

# STANDARDS FOR ALKALI INPUT IN BLAST FURNACES<sup>1</sup>

Maarten Geerdes<sup>2</sup> Gustavo Cegna<sup>3</sup> Pedro Contreras<sup>4</sup> Carlos González<sup>5</sup> Fernando Liceaga<sup>6</sup> Oscar Lingiardi<sup>7</sup> Hisko Toxopeus<sup>8</sup>

#### Abstract

Operational standards for the alkali input in blast furnaces are generally set as the sum of potassium and sodium oxide per ton hot metal. This approach does not take differences in operational conditions nor the distinction between Na<sub>2</sub>O and K<sub>2</sub>O into account. In the present paper it is shown, that the alkali standard can be based on the K<sub>2</sub>O "carrying capacity" of the slag. The major determinants of the K<sub>2</sub>O carrying capacity are the basicity of the slag and the slag volume. The K<sub>2</sub>O carrying capacity is estimated from blast furnace operational data. The elimination of Na<sub>2</sub>O is adequate as long as the Na<sub>2</sub>O input is lower than the K<sub>2</sub>O input. Elimination of alkali with the top gas and dust can occasionally be observed, but is not taken into account for deriving input standards. Verification of the model is carried out by comparing the operating conditions and alkali balances at AHMSA, Mexico, Ternium Siderar, Argentina and Cap/CSH, Chile.

Key words: Blast furnace; Alkali; Sodium; Potassium.

- <sup>1</sup> Technical contribution to the 6<sup>th</sup> International Congress on the Science and Technology of Ironmaking – ICSTI, 42<sup>nd</sup> International Meeting on Ironmaking and 13<sup>th</sup> International Symposium on Iron Ore, October 14<sup>th</sup> to 18<sup>th</sup>, 2012, Rio de Janeiro, RJ, Brazil.
- <sup>2</sup> Director, Geerdes Advies, geerdes@geerdespartners.com.
- <sup>3</sup> Process engineer, Ternium/Siderar, Argentina, c.gcegna@terniumsiderar.com
- <sup>4</sup> Blast Furnace manager, CAP/CSH, Chile, pcontreras@csh.cl.
- <sup>5</sup> Former Blast furnace Technical manager, CAP/CSH, Chile, presently at BHP Billiton, Chile, Carlos.CF.Gonzalez@bhpbilliton.com.
- <sup>6</sup> BF Technical manager, GAN/AHMSA, Mexico, fliceagamartinez@gan.com.mx
- Ironmaking Technical manager, Ternium/Siderar, Argentina, olingiardi@ternium.com.ar.
- <sup>8</sup> Ironmaking Consultant, hisko.toxopeus@xs4all.nl.

# **1 INTRODUCTION**

Alkali, sodium and potassium, are unwanted elements that enter the blast furnace with the ferrous burden, recycled materials, coke and coal. The alkali effects coke reactivity, contributes to the formation of scaffolds on the blast furnace walls and can attack refractories. They take part in a cycle of vaporization and condensation. From measurements of quenched blast furnaces it has been observed, that the amount of recirculation is about 3-10 times the input.<sup>(1)</sup>

ISSN 2176-3135

The alkalis in the blast furnace have various effects on operation.<sup>(2,3)</sup> From a chemical point of view, alkali acts as a catalyst for the solution loss reaction (C+ CO<sub>2</sub>  $\rightarrow$  2CO). It means that at high alkali input the fuel rate is slightly higher. This effect is generally rather small. A second effect is, that physical degradation of coke and ferrous materials is promoted, which leads to a poorer permeability and can affect productivity at high production rates.

Moreover, alkali can lead to formation of scaffolds in the furnace: solid material adhered to the wall in the stack of the furnace. The effect of the formation of scaffolds is that the burden descent deteriorates, in extreme cases, leading to hanging and slipping. Also in scabs, formed from cohesive material in the bosh/belly area, high levels of alkali have been observed. Finally, the refractory materials, especially carbon-based refractories, can be attacked by alkali, affecting campaign life. Therefore, alkali control in the furnace and prevention of scaffold formation require attention from the blast furnace operator.

