LIME DISSOLUTION IN SIMULATED INITIAL STAGE OF BOF PROCESS*

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Resumo

O foco deste estudo é avaliar a capacidade de dissolução das partículas de cal a uma temperatura próxima da fase inicial de sopro do processo BOF. Os testes foram realizados em um forno elétrico utilizando amostras de Cal com diâmetros de 6 mm e 9 mm, 80% e 100% calcinadas em diferentes basicidades de escoria. Os resultados mostram que com o menor nível de calcinação a dissolução foi mais rápida. Podendo ser atribuído a algumas diferenças na porosidade da cal ou um efeito de formação de espuma observado durante os testes devido à evolução do CO2 da calcinação restante. O aumento na basicidade da escória resultou na redução da taxa de dissolução que pode ser atribuída a uma precipitação de fase sólida mais densa na interface das partículas aumentando a viscosidade da escória e reduzindo a porosidade da partícula. A partir de um modelo de regressão linear o nível de calcinação mostrou maior efeito sobre o coeficiente cinético do processo de dissolução seguido do tamanho de partícula. O efeito mais fraco foi a basicidade da escória. Este resultado sugere que a área de contato cal escória parece ser mais significativa do que a viscosidade no processo de dissolução de cal nos presentes experimentos.

Palavras-chave: Dissolução da Cal; Granulometria; Calcinação Cal; Basicidade.

LIME DISSOLUTION

Abstract

The focus of this study is to evaluate the dissolution ability of different lime particles size and calcination levels submitted to different slag chemistry, at temperature close to that of early stage of BOF process blowing time. Tests conducted in a small electrical furnace using lime samples of 6 mm and 9 mm particle size and 80% and 100% calcinated at different slag basicity reported results showing that lower lime calcination level produced the faster dissolution process. These results might be attributed to some differences in lime porosity or a foaming effect observed during the testes due to CO2 evolution of remaining calcination. The increase of slag basicity resulted in reduction of lime dissolution rate, which might be attributed to a denser solid phase precipitation at the interface lime particle-slag that might increase slag viscosity as well reduce particle porosity. From a multilinear regression model, lime calcination level showed the strongest effect on kinetic coefficient of lime dissolution process, followed by particle size. The weaker effect was from slag basicity. This result suggests that lime-slag contact area seems to be more significant than viscosity in the lime dissolution process of present experiments.

Keywords: Lime Dissolution; Particle Size; Lime Calcination; Basicity.

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1 INTRODUCTION

Lime dissolution during BOF process has being investigated through a collaborative work between RDBR (12º ArcelorMittal research center) and IFES. It involves the usage of laboratories and human resources from IFES (Federal Institution of Espirito Santos state) through a research contract with FACTO (Foundation for supporting the development of science and technology), partially sponsored by recent created EMBRAPII, a federal institution that has the mission to stimulate Companies-University joined research.

The focus of this study is to evaluate the dissolution ability of two different lime particles size with two different levels of calcination each, submitted to different slag chemistry, at temperature close to that of early stage of BOF process blowing time.

This initiative was carried out to give support to more comprehensive studies that aim at producing very low point P in steel (lower than 60ppm), as well as reducing BOF slopping and oxygen lance scull build up occurrences.

2 METHODOLOGY

Some limestone collected from Tubarão steel plant with the composition presented in Table I was used to prepare limes particles at IFES laboratory.

Table I – Limestone used as a raw material for lime production at IFES laboratory.

|	CaCO$_3$	SiO$_2$	Al$_2$O$_3$	S	P	Moisture max
Limestone	96,86	1,32	0,18	0,047	0,046	3,0

Two levels of limestone calcination were arbitrary defined as 100% and 80% for the two particle sizes also arbitrary defined as 6 and 9 mm.

Calcination times to reach the above calcination level was previously defined by a set of calcination tests performed at 950°C[1] summarized in figure 1.

In order to avoid lime deterioration effects in tests, only the material necessary of each teste was previously produced. In this case, the lime was kept inside the furnace which temperature dropped from the calcination one to 250°C for 30 second just before its utilization in dissolution testes.

