DEPHOSPHORISATION OF HOT METAL

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ABSTRACT

In a tough economic climate and faced with increasing environmental awareness, Japanese steelmakers developed a number of processes in the early 1980's to desiliconise and dephosphorise hot metal prior to decarburisation in the BOF. These processes used both CaO and Na₂O based slags. Dephosphorisation has not been considered an issue in Australia due to the abundance of low phosphorus ores. The BOF has been capable of removing phosphorus without excessive impact on the productivity of the furnace. However, the availability of low phosphorus ores is not something that should be taken for granted, particularly, if the ability to use lower grade ores results in a large increase in useful domestic ore reserves. This paper summarises the technologies available for dephosphorisation of hot metal using both CaO and Na₂O based slags. It can be seen that a reduction in the phosphorus concentration of hot metal below 0.010% can be achieved prior to decarburisation using a relatively simple process and resulting in significant cost savings.

1. INTRODUCTION

The detrimental effects of excessive phosphorus in iron and steel have been recognised for a long time. Subsequently, the removal of phosphorus from iron and steel has always been considered a primary processing requirement. Today, steel is used for applications requiring greater strength under increasingly adverse conditions, and subsequently there is greater demand to reduce the levels of undesirable solutes such as phosphorus. Phosphorus is known to reduce ductility, raise the ductile to brittle transition temperature and reduce the fracture toughness at all temperatures. It reduces resistance to stress corrosion and hydrogen induced cracking and promotes cracking in the heat affected zones of welded steel.

Development of satisfactory dephosphorisation techniques has been driven by the concurrent development of other steelmaking technologies. The domination of continuous casting technology...
has required lower phosphorus levels in steel. During continuous casting, phosphorus segregates to the centre of the slab resulting in severe localised brittleness. Phosphorus segregation can also result in hot shortness on slab reheating.

The longer cast times associated with continuous casting requires higher tap temperatures from the BOF vessel. This, in turn, results in phosphorus reversion from the slag to the metal that can only be avoided through using very high slag volumes, double slag practices or external dephosphorisation of hot metal prior to charging into the BOF. In addition to customer demands and changing technology, the need for steelmakers to effectively dephosphorise iron becomes more important as sources of low phosphorus containing ore become scarce.

A number of studies have been carried out in Japan to reduce the amount slag used in the BOF. Minimum slag practices have been applied to almost all Japanese BOF and significant cost reductions have been realised through the external desiliconisation and dephosphorisation of hot metal prior to decarburisation in the BOF. In addition, there are attractive recycling opportunities with such plant configurations.

2. BENEFITS OF DEPHOSPHORISATION

An economic relationship exists between the pretreatment of hot metal, the productivity of the decarburisation furnace, the quality of hot metal and the relative cost and availability of scrap. It was with these factors in mind that Japanese steelmakers developed a number of processes for the pretreatment of hot metal, which enabled a reduction in the volume of slag required for the conversion of pig iron to steel and reduced on the load on the decarburisation furnace, thus increasing the productivity of these units. In the early 1980's a number of commercial plants were commissioned, their capacities ranging from 30,000 to 650,000 tonnes per month of treated metal.

In order to dephosphorise the hot metal, it is imperative to remove silicon first. Thus steelmakers who pretreat hot metal for the removal of phosphorus initially desiliconise and then dephosphorise. The benefits of desiliconisation and dephosphorisation have been reported by a number of authors (Harrison, 1959; Koros, 1984; Itoh, 1983; Kurose et al, 1989):

1. A reduction in converter slag volume; increased iron yield and reduced converter lining wear.
2. Increased converter productivity with more control and predicability.
3. A reduction in the amount of phosphorus in the steel.
4. Alloy conservation through the recovery of Nb, V and Ti in the hot metal.
5. A reduction in the amount of CaO and MgO required per tonne of treated steel.
6. An increase in the amount of Mn recovery in the BOF.
7. With little or no phosphorus load on the BOF, it is much more capable of producing high carbon heats at low temperatures.
8. A reduction in the FeO content of any carryover slag into the ladle reduces the formation of aluminates in the steel.
9. With increased confidence in BOS process due to greater control, it becomes possible to tag without analysis reducing process time, and
10. A reduction in the scrap to hot metal ratio.
3. EXTERNAL DEPHOSPHORISATION OF HOT METAL

Steel can be dephosphorised either as iron direct from the blast furnace prior to decarburisation in the BOF, in the BOF itself, or in the ladle following decarburisation. The thermodynamics of dephosphorisation indicate that significant rephosphorisation takes place at higher temperatures. Therefore, the most energy efficient process location for dephosphorisation is directly after the iron making stage, when the temperature of the hot metal is between 1250 and 1400°C. After decarburisation, the temperature of the steel is typically between 1500 and 1650°C.

