Recent Advances in Understanding Phosphorus in Oxygen Steelmaking

Geoffrey Brooks[1]

1.Professor, Swinburne University of Technology, Melbourne, Victoria, 3160. Email: gbrooks@swin.edu.au

Keywords: Steelmaking, Slag Chemistry, Industrial Data

ABSTRACT

The control of phosphorus in steelmaking is one of the famous challenges of pyrometallurgy. It is well established that highly basic slags, the presence of FeO in the slag and lower temperatures (less than 1650 °C) are favourable for phosphorous removal. The thermodynamics of this reaction have been extensively studied under laboratory conditions and the general trends confirmed through industrial trials. However, in general, phosphorus slag/metal distributions measured in industry are far from equilibrium and quite specific to the oxygen steelmaking technology being used. This variability was quantified by Urban and co-workers, who found that the phosphorus partition ratio measured in plants varied with blowing practice, stirring intensity and even converter life. Some recent kinetic studies by Dogan and co-workers have shown how the kinetics of these reactions vary with FeO content and dissolved sulphur at the droplet scale. A global kinetic model by Rout and co-workers provides meaningful predictions of where dephosphorisation occurs in an industrial BOF and some recent heat transfer modelling by Madhavan and co-workers implies that temperature difference between droplets and slag has a role to play in explaining why equilibrium is not achieved. This paper will review the current state of knowledge and provide suggestions on predicting phosphorous removal for industrial operations and how greater removal could be achieved.

INTRODUCTION

The control of phosphorus is one of the central challenges facing steelmakers. In Oxygen steelmaking, it is well established that maintaining a slag with high basicity (high CaO and MgO), low tapping temperatures (<1650 °C) and high FeO will promote the removal of phosphorus from steel. High basicity also means high flux additions and added expense, low tapping temperatures may necessitate reheating the steel between steelmaking and casting, and high FeO contents in the slag will adversely affect yield. As a result, steelmakers are always looking for ways to minimise phosphorus coming into their feed materials and the adverse effects associated with removing phosphorous.

Phosphorus in even low quantities (above 0.1wt.%) can adversely affect ductility, fracture toughness, and cause hot shortness. Ironmaking conditions are not ideal for removing phosphorous, that is, reducing conditions encourage both Fe and P formation from their oxide states. In general, phosphorus is either removed from hot metal from a post blast furnace operation before entering the oxygen steelmaking or in the oxygen steelmaking furnace, typically below 0.010 wt.% in the tapped steel depending on the requirement of the grade being produced (Turkdogan, 1996). Some steelmakers use a two staged oxygen steelmaking process to remove phosphorus from hot metal, as a means of minimising flux addition, though this is also likely to lower overall productivity.

The thermodynamics of phosphorus removal has been extensively studied (Asiss et al., 2015). A recent review identified twenty-four different equilibrium relationships proposed in the literature (Urban et al, 2015), based on different models for dealing with the complex solution behaviour of PO_4^{3-} anion in slags. It is well beyond the scope of this paper to critically review this vast literature but to note that many of the equilibrium relationships take the following form:

$$\log (\%P)/[\%P] = A/T + 2.5 \log (\%Fe) + B. (\%CaO) + C. (\%MgO) - D \qquad (1)$$

Where () indicates slag, [] metal, T is temperature in Kelvin, concentrates are in wt.% and A, B. C and D are constants

This equation shows:

(a) the importance of temperature on phosphorus partition in slags – phosphorous oxide becoming less stable with temperature – with the ratio (%P)/[P] decreasing from approximately 50 at 1620 °C for a commercial BOF operation to below 35 at 1690 °C (Urban et al., 2015). High tapping temperatures (>1650 °C) reflect processing requirements post steelmaking and the superheat required at the casting machine.

(b) the importance of FeO in the slag to provide dissolved oxygen into the metal for reaction with dissolved P (i.e. the least stable oxide in the slag will be accompanied by significant dissolved oxygen), other relatively unstable oxides (SiO_2 and MnO) will also provide dissolved oxygen but FeO content in the slag is major variable. Increasing the FeO content of the slag from 14 wt.% to 24 wt.% can typically double the partition ratio in industrial furnaces (Urban et al., 2015). Increasing FeO in the slag effects yield from the operation and is itself controlled by the carbon content of the steel, so in many cases not a variable that can be easily manipulated i.e. the FeO content of the slag is set by the grade of the steel being tapped (Turkdogan, 1996).

