

PHOSPHORUS CONTROL IN DRI STEELMAKING

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Abstract

This paper is a brief review of some of the pertinent metallurgical literature with respect to the control of phosphorus when direct-reduced iron is used in steelmaking processes. The chemical principles for the distribution of phosphorus between slag and metal in steelmaking processes have been fairly well treated in the literature. Some selected examples are taken from certain references to illustrate the relationships between critical components, such as  $\text{CaO/SiO}_2$  ratios,  $\text{FeO}$  content, and temperature as being the principle variables.

## Abstract (cont'd)

Additional production experience gained with relatively high phosphorus content (0.10 to 0.15% P) has also been reported in the technical literature. Some of the data from technical papers involving steelmaking with high percentages of DRI containing phosphorus contents up to 0.12% P are reviewed and compared with the thermo-chemical equations from the metallurgical literature.

The information from a thermo-chemical standpoint, as well as production experience, shows that the control of phosphorus follows straightforward metallurgical principles. It is a relatively easy matter to produce steels containing less than 0.015% P, even when using up to 80% of DRI containing 0.12% P. Steelmaking practices for control of phosphorus in this manner do not require major practice changes, but will result in some additional flux and energy requirements.

## INTRODUCTION

Phosphorus control has been a long term consideration in all steelmaking processes. Much of the technology dates to the use of Bessemer converters for the production of steel from high phosphorus iron ores. Similar considerations were also directed toward basic open hearth steelmaking, with the attention paid toward phosphorus control related to the amount of phosphorus in the charge materials. The early metallurgical texts all have sections dealing with thermo-chemical principles that control the removal of phosphorus in the steelmaking process.

## Introduction (cont'd)

As each steelmaking process evolution occurred, appropriate thermo-chemical principles, specifically relating to the process, have been developed and published in numerous technical papers. This has been true with respect to electric furnace steelmaking, basic oxygen furnace steelmaking, and also the present subject, DRI (Direct Reduced Iron) steelmaking. Therefore, this paper will attempt to summarize some of the relevant technical literature on the subject, highlight the basic thermo-chemical principles involved, and reference to actual production experience.

The current attention being directed to the control of phosphorus with continuous feeding of DRI materials to electric furnaces is related to two principle market factors. The first is the availability of direct reduced from iron ores containing relatively higher amounts of phosphorus, and which is presently an item of international commerce. The second is the increasingly stringent product quality demands for lower sulfur and subsequently phosphorus in many steel products. Both of these factors have caused many steelmakers to express renewed interest in the control of phosphorus in DRI steelmaking.

## BASIC SLAG CHEMISTRY

### Operating Practices

The dominant process variables relating to phosphorus distribution (amount of phosphorus contained in the slag divided by the amount of phosphorus dissolved in the metal) are widely recognized to be: (1) slag basicity ( $\text{CaO}/\text{SiO}_2$ ), (2) temperature, (3) iron oxide content ( $\text{FeO}$ ), (4) slag fluidity, and (5) slag and metal mixing. A working understanding of the interrelationship of the above factors can readily result in the attainment of low phosphorus steel products with relatively high phosphorus charge materials; and without significant costs related to productivity or flux materials.

The production of low sulfur containing steels has caused many steelmakers to be concerned that steelmaking practices for phosphorus removal may be similar to those for sulfur removal. However, the thermo-chemistry of the system allows a much easier process result to be achieved in the case of phosphorus than for sulfur. The phosphorus distribution attainable in simple steelmaking slags is approximately 10 times greater than a similar sulfur distribution (a range of 80 to 120 for oxidizing slags). While similar product specifications may be given for both sulfur and phosphorus (both at about 0.015%), the furnace charge materials do not need to be restricted to the same degree for both elements.