There are essentially two slag systems used for the external dephosphorisation of hot metal. CaO-CaF² based slags have been very successful at dephosphorisation, sometimes aided by an oxidant such as Fe₂O₃ or O₂. Another system used for dephosphorisation is that which utilises Na₂O-SiO₂ based slags. Na₂O is usually introduced as soda ash Na₂CO₃. These fluxes are generally more effective than CaO based fluxes, and have been shown to be effective desulphurisers. There are, however, significant environmental concerns associated with their use, particularly the evolution of sodium vapour.

There is quite a range of plant configurations used to pretreat hot metal (Ishihara, 1985), each developed based on the currently existing steelmaking plant and needs. The simplest hot metal pretreatment process was developed by NSC. Desiliconised hot metal [Si ≤ 0.1-0.15%] is injected with Na₂CO₃ and Fe₂O₃ in the hot metal charging ladle. The slag formed is then raked off. This method was used at the Yawata works to produce stainless steel.

SMJ developed a process known as SARP (Sumitomo Alkalai Refining Process), which utilises soda-ash injection at the rate of about 19kg/thm in a torpedo ladle following desiliconisation in the blast furnace runner to Si < 0.10%. During Na₂CO₃ injection, the phosphorus content of the metal decreases from 0.1 to 0.005 % and sulphur decreases from 0.05 to 0.002%. This process has the additional benefit of being able to economically extract the water soluble Na₂O component of the slags in subsequent treatment for recycling. The slag remaining, rich in phosphorus and sulphur, can then be sold as an agricultural commodity.

Desiliconisation is performed prior to treatment with Na₂CO₃ as when Na₂CO₃ reacts with silicon to form a metasilicate, free carbon is formed. This free carbon is very reactive and will react with Na₂CO₃ reducing the sodium available for dephosphorisation. It is important to control the temperature during hot metal treatment. This can be achieved through the concurrent injection of mill scale, (Fe₂O₃ + FeO), which will preferentially react with free carbon and thus conserve a reserve of Na₂CO₃ for dephosphorisation and desulphurisation (Fuwa et al, 1984).

An example of a CaO based external dephosphorisation process is ORP (Optimum Refining Process), used at the Kimitsu works of NSC. In this process, a CaO-CaCl₂ flux is used to dephosphorise and desulphurise desiliconised hot metal in the torpedo ladle prior to decarburisation. NSC found that steelmaking time could be reduced from 56 to 34 minutes and steelmaking flux consumption reduced from 46.6 to 29.0 kg/thm (Chihara, 1986).

4. FACTORS AFFECTING DEPHOSPHORISATION

The factors affecting dephosphorisation are well understood due to the comprehensive amount of detailed thermodynamic studies conducted by various researchers over the last 80 years. A slag rich
in basic components is critical in lowering the activity coefficient of phosphorus. Basic components include CaO, Na₂O and MgO. The exothermic nature of the dephosphorisation reaction means that a higher distribution of phosphorus between the slag and the metal is possible by lowering the temperature of the reaction. A regularly referred to equation that describes the phosphorus distribution in terms of these factors is given by (Healy, 1970):

\[
\log \left( \frac{P}{[P]} \right) = \frac{22350}{T} - 16.0 + 0.08 \times (\% CaO) + 2.5 \times \log(\% Fe_{\text{metal}})
\]  

(1)

A high oxygen partial pressure at the slag-metal interface increases the distribution ratio, and this is characterised by a high activity of FeO in the slag phase. The concentration of FeO in the slag phase cannot be too high, however, or the concentration of active bases may be reduced to the detriment of the phosphorus distribution. It is possible to increase the chemical activity of FeO in the slag phase without increasing the concentration of this oxide through the addition of CaF₂ (Turkdogan and Pearson, 1953). From a kinetic point of view, intense stirring to maximise interfacial area is important, and the slag phase must be sufficiently fluid to encourage diffusion from the interface to the bulk phase. CaF₂ is commonly added to steelmaking slags to improve fluidity.

In slags containing in excess of 25% CaO, the phosphorus distribution has been found to be dependent on the concentration of CaO only (Balajiva et al, 1946, Healy, 1970; Vajragupta, 1948; Kor, 1977) however at lower concentrations of CaO, other slag components have a significant effect, and the relative dephosphorisation strength of these components with respect to CaO need to be taken into account. Balajiva et al (1946, 1947) determined that the logarithm of the phosphorus distribution, \( L_p \), was dependent upon the logarithm of the composition of the slag expressed in percent weight CaO. Suito et al (1981, 1982, 1984) determined similar log–log relationships, incorporating values for the CaO equivalencies of MgO, Na₂O, BaO, MnO, FeO, CaF₂ & P₂O₅. More recent works have chosen log–linear relationships in determining expressions for \( L_p \) (Turkdogan, 1996; Suito and Inoue, 1982; Kunisada and Iwai, 1987; Zhang et al, 1985).