(c) the importance of providing basic oxide fluxing agents to stabilise the phosphorus in the slag phase. Lime/silica weight ratios (an approximate measure of “basicity” commonly used in industry) range from two to four depending on the grade of the steel and the operating temperature of the steelmaking furnace. Increasing the lime/silica ratio from 2.6 to 4.0 in BOFs can typically double the partitioning ratio of phosphorus but at the cost of extra flux and the risk of creating a high liquidus temperature slag that may not be practical to melt or easily tap from the vessel (Urban et al., 2015).

There are variations to the relationship shown in equation 1 (e.g. a temperature term is introduced to reflect the impact temperature on the activity of CaO and MgO) and significant debate about which is the most accurate formulae but these debates, in part reflect the variation in experimental data and difficulties in controlling and measuring all variables accurately in high temperature experiments (Assis et. al., 2015). An important complication is the tendency of phosphorus oxide to dissolve into a solid solution with solid calcium silicate phases that can exist in steelmaking conditions, particularly early in the blow when temperatures in the vessel can be below 1600 °C, and various researchers have attempted to measure this behaviour in experiments and pilot plant testing (Millman et al., 2013)

The large body of work in quantifying the behaviour of phosphorus in steelmaking systems whilst providing an excellent basis by which to qualitatively understand the general trends of oxygen steelmaking furnaces, they do not allow direct control of the process because these thermodynamic relationships over predict phosphorus partitioning significantly in industrial operation. Most industrial furnaces are not at equilibrium regarding phosphorus and this paper explores the reasons for this and recent work in trying to provide a better predictive basis for phosphorous behaviour in Oxygen steelmaking.

NON-EQUILIBRIUM CONDITIONS IN OXYGEN STEELMAKING

There is clear evidence that industrial oxygen steelmaking operations are not at equilibrium regarding phosphorus at the completion of the blow. An extensive review of plant data from around the world (including data from 30 plants) by Urban et al. (2015) found that tapped phosphorus partitioning ratios (P)/[P]) for oxygen steelmaking operations are far from equilibrium. For top blown (BOF) operations the (P)/[P] ratio may vary from 50 to 100, whilst combined blowing operations vary between from 80 to 140 and bottom blown between 100 to 200. Urban et al. reported that calculated equilibrium ratios over the range of conditions considered for these industrial systems ranged from 200 to 700. Turkdogan (1996) also recognised these differences had plant data showing that the greatest deviation from equilibrium could be found for top blown BOFs producing steel below 0.1 wt.% C, where-as, bottom blowing (Q-BOP) operators were tapping close to equilibrium regarding phosphorous.

Urban et al (2015) provided industrial data show that tapped phosphorus partition ratios in top blown BOFs were influenced by slag splashing, introduction of inert gas bottom stirring and converter life. They concluded that phosphorus partitioning in most oxygen steelmaking vessels is kinetically controlled, that bottom blown vessels are closest to equilibrium (which is consistent with Turkdogan (1996)) and that increased stirring in the vessel is important to improving the kinetics. They also concluded that equilibrium-based relationships could not be used to control industrial operations and that each plant needed to develop empirical models based on statistical techniques to predict their phosphorous partitioning ratios at tapping.

In addition to plant data, which is dominated by at “turn down” (a few minutes before tapping) and/or “at tap” data, there has an extensive pilot plant study carried at MEFOS in Lulea using a 6 tonne top blown converter in which samples from different positions within the furnace were removed at regular intervals during the blow (Millman et al., 2013). This is the only known study in the open literature which quantified how phosphorus distributes itself in different phases at different stages of an oxygen steelmaking blow. The data generated from the study is detailed and difficult to interpret but the major findings regarding how dephosphorisation proceeded in this pilot plant study can be summarised:

i) Early in the blow (under ten minutes), the majority of phosphorus removed from the metal was present in a solid solution phase containing Ca_2SiO_4nd $Ca_3(PO_4)_2$

ii) After ten minutes, the liquid slag phase dominates the make of the slag layer and phosphorus previously in the solid solution phase is dissolved into the liquid phase.

iii) That amount of phosphorus in the slag phase is maximised below ten minutes and then is stable in the molten slag layer until tapping.

iv) The amount of phosphorus found in metal droplets in the slag emulsion reaches a maximum total quantity at the 10-minute mark in the blow and then decreases to zero after 15 minutes.

