

## THERMODYNAMICS OF BaO BEARING FLUXES

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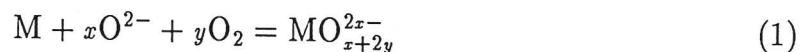
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**Synopsis:** Since BaO is more basic than CaO, BaO bearing fluxes are expected to be effective for refining particularly alloyed steels containing chromium or manganese. In this paper the thermodynamic properties such as phosphate, carbonate and sulfide capacities of BaO bearing fluxes including BaO–BaF<sub>2</sub> and BaO–MnO systems have been reviewed based on the works of the author's group. The thermodynamic effect of the addition of BaO to CaO saturated slags on their dephosphorization ability has been also examined. It has been shown to be of practical importance because their refining capacities are much improved with a little extra cost.

**Key words:** thermodynamics, refining, steel, hot metal, barium oxide, slag, phosphorus, sulfur, carbonate, chromium, manganese

### 1. Introduction

Unconventional, highly basic slags are to be used for producing ultra-pure steels, particularly when they contain oxidizable elements such as chromium or manganese, since most impurities are removed according to Eq.(1).



where the activity of oxide may be a measure of slag basicity. Barium oxide is expected to be a good candidate for attaining this purpose either as a major component or as an additive because of its strong basic nature.

In the present paper, the experimental findings by the author's group on thermodynamic properties of BaO containing slags are summarized.

### 2. The solubility of CO<sub>2</sub> in the BaO–BaF<sub>2</sub> melt

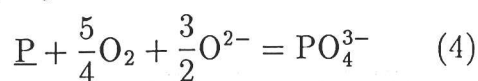
Since Wagner proposed to use the CO<sub>2</sub> solubility as a measure of slag basicity on the basis of Eq.(2)<sup>1)</sup>, it has been measured for many slag systems. Figure 1 shows the carbonate capacities of the BaO–BaF<sub>2</sub><sup>2)</sup> and BaO–MnO systems at 1573K, which are defined by Eq.(3).



The data were obtained in conjunction with the measurement of their sulfide capacities, which are described later.

### 3. Thermodynamic behavior of phosphorus in BaO bearing slags

Phosphorus may be removed from iron to slags by oxidation according to Eq.(4).



The phosphate capacity,  $C_{PO_4^{3-}}$ , which is defined as  $(\%PO_4^{3-}) / (P_{P_2}^{1/2} \cdot P_{O_2}^{5/4})$  based on Eq.(4), of the BaO-BaF<sub>2</sub> melts was obtained by measuring the distribution ratio of phosphorus between the slag and carbon saturated iron at 1473 and 1573K and is shown in Fig. 2. The phosphate capacity of this system is one of the largest among various basic slags as shown in Fig. 3. Accordingly, these slags are most suitable for dephosphorization of metals which contain oxidizable alloying elements. Figure 4 shows the phosphorus distribution ratio for carbon saturated chromium-iron alloys at 1573K<sup>3)</sup>. With increasing chromium content, the distribution ratio is lowered because of the negative value of interaction parameter of  $e_P^{Cr}$ . When this slag is used for dephosphorizing a carbon saturated 8mass%Mn-Fe alloy<sup>4)</sup>, the distribution ratio also drops significantly for the same reason as with chromium-containing metals as shown in Fig. 5. The activity of BaO in this system at 1473 and 1573K was determined by equilibrating the slag with Ag-Ba alloys in a CO atmosphere and is shown in Fig. 6.

As stated earlier, the BaO-BaF<sub>2</sub> slag is not suitable for effective dephosphorization of metals containing a large amount of manganese. For this reason, the phosphorus distribution ratios between the BaO-MnO slag and carbon saturated Fe-Mn alloys were determined in a CO atmosphere at 1573 to 1673K as a function of MnO content. As are shown in Fig. 7, the distribution ratio is high enough to dephosphorize alloys containing manganese up to 40mass%, and the phosphate capacities are almost equal to those of the BaO-BaF<sub>2</sub> system. The reason why this system has a low melting temperature would be the presence of a small amount of carbon up to 0.3 mass% as carbide. More details will be discussed elsewhere.

