

Dephosphorization of Liquid Ferromanganese

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1. Introduction

Ferromanganese is used as deoxidizing and alloying agent in steelmaking. In order to produce high quality steel, it is desirable to have phosphorus contents in the ferromanganese less than 0.25%. However, the ferromanganese alloys produced in India continue to have high (>0.4%) phosphorus levels. There are no established methods existing for lowering the phosphorus levels in ferromanganese.

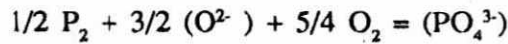
In the conventional production of ferromanganese based on carbothermic reduction of manganese ores, virtually all the phosphorus contained in the ore enters the ferromanganese alloy. Attempts have been made to remove phosphorus from manganese ores [1]. The majority of manganese ore deposits in central India have relatively high (> 0.3%) phosphorus levels. Since phosphorus is intimately associated with manganese [1], physical beneficiation is unsuitable and chemical beneficiation is necessary. Phosphorus removal through chemical beneficiation requires comminution, flotation and/or leaching to be followed by agglomeration. However, this route is highly energy intensive whose techno-economics is not considered favourable [1].

Dephosphorization of liquid FeMn can be a more viable alternative to removal of phosphorus from the ores using mineral processing techniques. Phosphorus removal from liquid ferromanganese by conventional methods under oxidising conditions is usually accompanied by a significant loss of manganese because the oxide of manganese is more stable than that of phosphorus at smelting temperatures [2]. If we want to prevent loss of manganese, the alternate method could be removal of phosphorus under reducing conditions but then the reaction product would be a phosphide which is considered environmentally unfriendly [3]. Research and development work in this area is going on at several well established R & D centers and universities all over the world [4-7]. This paper summarizes the various approaches followed by different investigators and the experience we have had while conducting trials at NML.

2. Approaches

Dephosphorization of liquid FeMn has been investigated along three different reaction schemes as follows :

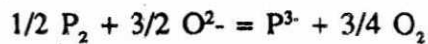
- i) Reaction with basic fluxes under oxidizing condition, wherein the product formed is a phosphate. The reaction can be expressed as :



and phosphate capacity (CPO_4^{3-}) which is the ability of a flux to contain phosphorus as phosphate ion is defined as :

$$CPO_4^{3-} = (\text{pct } PO_4^{3-}) / \left(\frac{P^{1/2}}{P_2} \cdot \frac{P^{5/4}}{O_2} \right)$$

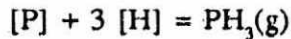
- ii) Reaction with basic fluxes under reducing conditions wherein phosphorus is removed as a phosphide as follows :



and the phosphide capacity (CP^{3-}) is defined as

$$CP^{3-} = (\text{pct } P^{3-}) \cdot \frac{P^{3/4}}{O_2} / \frac{P^{1/2}}{P_2}$$

- iii) Removal of phosphorus in vapour form as phosphine gas (through reaction between phosphorus and hydrogen dissolved in liquid metal) as follows [8] :



However, release of phosphine into open atmosphere would not be environmentally acceptable.

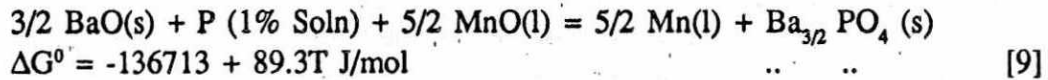
Presence of phosphide in the slag is also likely to cause formation of phosphine when in contact with moisture, thus, rendering the 2nd approach undesirable. In view of these environmental concerns, the favourable choice is considered to be dephosphorization of ferromanganese under oxidizing conditions. Additional advantages of the oxidizing conditions are following:

- a. Activity coefficient of phosphate is much less ($\gamma_{Ca_{1.5}PO_4} = 0.52$ in a $CaF_2 - CaO$ soln [3]) compared to the activity coefficient of phosphide ($\gamma_{Ca_{1.5}P} = 16.4$ in a $Ca - CaF_2$ soln [13]) in molten basic fluxes; thus the flux consumption is much less for the formation of phosphate.
- b. Under oxidizing conditions, there is no need to achieve lower oxygen pressure by adding deoxidisers.
- c. Under oxidizing conditions, reaction is favored at lower temperatures.