Alkali control is mostly done by setting a maximum value for the input of the sum of potassium and sodium oxide, expressed in kg/tHM. We have discussed earlier,<sup>(4)</sup> that this approach neglects differences between sodium and potassium behavior. In the present paper we have developed a methodology to set operational standards for alkali input taking differences in slag basicity and slag volume into account as well as differences of the amount of alkali eliminated via the top. The present study is based on data of operating furnaces.

# 2 POTASSIUM AND SODIUM

### 2.1 Differences in Properties of Na and K

The two types of alkali, sodium and potassium, behave slightly different. Sodium is more easily removed from the furnace with slag as well as via the top gas.<sup>(2)</sup> Moreover, in most furnaces the potassium input is higher than the sodium input. Therefore, for our purposes it is sufficient to observe the potassium balance. Only in situations where the sodium input is higher than the potassium input, both have to be observed.

The focus on potassium is also based on operational considerations. In figure 1 we show the content of  $K_2O$  and  $Na_2O$  during a chilled furnace condition. It is clear from the figure, that during a chilled condition the  $K_2O$  is eliminated with the slag, while  $Na_2O$  is constant. As soon as the furnace is heating up the  $K_2O$  is retained within the furnace. The amount of accumulated  $K_2O$  is indicated in figure 1. In addition it can be observed, that scaffolds formed in a blast furnace contain much more potassium than sodium.<sup>(5)</sup>







### 2.2 Monitoring Alkali During a Cast

Figure 2 shows typical examples of the  $K_2O$  and  $Na_2O$  in slag during a cast. The left hand figure shows the slag composition during a cast, the right hand figure the correlation between slag basicity and slag  $K_2O$ %. The hot metal silicon is also shown.



**Figure 2**. Slag  $K_2O$  % during a cast and the correlation between basicity B3 and  $K_2O$  % during a cast. A: Ternium Siderar BF2, B: CAP/CSH BF1.

The slag K<sub>2</sub>O% can vary strongly during a cast. This means that slag sampling becomes very important when assessing the alkali balance. The strong correlation between basicity and slag K<sub>2</sub>O% suggests that they are continuously in equilibrium.

### **3 POTASSIUM REMOVAL AND MAXIMUM LOADS**

The  $K_2O$  input of the furnace is eliminated with top gas and with slag. The elimination of  $K_2O$  with top gas varies from furnace to furnace and is dependent on operating

mode. Alkali elimination with the top gas increases with a higher central gas flow, more dust to the gas system and a higher top gas temperature. The fraction of  $K_2O$ -load that is eliminated with the top gas, is generally small (section 4). Therefore it is not taken into account when developing an input standard for the  $K_2O$  load (in kg  $K_2O$ /tHM).

ISSN 2176-3135

The major part of  $K_2O$  is eliminated with the slag.<sup>(6)</sup> The  $K_2O$  "carrying capacity" of the slag depends on slag chemical composition, slag volume and -to a minor extent- slag temperature. Figure 3 shows the outline of a simple model for elimination of  $K_2O$  from a blast furnace. In section 4, the model is verified with independent operational data.

Input		Within BF		Output	
					Potassiumeliminated with top gas
Input from ferrous,			>	Top gas/dust	Furnace specific,
recycled materials,					correlates with top gas temperature
coke and coal	$\rightarrow$	Potassium			
		pool	$\rightarrow$	Potassium eliminated	Potassium capacity of slag
				with slag	depends on basicity

Figure 3. Outline of a simple model for elimination of potassium from a blast furnace.