Slag chemistry used in dissolution testes at 1400°C is presented in table II. They were defined from literature studies of BOF slag evolution during the early stage of oxygen blow[2]. Some properties were estimated through software FactSage 7.0 calculation (table III). These compositions were produced using high purity oxides except CaO that was from experimental lime particles.
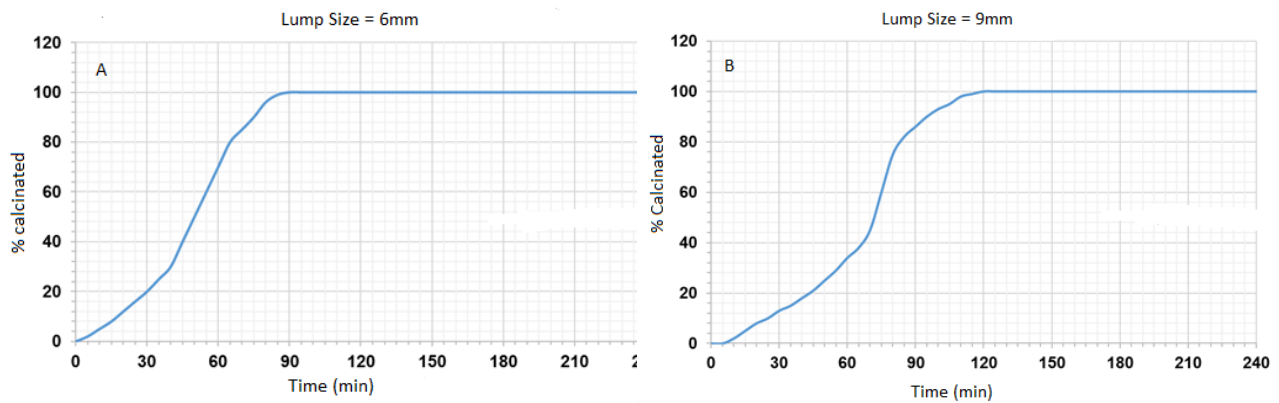
Figure 1: Limestone calcination curves

Table II – Final slag composition aimed for dissolution tests.

Slag	Basicity	Chemical Composition (%By weight)			
		CaO	SiO$_2$	FeO	MgO
1	1,25	35	28	33	4
2	2	35	17,5	43,5	4
3	3	35	11,67	49,33	4
4	4	35	8,75	52,25	4

Table III – Some predicted slag properties at 1400ºC.

Basicity	% Liquid	% de Solid MgO	aCaO
1,25	100,00	0,00	0,05
2,00	100,00	0,00	0,18
3,00	99,57	0,43	0,37
4,00	98,93	1,07	0,51

Lime dissolution tests were performed in a 3 Kg electrical resistance furnace with inert atmosphere as illustrated by figure 2.
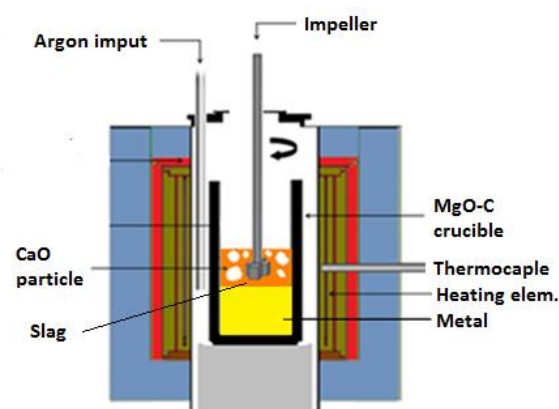
Figure 2: Lime dissolution experimental set up.

The experimental set up was design to use an especial hot metal, previously produced from a re-carburization of steel. This strategy was adopted in order to avoid

test contamination as well as to obtain a better thermal control of dissolution experiments. After 997g of metal melt at 1400°C, slag forming materials (total of 50 gr) were added and the crucible was homogenized for 2 minutes using an impeller rotating at 400rmp.

