DEPHOSPHORISATION IN BOF STEELMAKING

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ABSTRACT

Phosphorus content in hot metal has been increasing in the last years at Huachipato Steel plant, as low phosphorus iron ore availability has been decreasing, with a clear tendency to continue the same trend.

This has led to study the phosphorus slag-metal partition ratio at the BOS furnaces both in high carbon and low carbon steelmaking. Steel and slag samples were taken both for high carbon and low carbon steels. Some samples were also taken during the blow to evaluate slag composition evolution. Blowing practices at CSH consider obtaining high carbon steels via catch-carbon practices. Blowing patterns are designed to obtain partition coefficients around 80 for high carbon steels. Low carbon steels, with harder blowing practices, attain values close to 100. Vanadium behaves very much like phosphorus, and its average partition coefficients measured are around 200 for high carbon steels, and 400 for low carbon steels.

Both phosphorus and vanadium presence in the BOF high carbon steelmaking slags have been examined by optical and scanning electronic microscopy, and chemical analysis of the different phases present have been done by energy dispersive spectroscopy (EDS).

The mathematical correlation model developed is used to predict phosphorus content obtained in steel after blowing, using operational practices of the year 2007. The calculation considers the phosphorus in the converter charge, the temperature and carbon attained after blow, as well as slag basicity and FeO contents.

The results are compared with the expected theoretical equilibrium slag-metal partition ratio, and the percentage of approach to equilibrium is calculated. While this value stays around 20% for high carbon steels, it is slightly over 30% for low carbon steels. The results are also used to predict reblow frequency at different phosphorus contents in hot metal. Since this parameter grows strongly as phosphorus of the hot metal continues to increase, it leads towards changing operational practices to obtain high carbon steels with acceptable phosphorus levels.

INTRODUCTION

Compañía Siderúrgica Huachipato (CSH) Steel plant's blast furnaces have worked during the last years with pellets from Compañía Minera del Pacífico (CMP) and magnetitic lump iron ores as iron sources. While CMP pellets show only 0.017%P contents, whereas the lump magnetitic ores feature moderate phosphorus content, averaging 0.075%P. Therefore hot metal sent to the LD converters is low phosphorus, around 0.060%P, and showed excellent operation characteristics. High carbon steels could be blown with the catch-carbon method, shortening blowing times and increasing steel yield.

During the last year, availability of these ores decreased sharply, charging frequently hematitic high phosphorus lump ore in the blast furnaces, with 0.290%P contents as a typical value. Obviously phosphorus in hot metal increased seriously, getting up to 0.125%P. Under these circumstances operation started to be slightly disrupted, showing frequent reblows due to high phosphorus in the obtained steel baths. As in the near future only lump ores with even higher phosphorus contents shall be available, as shown in Table 1, hot metal phosphorus content shall be increased to higher values, and serious operation problems at the LD converters must be expected. This has led to study the phosphorus slag-metal partition ratio at the BOS furnaces both in high carbon and low carbon steelmaking in different blowing conditions.

Table 1: Chemical composition of CMP iron pellets and lump ores available at Huachipato steel plant in the last years and in the near future

	Fe%	SiO_2%	Al_2O_3%	CaO%	MgO%	P%	V%	S%
CMP pellets	65.00	2.50	1.00	1.00	0.70	0.017	0.200	0.060
Lump magnetitic ore	62.12	6.45	1.27	1.46	1.36	0.075	0.350	0.080
Lump hematitic ore	62.03	6.45	1.27	1.03	0.99	0.290	0.200	0.070
Hi-phos. lump ore	65.00	2.50	1.00	1.00	0.70	0.500	0.080	0.060

Note: that magnetitic lump ore has a significant vanadium content, somewhat lower for pellets and hematitic lump ore, and low for hi-phosphorus lump ore.

BOF Operation

Huachipato steel plant produces both low and high carbon steels for the local market. Low carbon steels are normally hard-blown to reach 0.04%C. High carbon steels for grinding media is one of Huachipato's strong going products. These steels are normally produced via the catch-carbon process with soft-blowing techniques to get low phosphorus and vanadium values in the steel bath. The two different blowing techniques are detailed in Tables 2 and 3.