# 3.1 Potassium Removal With Slag

In the situation where no accumulation of K<sub>2</sub>O takes place inside the blast furnace, the K<sub>2</sub>O eliminated with the slag equals the input (in kg/tHM) minus the amount of K<sub>2</sub>O eliminated with the top gas. The expected K<sub>2</sub>O content of the slag is the amount of K<sub>2</sub>O in the slag divided by the slag volume. We assume that there is an operational "carrying capacity" for K<sub>2</sub>O in the slag that only depends on basicity. We have chosen to work with the three component basicity B3 (CaO+MgO/SiO<sub>2</sub>), since the three component basicity takes the competition between alkali and Mg<sup>2+</sup> into account. However, we present graphs with two-component basicity (CaO/SiO<sub>2</sub>) as well. A linear relation between basicity B3 and slag K<sub>2</sub>O is a simplification of reality, because the K<sub>2</sub>O% in slag will also depend on other components of the BF slag as well as, slag temperature.

In order to find the maximum slag  $K_2O\%$ , we have made an analysis of monthly average data of twenty operating blast furnaces. The results are shown in Figure 4, where a line indicates the operational maximum slag  $K_2O$  content. This can be written as  $K_2O\%_{max}$ = 2,32 -1,2\*B3, where  $K_2O\%_{max}$  is the maximum  $K_2O$  operationally observed and B3 is the three component basicity. The data come from about 20 furnaces for which we had monthly data available. We eliminated furnaces with very high  $K_2O$  loads (> 2,3 kg  $K_2O$  /tHM) and with high  $Al_2O_3$  (> 15%) in the slag. The figure is intended to be used for a basicity between 1,25 and 1, 45. At a lower basicity (B3<1,25) the linear equation cannot be used.

(When using the 2-component basicity B2=CaO/SiO<sub>2</sub>, the formula reads:  $K_2O= 2,19-1,32*B2$ , applicable if B2>1,0, estimated for MgO = 8% and Al<sub>2</sub>O<sub>3</sub>=11%.).



**Figure 4**. Slag  $K_2O$  content for various furnaces, monthly averages. The red line shows the assumed maximum slag  $K_2O\%$  for basicity ((CaO+MgO)/SiO2) in the range 1,25-1,45 in our model.

### 3.2 Potassium Removal With Top Gas

If part of the potassium is removed with the top gas, be it in a form of  $K_2O$  or KCN, then we would expect that the potassium is removed with the hot central gas flow and/or associated with the dust leaving the furnace. Therefore, a correlation between the top gas temperature and the potassium balance is to be expected if a substantial amount of alkali leaves the furnace via the top. More specifically: we would expect to find a correlation between (K<sub>2</sub>O input- K<sub>2</sub>O output via slag, in kg/tHM) and the average top gas temperature or even the central top gas temperature. In some cases such a correlation can be found and in other cases we did not find such a correlation. See figures 5 and 8. In developing standards for of K<sub>2</sub>O input we assume that none of the K<sub>2</sub>O is eliminated with the top gas.



**Figure 5.**  $K_2O$  removed with top gas (in kg/tHM) as a function of top gas temperature. The figure shows monthly averages for the difference between  $K_2O$  input and output via slag for four different furnaces and linear regression lines for the four furnaces.

The maximum allowable K<sub>2</sub>O input can be estimated with the formulas in section 3.1 by taking slag volume and basicity into account. The results are shown in figure 6. It is based on the assumption that no K<sub>2</sub>O leaves the furnace out of the top and that the maximum allowable slag K<sub>2</sub>O content is given by the formula presented in section  $3.2 \text{ K}_2\text{O}\%_{\text{max}}$ = 2,32 – 1,2\*B3 (or 2,19-1,32\*B2 at 8% MgO and 11% Al<sub>2</sub>O<sub>3</sub>).

ISSN 2176-3135



**Figure 6**. The maximum allowable  $K_2O$  input (monthly average) assuming no elimination of  $K_2O$  via the top for different slag basicity and slag rates. At the left hand side a graph based on 3-component basicity, on the right hand 2-component basicity. Slag rates are indicated on the right side of the graphs. For details see text.