Figure 8 shows the effect of BaO addition to the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> slag at double saturation

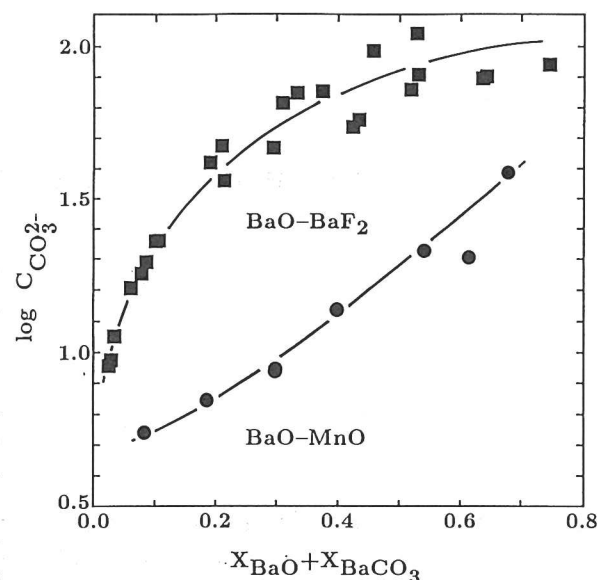


Fig. 1. Carbonate capacities of the BaO-BaF<sub>2</sub> and BaO-MnO systems at 1573K. Partial pressure of CO<sub>2</sub> is  $3.04 \times 10^3$  Pa.

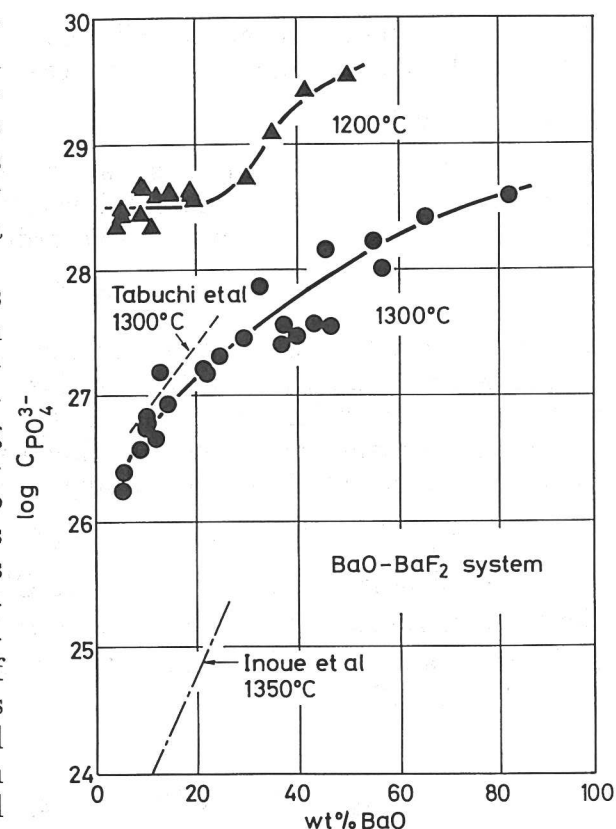


Fig. 2. Phosphate capacities of the BaO-BaF<sub>2</sub> system at 1473 and 1573K.

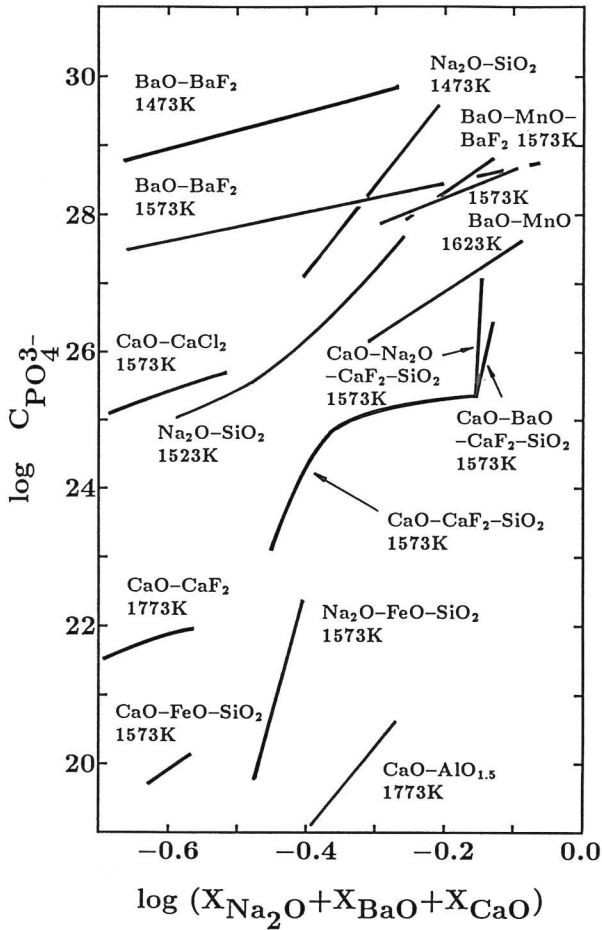


Fig. 3. Phosphate capacities of various flux systems.