3. Thermodynamic Considerations

In view of the advantages listed above, much attention has been devoted to dephosphorization of ferromanganese under oxidizing conditions using basic fluxes, preferably BaO based fluxes as discussed later in section 5. The main problem with such an oxidizing scheme is a possible loss of manganese. However, by analysing

the Ba-P-O predominance diagram (Figure 1), Goel and Srikanth [9] have shown that there is a narrow range of a oxygen pressure in which it is thermodynamically feasible to remove phosphorus selectively under oxidizing conditions (without oxidizing manganese) by reacting the alloy with a BaO-saturated slag rich in MnO. Even though the predominance diagram was constructed assuming unit activity of all the condensed phases the above authors also considered the dephosphorization under more realistic operating conditions (non standard states) as follows:



The equilibrium constant K for the above reaction is expressed as :

$$K = \frac{a_{\text{Mn}}^{5/2} \cdot a_{\text{Ba}_{3/2} \text{ PO}_4}}{a_{\text{BaO}}^{3/2} \cdot h_{\text{P}} \cdot a_{\text{MnO}}^{5/2}}$$

$$h_{\text{P}} = \frac{a_{\text{Mn}}^{5/2} \cdot a_{\text{Ba}_{3/2} \text{ PO}_4}}{a_{\text{BaO}}^{3/2} \cdot K \cdot a_{\text{MnO}}^{5/2}}$$

where a_i is the Raoultian activity of components and h_p is the Henrian activity of the phosphorus dissolved in ferromanganese (1% solution as standard state). From above expressions, it is clear that for achieving lower h_p , the desirable conditions are:

- a. Lower activity of reaction product
- b. High activity of BaO
- c. High activity of MnO (>0.5)
- d. High value of K, which is possible at lower temperature.

The activities of manganese in Mn-Fe-C melts as calculated by Healy (10) are shown in Figure 2.

4. Effect of C, Mn, Si, Levels on Dephosphorization

Figure 3 shows a plot of phosphorus activity, h_p , versus phosphorus content of the liquid alloy at 1873 k [9]. This figure indicates that phosphorus removal should be easier from high carbon ferromanganese alloys because of a strong repulsive interaction between carbon and phosphorus.

Fuzita et al. [7] have studied the feasibility of dephosphorization of Fe-Mn-C alloy through the oxidizing route using BaCO_3 and found that the phosphorus removal

is favored by : (a) lower temperatures, (b) prevention of contamination of the flux by SiO_2 , in order to keep the BaO content as high as possible. They noted that dephosphorization efficiency does not increase beyond a certain carbon level (which is slightly lower than that of the solubility limit of carbon in ferromanganese).

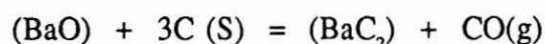
They also studied the influence of manganese content and found that the dephosphorization efficiency decreases with increasing manganese content. On conducting tests at moderate temperatures of 1300°C they were able to remove phosphorus effectively from high carbon Fe-Mn alloy using BaCO_3 , attaining a (% P)/[% P] ratio about 15. Their findings are further substantiated by recent studies reported by Watanabe et. al. [12]. Figure 4 shows that at a fixed T the equilibrium partition ratio for phosphorus between the slag and metal increases with a decrease in manganese content of the alloy.

Dephosphorization efficiency decreases with higher initial silicon content. Lee [11] reported that the best results can be obtained when the molten alloy has silicon content less than 0.1% by weight. They carried out dephosphorization of two ferromanganese alloys, one having a silicon content of 0.66% and the other desiliconized melt having a silicon content of 0.27% with a barium oxide containing agent under oxidizing conditions. Phosphorus content got reduced from initial level of 0.31% to 0.19% for the desiliconised melt whereas there was no effect on the melt containing 0.66% silicon.

5. Development of Suitable Fluxes for Effective Dephosphorization

Amongst the various reagent systems reported in the literature, BaO based fluxes are the most effective because of their high phosphate capacity (Figure 5). The phosphate capacity of BaO-MnO flux is as high as that of BaO- BaF_2 flux and much higher than those of any CaO bearing fluxes. The problem with BaO-MnO flux is the high melting points of pure components, 2198 and 2058K respectively. It is, therefore necessary to develop BaO-MnO flux by adjusting the composition in such a way that would melt at moderate ($<1500^\circ\text{C}$) temperatures. As shown in Figure 6, Fuzita et al. [7] reported that the addition of MnO helps lowering down the melting temperature of the flux (BaO-MnO).