With the slag homogenized and temperature stabilized, lime particles (17.5g) were added and kept under the same impeller mixing speed for more 5 minutes, period during which two slag samples were taken at 2.5 minutes time steps. Table IV summarize all the steps of present 20 dissolution experiments.

Slag sample was crushed and washed in water to measure non dissolved lime. Due to the small amount of slag it was not possible to perform elemental chemical analysis.

Table IV – Steps of lime dissolution experiments

Tempo (min)	Procedures
-	Temperature tunning
0	Slag forming addition
2	Lime addition
4,5	Slag sampling
7	Slag sampling

3 RESULTS AND ANALYSIS

Table V summarizes the results of non-dissolved lime of all the experiments obtained by hydration of slag samples. Table VI presents the results of dissolved lime after de-hydration (draying). Both results are comparable as observed by figure 3, which show a consistency between them.

Table V – Summary of lime dissolution experimental results.

FeO/SiO2	Calcination level (%)	80%	80%	100%	100%	100%
	Sampling time (min)	2.5 '	5	2.5 '	5	5
1.18	Hydrated Free lime weight (g)	0.00	0.00	4.32	0.00	6.90
2.49		0.00	0.00	7.57	0.50	8.06
4.23		1.05	0.00	8.10	1.70	10.41
5.97		1.30	0.00	9.70	4.89	11.13

(Particle size (mm): columns under "6" = 80%, 80%, 100%, 100%; column under "9" = 100%)

Tabela 1 – Percentage of lime dissolved in slag.

FeO/SiO2		Particle size (mm)				
		6mm		6mm		9mm
	Calcination level (%)	80%	80%	100%	100%	100%
	Sampling time (min)	2.5 '	5	2.5 '	5	5
1.18		100.00	100.00	81.32	100.00	70.16
2.49	% Lime Reacted	100.00	100.00	67.26	97.84	65.14
4.23		95.46	100.00	64.97	92.65	54.98
5.97		94.38	100.00	58.05	78.85	51.87
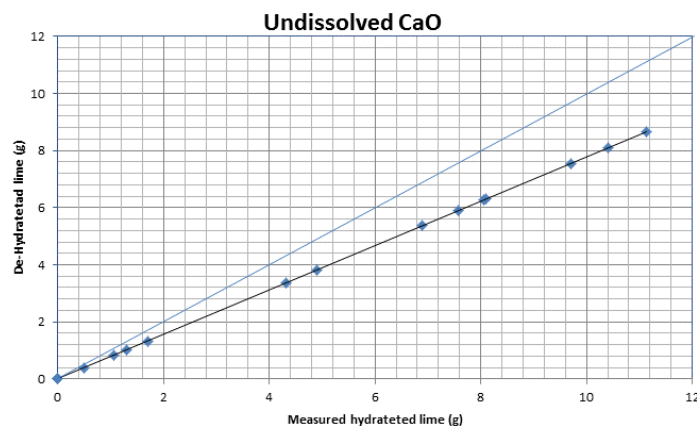
Figure 3: Comparison of non-dissolved CaO obtained from two different methods

Figure 4 summarize the results of dissolution tests. Faster dissolution was found from lower calcination level (80% Calcinated lime), lowers initial FeO/SiO2 slag relation and lower particle size.