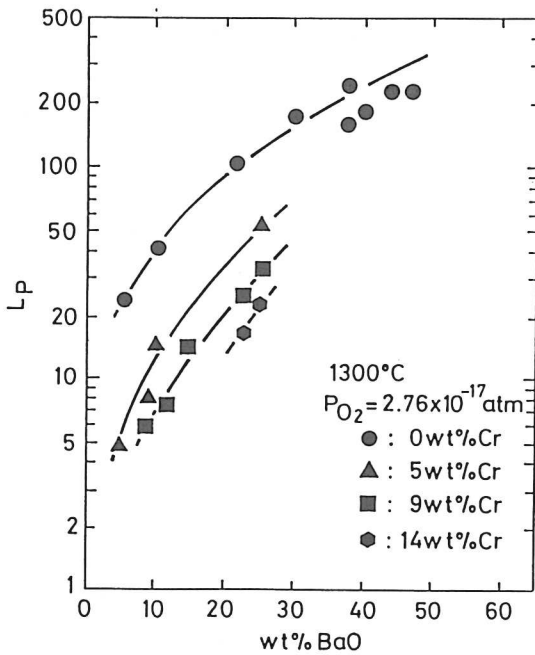


Fig. 4. Phosphorus partition ratio between Fe-Cr-C<sub>satd.</sub> alloy and BaO-BaF<sub>2</sub> melts as a function of BaO content at 1573K.

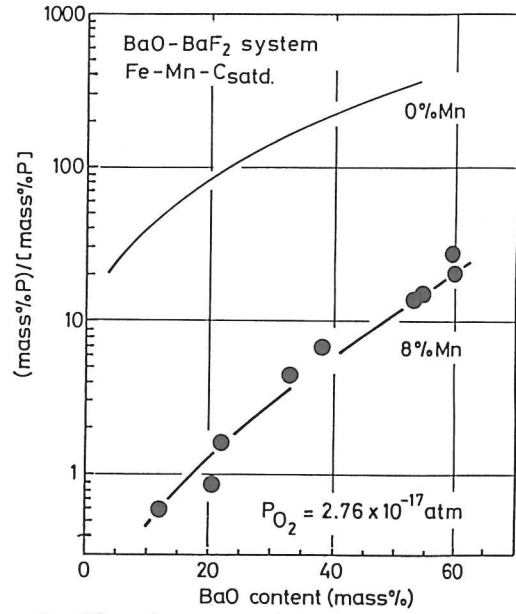


Fig. 5. Phosphorus partition ratio between Fe-8mass%Mn-C<sub>satd.</sub> alloy and BaO-BaF<sub>2</sub>-MnO melts as a function of BaO content at 1573K.

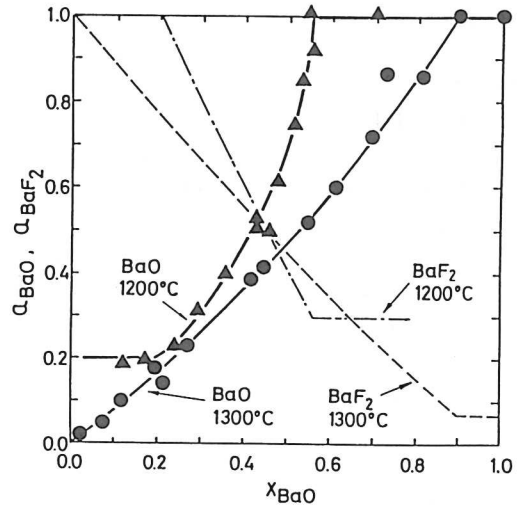


Fig. 6. The activities of BaO and BaF<sub>2</sub> for the BaO-BaF<sub>2</sub> system at 1473 and 1573K.

