4th International Conference on Molten Slags and Fluxes, 1992, Sendai, ISIJ

KINETICS OF HOT METAL DEPHOSPHORIZATION USING LIME BASED SLAGS

Brian MONAGHAN, Roger POMFRET and Kenneth COLEY

Department of Metallurgy and Engineering Materials,
University of Strathclyde, Glasgow, U.K.

Synopsis

An investigation has been carried out to assess the effects of lime based slags containing SiO_2. CaF_2 and Fe_2O_3 on hot metal dephosphorization at 1330°C.
It was found that the kinetics of dephosphorization is first order with respect to phosphorus in the metal, and optimum dephosphorization was achieved with 50% Fe_2O_3 in the slag.
Increasing the CaF_2 beyond 12.5% reduces the rate of dephosphorization and lessens the amount of phosphorus removed.
Increasing the V-ratio from 2 to 3 had no effect on the rate of dephosphorization.

Key Words

Dephosphorization; kinetics; ironmaking; calcium fluoride; v/ratio; basicity; phosphorus; iron oxide.

I. Introduction

The increase in demand for low phosphorus steels coupled with an increase in the phosphorus levels of the raw materials used in steelmaking, has given impetus for research into the removal of phosphorus from iron and steel.

The removal of phosphorus from iron and steel is an oxidation reaction and requires a basic slag. Slags used for dephosphorization in general contain Na_2O or CaO. Na_2O based slags are more powerful dephosphorizing agents than CaO based slags [1], but the CaO based slags are preferred because of the process and environmental problems involved in using Na_2O [2].

The majority of work carried out on dephosphorization has involved equilibrium studies of the phosphorus partition between slag and metal and there is only limited information on the kinetics of dephosphorization [3], [4], [5], [6], [7], [8].

This investigation was set up in association with British Steel, Ravenscraig primarily to evaluate slags in the $CaO-SiO_2-Fe_2O_3$ system, some with the addition of CaF_2, suitable for hot metal dephosphorization in the convertor and to obtain kinetic data on dephosphorization using these slags.

II. Experimental

Slag constituents CaO, SiO_2 and CaF_2 were weighed and mixed. This mixture was then melted in an induction heated graphite crucible, then poured into a steel mould and allowed to cool to room temperature. The fused glassy slag was crushed and mixed with haematite to give a slag of the desired composition.

5kg of Sorel iron (4.3%C, 0.18%Si, 0.009%Mn, 0.027%P, 0.006%S), with ferrophosphorus (26%P, 1.5%Si) added to give the desired starting phosphorus level, was melted in a graphite crucible (inner diameter: 11cm, height: 21cm) in an induction furnace. It was raised to 1330°C (+/−10°) and a metal sample was taken. 500g of prefused slag was added to the surface of the metal. Alternate metal and slag samples were taken every minute for 30 minutes. The metal samples were obtained by suction using a silica tube and analyzed for phosphorus using a vanadium molybdate colorimetric method. The slag samples were taken by means of a steel scoop and analyzed by atomic absorption spectrophotometry.

III. Results & Discussion.

1) Kinetics of Dephosphorization

Fig. 1 shows the results for experiments with two initial phosphorus levels, and it can be seen that the rate of phosphorus removal increases with increasing initial phosphorus content of the metal.

The results were tested for zero, first and second order kinetics with respect to phosphorus in the metal.

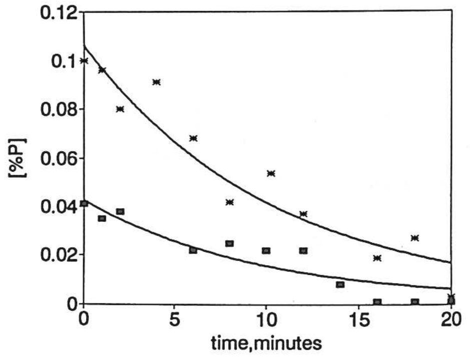

Fig 1 Effect of initial [%P]

If dephosphorization was zero order with respect to phosphorus in the metal, then the rate of dephosphorization would be independent of the initial phosphorus content of the metal. This is clearly not the case as can be seen in Fig. 1 where increasing the starting phosphorus increases the rate. Therefore dephosphorization is not zero order with respect to phosphorus in the metal.

First order dephosphorization with respect to phosphorus in the metal can be represented by the following equation:

$$\frac{[\%P] - [\%P]_e}{[\%P]_0 - [\%P]_e} = \exp(kt) \qquad (1)$$

where $[\%P]_0$ is the initial %P, $[\%P]_e$ is the equilibrium %P, k is a first order rate constant, and t is the time.