Watanabe et al. [12] have reported that the BaO-MnO flux may melt at hot metal temperatures ($1300-1400^\circ\text{C}$) because of the presence of small amount of carbon but the reaction mechanism is not clear. The reaction can be expressed as :



The carbon content of the BaO-MnO flux increases with increasing BaO content and temperature and decreasing partial pressure of CO (Figure 7 a, b, c). The presence of BaC_2 ranging from 1.13 to 7.91 mass pct in the BaO-MnO flux would have a strong effect on the melting temperature drop of BaO-MnO flux.

Efforts are being made at NML to develop a suitable BaO-MnO flux which would melt at moderate (<1500°C) temperatures which is desired for effective dephosphorization of ferromanganese. In view of the high cost of BaO, tests are being conducted to replace part of BaO by CaO. We have conducted some tests using small quantities of BaO in lime based eutectic slag.

6. Results of Preliminary Trials at NML

Preliminary tests were not very encouraging because crucible used was of sillimanite which eroded heavily during melting test and contaminated the slag phase accompanied by huge loss of manganese. Subsequent experiments were carried out in graphite crucibles. This stopped the loss of manganese into the slag phase. About 30% phosphorus was found to have transferred into the slag phase.

Results of recent trials have shown encouraging trend. Efforts are underway for the development of BaO-MnO fluxes. Subsequent experiments are being planned to be carried out in a graphite resistance furnace (TAMMANN) using BaO based fluxes for effective dephosphorization.