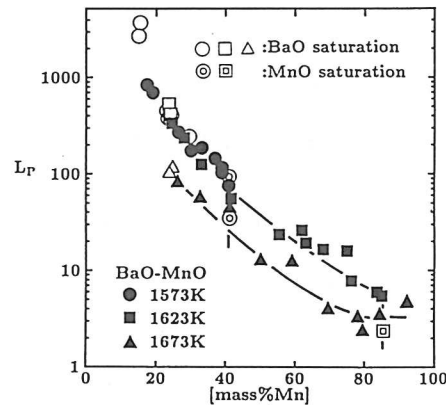


Fig. 7. Phosphorus partition ratio between Fe-Mn-C<sub>satd.</sub> alloy and BaO-MnO melts as a function of Mn content of alloy at 1573, 1623 and 1673K.

tion with CaO and  $3\text{CaO} \cdot \text{SiO}_2$  at  $1573\text{K}^5$ ). By adding BaO up to 26 mass% the distribution ratio increases by a factor of 10. However, this enhancing effect is much smaller than that of  $\text{Na}_2\text{O}$  addition. For example, 1.4 mass% of  $\text{Na}_2\text{O}$  addition is equivalent to 26 mass% BaO.

An improving effect of BaO addition to MgO or CaO saturated slags was studied by measuring distribution ratios of phosphorus between the slags and molten iron at  $1873\text{K}$ , together with the solubility of MgO or CaO. Figure 9 shows the contours of the phosphorus distribution ratio,  $L_P$ , for the MgO saturated BaO-SiO<sub>2</sub>-FeO system in which the sum of mole fractions of BaO, SiO<sub>2</sub> and FeO are taken to be unity, excluding MgO, Fe<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub><sup>6</sup>). Naturally,  $L_P$  increases with increasing  $X'_{\text{BaO}}/X'_{\text{SiO}_2}$  with constant  $X'_{\text{FeO}}$ . With constant  $X'_{\text{BaO}}/X'_{\text{SiO}_2}$ ,  $L_P$  increases with increasing  $X'_{\text{FeO}}$  and reaches a maximum and then decreases. Similar behavior is well known for the CaO-SiO<sub>2</sub>-Fe<sub>2</sub>O system.

Figure 10 shows the effect of BaO addition to the CaO saturated BaO-SiO<sub>2</sub>-Fe<sub>t</sub>O system<sup>7</sup>). The favorable effects depend on the SiO<sub>2</sub> content. They are an order of magnitude larger than those of MgO saturated slags. The same data are expressed in Fig. 11 in terms of mass% FeO for comparison with other CaO saturated slags. The present system has phosphate capacities nearly equal to those of the CaO-CaF<sub>2</sub>-SiO<sub>2</sub> system and far larger than those of the CaO<sub>satd</sub>-SiO<sub>2</sub>-Fe<sub>t</sub>O or CaO<sub>satd</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>t</sub>O system. A smaller amount of BaO than CaF<sub>2</sub> is needed to retain the same level of phosphate capacity but the relatively expensive cost of BaO should be considered before widespread use in ladle treatment of steels.

#### 4. Sulfur in BaO-BaF<sub>2</sub> and BaO-MnO slags

The sulfide capacities of two BaO bearing systems were measured by equilibrating the slags with silver in an Ar-CO-CO<sub>2</sub> mixture, where the partial pressure of CO<sub>2</sub> was controlled at a low level to maintain low BaCO<sub>3</sub> content.

Figure 12 shows their sulfide capacities vs BaO+BaCO<sub>3</sub> content at 1473 and 1573K,

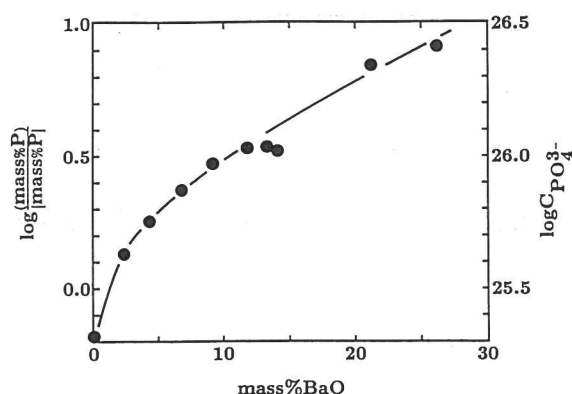


Fig. 8. Effect of BaO addition to CaO<sub>satd</sub>-CaF<sub>2</sub>-SiO<sub>2</sub> melts on the phosphorus partition ratio at  $1573\text{K}$  with oxygen partial pressure of  $2.80 \times 10^{-12}\text{Pa}$ .

