

## Lecture 8: Dephosphorization Reaction

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### Preamble

Phosphorus removal from hot metal is the most important refining reaction. Phosphorus has atomic number 15 and it can give up all 5 electrons from its outermost shell to become  $P^{5+}$  or accept 3 electrons to become  $P^{3-}$  to attain stable configuration. This means that phosphorus can be removed both under oxidizing as well as reducing conditions. But removal of phosphorus under reducing conditions is not practical since its removal is highly hazardous. Thus P removal is practised mostly under oxidizing conditions.

### Equilibrium Considerations:

Phosphorus removal reaction



$$\Delta G^\circ = -740375 + 535.365T \text{ J/mol}$$

At  $T > 1382K$ ,  $\Delta G^\circ$  becomes positive which results in decomposition of  $P_2O_5$  to P and O. Thus removal of phosphorus requires that  $a_{P_2O_5}$  must be reduced.

$$K_P = \frac{a_{P_2O_5}}{[wt\% P]^2 [wt\% O]^5} \quad (2)$$

Now

$$[wt\% O] = a_{FeO} [wt\% O]_{sat.} \text{ and} \quad (3)$$

$$\log[\text{wt}\% \text{ O}]_{\text{sat.}} = -\frac{6320}{T} + 2.734 \quad (4)$$

By equation 2 and 3 and replacing  $a_{\text{P}_2\text{O}_5}$  by using Raoult's Law and after rearrangement

$$\frac{N_{(\text{P}_2\text{O}_5)}}{[\text{wt}\% \text{ P}]^2} = \frac{K_P (a_{\text{FeO}})^5 [\text{wt}\% \text{ O}]_{\text{sat.}}}{\gamma_{\text{P}_2\text{O}_5}} \quad (5)$$

$\gamma_{\text{P}_2\text{O}_5}$  is activity coefficient of  $\text{P}_2\text{O}_5$  in slag. The LHS of equation 5 is index of dephosphorization and denotes distribution of phosphorus between slag and metal. Higher value of LHS demands low  $\gamma_{\text{P}_2\text{O}_5}$  in a slag of a given composition.

### How low $\gamma_{\text{P}_2\text{O}_5}$ should be?

Consider dephosphorization in a slag of  $a_{\text{FeO}} = 0.31$  at 1773K. Initial %P in metal is 0.1 and mole fraction of  $\text{N}_{\text{P}_2\text{O}_5}$  in slag = 0.01. Let us calculate  $\gamma_{\text{P}_2\text{O}_5}$  which will allow dephosphorization.

$$\log K_P = \frac{38668}{T} - 27.96 \quad (6)$$

At 1773 K,  $K_P = 7.06 \times 10^{-7}$

$[\text{wt}\% \text{ O}]$  can be determined by equation 3 and 4. We substitute the values in equation 5. We get  $\gamma_{\text{P}_2\text{O}_5} = 4.16 \times 10^{-16}$  Now the question before us: how to attain such a low value of  $\gamma_{\text{P}_2\text{O}_5}$  in a slag of given composition? Such a low value of  $\gamma_{\text{P}_2\text{O}_5}$  can be attained when we use basic oxides which have a very strong tendency to form a stable chemical compound. The different basic oxides have different ability to lower  $\gamma_{\text{P}_2\text{O}_5}$ . The following expression describes the relative effects of basic oxides on  $\gamma_{\text{P}_2\text{O}_5}$ .

$$\log \gamma_{\text{P}_2\text{O}_5} = -24.64 \left[ N_{\text{CaO}} + 0.682N_{\text{MgO}} + 0.591N_{\text{MnO}} + 0.545N_{\text{FeO}} - 0.091N_{\text{SiO}_2} \right] - \frac{42000}{T} + 23.58 \quad (7)$$

Alkaline oxides  $\text{Na}_2\text{O}$  and  $\text{BaO}$  are stronger than  $\text{CaO}$  but they are corrosive to the refractory lining and hence not used.

Consider a slag  $N_{\text{CaO}} = 0.56$ ,  $N_{\text{MgO}} = 0.12$ ,  $N_{\text{MnO}} = 0.06$ ,  $N_{\text{FeO}} = 0.1$  and  $N_{\text{SiO}_2} = 0.6$

We calculate  $\gamma_{\text{P}_2\text{O}_5}$  at different temperatures

T (K)	$\gamma_{\text{P}_2\text{O}_5}$
1773	$1.74 \times 10^{-18}$
1823	$0.778 \times 10^{-18}$
1873	$0.324 \times 10^{-18}$

Decrease in temperature increases  $\gamma_{\text{P}_2\text{O}_5}$  which favours dephosphorization reaction.