This model gave a good fit to the experimental results as seen in Fig. 1, where the solid lines are the best fit non-linear least squares regression lines using equation (1).

Although not shown in this paper the results were also tested for second order behaviour but this model gave a very poor fit to the experimental data.

It is therefore believed that dephosphorization is first order with respect phosphorus in the metal. This is in good agreement with other reported work [3-8].

If dephosphorization was first order then the likely rate limiting steps could be one or more of the following reactions :

a) Chemical reaction at the slag metal interface.
b) Mass transport control in the metal phase.
c) Mass transport control in the slag phase.

but , at present we have insufficient data to distinguish between these.

Mori et al [3], [4], [5], proposed a first order two film model based on both mass transport control in the metal and slag whilst Kitamura et. al [7], and Robertson et al [8], proposed a first order coupled reaction model based on mass transport control.

2) Effect of Fe_2O_3

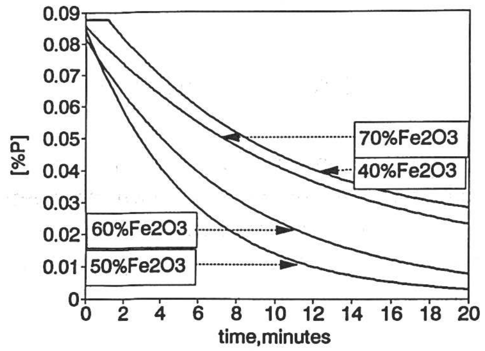

Fig 2 Effect of $\%Fe_2O_3$.

Fig. 2 shows the effect of the Fe_2O_3 content of the slag, where for clarity the results are shown as the best fitted first order lines. There is not a simple linear relationship between the Fe_2O_3 content of the slag and the rate of dephosphorization. Slower rates of dephosphorization were obtained with 40% and 70% Fe_2O_3 in the slag compared to 50% and 60%Fe_2O_3.

In addition the final phosphorus level achieved with 70 & 40% Fe_2O_3 is much higher than that achieved using 50 & 60%. Thus the best dephosphorization occurs between 50% and 60% Fe_2O_3. This is seen as the optimum level for dephosphorization in our experiments. The lower rates on either side of this composition can be explained as follows:

The 40% Fe_2O_3 slag is not sufficiently oxidising, thus limiting the slags ability to remove phosphorus down to a low a level, and slowing down the rate of phosphorus removal, whilst at the higher iron oxide level of 70% Fe_2O_3, there is a dilution effect, considerably reducing the amount of lime present in the slag. This would raise the final phosphorus content of the metal as the slag would have a lower phosphorus capacity, and also reduce the rate of dephosphorization.

50%–60% Fe_2O_3 is seen as a compromise between these two conditions. Optimum levels of iron oxide for dephosphorization have been reported by other workers. Balajava et al [9], obtained an optimum %FeO in the slag for dephosphorization of 14–16% at 1685°C. The different optimum levels of iron oxide in the slag are thought mainly to be the result of different working temperatures.

3) Effect of CaF_2

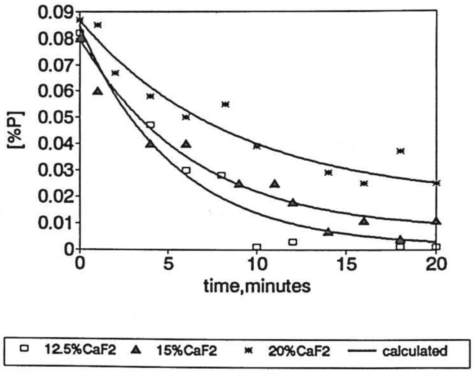

Fig. 3 Effect of CaF_2.

Fig. 3 shows the effect of CaF_2 additions and shows that increasing the CaF_2 beyond 12.5% decreases both the rate of dephosphorization and the amount of phosphorus removed.

Ito and Sano [10] measured the effect of %CaF_2 on the phosphorus partition and the phosphate capacity of slags and obtained similar results. They suggested that the explanation was that at high levels of CaF_2, the phosphate capacity of the slag and the phosphorus partition are lowered because CaF_2 has a dilution effect on the slag basicity. Simonov et al [11], obtained similar results.