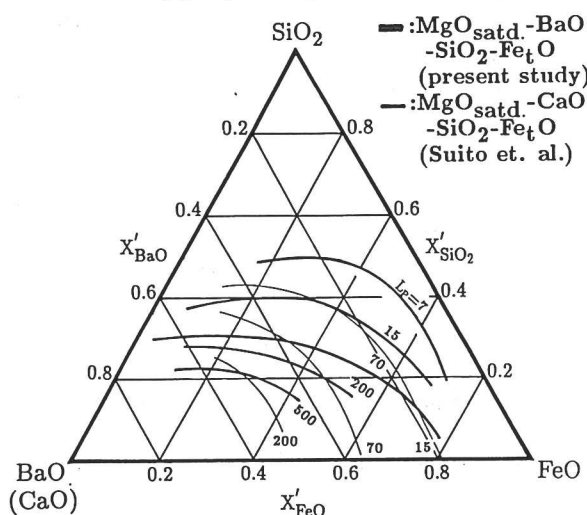


Fig. 9. Contours of the phosphorus partition ratio between MgO<sub>satd</sub>-BaO-SiO<sub>2</sub>-Fe<sub>t</sub>O slags and liquid iron at  $1873\text{K}$ .

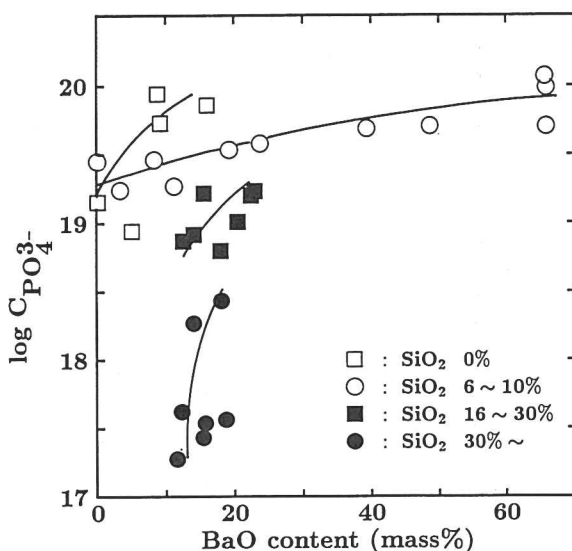


Fig. 10. Phosphate capacities of the CaO<sub>satd</sub>-BaO-SiO<sub>2</sub>-Fe<sub>t</sub>O system at  $1873\text{K}$ .

which are far larger than any slag systems investigated so far<sup>8)</sup>. The deteriorating effects of FeO, SiO<sub>2</sub>, BaCl<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub> on the sulfide capacities of the BaO-BaF<sub>2</sub> system were observed whereas the BaO-BaF<sub>2</sub> slag saturated with CaO has a slightly higher sulfide capacity than that without CaO. The solubilities of S as BaS in the slag were observed to be 1.14, 2.30, 4.48, 3.88 and 3.06 mass% for those having initially 10, 20, 40, 60 and 80 mass% BaO at 1473K.

The BaO-MnO slag is very effective for dephosphorization of the Fe-Mn alloys as described earlier and is expected to be the same for desulfurization. Its sulfide capacity at 1573K was found to be almost equal to that of the BaO-BaF<sub>2</sub> system.

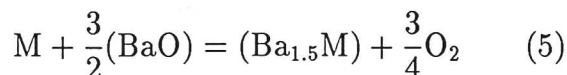
## 5. Chromium and Manganese in the BaO bearing slags

In association with Fig. 4 for phosphorus distribution between the BaO-BaF<sub>2</sub> slag and carbon saturated Fe-Cr alloys, the chromium distribution,  $L_{Cr}$ , was studied as shown in Fig. 13<sup>3)</sup>. As BaO content increases,  $L_{Cr}$  increases and the activity coefficient of CrO<sub>1.5</sub>,  $\gamma_{CrO_{1.5}}$ , decreases. This indicates that CrO<sub>1.5</sub> behaves as an acid oxide in this slag system. The loss of chromium on oxidative dephosphorization of chromium containing metals is expected to be very small.