This analysis implies that the formation of a solid solution phase early in the blow (when the temperature in the slag layer well below 1600 °C and solid phases are thermodynamically stable) is the dominant mechanism in controlling the overall removal of phosphorous. This conclusion does not consider the possibility that the solid solution samples measured from the samples were formed during the cooling of the samples post sampling, as these are the very phases expected to form upon cooling of a molten steelmaking slag. Also, the recognition of the potential importance of the solid solution in removing phosphorus is difficult to relate to the overall observations of Urban et al. (2015) that increased mixing in the vessel is key to the kinetics of dephosphorisation. It is also hard to understand why the total phosphorous removal is stable after 10 minutes given that gas injection is still mixing the overall system beyond ten minutes. The indication that droplets found in the slag emulsion have less and less phosphorous further suggests that the role of droplets in dephosphorisation may be crucial in the slowdown of dephosphorisation observed in the pilot plant study.

DROPLET KINNETICS AND DEPHOSPORISATION

The role of droplet formation and the chemical behaviour of these droplets in steelmaking slags has been the subject of extensive study in the last 20 years, with groups at McMaster University and Swinburne University of Technology working on both modelling and fundamental experimental aspects of these systems (Gu et al., 2017; Rout et al., 2018). Fully reviewing this literature is beyond the scope of this paper but a few key points from the most recent published studies from these groups can be summarised, as follows:

A) Droplets of iron containing carbon and phosphorus readily “bloat” when reacted within steelmaking slag, with nucleating CO gas bubbles being entrapped with the metal droplets, effectively lowering the density of droplets, and promoting their movement upwards in a slag. The buoyant droplets spend between 30 to 60s in a bloated state depending on the amount of carbon available, the FeO content of the slag and other parameters (Gu et al., 2017). These observations have been made using X-ray fluoroscopy in laboratories and there is also plant sample that support this observation (i.e. iron droplets in the slag emulsion “bloat”).

B) Small droplets (1g) of iron containing carbon and phosphorus react very quickly in a steelmaking slag, with phosphorous in the metal being reduced from 0.088 wt.% to below 0.04 wt.% within 20 seconds.

C) After an initial rapid dephosphorisation, the formation of CO starts consuming dissolved oxygen available for phosphorus oxidation and some reversion of phosphorus can occur within the droplet. Both the nucleation of gas bubbles and the blocking of reaction sites at the gas/metal interface is influenced by slight changes in sulphur content in the metal droplets.

D) Models of the bloating behaviour extended to the industrial BOF scenario by Rout et al. (2018) calculated the rate of different refining reactions in three different regions of the furnace, namely, (i) the jet impact region, (ii) the slag-bulk metal zone and (iii) the slag metal droplet emulsion zone and predicted that the reaction between droplets and the slag dominated the dephosphorisation kinetics. The model further predicted that the rate of dephosphorisation slowed down after 10 minutes in the blow because there was insufficient carbon in the metal to “bloat” droplets and this resulted in significant less residence time of the droplets and thus slower kinetics. When validating the models developed against industrial data, there was some evidence to suggest that variations in the FeO content in the emulsion slag layer could influence the final phosphorus level of the product steel through both changes in the thermodynamic drive and kinetics of the droplet reaction kinetics. In the modelling of Rout et al. (2018), the temperature at the droplets and emulsion was estimated using simplistic models and the droplets were assumed to be uniform in temperature during their time in the emulsion.

The modelling work of Rout et al. (2018) did successfully capture several key aspects of steelmaking kinetics but the models were limited by a lack of reliable kinetic model for predicting FeO formation in steelmaking conditions – the kinetics of FeO were estimated by difference (i.e. calculate the kinetics of the other reactions and assume the remaining oxygen reacts with iron to form FeO) – and a simplistic treatment of heat transfer during the steelmaking process, particularly, in relation to the temperature of droplets generated from the impact region of the furnace and the gradients in the droplets as they react in the slag emulsion.