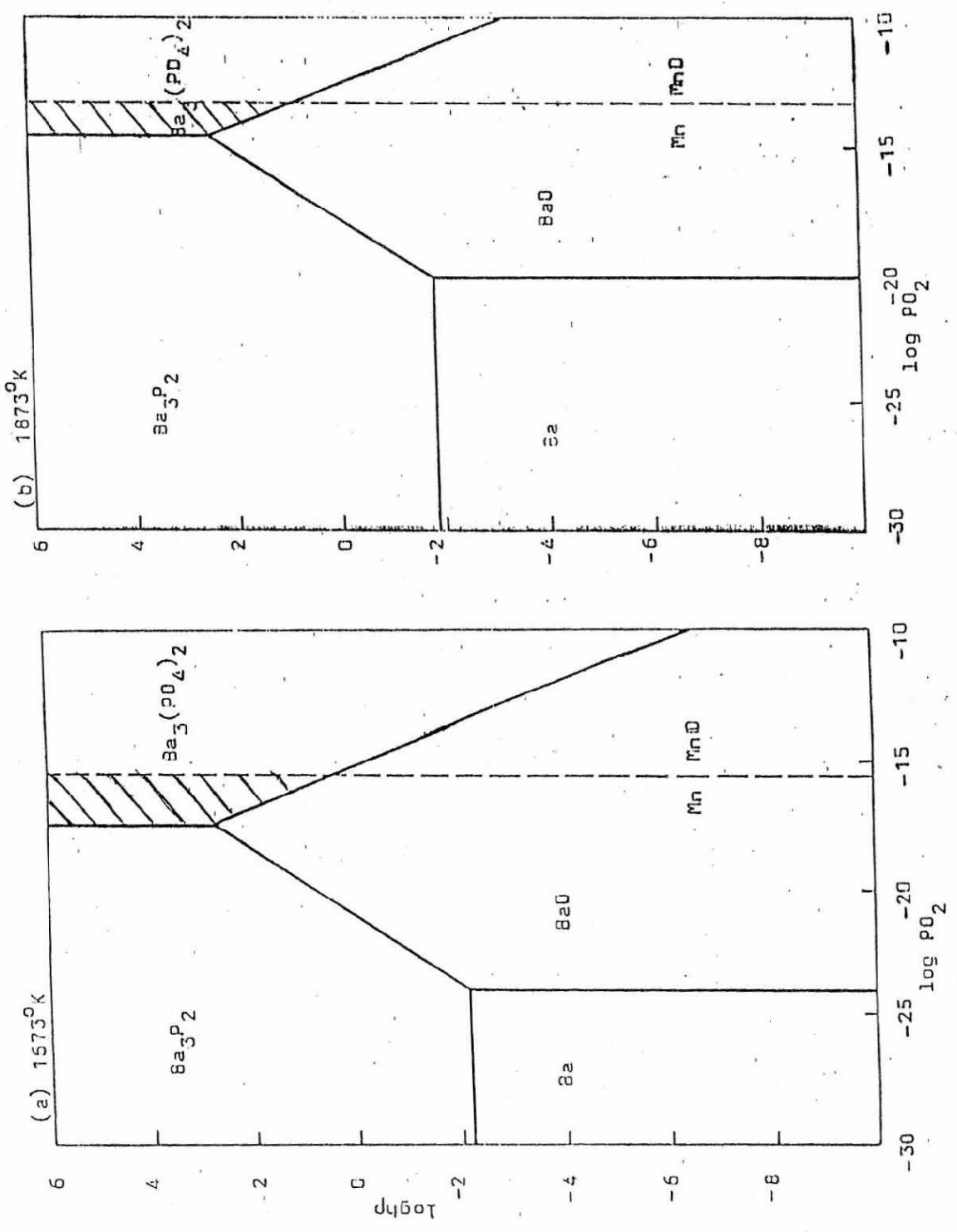
7. Summary

1. It is clear from the literature reviewed that dephosphorization of ferromanganese under oxidizing conditions has several advantages over that under reducing conditions even though there may be some loss of Mn :
 - a. Dephosphorization under reducing condition is not environment friendly.
 - b. Dephosphorization under oxidizing condition is favored at lower temperature.
 - c. Flux consumption for dephosphorisation under oxidizing conditions is much less than under reducing conditions.
2. Amongst the various fluxes reported to be investigated, BaO based fluxes are known to be most effective for dephosphorization of ferromanganese.
3. Under oxidizing conditions there is a narrow range in which it is thermodynamically feasible to dephosphorize molten ferromanganese, without oxidizing manganese, by reacting the alloy with a BaO-saturated slag rich in MnO.
4. In view of the high melting points of BaO as well as MnO, an attempt will be made to melt the flux in a graphite crucible in presence of small amount of carbon or by adjusting composition using various additions in order to melt them at moderate temperatures (<1500°C).
5. Studies are underway on dephosphorization of ferromanganese to develop a viable process for reducing phosphorus content (from >0.5% to <0.25%) using BaO-MnO based basic fluxes.

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Figure 1 - Predominance Area Diagrams for Ba - P - O (solid lines) & Mn-O (dashed lines).



