THERMODYNAMIC CONSIDERATIONS IN METAL EXTRACTION

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Chemical thermodynamics can be used to ascertain the feasibility of a given chemical reaction. It permits quantitative calculation of the state of equilibrium of a system. Conversely, the concepts of chemical equilibria can be used to find out conditions for making a desired reaction feasible.

In this paper, the basic concepts are briefly reviewed and then applied to Zn-C-O, M-S-O, Ba-P-O systems to analyse the main chemical reactions encountered in the pyrometallurgical processes for zinc extraction, roasting of sulfides, and removal of phosphorus from molten metal, respectively. Finally, the zinc fuming from lead blast furnace slag is analysed by assuming chemical equilibia between the slag and the gas phases.

INTRODUCTION

In general, a process for extraction of metals has two components :

Severance : produces, through chemical reactions, two or more new phases, one of which is much richer in the valuable content than others.
Separation : involves physical separation of one phase from the others

Three types of processes are used for accomplishing severance :

Pyrometallurgical :   chemical reactions take place at high temperatures
Hydrometallurgical :   chemical reactions are carried out in an aqueous media
Electrometallurgical : involves electrochemical reactions

Advantages of pyrometallurgical processes :

1.   Option of using cheap reducing agents, (such as C, CO). As a result, the unit cost is 5-10 times lower than that of the reductants used in electrolytic processes where electric power often is the reductant.

2.   Larger throughput per unit reactor volume.

3.   Enhanced reaction rates at high temperatures

4.   Simplified separation of (molten) product phases at high temperatures

5.   Simplified recovery of precious metals (Au, Ag, Cu,) at high temperatures

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6. Ability to shift reaction equilibria by changing temperatures

7. Existence of high temperatures helps forming of metals into useful shapes / commodities

THERMODYNAMICS

Let us understand the link between the thermodynamics of a reaction and its chemistry.

The Gibbs free energy, G, of a system can be described as the energy in the system available to do work. It is one of the most useful state functions in thermodynamics as it considers only variables contained within the system, at constant temperature and pressure.

It is defined as :

$$G = H - TS \tag{1}$$

Here, T is the temperature of the system and S is the entropy, or disorder, of the system. H is the enthalpy of the system, defined as;

$$H = U + pv \tag{2}$$

Where U is the internal energy, p is the pressure and v is the volume.

To see how the free energy changes when the system is changed by a small amount, we can differentiate the above functions :

$$dG = dH - TdS - SdT \tag{3}$$

and;

$$dH = dU + pdv + vdp \tag{4}$$

From the first law,

$$dU = dq' - dw \tag{5}$$

and from the second law,

$$dS = \frac{dq'}{T} \tag{6}$$

we see that,

$$\begin{aligned} dG &= dq' - dw + pdv + vdp - TdS - SdT \\ &= -dw + pdv + vdp - SdT \\ &= vdp - SdT \end{aligned} \tag{7}$$

since work, . $dw = pdv$

The above equation shows that if the temperature and pressure are kept constant, we see that the free energy does not change. This means that the Gibbs free energy of a system is unique at each temperature and pressure.

At a constant temperature $dT = 0$ and so

$$dG = vdp \tag{8}$$

We can find G for the system by integration. To do this we need the system's equation of state, to give a relationship between v and p.

We will consider an ideal gas. For one mole of an ideal gas the equation of state is;

$$v = \frac{RT}{p} \tag{9}$$

so (8) becomes

$$dG = RT\frac{dp}{p} \tag{10}$$

Integrating :

$$G = RT\ln(p) + const. \tag{11}$$

This we can express as

$$G = G^\circ + RT\ln\left(\frac{p}{p^\circ}\right) \tag{12}$$

We define G° to be the standard free energy at the standard pressure, p°. These standard values are nothing more than lower integration constants, but using them is very useful, as we shall see. They are a consequence of the fact that one can only describe energy changes absolutely - there is no absolute energy scale, so the energy value we give to a system is arbitrary.