## Operating Practices (cont'd)

With the marketplace continuing to demand lower sulfur levels, it is necessary to understand the relationship between practices designed for low sulfur, and those practices designed for low phosphorus. Low sulfur steelmaking practices require a basic slag, but under conditions of very low iron oxide content (strongly reducing). However, the similar basic slags for phosphorus removal require an oxidizing slag (containing about 0.15% to 0.25% FeO) for efficient phosphorus removal. Moreover, sulfur removal is favored by high temperatures while phosphorus is favored with lower temperatures.

Effective production practices for the simultaneous production of low phosphorus and low sulfur steel will require two stages of the refining process. The electric furnace process lends itself to relatively high speed dephosphorization occurring during meltdown and the oxygen blowing with slag flushing, followed by a transition to a sulfur refining phase with a corresponding reduction in slag oxidation potential.

Because the oxidation potential of the slag exerts a dominant effect upon the phosphorus distribution ratio, an attempt to desulfurize without physically removing oxidizing slags containing high phosphorus levels will result in rather complete reversion of the phosphorus from the slag into the metal bath during desulfurization.

## Process Chemistry (References)

The following paragraphs will contain a review of the dominant thermo-chemical principles that may be used to quantify expected results for a given steel-making practice. One of the earlier, more practical reviews of slag metal chemistry and phosphorus reactions was given in 1953 by Derge and Tenenbaum

In the Derge and Tenenbaum review of slag metal reactions, relationships identifying the effect of basicity, slag oxidation, and temperature are identified and equilibrium constants derived. However, the simultaneous interaction of these variables is not considered.

The work by Healey (2) in 1973 is directed to providing the steelmaker with a useful set of parameters that may be combined in one equation for calculation of a phosphorus distribution equation. In his review, Healey brings together the

of several contributors and the results of interpretation of published empirical data. From his studies, Healey determines the following equation for estimating phosphorus distribution:

$$\text{Log} \frac{(\%P \text{ in Slag})}{[\%P \text{ in metal}]} = 22350/T - 16.0 + 2.5 \log \%Fet + 0.08 \times \%CaO$$

While the technical literature with regard to DRI steelmaking in general is rather extensive, specific reference to the behavior of phosphorus is a subject of relatively few papers at the present time. A principle difference with regard to the control of phosphorus in DRI steelmaking is associated with the form of the element in the DRI material. It has become generally recognized that phosphorus in DRI materials remains associated with the gangue

Process Chemistry (References) (cont'd)

minerals as a phosphorus oxide. This is illustrated in some detail by Frohberg, Pantke, and Queens (3), who propose that the removal of the phosphorus oxide directly to the slag can be accomplished at a much lower basicity ratio than would otherwise be predicted. Additionally, they identify that slags resulting from the processing of high percentages of DRI may contain rather large quantities of MgO and Al<sub>2</sub>O<sub>3</sub>.

Frohberg, Pantke, and Queens (3) have also proposed a slag model based on electrolytically disassociated ions from the slag components. It is intended that an ionic model of the slag would simplify proper consideration of all acid and basic components. In their treatment of ionic slag activity, an expression "pO" is developed which represents the equivalent of a basicity ratio. In a similar manner, the activity of the iron ions is calculated to determine an ionic equivalent for the oxidation capacity of the slag called pFe. The utilization of this concept is shown to be effective for complex slags involving FeO-CaO-MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> in a multi-component system and fluid steel baths. The theoretical relationships, when combined with empirical data and regression analysis, yields the following phosphorus distribution equation:

$$\text{Log } K = \log \frac{(\text{PO}_4)^{3-}}{[\text{P}]} + 4 \text{ pO} + 2.5 \text{ pFe}$$

## Process Chemistry (References) (cont'd)

A similar paper has been prepared by Froberg and Queens (4) which was presented in the "Seminar on the Utilization of Pre-Reduced Materials in Iron and Steelmaking," Bucharest, 24-28 May 1976. This paper is similar to the previously cited paper but may be more generally available.

While there are, no doubt, many additional technical papers which could be cited, the preceding should serve as a useful basis to indicate thermo-chemical principles for the consideration of phosphorus control in DRI steelmaking.

