Rate of Lime Dissolution in Converter Slag

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Abstract

The dissolution rate of burnt lime in slag is a key parameter in the steelmaking process with the slag playing an important role in the refining of, for example sulphur and phosphorus. In the day to day operation in the steelshop there are two parameters available to judge whether the lime matches the quality standards: size distribution and reactivity. When these parameters are linked to the parameters of the dissolving mechanism, the size is a derivative for all the macroscopic parameters (i.e. parameters particle heating, external diffusion), the reactivity is the derivative for all the microscopic parameters (i.e. internal surface, porosity, apparent density). By carrying out a factorial 2 * 2 * 5 experiment (size, reactivity, time) it has been shown that the reactivity is high and never impedes the dissolution rate. Rather, lime sample size accounts for the constraint in dissolution. Knowing that the reactivity is by definition the affinity of lime for water, it is obvious that lime with a higher reactivity will suffer more from weathering than lime with a low reactivity. It is advised to fit the reactivity of the lime to the size of the lime or to introduce extra precautions to prevent the lime from weathering.

Introduction

In the basic oxygen steelmaking process the slag in the BOS converter plays an important role in respect of refining aspects and refractory life expectancy. In order to control the process properly a slag formation strategy is planned: the slag path (i.e. the evolution of the liquid slag composition during the process). The lime dissolution rate defines the dosage strategy of the burnt lime, which is the most important slagformer.

In the BOS 2 shop of CORUS IJmuiden problems were sometimes experienced with slag formation in the converter and with lime storage in bins during the summers. To ensure the phosphorus and sulphur raffinage, it was sometimes necessary to add 20 to 40 % more lime than usual to the slag. The origin was of these problems was not clear. Therefore a R&D investigation was undertaken. An objective was to guarantee the lime quality in the future by defining a way of characterising the lime quality.

The overall objective of this study was to find a way to improve the process control of slag formation in the BOS converter by a better control of the planned strategy of slag formation. To do so it was necessary to find out which parameter influence the slag formation most. As lime had a large contribution to the final slag consistency, it was obvious that the rate of lime dosing and rate of lime dissolution played an important role in the slag formation. In the past R&D tried to define the quality of lime by means of parameters that should be related to the refining properties of the lime. This lime quality was made up of the internal surface (B.E.T.), porosity, reactivity (slaking test), apparent density and size distribution[1,2,3]. These parameters were chosen after studying the lime dissolution mechanism. From literature review it was

established that the mechanism of lime dissolution in slag followed a sequence of several processes, namely:

1. Heating of the lime, while a slag layer solidified around the lime particles[4].
2. Reliquefying the 'frozen' slag layer and penetration of the lime by the slag[5,6,7,8].
3. Diffusion of slag components through a stagnant diffusion layer around the lime particle[1,2,3,4,5].
4. Breaking down of the crystal lattice of the lime into separate crystallites[3,9].
5. Dissolving the separate crystallites in the slag[3,9].

In the day to day operation of a BOS shop the quality of lime is defined by its reactivity and size distribution. It is known from the lime burning process[3] that the reactivity is related to the burning temperatures and the residence time of the lime in the burning process. The other microscopic parameters (i.e. internal surface (B.E.T.), porosity and apparent density) are also determined by the lime burning temperature and residence time[3]. The concept is that the reactivity is a representative measure for all the microscopic properties of the lime. The main advantage being the simplicity of measuring the reactivity. The macroscopic process steps (heat penetration and diffusion toward the particle) are represented by the size of the particles. The question to answer first is: what is more important, the reactivity of the lime or the size of the lime particles. Or to rephrase the question: what is more important, the microscopic or the macroscopic properties of the lime. To answer this question a series of experiments was performed in the metallurgical laboratory of CORUS Research Development and Technology.

The reactivity and size distribution of the lime

The reactivity of the lime is measured by the slaking test (i.e. dissolution of lime into water). The slaking test is performed in an insulated vessel with an exact amount of water, an exact amount of lime (of a definite size) is added to the water at the start of the test. The water and lime are stirred vigorously and the heat of the reaction will rise the temperature, which is measured on-line[9,10,11,12]. The result of the slaking test is a rise in temperature per minute, which is a measure for the rate of reaction with water. Due to the weathering of the burnt lime the reactivity is not an absolute measurement. Weathering is an external influence and not a direct property of the lime itself. Therefore reactivity will be determined by the inconsistent down grading of the lime by the weathering.