Table 2: Blowing pattern for low-carbon steel: %C< 0.04

Time (min)	Lance height (m)	Oxygen flow(Nm^3/min)
00 – 05	1.9	310
05 – 15	1.5	310
15 – end	1.3	310

Table 3: Blowing pattern for high-carbon steel: 0.10 < %C< 0.80

Time (min)	Lance height (m)	Oxygen flow(Nm^3/min)
00 – 05	2.0	310
05 – end	1.8	260

After blow at the converter phosphorus values obtained in 2007 average 0.010% for low-carbon steels, and 0.015% for high carbon steels. Vanadium values were 0.004% and 0.010%, respectively. Required reblows due to high phosphorus in the bath have been evaluated for the two different blowing patterns, as well as for different average hot metal phosphorus:

Table 4: Reblows for different phosphorus contents in hot metal

Time period	%P hot metal	low carbon steel (% reblow)	high carbon steel (% reblow)
First half 2006	0.062	0.05	< 2.0
Complete 2006	0.094	0.33	4.8
Complete 2007	0.111	0.92	8.4

While during the first half of 2006 operation showed no problems concerning phosphorus contents in the steel bath, the percentage reblow values became significant as phosphorus increased in hot metal, disrupting operation stability.

METHODOLOGY

For statistical analysis data was taken from steelshop operation of the years 2006 and 2007. Steel bath samples were taken form the converter through a *lolly-pop* type sampler. Chemical analysis was made by optical spectroscopy in an ARL equipment. Slag samples were taken by immersing a steel rod in the liquid slag in the converter, and analysis was made with a X-ray fluorescence equipment. Data was revised for completeness.

For slag characterization and analysis, samples were taken for optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The slag samples were taken immersing a steel rod in the liquid slag in the converter. They were mounted both perpendicular and flat in the briquette and polished without use of water to avoid reaction with undissolved lime. Chemical analysis through EDS was made in several locations of both samples, as to have at least 5 analyses of each phase present.

RESULTS AND DISCUSSION

Phosphorus Slag-metal Partition Ratio

Phosphorus slag-metal equilibrium partition ratios in steelmaking have been extensively studied. Different authors [1, 2, 3] developed correlations to estimate phosphorus slag-metal partition ratios. Literature of industrial BOF processes indicate that practical results are far from equilibrium, reaching approach to equilibrium values rarely higher than 30% at the end of the process [4]. Furthermore, as industrial processes run normally on lime saturated slags, dissolved %CaO contents are difficult to establish, making statistical evaluations more difficult, rendering low correlation coefficient R values. Nevertheless such analysis is useful for practical purposes in evaluating operation procedures [5] and estimating production stability.

Phosphorous slag-metal partition ratios in BOF steelmaking at CSH have been evaluated for the two different blowing patterns and for increasing phosphorus content in the hot metal, based on actual values of the years 2006 and 2007.

As the BOF process is essentially an interaction between the liquid bath and the slag, early development of the latter is very important, and lime has to be added according to hot metal quantity and silicon content. Lime is charged during the first minutes of blowing, while dolomite for MgO is added after ignition. Nevertheless, very often Slag basicity runs on very high values, as lime is normally used to control slopping. Slag and steel bath characteristics are detailed in Tables 5 and 6.

Table 5: Average Slag characteristics for low and high carbon steels

Steel type	**%FeO**	**%CaO**	**%MgO**	**% SiO_2**	**% P_2O_5**	**% V_2O_5**	**% Al_2O_3**
Low carbon	17.34	46.34	6.78	8.21	2.27	2.94	2.79
High carbon	15.89	48.04	7.33	8.68	2.21	2.91	2.94

Table 6 : Average steel characteristics and partition coefficients for low and high carbon steels

Steel type	**$\%C_{steel}$**	**$\%P_{steel}$**	**$\%V_{steel}$**	**Temp °C**	**%(P)/[P]**	**%(V)/[V]**
Low carbon	0.038	0.0094	0.0036	1656	114.2	483.3
High carbon	0.280	0.0163	0.0156	1646	69.9	208.9