## PRODUCTION EXPERIENCE

### General Observations:

The author has had experience in the development of steelmaking practices for the production of a wide variety of steel grades with the utilization of DRI materials representing a wide range of chemical analyses. In almost all cases, the effective practices to control final phosphorus contents to the desired product levels were accomplished. The only significant situation in which phosphorus control was not able to be achieved was in the production of steel grade AISI 52100.

### General Observations (cont'd)

In this particular situation, the steelmaking practices were developed to recover a maximum amount of high residual chromium from AISI 52100 steel turnings. These melting practices were developed to minimize oxygen input during meltdown. The entire meltdown and refining process was conducted at very low oxidation potentials. In accordance with the thermo-chemical principles reviewed above, it would be expected that such conditions would not be favorable for the development of a high phosphorus distribution ratio. As may be expected, the final production results when using batch charged DRI containing approximately 0.10% P, resulted in high final phosphorus levels in the product.

In the above situation, process economies depended strongly upon the maximum recovery of chromium from residual scrap. The chemistry of AISI 52100 is a nominal 1.00% carbon. Therefore, it is not possible to develop slag chemistries consistent with phosphorus removal without suffering high chromium losses to the slag. In general, it is only in rather unique situations, as described above, in which it may not be economically possible to achieve the desired control of phosphorus.

### General Observations (cont'd)

In contrast to the production experience of AISI 52100 as mentioned, steel-making practices were developed for cost effective production of plate steels for construction of nuclear pressure vessels. Practices involving both continuous charging and batch charging of DRI materials containing from 0.060 to 0.100% P., were developed to provide final product specifications of 0.015% P. max. and 0.015% S. max. In these practices, oxidizing conditions were maintained during meltdown and into the early stages of refining. To avoid the reversion of phosphorus from slags during the subsequent desulfurization practice, extensive flushing of the oxidizing furnace slag was required prior to the finishing slags. Required product specification chemical results were obtained.

### Production Experience:

Perhaps the most dramatic production experience which relates to effective control of phosphorus in DRI steelmaking has been published with regard to operations at SIDOR in Venezuela. The local Cerro Bolivar iron ore contains a relatively high amount of acid gangue and phosphorus. The published steel-making results by Miller (5) review the operations with up to 84% of DRI continuously charged to the electric furnaces. The DRI material produced from this iron ore in the middle of 1980 had an acid gangue level of 4.70% to 5.20% and a phosphorus level of 0.090% to 0.130%. It is stated that practices at

## Production Experience (cont'd)

that time were adequate to continuously cast heats with phosphorus levels under 0.014%. However, the author states that high acid and total gangue contents require high lime charges and power requirements, resulting in increased steel costs

experience at SIDOR may be found in results published by Acosta and Steindor (6) in which the Cerro Bolivar iron ore is the raw material for DRI production.

## CONCLUSIONS

The above remarks have been prepared to help avoid some of the confusion which is apparent by steelmakers who are focusing their attention on the production of low sulfur products. In many cases, the person not familiar with slag chemistry, has often confused the practices and costs required for low sulfur to be similar with regard to phosphorus.

The reality is that the removal of phosphorus is rather simple with respect to that of sulfur. The thermo-chemical discussion and references confirm that easily controlled steelmaking slags can contain more than 10 times the amount of phosphorus as compared with sulfur. Phosphorus is readily removed by oxidizing slags, at relatively lower temperatures, and with basicity ratios in the range of approximately 2.

## Conclusions (cont'd)

Steelmaking practices that use 100% DRI materials containing up to 0.110% P have been effective in producing flat rolled products with a final phosphorus content of 0.014%. Steelmaking practices that require final sulfur contents that approach 0.010% must have sufficient slag removal prior to desulfurization to avoid reversion of phosphorus from the slag to the metal under conditions of strong deoxidation.

The development of appropriate steelmaking practices must therefore recognize the thermo-chemical principles that control phosphorus distribution. Proper application of these principles will result in effective phosphorus control with minimal impact on steel productivity or steelmaking costs.

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