In literature[9] it is proposed to use a recalcination treatment at 910 $^{\circ}$C before the actual reactivity test. This temperature was chosen to remove water and carbon dioxide from the lime. The recalcination re-establishes the original reactivity of the lime immediately after the burning process in the rotary kiln. Previous research showed that within the available time span only water absorption will take place. For the removal of water from the lime a temperature of 630 $^{\circ}$C is high enough to recalcinate the lime.

The reactivity of lime stems from the decisions made in process control during the burning of the limestone. The selection of a specific burning temperature and a residence time in the rotary kiln determines the reactivity of the lime simultaneously with the specific surface, the pore distribution and the apparent density[3]. This justifies the statement that reactivity can be regarded as a representative for the microscopic parameters. Because the weathering is reversible[1,9] it is clear that the weathering does not affect the intrinsic quality of the lime.

The size distribution can be influenced by the limestone crusher and the choice of the size fraction. Previous research was carried out at CORUS IJmuiden[13] in order to optimise the size distribution. It concluded that a small size would be optimal, but sizes below 7 mm would be ejected from the converter by the off-gases. This restriction is an economical consideration: the size distribution should be chosen such that the size is minimal and that the losses (size below 7 mm) are as low as possible. Typically the size distribution is such that 80% of the lime is in the range of 10 mm to 20 mm.

Experiments

In an induction furnace 20.5 kg iron was melted and mixed with 21 kg steel to form a liquid steel melt (2.0% C - 0.04% Mn - 0.025%P - 0.01% S - 0.25% Si) of 1550 ^{o}C. On top of the liquid steel 160 to 170 grams of synthetic slag was added. The synthetic slag was made by mixing and melting 40 w-% SiO_2, 45 w-% FeO and 15 w-% CaO, this slag being typical for the slag composition in the converter in the period before the main blow. At this time the oxygen lance is in a high position to form and mix the slag.

A set of high reactive lime samples (R=31 to 45°C/min) and a set of low reactive samples (R=10 to 15°C/min) were burned in a well controlled furnace. Both sets of samples contained five small bars of lime (10*10*40 mm) and five large bars of lime (20*20*40 mm). The chemical analysis of the lime is given in table 1. The samples were transported under absolutely dry conditions to IJmuiden to prevent weathering of the lime. The four different samples (small and large high reactivity, small and large low reactivity) were mounted together on a submerging device and were simultaneously submerged into the slag. During the experiments the induction power was reduced to a minimum in order to maintain a slag layer of constant thickness.

The first set of samples was submerged for 10 seconds without preheating, the second set of samples was submerged for 30 seconds. The following sets (third, fourth and fifth set) involved preheating for 60 seconds in an oven at about 1500 ^{o}C. The third set was submerged for 60 seconds, the fourth set for 120 seconds and the fifthset was submerged for 180 seconds. After each submerging of a set of lime samples the slag was completely removed from the steel and fresh synthetic slag was applied on top of the steel. The steel was reheated to 1550 ^{o}C before submerging the next set of samples.

After having been submerged in the slag the samples were cooled down and dismantled. The samples were sawn in half and embedded in an inert resin. Photographs were taken of the cross-section of these embedded lime samples. A typical example of these photographs of a set of slag submerged lime samples is given in figure 1. An outline of such a sample is depicted in figure 2. Seen from the lime core, lime is distinguished in the centre of the sample, surrounded by an area of lime in which slag had penetrated. On the outer side of the sample slag that had adhered to the lime sample can be seen.

The parts of the samples that had not been embedded in resin were analysed microscopically and examined applying X-ray microanalysis technique. The samples were polished using Al_2O_3-polishing paper (there was no Al_2O_3 in the slag nor in the lime). A microprobe was moved in a straight line along the cross-section of the sample. While doing so, the probe analyses the sample locally for the elements Ca, Fe, Si, Mg, O. Typical results of these

analyses are shown in figure 3. The dashed vertical lines show the boundaries between the slag layer, the penetration layer and the pure lime core. From these results the average composition of the layers can be calculated. The average composition of the three distinct layers is given in table 2.