The standard for alkali that we propose can be based on the maximum allowable  $K_2O$  load of slag as shown in figure 4. In order to accommodate for variations in basicity as well as in alkali content and slag volume of the raw materials a safety margin has to be taken into account. The operator can decide to choose for 80% or 90% of the maximum slag carrying capacity. As an example, choosing a safety margin of 80% the present methodology leads to a max  $K_2O$  load, as an annual average:

K<sub>2</sub>O max (in kg/tHM)= 0,8\* slag vol (in kg/tHM)\* (2,32-1,2B3)/100,

where B3 is the three component basicity (CaO+MgO)/SiO<sub>2</sub>. This is applicable for the range of B3 between 1,25 and 1,45 and as long as Na<sub>2</sub>O load is <  $K_2O$  load.

# 4 MODEL VERIFICATION

# 4.1 Maximum K<sub>2</sub>O Loads

In Figure 7 and Table 1 we compare the  $K_2O$  loads of our companies with the maximum loads according to the method derived in section 3.1. The figure shows daily average data. The line describing the maximum  $K_2O\%$  in the slag is also the line through the higher  $K_2O\%$  operationally observed.



Figure 7. K<sub>2</sub>O in slag, daily averages for AHMSA, Siderar and CAP/CSH.

Table 1 shows, that CAP/CSH and Siderar are below the maximum allowable  $K_2O$  loads and are having some possibility to increase  $K_2O$  loads before scab formation can be expected.

ISSN 2176-3135

Company	period	K <sub>2</sub> O input	Max K <sub>2</sub> O input	Slag vol	Basicity B3
Siderar BF2	March 2011	1,02	1,52	198	1,295
Siderar BF2	Oct 2011	1,41	1,62	207	1,28
AHMSA BF5	2011	2,7	2,67	286	1,156
CAP/CSH BF2	Dec 2010	1,1	1,52	175	1,21

**Table 1**. K<sub>2</sub>O input and maximum allowable K<sub>2</sub>O input compared for our furnaces

AHMSA is able to keep the scab formation under control by adjusting basicity downward and by taking corrective actions as soon as required, i.e. as soon as scab formation is observed from process data like heat losses and burden descent. Figure 7 shows, that AHMSA operates its blast furnace at a lower the basicity in order to control  $K_2O$  output. The figure shows that model and reality are well in line, however, AHMSA works with a basicity below 1,25.

# 4.2 K<sub>2</sub>O Eliminated Via the Top Gas

The K<sub>2</sub>O eliminated with the top gas (K<sub>2</sub>O<sub>tg</sub>) is estimated as the K<sub>2</sub>O input minus K<sub>2</sub>O output via slag. We expect that a correlation between K<sub>2</sub>O<sub>tg</sub> and top gas temperature should exist. However, such a correlation was not manifest from our data. Consequently we assume that no K<sub>2</sub>O is eliminated via the top of the furnace.

Kurunov et al.<sup>(7)</sup> have indicated that in their situation the elimination of alkali with the top gas is estimated as 2-8% of the input. So, in a simple approach, the elimination of K<sub>2</sub>O via top gas should not be considered when setting a standard for the input of K<sub>2</sub>O in kg/tHM.



**Figure 8**. (a) Correlation between  $K_2O$  input minus output for Ternium Siderar BF2; (b) correlation between  $K_2O$  input minus output and top gas temperature for CAP/CSH BF2.

# **5 DISCUSSION**

# 5.1 Alkali Input Standards Compared

In an earlier paper<sup>(4)</sup> we have shown the graph of figure 9, where annual average input data are correlated with slag basicity for a large number of companies. The figure shows, that at a level of 1,6-1,7 kg K<sub>2</sub>O/tHM input and at a standardized slag volume of 250 kg/t companies tend to lower basicity. The standard derived in

Figure 4 for the situation of a basicity B3 of 1.35 and a slag volume of 250 kg/tHM is max input is 1,75 kg/tHM. This compares well with the data shown in Figure 9.