Lime dissolution process is a well-known solid-liquid interfacial phenomenon where de Ca+ dissolution rate seems to be regulated by diffusion mechanism in a solid-liquid boundary layer, where more dense solid phase precipitation in lime surface is reported to impair dissolution rate by their effect on reducing liquid solid interface area and diffusivity[3]. Also, some slag properties like viscosity and interfacial tension might influence liquid infiltration inside lime particle porous.
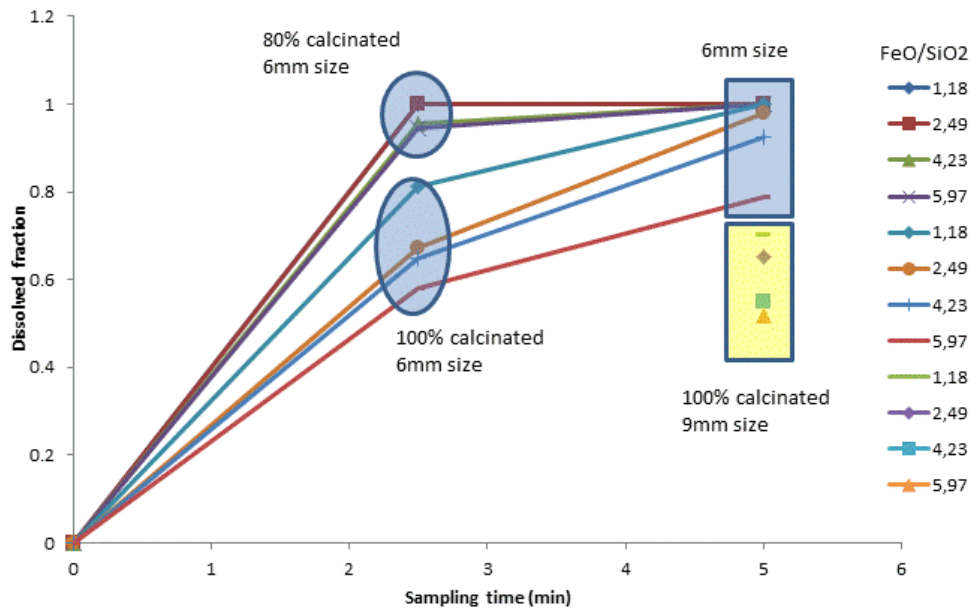
Figure 4: Summary of lime dissolution experiments

From thermodynamic point of view, some results from calculation obtained using CEQCSI software predict that the increase of FeO/SiO2 relation might result in solid phase precipitation like: 3CaO.SiO2 (C3S) and (Mg,Fe)O solid solution (MGW) which is summarized in figure 5.

These results motivates speculation that there might be two control mechanism affecting lime dissolution: one related to the more dense shell formation around lime particle by C3S precipitation and the other due to the change in liquid slag properties, like viscosity or interfacial tension that would reduce slag infiltration into solid phases.

In fact, simulation results from CEQCSI show also that solid fraction precipitation at higher FeO/SiO2 rate increase slag viscosity significantly (figure 6). This approach however was not predicted by Factage 7.0 calculation, which reported a lower value of viscosity.

For the possible mechanism presented above, a 100% liquid slag prediction would be not consistent to the reduction of lime dissolution observed in experiments associated to the increase of FeO/SiO2 slag ratio, unless some effect of increasing surface tension could takes place and reduce liquid slag wetting to lime particles.
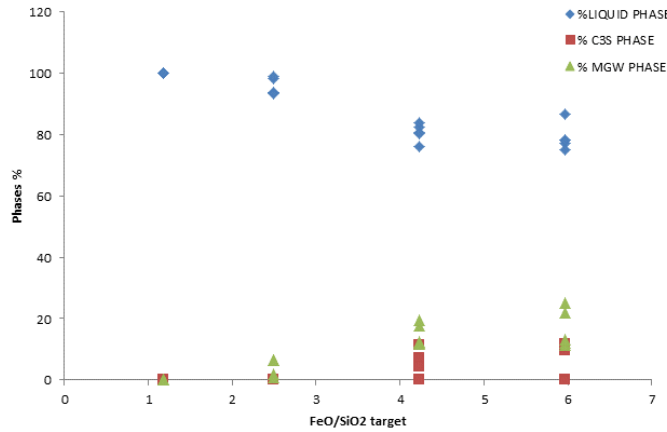
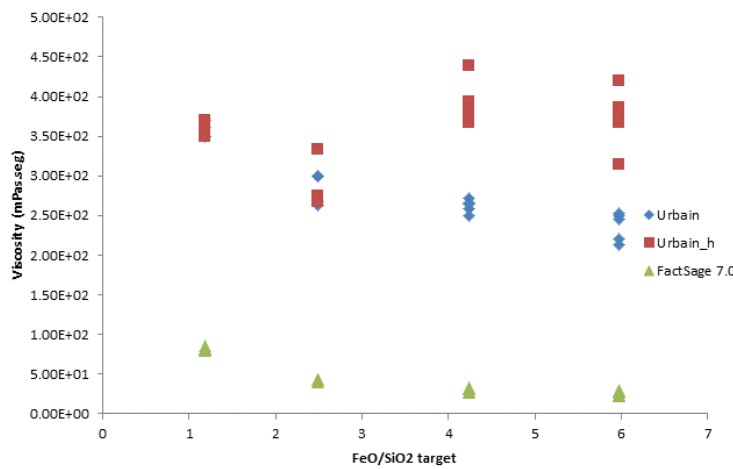Figure 5: Some predictions of phase's precipitation in function of FeO/SiO2 relation.