From photographs of the sets of submerged lime samples the average thickness of the penetration zone and the average reduction of the thickness of the lime core were measured by graphical integration and dividing the result by original width of the sample. These data were used as input for analysis of variance. The results are presented in table 3 and the outcome of this statistical analysis is shown in the figures 4a-d. A clear distinction is shown between the large and small size samples, whereas the high and low reactivity samples show no difference. A significant dependency on sample size and submerging time was found. There was significant (95% confidence) non-influence of the variations in the reactivity. The interactions that were significant (95% confidence) were time with size and time with reactivity. From these results there is a strong influence of the size of the samples and only a small, second order influence of the reactivity of the lime. This does not mean that reactivity is not important, but rather that the reactivity is so high that it doesn't restrict the dissolution rate at all. The dissolution rate being restricted only by the size of the lime. As mentioned earlier the size is already optimal.

As frequently reported, the mechanism of lime in slag in the converter is a sequence of several processes. This dissolution mechanism is compared with the results of the experiments.

1. Initially the lime will be heated up by the slag[4]. A slag layer will solidify ('freeze') around the lime particles. This is observed in the experiments with non-preheated lime samples. These samples do not show any slag penetration or dissolution. Heating the lime is preliminary to any other process in the dissolution of the lime.
2. Following reliquefying the 'frozen' slag layer the lime will be penetrated by the slag[5,6,7,8]; the process of slag penetration being dependent on the pore size and the properties of the slag that penetrate the lime. The process of slag penetration depends also on the pore density (pores per unit surface). This leads to the statement that this process is a mixing of macroscopic and microscopic mechanisms. The comparison of the figures 4a+b with figures 4c+d demonstrate that dissolution of the lime takes place after the penetration of the slag.
3. If just one component is penetrating the pores preferentially, then this component must diffuse towards the lime particle through a stagnant diffusion layer[5,6,7,8]. This is a macroscopic process. The X-ray analysis using the microprobe line scan shows that there is only FeO_n ($FeO + Fe_2O_3$) and CaO in the slag penetration layer. From this fact is concluded that FeO_n diffusion into the lime particle does occur.
4. The next thing to happen is the break down of the crystal lattice of the lime into separate crystallites[3,9,14]. The ease of breaking down the lattice is related to the number of active attack sites in the pores and the accessibility of these sites (i.e. pore size). It is suggested that the active attack sites are located in the points of tangency between two crystallites. Even if this contention is not correct, lattice breakdown is a microscopic parameter.
5. The separate crystallites will eventually dissolve in the slag[3,9]. The slag present in the pores mainly consists of FeO_n molecules. Most likely calcium-ferrites will be formed. Calcium-ferrites have a low melting point and will be liquid at relatively low temperature. This makes it possible for the dissolved lime to leave the pores. When for instance calcium-

silicates would had been formed, the pores might have been blocked by the solid calcium-silicates and the lime dissolution would have stopped.

Discussion

The ultimate goal of lime additions in the oxygen steelmaking process is to create a slag in which all of the lime is dissolved at a certain moment. Therefore, while looking for a quality parameter for lime dissolution in the BOS shop operation, it is important to know which percentage of the lime added to the slag is actually dissolved in the slag. This is controlled by the lime dosing rate and the lime dissolution rate in the slag. The dissolution rate will be an amount of lime per unit surface area per unit time. When this is linked to the total surface of the particles (this is depending on the size distribution) the amount of lime dissolved in the slag could be known at any moment. The small sized lime particles cause a larger percentage of the lime to dissolve into the slag than the large lime particles. This is demonstrated by the analysis of variance. This effect is emphasized by the selection of percentages instead of an absolute rate of mass of lime dissoluted per unit time per unit surface. This selection shows the overall process of dissolution and this is the process which must be managed in the steelshop.

The very first question to answer is what is more important: the chemical and physical properties of the lime or the size of the lime. This question can be rephrased as: are the microscopic processes (i.e. slag penetration into the pores, breaking up the crystal lattices and dissolution of the crystallites) or the macroscopic processes (heating of the lime particles, diffusion towards the lime particle) the rate determining processes. As mentioned before the everyday practise of a steelshop will use the size distribution (a derived estimation of the macroscopic properties) and the reactivity of the lime (a derived estimation of the microscopic properties). The experiments confirm the mechanism as stated in the previous paragraph. The experiments show the influence of the size of the lime particles on the dissolution rate of the lime. A logical explanation for the influence of the partical size is given by the heating after charging the lime into the slag and the slag penetration into the lime. Whether the slag penetration is depending on the degree of preheating has not been investigated. It is the author's view that the slag will not penetrate beyond the heat penetration.