The activity coefficient of MnO in the BaO-BaF<sub>2</sub> system was studied together with the measurement of phosphorus distribution<sup>4)</sup>. Figure 14 shows that it significantly drops as BaO content increases and is slightly lower than that of the CaO-CaF<sub>2</sub> system. It is of interest that MnO apparently behaves as an acidic oxide in this very basic melt, although it is generally thought to be a weak basic oxide.

## 6. Thermodynamic behavior of antimony and arsenic under reducing conditions

An element M of the Va group form Ba<sub>1.5</sub>M with BaO under strongly reducing conditions as expressed by Eq.(5).



In connection with the removal of these

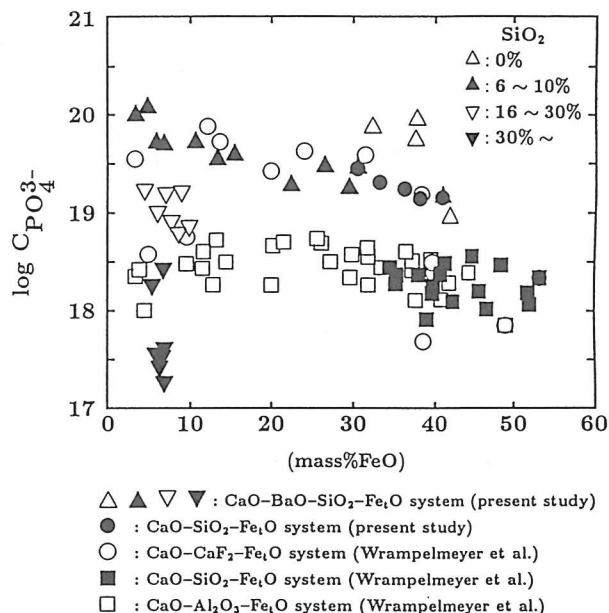


Fig. 11. Comparison of phosphate capacities among the CaO saturated systems at 1873K.

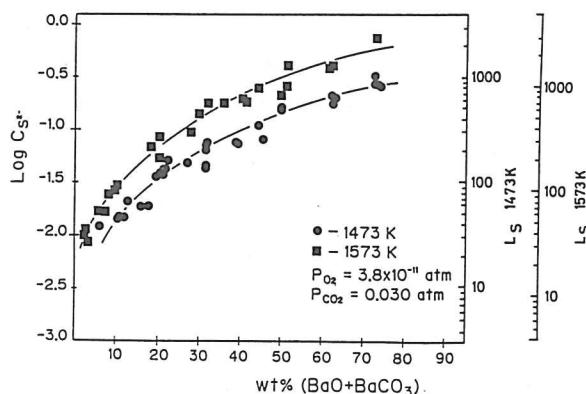


Fig. 12. Sulfide capacities of the BaO-BaF<sub>2</sub> system and sulfur partition ratio between BaO-BaF<sub>2</sub> slag and silver as a function of slag composition at 1473 and 1573K.

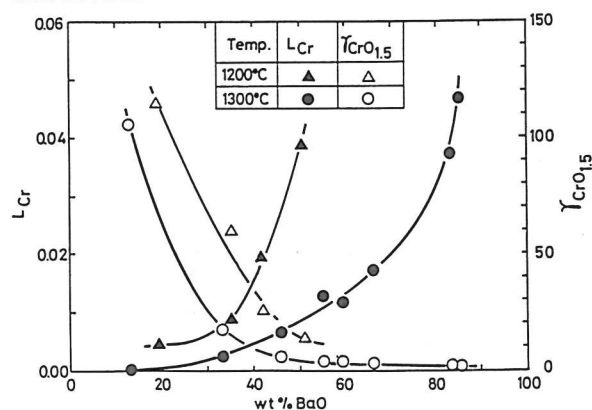


Fig. 13. Chromium partition ratio between BaO-BaF<sub>2</sub> melts and Fe-Cr-C<sub>satd.</sub> alloy and the activity coefficient of CrO<sub>1.5</sub> for the BaO-BaF<sub>2</sub> system at 1473 and 1573K.

tramp elements from steel scrap, the distribution ratios of As and Sb between the BaO-BaF<sub>2</sub> slag and silver were measured as function of the partial pressure of oxygen and the slag composition (Fig. 15)<sup>9)</sup>. The slope of the straight line in Fig. 15 representing the  $a_{\text{BaO}}$  dependence of antimony distribution ratio is 1.82, which is in reasonable agreement with 1.5, the expected value from Eq.(5). Comparison was also made between the experiment and theory for the dependence on the partial pressure of oxygen. These results confirm Eq.(5), showing that M is stabilized as Ba<sub>1.5</sub>M in this slag system. The similar behavior was also demonstrated for arsenic. Comparing with the CaO-CaF<sub>2</sub> system, the BaO-BaF<sub>2</sub> system was shown to be more effective in removing those elements from metals under reducing conditions.