Chemical Reactions

The free energy change, ΔG, of a chemical reaction is the difference in free energy between the products of the reaction and the reactants. If the free energy of the products is less than the free energy of the reactants there will be a driving force for the reaction to occur.

For the reaction

$$A + B \rightarrow C$$
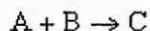
the free energy change,

$$\Delta G = G_C - G_A - G_B \tag{13}$$

$$= \Delta G^\circ + RT\ln\left(\frac{p_C}{p_A p_B}\right) \tag{14}$$

It is clear that the free energy change of a reaction is determined by the relative quantities of reactants and products.

The Equilibrium Constant

A chemical reaction will occur if the total free energy of the products is less than the total free energy of the reactants. (i.e. The free energy change for the reaction is negative.) If the system containing the reactants and products is closed (if there is no input of reactants, for example), the concentration of reactants will decrease and the concentration of products will increase as the reaction proceeds. This will alter the state of the system and therefore alter the free energy change for the reaction (see equation 14, above).

The reaction will continue if the free energy change remains negative. Hence, the system proceeds down a free energy gradient with respect to composition and this gradient provides the driving force for the reaction to proceed. The system alters the quantities of reactants and products in response to the driving force until a minimum in free energy is reached and the gradient is zero. This is a point of equilibrium.

At equilibrium the free energy change for the reaction is equal to zero:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{p_C}{p_A p_B} \right)$$
$$= 0$$

Therefore

$$\Delta G^\circ = -RT \ln \left(\frac{p_C}{p_A p_B} \right)_{equilibrium}$$
$$= -RT \ln K_p.$$

$$(15)$$

For the composition at equilibrium, the quotient is equal to K_p - the equilibrium constant for the reaction at constant pressure. We see that the equilibrium composition of the system is defined by the standard free energy change, ΔG°. Equation 15 provides a link between the thermodynamics of a reaction and its chemistry. ΔG° for a reaction is hence a very useful value to know.