To examine all the parameters (internal surface (B.E.T.), porosity, reactivity, apparent density), is more complicated than considering just size and reactivity. For the day to day operation it is sufficient to distinguish the macroscopic parameters, represented by the size distribution, from the microscopic parameters, represented by the reactivity. From literature on lime burning[3] and the fact that the reactivity is restorable after weathering by recalcination[9] it is concluded that the reactivity can be taken as a representative value for the lime quality. The reactivity can reflect an intrinsic lime quality if the effect of weathering is excluded[1].

With respect to the high reactivity, one should consider the fact that reactivity of the lime is by definition the affinity of lime to water. The redundant high reactivity of the lime leads to unnecessary weathering of the lime. The major effect of this is crumbling of the lime to a size below 7 mm. This will lead to an increase of the losses of lime being ejected from of the converter by the off gasses.

Conclusions

As suggested by previous research, the slag dissolves according the following sequential mechanism:
1. Heat penetration into the particles
2. FeO_n rich slag penetration into the pores of the lime
3. Diffusion of FeOn through a stagnant layer around the particle
4. Breaking down of the crystal lattice of the lime
5. Dissolving of the lime crystallites into the FeO_n slag and formation of liquid Calciumferrites

The above-mentioned mechanism requires a slag with a high FeO_n content to dissolve the lime rapidly. The high FeO_n content in the slag prevents the building up of calciumsilicate layers around the lime particle. Such a slag is present during the first stage of the oxygen blowing process in the converter and at the end when all the carbon is already oxidised. The lime in the slag is needed for refining purposes as well as to protect the refractory lining during the process. Therefore it is necessary to have the lime dissolve completely during the first stage of the process.

As the reactivity of the lime is very high, the dissolution rate is restricted by the size of the lime particles. The main conclusion is that the reactivity is redundant high. This might be necessary for the lime producer to meet the specifications regarding minimum reactivity, taking into account the standard deviation in the reactivity and the loss of reactivity due to weathering. For the steelshop it either calls for additional precautions to prevent weathering or a lower reactivity should be accepted (preferable while lowering the standard deviation, if possible).

The high reactivity means by definition more weathering of the lime. The reactivity should be fitted to the size distribution to avoid weathering as much as possible. The reactivity can reflect an intrinsic lime quality when the effect of weathering is excluded.