Figure 6: Prediction of slag viscosity: Urbain → liquid slag; Urbain_h → all slag phases

It is important to note that there is a relationship between FeO/SiO2 ratio and Basicity (CaO/SiO2) as presented in figure 7. Therefore and increase in FeO/SiO2 is mainly imposed by the reduction of SiO2 that, for the same amount of added CaO, will result in an increase of basicity which explain the C3S precipitation.
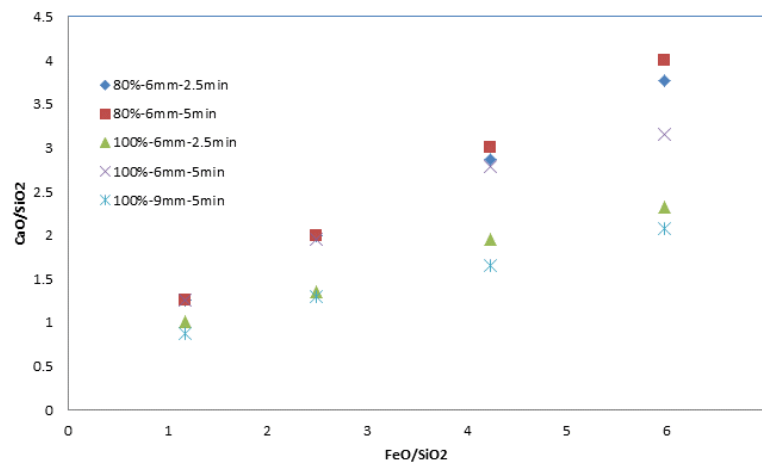

Figure 7: Relation between FeO/SiO2 and basicity

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The results of presents experiments suggests that, in conditions where SiO2 regeneration from hot metal Si is low, lime dissolution behavior would be hindered by the increase of basicity at lower T in condition where FeO content is still low. Therefore in order to speed up slag formation, some silica should be added to keep the basicity under a certain low level as well as a soft blowing practice should be adopted to increase FeO content in slag.

On the contrary, at high hot metal Si, basicity is low and therefore lower FeO is sufficient to keep higher lime dissolution rate, so hard blow strategy is enough to get good slag formation without excessive increase slag volume.

The above discussions have been oriented by thermodynamic calculation, which have some inaccuracy. Therefore in order to validate it some microscope analysis of undissolved lime residues should be performed.

Another important result extracted from figure 4 is the clear influence of calcination level of lime in its dissolution rate in slag. It was already documented that with the increase of calcination level there is a tendency for lime particle to increase density. Therefore, lime porosity would be reduced with the increase of calcination level and, as a consequence, less slag infiltration in lime particles would be expected and so lower dissolution rate. However, it was also observed that the remaining carbonation during dissolution test generated a higher foam slag due to the CO2 evolution. This effect can improve dissolution rate through the increase of Ca+ diffusion in lime-slag boundary lower. Therefore without a close view on the effect of calcination level in lime porosity it is impossible to identify the actual phenomenon that increased lime dissolution rate a lower calcination level.

It seems that endothermic characteristic of calcination process that would provoke a drop in temperature around lime particle is probably being dispersed very fast, avoiding an increase of slag viscosity locally close do dissolution front.

