratio is for longer upper the value 1 ($V_t > V_0$).

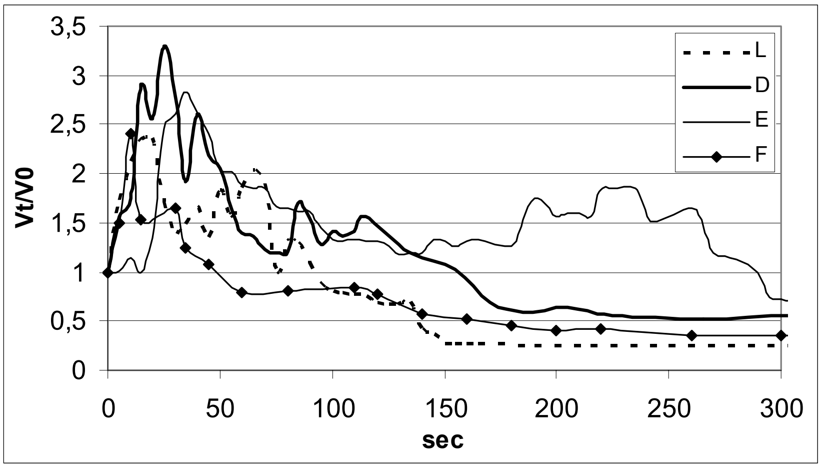

Figure 6: volume ratio for slag samples with recycling material (D and L) and without recycling material (L and F)

The graph of Figure 7 shows the experiments with slag samples without recycling material. The sample L has the better behavior with high volume ratio and better foam stability. The chemical analysis, reported in Table 1, show that the slag L is the one that has higher %FeO. This is in related to the fact that higher FeO in the slag favours the reaction with carbon.

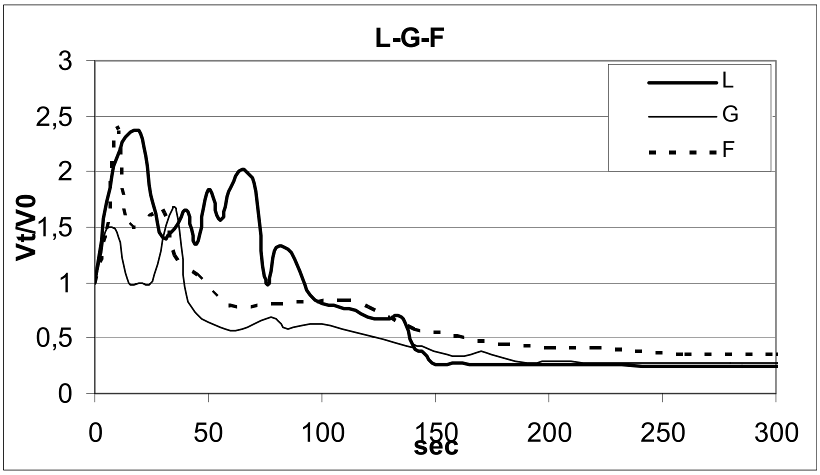

Figure 7: Volume ratio for slag samples without recycling material (L, F and G)

The graph of Figure 8 shows the comparison between the slag L without recycling material and the slag D with recycling material. Both samples have the same value of FeO.
The slag D has a higher volume ratio and better stability, although this one has a little lower SiO2 and higher S. In fact from literature higher SiO2 and lower S are favourable factors for the foaming slag stability.

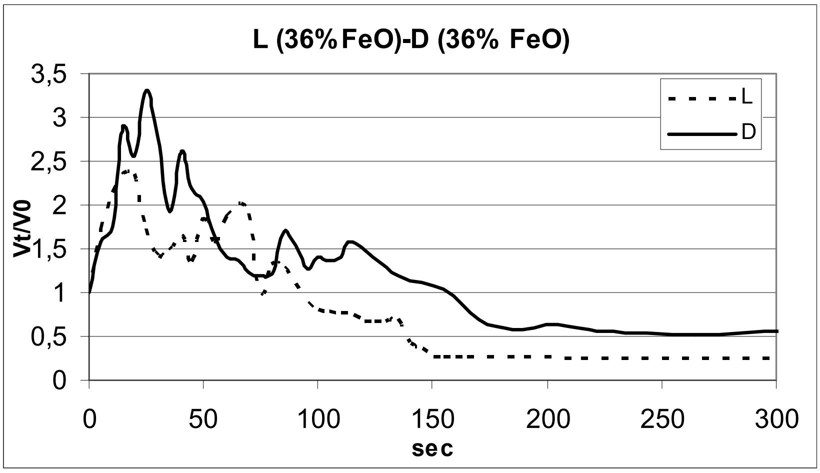

Figure 8: volume ratio for slag samples L without recycling material and D with recycling material at same FeO

The graph of Figure 9 shows the comparison between the slag L without recycling material, the slag D with recycling material at the same %FeO and the slag A with recycling material with higher %FeO. The slag A has a highest volume ratio, in according with the high FeO, but a lower stability. This slag has a lower value of SiO2 and higher S, factors that make worse the foaming stability.