## 7. Conclusions

As stated in Introduction, all experimental findings support BaO as an excellent component of the slags for removing unfavorable impurities. However, because it is relatively expensive and hazardous, its application in practice would be limited to the refining of precious metals. In this case the recycling or treatment of the slags after use must be considered.

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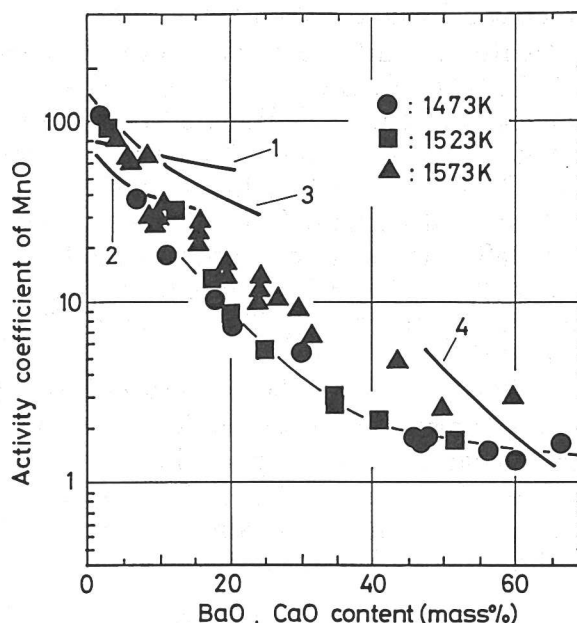


Fig. 14. Activity coefficient of MnO for the BaO-BaF<sub>2</sub> system at 1473, 1523 and 1573K compared with that for CaO bearing systems. 1: Smith and Davis, CaO-CaF<sub>2</sub>-MnO, 1773K,  $X_{\text{MnO}}=0.005$ , 2: Smith and Davis, CaO-CaF<sub>2</sub>-MnO, 1773K,  $X_{\text{MnO}}=0.24$ , 3: Inoue and Suito, CaO-CaF<sub>2</sub>, 1773K, 4: Simeonov and Sano, CaO-CaF<sub>2</sub>-16mass%SiO<sub>2</sub>, 1573K.

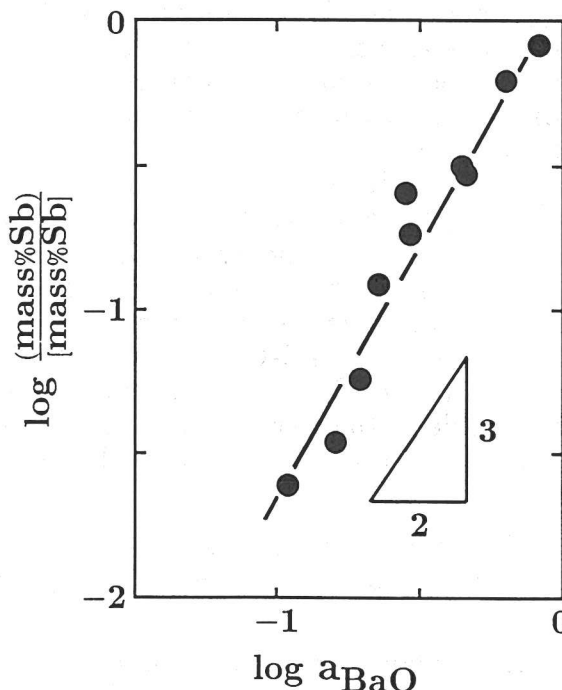


Fig. 15. Dependence of antimony partition ratio between Cu and BaO-BaF<sub>2</sub> melts on the activity of the BaO at 1573K at the oxygen partial pressure of  $2.80 \times 10^{-14}$  Pa.