Going back to figure 4, the effect of increasing particle size is straightforward explained by the reduction of specific contact area. In fact lager particle size with similar porosity will offer to the dissolution front a smaller area.

From experimental data it is possible to tune a kinetic model. The classic model described by equation 1 was used:

(1)
$$\frac{dW}{dt} = k \cdot (a_{CaO} - 1)$$

Where W is lime weight (Kg), t is time (min), K is coefficient (Kg/min) and a is CaO activity.
This model states that dissolution rate (loss of lime weight (W) with time (t)) of certain weight of CaO (lime) is monotonically related to the difference between CaO activity in slag (reference state as pure CaO) and its value at hypothetical CaO saturation where its activity would be equal to one, modulated by a coefficient (k) that introduce the interfacial solid-liquid resistance to the dissolution process (boundary layer effect).

The integration of equation 1 produces the following expression:

$$(2), \qquad Ln\left(\frac{W}{W_0}\right) = k \cdot (a_{CaO} - 1) \cdot (t - t_0)$$

where the subscript W 0 means the weight beginning of lime addition test (Kg), W is lime weight (Kg), t is time (min), t0 is time started the addition, K is kinetic coefficient (Kg/min) and a is CaO activity.

Using the experimental data we can predict k from equation 2as shown in figure 8 for different basicity. From these results, a statistical model was built (a multi-linear model) relating "k" to the trials conditions variables as basicity; particle size and calcination level of lime. The summary of regression coefficients and others statistical tests are shown in table VIII. The adjusted R square is 98.52 with a very low p-value which means a very good adjustment of this model to the data (figure 9).
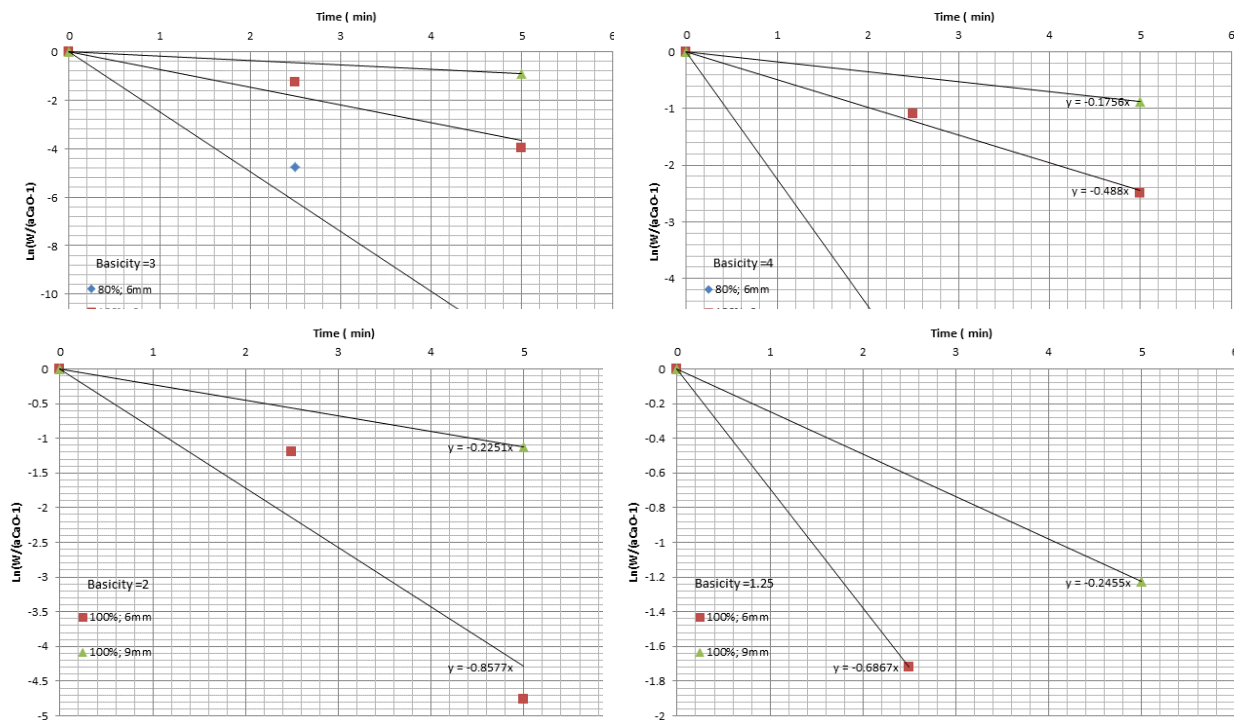