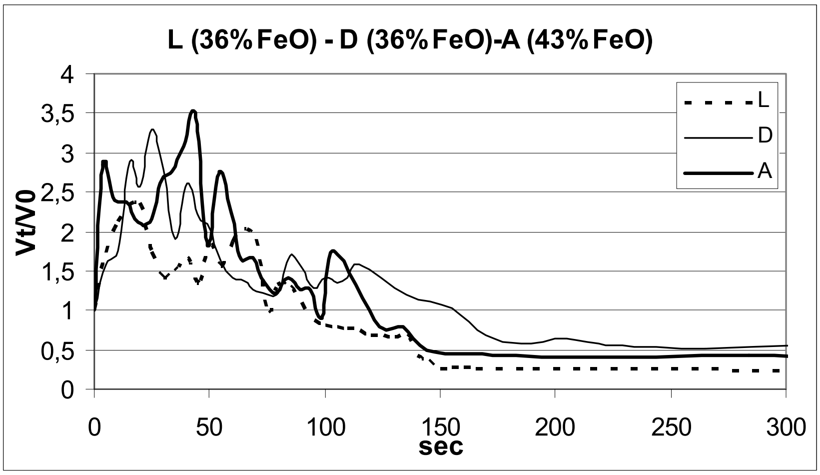

Figure 9: volume ratio for the slag samples L, D and A

The graph of Figure 10 shows the comparison between the slag L without recycling material, the slag D with recycling material at the same %FeO and the slag E with recycling material with little lower %FeO. This slag presents the best foaming behavior. The volume ratio is lower than slag D according to the lower %FeO, but higher than slag L without recycling material. The foaming stability is the best one and this in agreement with the chemical analisys: high SiO2 and low S.

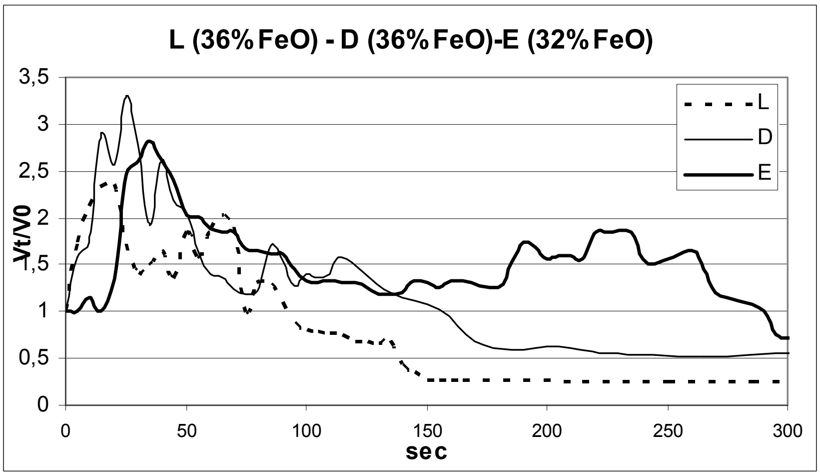

Figure 10: volume ratio for the slag samples L, D and E

CONCLUSION

The experimental results are confirmed the general principles of foaming practice:

- the graphs of Figures 8 and 9 confirm the influence of SiO_2: higher SiO_2 improve the foaming stability;
- the graphs of Figures 8 and 9 show that higher S make worse the foaming stability;
- the graphs of Figures 6, 8, 9 and 10 show that the presence of recycling material improve the foaming behavior:
    - the volume ratio is higher than without recycling material
    - the foaming stability is better than without recycling material

A plausible explanation of these phenomena is that the C2S present in the recycling material, as the second phase particles, can be nucleation sites for small CO bubbles increasing the number of bubbles and the final foam volume. Moreover the effective viscosity increases, with consequent increase of bubble stability.
The following pictures show the foaming behavior for the slag L without recycling material. The pictures are taken at 0, 30, 60, 90, 120, 150, 180, 210 sec.