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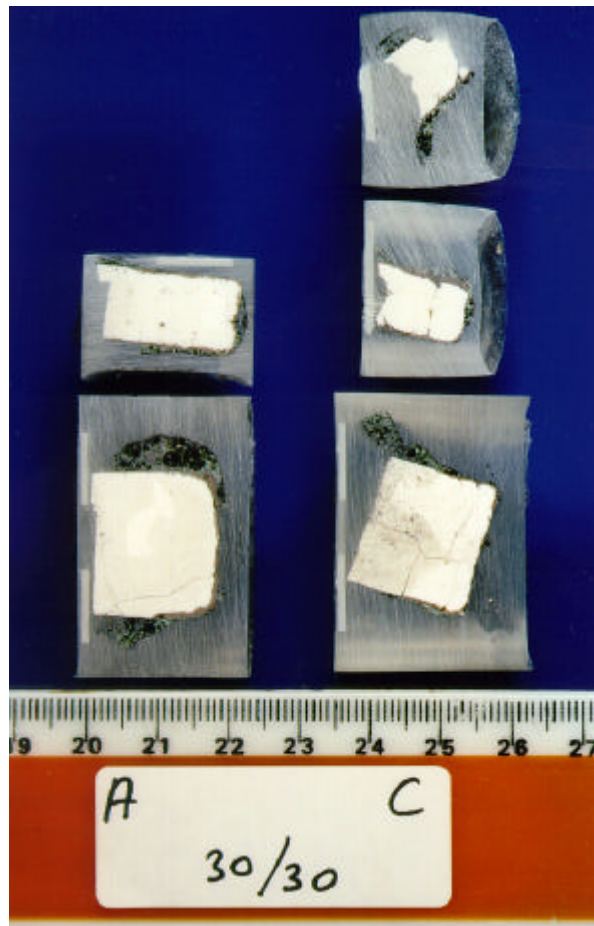
Figure 1   A set of slag dipped lime samples
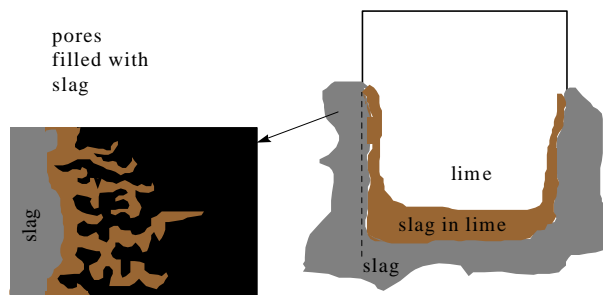
Figure 2   Outline of the slag dipped lime sample
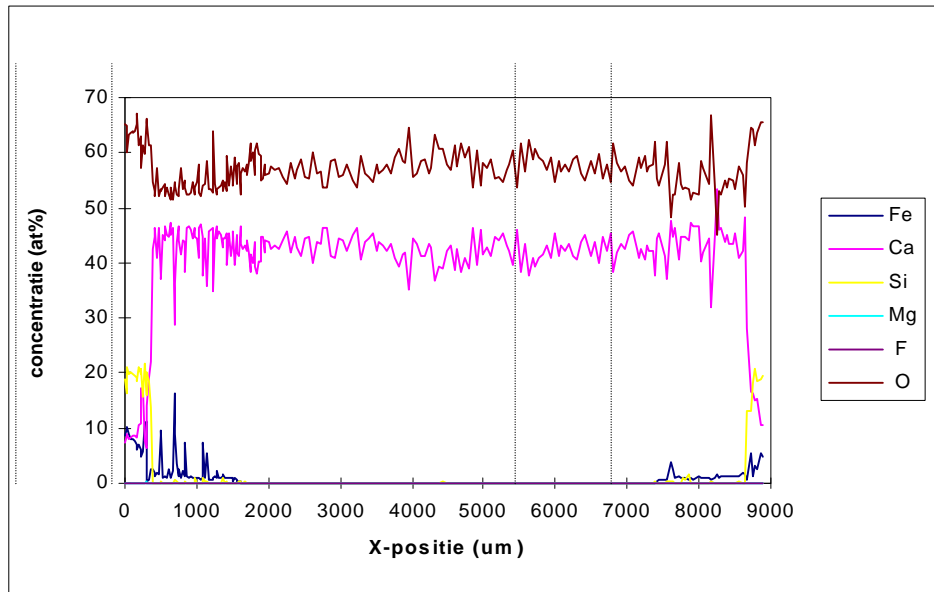
Figure 3   A typical plot of the micro-probe line scan over the slag dipped lime sample
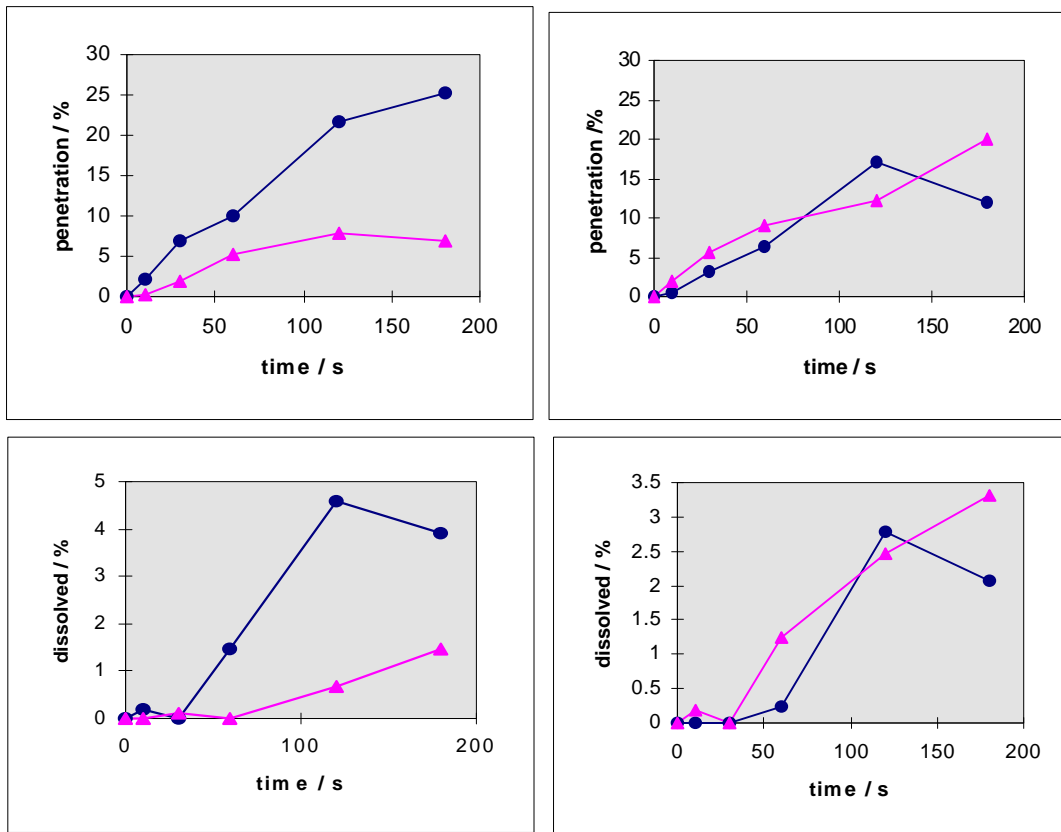
Figure 4a (left hand, top) slag penetration in the lime sample, the x-axis shows the time of dipping in the slag; ▲ results for the large samples; ● results for the small samples.