Figure 8:   Prediction of kinetic coefficient (k)

Table VII: summary of statistical multi linear correlation

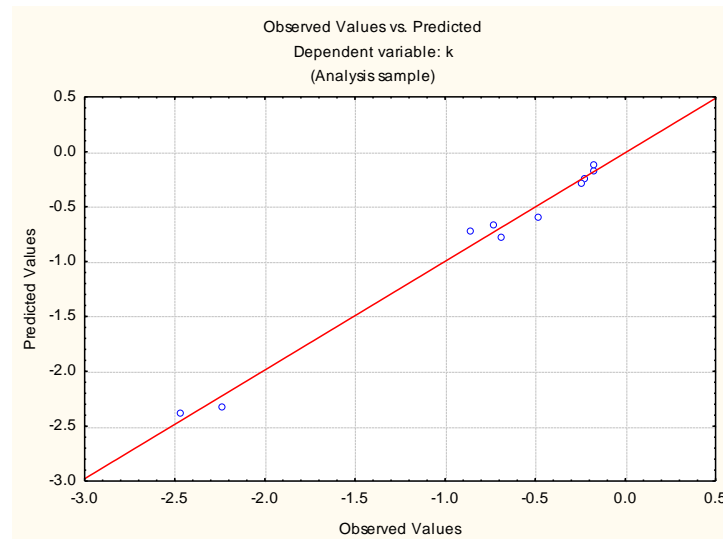| Effect	Parameter Estimates (Spreadsheet1) Sigma-restricted parameterization					
	k Param.	k Std.Err	k t	k p	-95.00% Cnf.Lmt	+95.00% Cnf.Lmt
Intercept	-10.4465	0.459720	-22.7235	0.000000	-11.5714	-9.32159
burning level	8.6157	0.469657	18.3446	0.000002	7.4665	9.76488
basicity	0.2615	0.135409	1.9310	0.101699	-0.0699	0.59281
lump size	1.4570	0.216554	6.7282	0.000525	0.9271	1.98691

Figure 9: Fitness of the multilinear model of kinetic coefficient

From coefficients of table VII, reduction of calcination level or basicity or particle size would lead a lower "k" value which means a faster dissolution rate. As these variables were standardized between zero and one, we can notice that calcination level was the more influenced variable followed by particle size. Basicity showed weakest effect. This result suggests that lime-slag contact area seems to be more significant than viscosity in the lime dissolution process of present experiments.

As long as high basicity process is a restriction for BOF process, fast slag formation that requires fast lime dissolution would be regulated mainly by variables that determine lime-slag interfacial area (particle size; porosity and slag foaming) and FeO content, which would regulate viscosity at a certain temperature avoiding solid phase precipitations at early stage of slag formation. Temperature, itself is one of the most important variable that affects strongly slag formation: the highest one the better.

4 CONCLUSIONS

Tests results using lower lime calcination level did no reduced lime dissolution rate; on the contrary these tests reported a faster process than the others that used 100% Calcinated lime. These results can be attributed to some differences in lime porosity (higher in 80% Calcinated materials) or a foaming effect observed during the tests due to CO2 evolution of remaining calcination.
The increase of slag basicity resulted in reduction of lime dissolution rate, which can be attributed to a denser solid phase precipitation at the interface lime particle-slag that might increase slag viscosity as well reduce particle porosity.
Lime calcination level was the strongest effect on kinetic coefficient of lime dissolution process, followed by particle size. The weaker effect was from slag basicity. This result suggests that lime-slag contact area seems to be more significant than viscosity in the lime dissolution process of present experiments.

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