The large quantity of experimental data has aided the development of a number of semi-empirical relationships. These expressions are derived either using the molecular approach of Balajiva et al or the more sophisticated ionic approach of Flood and Grjotheim (1952). The expressions developed by Turkdogan and Pearson (1954) and Suito et al include CaF₂ as an explicit term, with an approximately equivalent effect on dephosphorisation as CaO. Other works (Kor, 1977, Kawai et al, 1984) have suggested that CaF₂ has a much lower effect than CaO on the dephosphorisation of iron. The equations of Healy and Zhang et al do not include terms for the effect of CaF₂ and therefore are limited in their applicability.

So far only slag systems under oxidising conditions and at steelmaking temperatures have been considered. The semi-empirical equations attained from these experimental results cannot be applied to dephosphorisation of hot metal for two reasons. Firstly the high carbon content of hot metal means that the interfacial partial pressure is very low and is in fact controlled by the carbon- oxygen equilibrium, resulting in a very concentration of FeO in the slag phase. Secondly, the temperature of the reaction when dephosphorisation takes place external to the decarburisation furnace is between 200 to 300°C cooler.

In the study of dephosphorisation using CaO based slags under reducing conditions, very little use is made of empirical equations. The use of CaO based slags for the dephosphorisation of carbon saturated iron have been studied by a number of workers (Ito and Sano, 1985; Simeonov and Sano,
The distribution of phosphorus increases with increasing slag basicity and oxidising power of the slag, and an ideal balance can be achieved through use of the correct combination of bases and oxidisers. These findings are in agreement with the results of studies on the dephosphorisation of steel. The replacement of SiO₂ by CaF₂ results in an increased phosphorus distribution however the replacement of CaO by CaF₂ at constant SiO₂ content results in a decrease in the phosphorus distribution, in contrast to the reported effect of CaF₂ additions under oxidising conditions (Simeonov and Sano, 1985). An increase in temperature has a negative effect on the phosphorus distribution under reducing conditions.

The thermodynamics of Na₂O-SiO₂ slags in equilibrium with carbon saturated iron have been well studied (Pak and Fruehan, 1986; Tsukihashi et al, 1984; Inoue and Suito, 1982, 1985; Maddocks and Turkdogan, 1949, 1952; Van Niekerk and Dippenaar, 1992). It has been determined that the oxygen partial pressure at the slag-metal interface is controlled by the equilibrium between carbon and Na₂O. The substitution of Na₂O by CaO, BaO or MgO was found to decrease L_p, while the addition CaO to a 3Na₂O-SiO₂ slag increased L_p. There is very limited data on the effect of CaF₂ on Na₂O-SiO₂ slags. Van Niekerk and Dippenaar suggested that the phosphorus capacity of Na₂O-SiO₂-CaO based slags was decreased by the addition of CaF₂ due to a reduction in the formation of fluorophosphates, however, this was not proven conclusively. Suito and Inoue [33] only had two data points to demonstrate the effect of CaF₂ on the phosphorus capacity Na₂O-SiO₂, however these results indicated that CaF₂ decreases the phosphorus distribution.

Recent work by Johnston (1997) has shown CaF₂ has a detrimental affect on L_p, while additions of CaO improve L_p. It can be argued that these results are translatable to steelmaking conditions and that perceived improvements in L_p as a result of an increased concentration of CaF₂ are actually a reflection of the increased activity of FeO in the slag phase. The results are shown in Figure 1.

![Figure 1. Effect of CaO and CaF₂ on the distribution ratio between carbon saturated iron and 38%Na₂O-62%SiO₂ slag.](image-url)
5. CONCLUSION

The removal of phosphorus is a principle steelmaking process requirement. It is now possible to reduce the phosphorus concentration in hot metal from above 0.1% to below 0.010% by the treatment of hot metal prior to decarburisation. There are possibilities for a significant reduction in the total conversion cost from iron ore to steel if hot metal is desiliconised and dephosphorised prior to decarburisation in the BOF. In order to compensate for the lack of FeO in hot metal slags, very basic slags are required to remove phosphorus. CaF₂ is detrimental to the equilibrium phosphorus distribution under reducing conditions and the use of CaF₂ should be restricted to that required to ensure sufficient slag fluidity.

6. REFERENCES