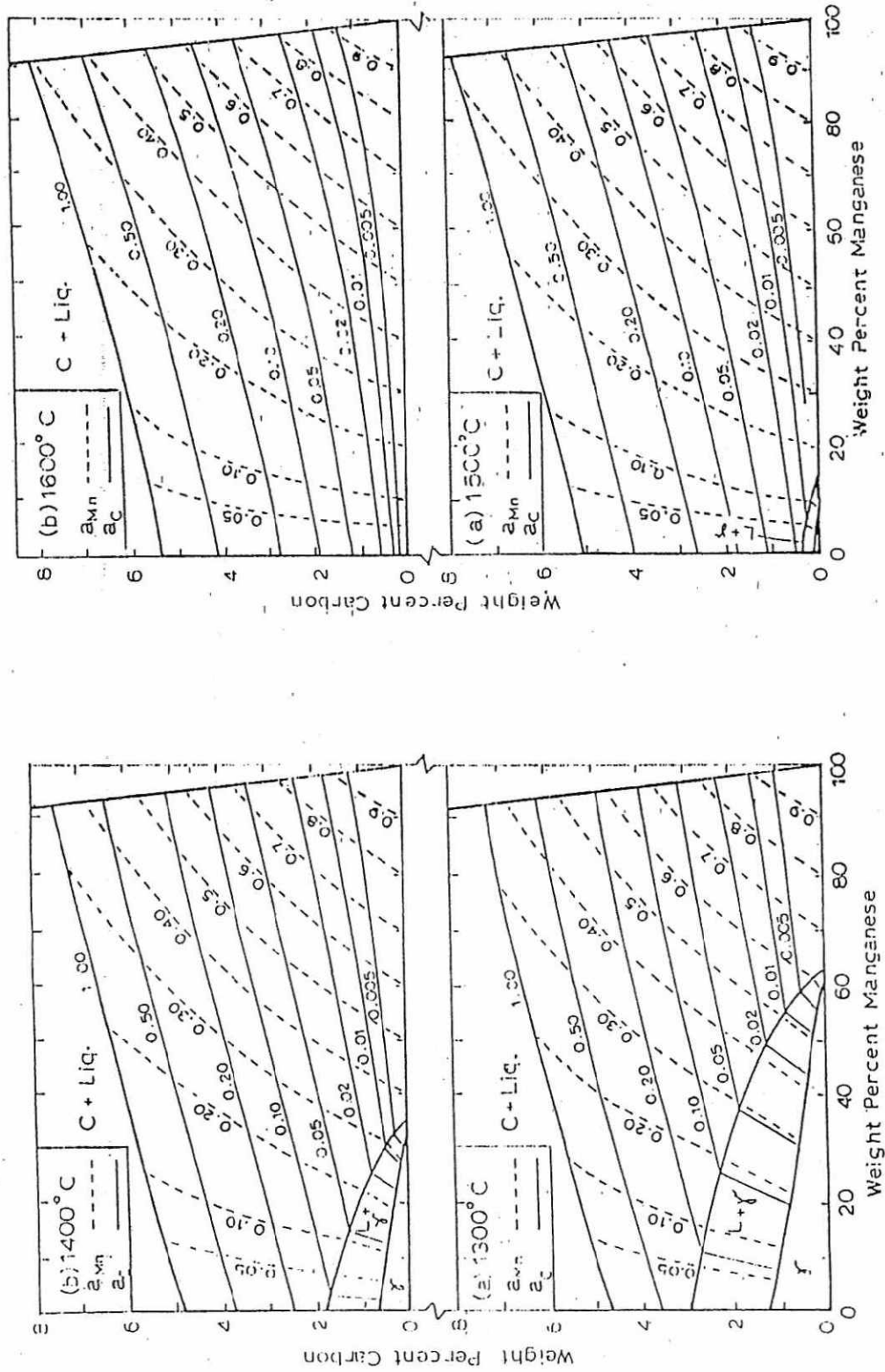


Figure 2 - Activities of carbon and manganese at 1300 - 1600°C. Standard states are graphite for carbon and pure liquid for manganese (9)