ISSN 2176-3135



Figure 9. K<sub>2</sub>O loads and basicity (B3) in a large number of companies.

Kurunov et al. indicated in a recent paper,<sup>(7)</sup> that for the conditions of their furnaces at NLMK (Novolipetsk, Russia) a maximum  $K_2O$  load of 2,2 kg/tHM can be eliminated by slag. According to the estimating methodology in the present paper, we calculate a maximum of 2,3 kg/tHM (based on a B2 of 1,041 and a slag volume of 285 kg/tHM). These independent studies are in good agreement.

# 5.2 Effects of Slag Chemistry

We have shown earlier<sup>(4)</sup> that the  $K_2O$  content shows a close correlation with the "solubility" of  $K_2O$  in slag as well as its reduction degree. At that moment we proposed, that the "solubility" depends mainly on the slag basicity and that the reduction degree is closely correlated with slag MnO%. Slag MnO% was used as an indicator of the progress of the reduction of metaloxides. Analysis of operational data has taught us, that slag MnO and slag basicity are as well correlated. Therefore, we use a correlation with (three-component) basicity only in the present paper.

It is possible to extend the model to lower basicity and/or to include a more sophisticated approach of the max  $K_2O$  content of blast furnace slag. It should be possible to include the competition between sodium and potassium and/or to include the effects of different slag compounds (like  $Al_2O_3$ , MnO) or temperature. Our preliminary indications are that the effect of temperature is relatively small.

For companies using the 2-component basicity, there is a need to include the effect of the MgO% in the slag. In a theoretical study, Ivanov, Savov and Janke<sup>(8)</sup> have shown, that increase of MgO% in slag accelerates alkali evaporation and increase of  $Al_2O_3$ % decreases alkali evaporation. For extension to lower basicity, higher alkali loads and differences in slag chemistry, there is a need for more companies participating in a data and operational experience exchange as well as application of thermodynamic models, which take interactions between the various positive ions within the molten slag into account. A relatively simple concept is application of the concept of "optical basicity". The optical basicity describes slag basicity in terms of the extent of electron donation by a metal to oxygen and makes it possible to discriminate the effects of various metal ions.<sup>(9)</sup>

# 5.3 High Alkali Input and Scaffold Formation

A number of companies have experienced high alkali input due to their local raw material supply. Methods have been developed to control the amount of circulating

alkali within the furnace by various methods, like coke charging at the wall, cleaning operations by low basicity and/or low burden level and others.<sup>(10-13)</sup>

ISSN 2176-3135

At AHMSA<sup>(14)</sup> a method has been developed to work with alkali levels up to 4,5 kg/tHM (2-2,5 kg K<sub>2</sub>O/tHM). This includes a method to eliminate as much fines as possible from the burden. In doing so the chance on scaffold formation becomes very much lower. Second, as soon as indications of scaffold formation are manifest from the unstable burden descent and high pressure, a cleaning action is carried out. This cleaning action consists of lowering the burden level to 14-15 meter above the tuyeres, (9 m below stockline), while keeping the top temperature under control with water sprays. During the period of low burden level the scaffolds will fall into the furnace and the normal operational conditions are restored as soon as the burden level has been recovered.

# 5.4 Small and Large Furnaces

In addition, we investigated the question, whether or not larger furnaces are more forgiving for K<sub>2</sub>O than smaller furnaces. We expected that large furnaces have a higher slag K<sub>2</sub>O content at the same basicity and slag volume, since there is more cold, unreduced material in the wall area of a large furnace and because large furnaces are normally operated at a higher pressure, allowing the equilibrium K<sub>2</sub>O +  $C \rightarrow K + CO$  to be pushed to the left hand side. So the idea was, that especially in the wall area of a larger blast furnace more unreduced K<sub>2</sub>O is available than in a small furnace. This would result in higher slag K<sub>2</sub>O content at the same input and basicity. We selected companies operating a larger and a smaller furnace. The analysis showed that larger furnaces have a lower slag K<sub>2</sub>O than smaller furnaces at the same basicity level. So our idea that large furnaces are more forgiving than small furnaces was not confirmed.