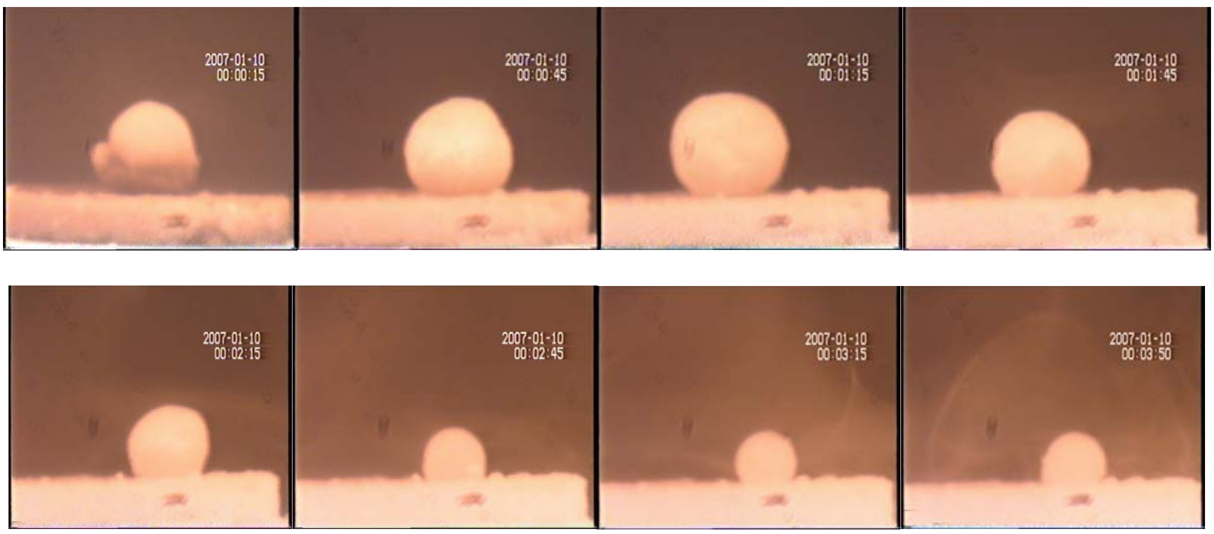

Figure 11: pictures at 0, 30, 60, 90, 120, 150, 180, 210 sec for the sample L without recycling material

The following pictures show the foaming behaviour for the slag E with recycling material at the same time. As shown in the graph of Figure 10, the foam with recycling material is much more stable than the case without injection recycling material.

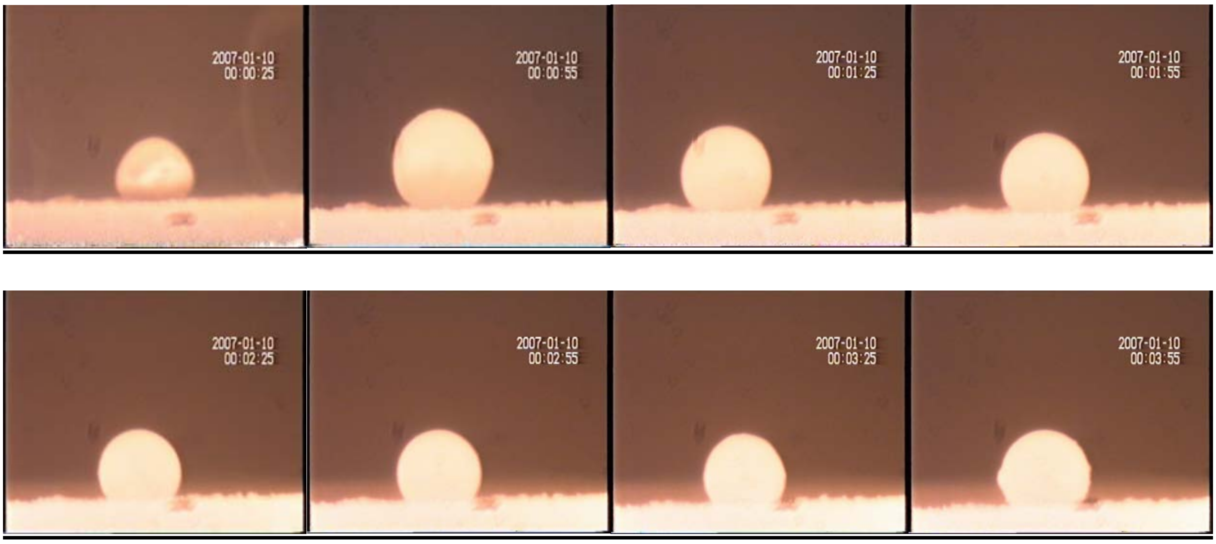

Figure 10: pictures at 0, 30, 60, 90, 120, 150, 180, 210 sec for the sample E with recycling material

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