FIG: 3. ACTIVITY OF PHOSPHORUS IN MOLTEN FERRO-MANGANESE AT 1873K

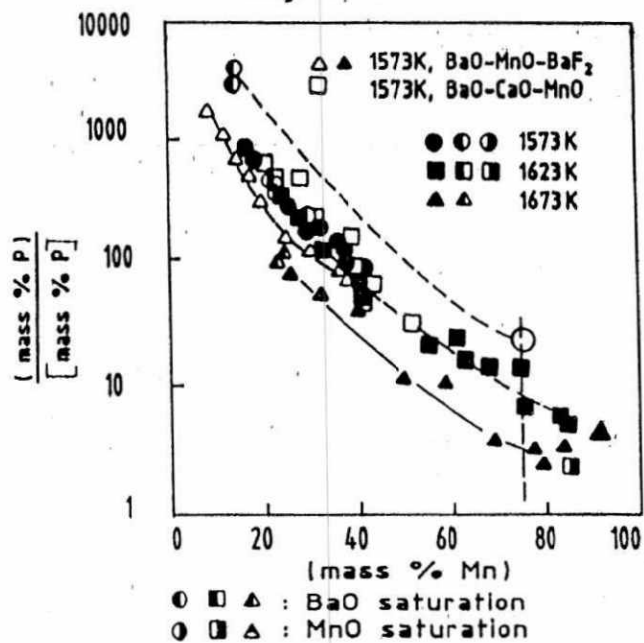
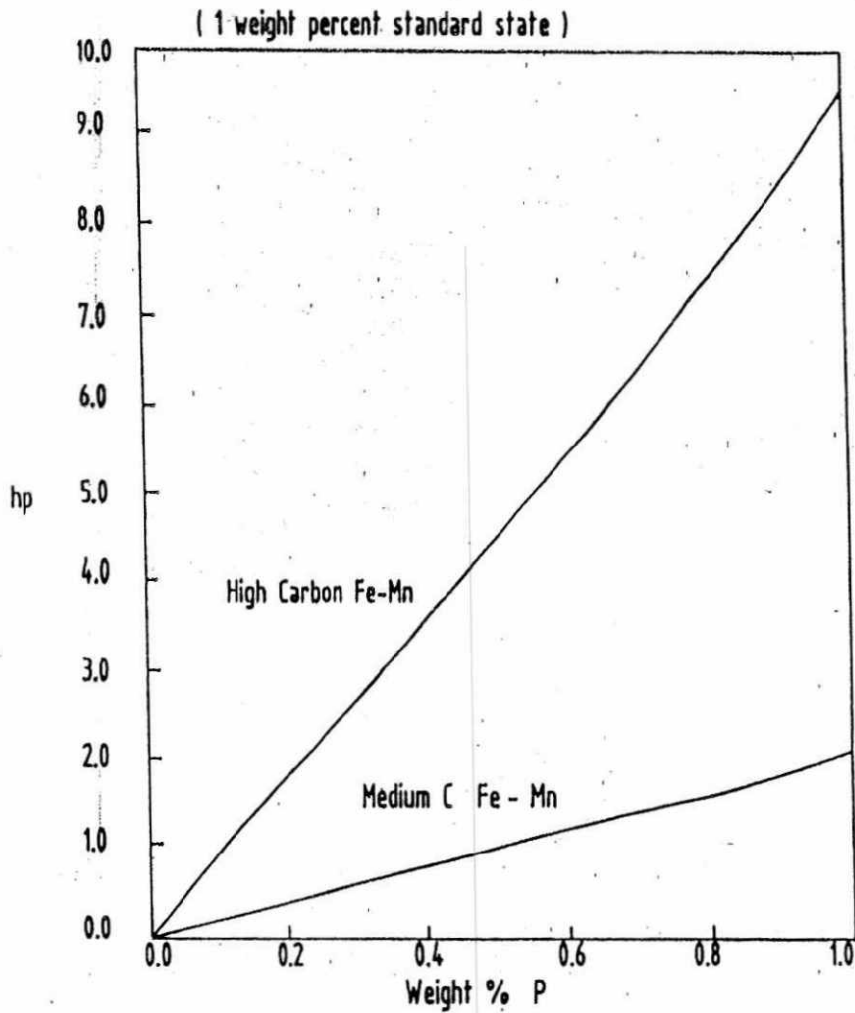


FIG: 4. PHOSPHORUS PARTITION RATIO BETWEEN THE BaO-MnO, BaO-MnO-BaF₂, AND BaO-CaO_{satd}-MnO FLUXES AND Fe-Mn-C_{satd} ALLOY AT 1573, 1623 AND 1673K AS A FUNCTION OF Mn CONTENT OF Fe-Mn-C_{satd} ALLOY .