# **6 CONCLUSIONS**

Methods generally used for setting a standard for alkali input in blast furnaces are insufficiently detailed. There are large differences between the behavior of sodium and potassium in a blast furnace. Potassium is more difficult to remove than sodium. The major part of potassium is eliminated with the slag phase in the form of K<sub>2</sub>O. The "slag carrying capacity" for K<sub>2</sub>O depends on basicity as well slag volume. A standard for alkali can in most steel plants be restricted to a maximum input for K<sub>2</sub>O.

We have quantified the slag carrying capacity based on the slag  $K_2O$  content of more than 20 operating furnaces. A relatively simple model allows the operator to check whether or not their standard for  $K_2O$  loads comes close to the maximum "K<sub>2</sub>O-carrying capacity". The results are in line with the operating results of furnaces of the authors.

# Acknowledgement

We are indebted to our colleagues on steel plants worldwide for sharing with us their insights and their data and esp. to John Ricketts, Arcelor Mittal, and Beatriz Fausta Gandra (Usiminas Ipatinga) for help during preparation of the manuscript.

# REFERENCES

- 1 Omori,Y. on behalf of committee on reaction within blast furnace: Blast furnace phenomena and modelling, (1987), Elsevier Applied Science, London
- 2 Babich, A., Senk, D., Gudenau, H., Mavrommatis (2008) Ironmaking, RWTH Aachen, Wissenschaftsverlag Mainz
- 3 Biswas, A. K., Principles of blast furnace ironmaking, (1981) Cootha Publishing, Brisbane , Australia

ISSN 2176-3135

- 4 Geerdes, M. and Toxopeus, H.: Alkali in a blast furnace, an operational approach (2011), Proc of the 8<sup>th</sup> Ironmaking conference, IAS 2011, 210
- 5 Suri, S. and Joshi, G. S. (2011): Causes and remedies for scab formation in blast furnaces, Proc of 24<sup>th</sup> national convention of metallurgical and material engineers, Ranchi, India, Jan 22, 2011
- 6 Ivanov, O., Savov, L., and Janke, D.: Alkali capacity and physical properties of Blast Furnace Type Slags, Steel Research Int 75 (2004) 7, p433-441
- 7 Kurunov, I. Titov, V. Arsamascev, A. Basov, V. and Tikhonov, D. (2011), Analysis of alkali removal influenced by blast furnace operating conditions. Proceedings of Metec 2011, session 13, p1
- 8 Ivanov, O., Savov, L. and Janke, D. (2004) Experimental studies of trhe alkali behavior in blast furnace type slags, Steel Research Int, 75, 442.
- 9 Duffy, J. A. (1993) A review of optical basicity and its applications to oxidic systems, Geochimica et Cosmochimica Acta, 57, 3961-3970
- 10 EC report 20586 KI-NA-20586 (2003): Investigation of Chlorine and Alkali behavior in the blast furnace and optimization of slag with respect to alkali retention capacity
- 11 Haberman, A., Schuster, E. and Schuster, G. (2005) Blast furnace control technique at operation with high alkali input, 5<sup>th</sup> ECIC, 3-2
- 12 Gladkov, N., Nikolaev, S. and Budnik, L. Metallurgy, 2,(1986), 12-14
- 13 Kurunov, F., Titov, V., Emel'yanov, V., Lysenko, S. and Arzamatsev, A.: Analysis of the behavior of alkalis in a blast furnace, Metallurgist, 53 (2009) 9-10, 533-542
- 14 Liceaga, F., Vidales, G., and Mata, R. Results of 3<sup>rd</sup> campaign of Blast Furnace 5 of AHMSA, Mexico, (2011), Proc of the 8<sup>th</sup> Ironmaking conference, IAS 2011, 148