4) Effect of V-Ratio

Increasing the V-ratio from 2-3 had no measurable effect on the rate of dephosphorization as seen in Fig. 4, where the V-ratio is defined as the mass ratio CaO/SiO_2.

This was surprising, as it has been widely reported in the literature [7], [9], [11], [12], that increasing the V-ratio increased the rate of

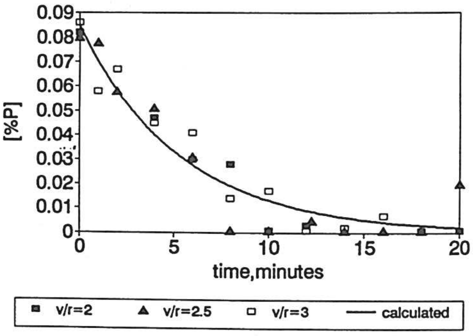

Fig 4 Effect of CaO/SiO_2

dephosphorization and gave a larger phosphorus partition.

The main difference between the findings of other workers and these results is the iron oxide content of the slags. This investigation used 50% Fe_2O_3, whilst previous investigations used much lower iron oxide levels.

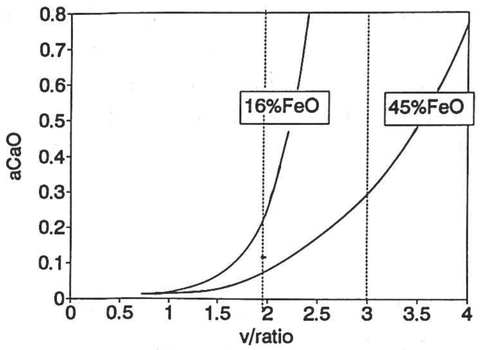

Fig 5 Lime activities in the $CaO-SiO_2-Fe_tO$ system.

An explanation for these results may be found in the fact that V-ratio is far too simplistic a measure of basicity and that perhaps what should be examined is the activity of lime.

The published data for the activity of lime in the $CaO-SiO_2-Fe_tO$ system [13] was replotted as a function of CaO/SiO_2 for 16% Fe_tO and 45%Fe_tO, Fig. 5 (45%Fe_tO corresponds to 50% Fe_2O_3). The diagram shows that for the low iron oxide case any increase in the V-ratio above 2 produces a large increase in the lime activity, whilst for the higher iron oxide case increasing the V-ratio from 2 to 3 only increases a_{CaO} from 0.08 to 0.3. It is believed that this difference in a_{CaO} for different FeO levels goes some way to explaining the fact that there is little , or no, effect of V-ratio at 50% Fe_2O_3.

Conclusions

It was found that the kinetics of dephosphorization is first order with respect to phosphorus in the metal.

Optimum dephosphorization was achieved at 50% Fe_2O_3 in the slag.

Increasing the CaF_2 beyond 12.5% reduces the rate of dephosphorization and lessens the amount of phosphorus removed.

Increasing the v/ratio from 2 to 3 had no effect on the rate of dephosphorization

ACKNOWLEDGEMENTS

The authors would like to thank the Science and Engineering Research Council and British Steel PLC, Ravenscraig Works for financial support for this work.

REFERENCES

1) K. Kunisada and H. Iwai: Trans. ISIJ 27 (1987), 332.
2) S. M. Cooper: Proceedings of Phosphorus in Steel Conference, University of Strathclyde (1987), 65.
3) K. Mori, S. Doi, T. Kaneko and Y. Kawai: Trans. ISIJ, 18 (1978), 261.
4) Y. Kawai, R. Nakao and K. Mori: Trans. ISIJ, 24 (1984), 509.
5) K. Mori, Y. Fukami and Y. Kawai: Trans. ISIJ, 28 (1988), 315.
6) H. Suito and R. Inoue: Trans. ISIJ, 24 (1984), 47.
7) S. Kitamura, N. Sato and K. Okohira: Trans. ISIJ, 28 (1988), 364.
8) D. G. C. Robertson, B. Deo and S. Ohguchi: Ironmaking and Steelmaking, 11 (1984), 41.
9) K. Balajva, A. G. Quarrell and P. Vajragupta: J. Iron and Steel Inst., (1946), 115.
10) K. Ito and N. Sano: Trans ISIJ, 25 (1985), 355.
11) S. Simeonov and N. Sano: Trans. ISIJ, 25 (1985), 1031.
12) T. Ikeo and T. Matsuo: Trans. ISIJ, 22 (1982), 495.
13) M. Timocin and A. E. Morris: Met. Trans., 1 (1970), 3193.