For low carbon steels multiple regression analysis on 500 heats showed the following Equation:

$$\log \frac{(\%P)}{[\%P]} = \frac{11913}{T} + 0.0066(\%CaO) - 0.0123(\%MgO) - 1.2270\,C + 0.00426(\%FeO) - 4.384$$

The main variables to influence phosphorus partition ratio are temperature and %CaO content. Low temperature strongly favors an increase of the phosphorus partition ratio, emphasizing the need for a good control of this operation variable. Contents of %CaO in the slag go on the same sense. At high basicity ratios changes in this parameter show only moderate influence on the expected results. On the other hand, %MgO appears to have a strong negative effect, as also seen in published results [4]. The statistical evaluation for low carbon steels shows low values for the multiple correlation coefficient R, only around 55%.

Partition ratio between slag and metal for vanadium behaves very much in a similar way as for phosphorus and operational variables influence it also the same way.

For high carbon steels, considering only 51 cases, the Equation was:

$$\log \frac{(\%P)}{[\%P]} = \frac{9736}{T} + 0.0023(\%CaO) - 0.0094(\%MgO) - 0.1910\,C + 0.00053(\%FeO) - 3.297$$

Again the main influencing variable is temperature, %CaO showing less importance, mainly at high basicities. Also %MgO acts in the same negative sense as for low carbon steels. The influence of the slag oxidation is much less important, as at higher carbon, %FeO variation is only slight. The value for the multiple correlation coefficient R is somewhat better, around 66%.

Working with slags with very high basicity means that large amounts of lime and magnesia remain undissolved [6]. This generates important basicity measurement errors and therefore better results are difficult to expect. Nevertheless, trials discarding very high Basicity Index heats did not show better multiple correlation coefficients.

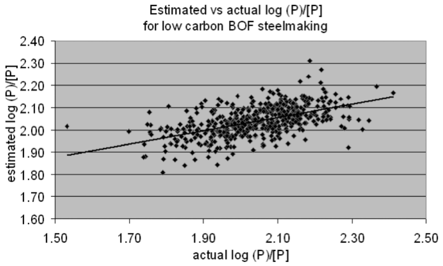

Figure 1a: Estimated and actual P partition ratio for low carbon BOF steelmaking

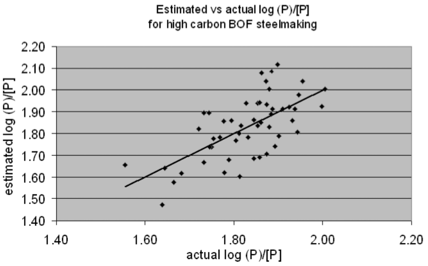

Figure 1b: Estimated and actual P partition ratio for high carbon BOF steelmaking

Phosphorous slag-metal partition ratios show values slightly over 100 for low carbon steels, and attaining values only between 70 and 75 for high carbon steels. These values are somewhat higher than those reported in the literature for lower basicity slags [6].

There is a strong correlation between the phosphorus and the vanadium partition ratios, both in low and high carbon steels, as it is shown in Figure 2. It is interesting to note that generating a combined phosphorus-vanadium partition ratio as L_{P+V} = (P+0.6*V)/[P+0.6*V] regression analysis for high carbon steels shows better results than for the phosphorus only partition ratio. Multiple correlation values of R get up from 66% to 75%. This is not the case for low carbon steels, where no improvement is found.

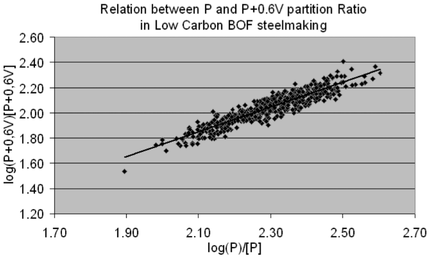

Figure 2a: Relation between P and P+0.6V partition ratio for low carbon BOF Steelmaking

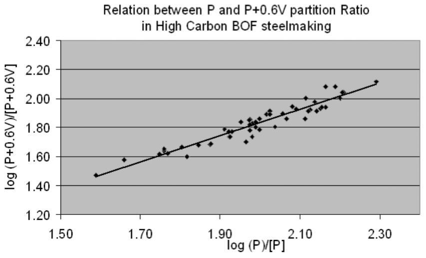

Figure 2b: Relation between P and P+0.6V partition ratio for high carbon BOF Steelmaking