## Effect of FeO and CaO on dephosphorization

Figure 7.1 shows the variation of dephosphorization index  $(\text{wt}\% \text{P}_2\text{O}_5)/[\text{wt}\% \text{P}]$  as a function of  $\text{wt}\% \text{FeO}$  for  $\text{CaO-FeO-SiO}_2$  slag at different basicities. The dephosphorization ratio increases with

Figure 7.1:

increase in FeO content of slag and becomes maximum in between 15-16% FeO at all basicities. Further increase in FeO beyond 15-16%, dephosphorization decreases. The above behaviour can be observed at all basicities of slag.

The above behaviour is due to the dual role of FeO. FeO is the source of oxygen for oxidation of P according to the following reaction

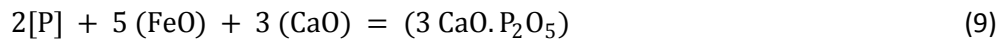


For a given basicity of slag, as FeO content of slag increases oxidizing power of slag increases and phosphorus oxidation according to reaction 8 will be favoured because CaO of slag decreases the activity of  $\text{P}_2\text{O}_5$  by forming a stable compound. Beyond the optimum value of FeO in slag FeO replaces CaO and may either combine with CaO or with  $\text{P}_2\text{O}_5$ . FeO is a weak base compared with CaO as a result of which the dephosphorization ratio decreases with addition of FeO beyond an optimum value.

The maximum dephosphorization ratio increases with the increase in the basicity of slag as can be seen in the figure 7.1. Higher basicity requires higher amount of CaO dissolved in slag. Any undissolved CaO will not be effective for dephosphorization. Optimum value of FeO is more or less independent of the basicity of slag. Thus control of FeO in slag is important for efficient dephosphorization.

### Conditions for dephosphorization:

Dephosphorization requires oxidizing and basic slag:



$$K_9 = \frac{a_{(3 \text{CaO} \cdot \text{P}_2\text{O}_5)}}{(a_{(\text{CaO})})^3 (a_{(\text{FeO})})^5 (a_{[\text{P}]})^2} \quad (10)$$

$$\frac{a_{(3 \text{CaO} \cdot \text{P}_2\text{O}_5)}}{(a_{[\text{P}]})^2} \approx \frac{(\text{wt}\% \text{P})}{[\text{wt}\% \text{P}]} = K_9 \times (a_{(\text{CaO})})^3 (a_{(\text{FeO})})^5 \quad (11)$$

- $a_{\text{CaO}}$  in slag should be high. This means slag should have free dissolved lime. High basicity of slag is required.
- $a_{\text{FeO}}$  in slag should be high; slag should be oxidizing. However for efficient dephosphorization the FeO content of slag should be in between 15 to 16%.
- Low temperature favours high  $K_9$ .

### Conditions for simultaneous removal of C and P

Removal of C and P both require oxidizing conditions but P removal is possible only when a basic and limy slag is formed. Consider the following reactions occurring simultaneously



$$K_{CO} = \frac{P_{CO}}{[wt\% C][wt\% O]} \quad (14)$$

$$K_P = \frac{N_{P_2O_5} \gamma_{P_2O_5}}{[wt\% P]^2 [wt\% O]^5} \quad (15)$$

It is assumed in eq. 14 and 15 that henrian activity is equal to (wt %). Both reactions 12 and 13 require oxygen but reaction 13 requires a slag which is basic in nature in addition to oxygen. Thus, if carbon and phosphorus are to be removed simulataneously, an important requirement is the availability of slag which acts as a sink for  $(P_2O_5)$ . Thermodynamically slag is required in which activity coefficient of  $P_2O_5$  is very low. The question is how low activity of  $P_2O_5$  should be?. This value can be determined by equations 14 and 15

$$\gamma_{P_2O_5} = \frac{K_P [wt\% P]^2}{K_{CO}^5 [wt\% C]^5 N_{P_2O_5}}$$

Replacing [wt% O] in equation 14 and 15, and after rearrangement,

$$(16)$$

From equation 16 one can determine the value of activity coefficient of  $P_2O_5$  which can lead to simultaneous removal of carbon and phosphorus.

Let us calculate the  $\gamma_{P_2O_5}$  when molten metal contains 2% C and 0.15% P and temperature  $T=1773K$ . The mole fraction of  $P_2O_5$  in slag is 0.1.

$$K_{CO} = \frac{1305}{T} + 1.979 \quad (17)$$

We can calculate  $K_P$  and  $K_{CO}$  from equations 16 and 17. Substituting all the values into equation 16 we get  $\gamma_{P_2O_5}$ . We can also calculate  $\gamma_{P_2O_5}$  at temperatures 1673K and 1873K. The results are given below

T(K)	$\gamma_{P_2O_5}$
1673	$1.6 \times 10^{-21}$
1773	$1.32 \times 10^{-22}$
1873	$1.42 \times 10^{-23}$

The calculations show:

- Both decarburization and dephosphorization are possible simultaneously in presence of slag in which  $\gamma_{P_2O_5}$  has extremely low value.
- Low temperature requires  $\gamma_{P_2O_5}$  in slag to be higher than at high temperature. Thus low temperature is favourable.

References for lectures 5 to 7

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