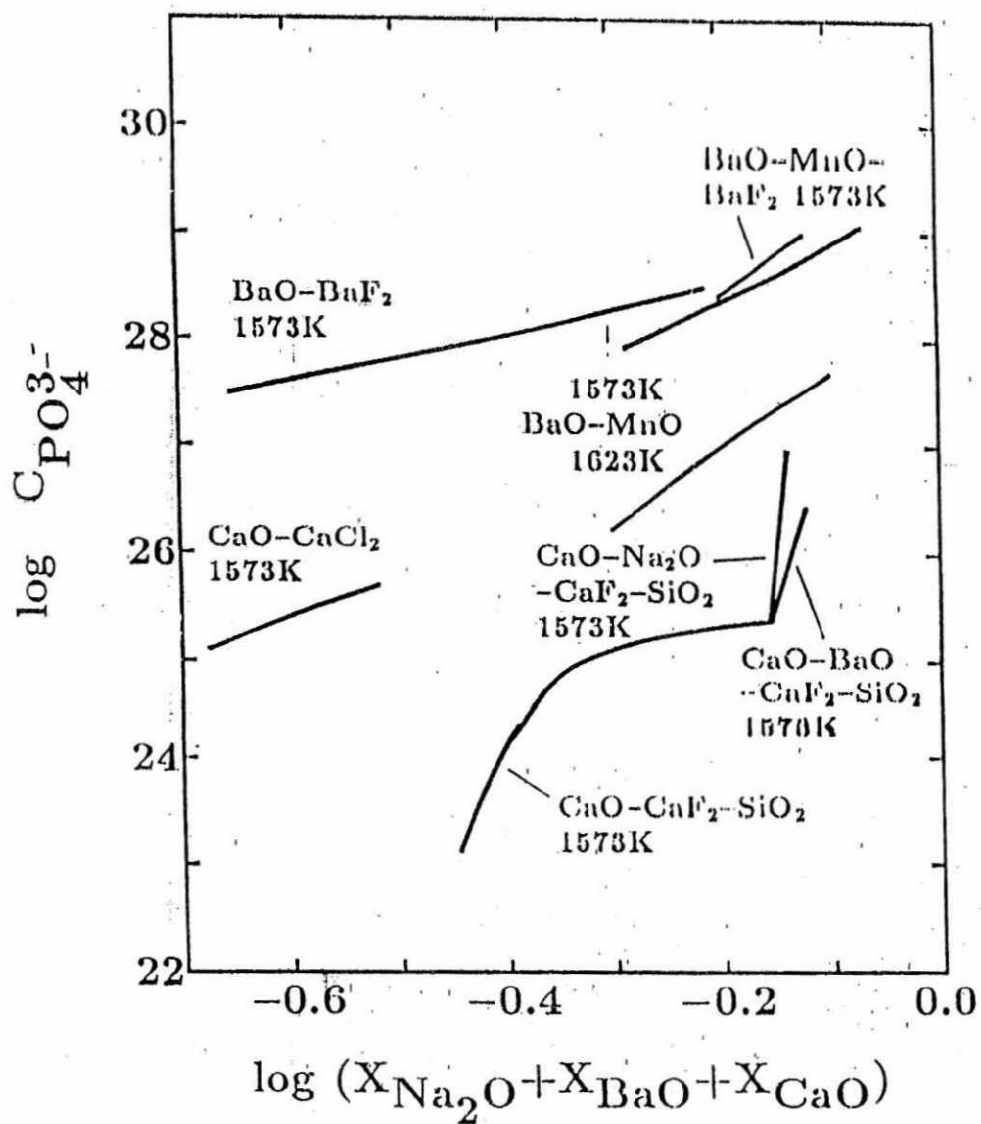


Fig. 5. — Phosphate capacities of various flux systems.

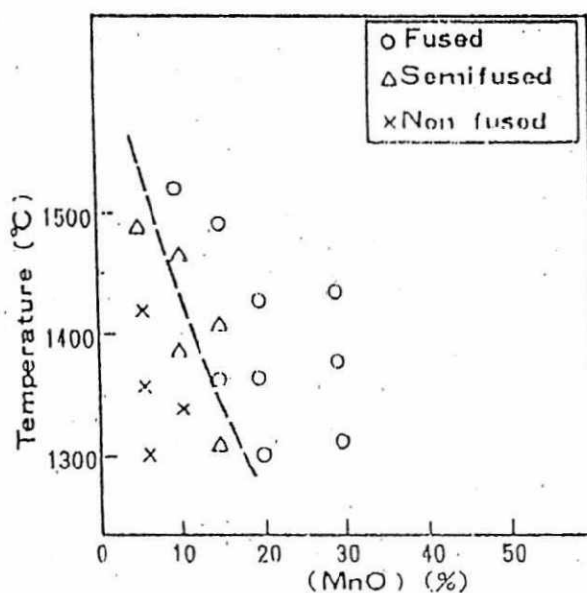


Fig. 6. Liquidus line of BaO-MnO obtained by the experiment of heating BaO-MnO₂ briquette.