Phosphorus Presence in the BOF Slag

Phosphorus in BOF steelmaking slags may be present in di-calcium silicate and, to a lesser extent, in di-calcium ferrite phases, while the presence of tri-calcium phosphate ($3CaOP_2O_5$) should also be possible in slags with lower basicities. Vanadium behaves alike phosphorus, and its presence should be looked in the same phases [7]. The way phosphorus and vanadium are present in the high carbon steelmaking slags was assessed in two samples of the same heat, taken at two different bath carbon levels, the first of them at 0.61%C, and the second one at 0.44%C. Chemical composition of the steel bath and the slag is shown in Tables 7 and 8. Phosphorous partition ratios for these samples are 35.66 and 67.38.

Table 7: Chemical composition of steel samples of high carbon heat 69469

Sample	%C	%Mn	%P	%S	%V	%Ti	Temp. °C
P1	0.64	0.12	0.051	0.018	0.017	0.002	1655
P2	0.44	0.10	0.023	0.015	0.011	0.002	1630

Table 8: Chemical composition of slag samples for high carbon heat 69469

Sample	%CaO	%MgO	%SiO_2	%FeO	%MnO	%Al_2O_3	%P_2O_5	%V_2O_5	%TiO_2
P1	53.59	4.96	10.52	12.14	3.72	1.85	4.16	2.24	0.71
P2	46.47	4.53	8.21	24.80	3.80	1.68	3.64	1.81	0.65

Electron microscopy of the slag samples shows the presence of three different phases, as shown in Figure 3, which were characterized both by appearance and chemical composition, which are shown in Table 9.

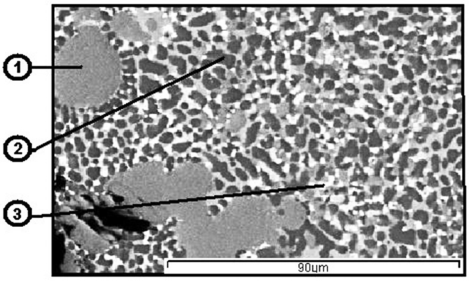

Figure 3a: High carbon BOF steelmaking slag sample composition showing three different slag phases

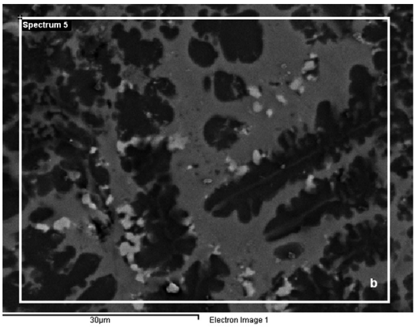

Figure 3b: Area of average chemical excluding free lime areas

- Phase 1: large grey rounded areas = basically free lime, with very little Mg, Mn and Fe.
- Phase 2: small dark grey areas, with a rounded lamellar solidification at the steel bar = basically calcium silicate, with some phosphorus and vanadium contents
- Phase 3: white or light grey matrix, basically calcium ferrite, with moderate phosphorus, vanadium and titanium contents.

Average chemical composition was measured in a bigger area, excluding free lime zones, as it is illustrated in Figure 3b and also indicated in Table 9.

Table 9: Chemical composition of different phases present in high carbon steel slags, measured by EDAX at the scanning electron microscope

Size. Form and color			%Ca	%Mg	%Si	%Fe	%Mn	%Al	%Ti	%V	%P
big	rounded	light gray	88.3	2.7		6.5	2.36				
small	rounded lamellar	dark gray	69.7	0.3	20.2	4.1				1.77	3.90
	matrix	white	21.4	7.3	3.4	60.8	4.81	0.29	0.15	0.97	0.79
AVERAGE COMPOSITION		CHEMICAL	49.6	6.0	7.4	23.5	2.25	2.14	1.79	4.80	2.33

While calcium silicate contributes to remove both phosphorus and vanadium, calcium ferrite contributes only slightly. On the other hand, the presence of large amounts of free lime, represented by the light grey phase, shows clearly that having as a goal an excessively high basicity does not contribute to a better dephosphorization.