The modelling work of Madhavan et al. (2021,2022) attempted to combine the insights around droplet kinetics from Rout et al (2018) and recent experimental work by Gu et al. (2017), with a rigorous treatment of heat transfer within the system. From available plant data and modelling of heat transfer in the impact region, Madhavan et al. (2022) estimated that the hot spot reaches a maximum of 2300 °C in the middle of a blow (approximately 10 minutes), and that droplets generated from the impact region heat the slag in the emulsion mainly by radiation, particularly in the first ten minutes of the blow. The model further predicts that the slag layer is consistently hotter than the hot metal bath, notably in the middle of the blow (50 to 100 °C) because of the heat transfer from the droplets to the slag emulsion region. The model further predicts that the slag and hot metal get closer in temperature in the last 5 minutes of the blow. There is limited industrial data available to confirm this prediction but these results do suggest that some of the slowing of the overall kinetics observed in dephosphorisation could be explained by the slag region near the reacting droplets in the emulsion becoming hotter, resulting in lowering of the thermodynamic drive to remove phosphorus, which in turn could expected to slow the kinetics. Certainly, there is a complex interplay between droplet generation, reaction within the droplets whilst in the emulsion and the transfer of heat between droplets and the surrounding slag, and this is likely to be important to understanding the overall kinetics of dephosphorisation in oxygen steelmaking.

CONCLUSIONS

There is significant evidence that top blown oxygen steelmaking vessels are far from equilibrium regarding phosphorus at the end of the blow. There is pilot plant data that suggests the majority of phosphorous removed from the metal is present in a solid solution phase containing Ca_2SiO_4 and $Ca_3(PO_4)_2$ and that metals droplets in the emulsion play a significant role in kinetic processes. Fundamental studies of droplet kinetics suggest that the “bloating” of droplets is significant in understanding the behaviour of phosphorus in steelmaking and that the low residence time of droplets towards the end of the blow may explain why the system is far from equilibrium. Heat transfer modelling of droplets in the slag emulsion show that the droplets transfer significant heat to that layer, and this is likely to affect the local kinetics of dephosphorisation. Models of oxygen steelmaking kinetics are limited by a lack of understanding of the kinetics of FeO formation, which is important as key phenomena such as decarburisation, “bloating” and phosphorus removal are strongly related to the FeO content in the slag.

In general, there is a lack of plant data particularly relating to behaviour of droplets in the emulsion, the temperature gradients within the process and how they change with time. The recent developments in understanding droplet behaviour have the potential to accurately model key aspects of the process but improved industrial data will assist in refining and improving these models. Insights into the kinetics of this reaction would allow more efficient use of fluxes and reduced environmental impact of the process.

ACKNOWLEDGEMENTS

I would like to acknowledge of the contribution of collaborators from Tata Steel, Swinburne University of Technology and McMaster University to my understanding of steelmaking kinetics, particularly, Akbar Rhamdhani, Ken Coley, Neslihan Dogan, Bapin Rout, Nirmal Madhavan and Aart Overbosch. I am particularly grateful to the long-term support of the Tata Steel Ijmuiden for much of the work described in this paper.

REFERENCES

Gu, K., Dogan, N. and Coley, K. 2017. The Influence of Sulfur on Dephosphorization Kinetics Between Bloated Metal Droplets and Slag Containing FeO, Met. Mat. Trans. B, 48B: 2343-2353.

Isis, A., Tyler, M., Seetharman, S., Fruehan, R., 2015. Phosphorous Equilibrium Between Liquid Iron and CaO-SiO2-MgO-Al2O3-FeO-P2O5 Slag Part 1, Met. Mat. Trans. B, 46B: 2255-2263.

Madhavan, N., Brooks, G., Rhamdhani, M., Rout, B., Overbosch, A., Gu, K., Kadrolkar, A., and Dogan, N., 2021. Droplet Heat Transfer in Oxygen Steelmaking, Met. Mat. Trans. B, 52B: 4141-4155.

Madhavan, N., Brooks, G., Rhamdhani, M., Rout, B. and Overbosch, A., 2022. Global Heat Transfer in Oxygen Steelmaking Process, Metals, 12: 992.

Millam, M.S., Overbosch, A., Kapilashrami, Malmberg, D. and Bramming, M., 2013. Some Observations and Insights on BOS refining, Ironmaking and Steelmaking, 40 (6): 460-469.

Rout, B., Brooks, G., Rhamdhani, A., Li, Z., Schrama, F. and Sun, J., 2018. Dynamic Model of Basic Oxygen Steelmaking Process Based on Multi-Zone Reaction Kinetics: Model Derivation and Validation, Met. Mat. Trans. B, 49B: 537-557.

Turkdogan, E., 1996, Fundamentals of Steelmaking, (Institute of Materials: London)

Urban W., Weinberg, M. and Cappel, J., 2015. Dephosphorisation Strategies and Modelling in Oxygen Steelmaking, Iron and Steel Technology. Iron and Steel Technology, April 2015; 91-102.