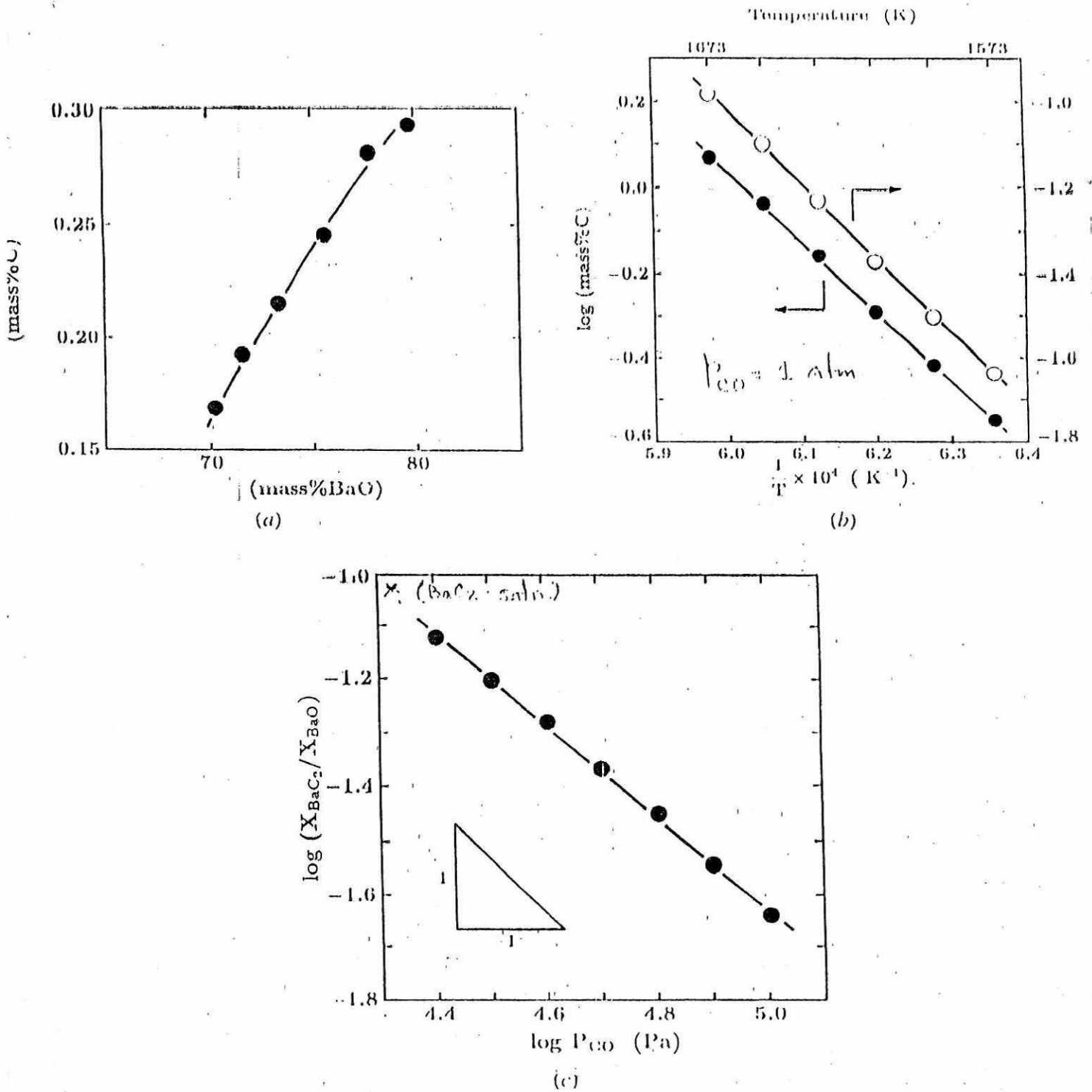


Fig. 7. --(a) Carbon content of the BaO-MnO flux at 1573 K at the oxygen partial pressure of 2.80×10^{-12} Pa as a function of BaO con of the flux. (b) Temperature dependence of carbon content of BaO-20 mass pct MnO flux. (c) Dependence of $X_{\text{BaC}_2}/X_{\text{BaO}}$ of BaO-20 mass MnO flux on partial pressure of CO at 1573 K.