BOF Steelmaking with High Phosphorus Hot Metal

Using operational values of hot metal charged, its silicon and phosphorus contents, a model was developed that permits to calculate the quantity of produced steel and slag, and the expected average phosphorus contents in the steel bath can be estimated both for low and high carbon steels. The maximum acceptable value for phosphorus in the steel bath allows to estimate the percentage reblows to maintain the product's quality. This value is very sensible to the standard deviation of the partition ratio, which is quite high, around a value of 25. The application of this model to the data of the year 2007 is shown in Table 10.

Table 10: Dephosphorization in the BOF converter. Data year 2007

BOF - CONVERTER DEPHOSPHORIZATION						YEAR 2007		
GENERAL DATA								
CHARGES	**Low carbon steel**	**High carbon steel**		**Low carbon steel**		**High carbon steel**		
				Si	**P**	**Si**	**P**	
Hot Metal	90	100	t	0.45	0.111	0.45	0.111	%
Iron scrap	5	5	t	0.45	0.111	0.45	0.111	%
Steel Scrap	25	15	t	0.10	0.020	0.10	0.020	%
PRODUCTION								
Steel	108.0	110.4	t					
Slag	13.01	12.20	t					
SLAG				**STEEL**				
	Low carbon steel	**High carbon steel**				**Low carbon steel**	**High carbon steel**	
IB(CaO/SiO_2)	5.70	5.70	%	Phosphourus actual Lp (actual)		0.008 104	0.012 73	%
CaO	51.3	59.2	%	Phosphourus equil.		0.002	0.003	%
SiO_2	7.1	8.2	%	Lp (equilibrium)		339	340	
FeO	20.0	15.0	%	Equilibrium approach		30.7	21.5	%
P_2O_5	1.93	2.23	%	Limit for reblows Lp (limit for reblows)		0.016 45	0.024 32	%
other	21.60	17.60		Reblown heats		0.80	7.05	%

Equilibrium phosphorus partition ratios calculated give very high values, usually around 300 or somewhat higher. These values are pretty close to those shown in the literature at high basicity values [4]. Normally Approach to equilibrium varies between 20% and 30%, depending on carbon contents.

CONCLUSIONS

The increase of the phosphorus content in hot metal at CSH has led to analyze the phosphorus partition ratio of the actual operation of the year 2006 and 2007. This study showed that phosphorus partition ratio depends very strongly on temperature, emphasizing the need for an excellent control of this operation parameter. Basicity is represented in the analyses by the %CaO content in the slags.

Statistical analysis of actual operation data shows correlation coefficient values up to 70%, probably due to the fact that excess quantity of lime leads to slag saturation and therefore to unreliable %CaO content data.

Vanadium partition ratio behaves very much in the same way as for phosphorus, mainly in high carbon steel heats. Vanadium plays an interesting role in dephosphorization of high carbon steels, as the statistical analysis shows that a combined partition ratio of phosphorus and vanadium shows some increase of the correlation coefficient.

A SEM analysis of high carbon slag shows that phosphorus and vanadium are mainly present in calcium silicates, while calcium ferrites have a more moderate content of these elements. Excessive lime additions are reflected only as free lime phases in the slags.
A model was developed to calculate the quantity of produced steel and slag, and the expected average phosphorus contents in the bath can be estimated both for low and high carbon steels. The model calculates the reblow percentage using the actual standard deviation of the phosphorus expected in the steel bath from the years 2006 and 2007.

Extrapolation of this analysis to higher phosphorus content in the ore shows that the use of high phosphorus lump ore takes hot metal phosphorus contents to levels over 0.200%.

Therefore phosphorus in the steel bath increases for low carbon steels, showing occasional reblows. Reblow percentage for high carbon steels blown with the catch-carbon practice start to be too high and blowing patterns have to be changed: high carbon steels must also be blown similar to low carbon heats so as to assure dephosphorization to acceptable levels.

Furthermore, the model indicates that values of phosphorus in the hot metal approaching 0.300% leads to an extremely high percentage of reblows, and a different approach has to be made to solve the problem. Bottom stirring with argon, in ways to be implemented at CSH, might lead to a better approach to equilibrium values rendering an acceptable operation at higher phosphorus content in hot metal.

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