Figure 4b (right hand, top) slag penetration in the lime sample, the x-axis shows the time of dipping in the slag: ▲ results of the hard burned samples; ● results of the soft burned samples.

Figure 4c (left hand, bottom) lime dissolution of the lime sample, the x-axis shows the time of dipping in the slag: ▲ the results of the large samples; ● the results of the small samples.

Figure 4d (right hand, bottom) lime dissolution of the lime sample, the x-axis shows the time of dipping in the slag: ▲ the results of the hard burned samples; ● the results of the soft burned samples.

Table 1   Chemical analysis of the lime

	small, low react.	large, low react.	small, high react.	large, high react.
CaO w-%	96.8	96.8	99.0	99.0
MgO	0.72	0.72	0.38	0.38
S	0.151	0.151	0.009	0.009
SiO_2	1.51	1.51	0.06	0.06
Al_2O_3	0.35	0.35	0.03	0.03
Fe_2O_3	0.19	0.19	0.08	0.08
CO_2	0.20	0.20	0.30	0.30
reactivity $^{o}C/min$	10	15	31	45

Table 2   X-ray analysis by microprobe line scans

composition weight-%	hard burned		soft burned	
	small	large	small	large
slag layer				
SiO_2	29,3	45,5	50,0	49,9
CaO	63,9	35,4	23,4	29,4
FeO	2,9	15,1	23,9	13,2
O (excess)	3,9	4,0	2,7	7,4
penetration layer				
SiO_2	0,3	0,5	0,2	0,2
CaO	86,1	78,0	91,5	89,6
FeO	2,8	5,1	4,7	3,7
O (excess)	10,8	16,4	3,5	6,5
lime core				
CaO	87,5	72,4	80	88
O (excess)	12,5	27,6	20	12

Tabel 3   Analysis of variance

major effects:	slag penetration		dissoluted lime	
degree of freedom	1	95%b.i.	1	95%b.i.
A = time	97.1	**34.7**	7.1	**17.8**
B = reactivity	lumbed		lumbed	
C = size	172.1	**61.5**	14.5	**36.3**
interactions				
degree of freedom	1		1	
AB	28.4	**10.1**	lumbed	
AC	40.8	**14.6**	2.9	7.3
BC	lumbed		lumbed	
ABC	lumbed		3.5	8.75
rest = lumbed	2.8		0.4	
degree of freedom	3		3	
significance criterium:		10.1		10.1