The Ellingham Diagram

The Ellingham diagram is essentially a graph representing the thermodynamic driving force for a particular reaction to occur, across a range of temperatures. It is also possible to compare the relative driving force for an element for oxidation or sulphidation in an environment containing both oxygen and sulphur as reactants. These reactions generally involve the reaction of a gaseous phase (the oxidising gas) with (almost) pure condensed phases (the metal and oxidised compounds).
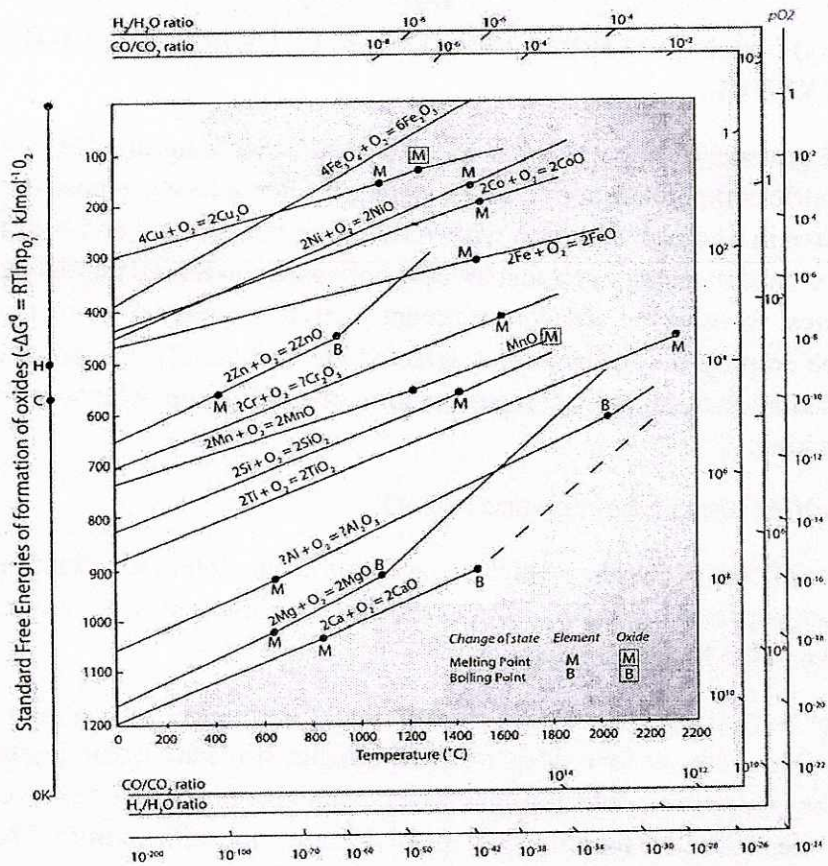
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Fig. 1 : Ellingham H. J. T., J Soc Chem Ind (London) 63 125 (1944)
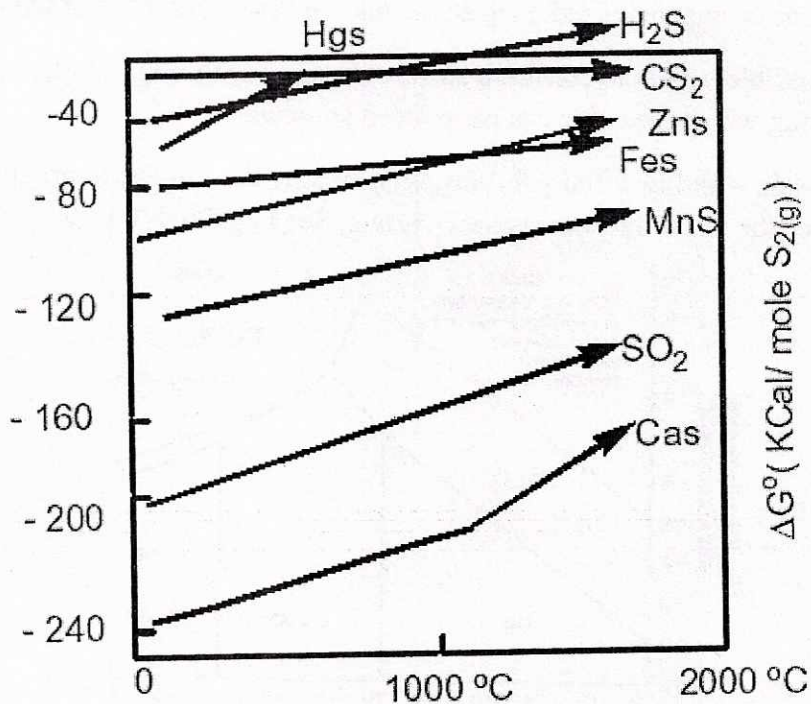

Fig. 2 : Ellingham diagram for metal sulfides

METALLURGICAL EQUILIBRIA INVOLVING PURE SOLIDS/ LIQUIDS AND GAS MIXTURES

Most chemical systems of importance to metallurgical processing involve solution phases-non-stoichiometric compounds, alloys, slags, mattes, molten salts etc. whose thermochemical properties behave in a complex fashion with variation in temperature and composition. Here we look at a few important examples that involve only pure condensed phases (solid or liquid) and gas mixtures, for which a simpler treatment (activity equals unity for pure condensed phases) may be employed. The examples selected are sufficiently complex as to illustrate methods of calculation and graphical representation of equilibrium behaviour for many other systems of this kind.

Roasting of sulfide ores and the system M-S-O

A large number of ores are oxides, which are amenable to maintain to reduction with the use of carbon. More expensive reducing agents, such as aluminum, may be necessary to reduce oxides far down in the Ellingham diagram.

The other major body of ores occurring in nature is that of sulfides. If we compare the Ellingham diagram for sulfides with one for oxides, we can immediately reach a technologically important conclusion: The inexpensive reducing agents carbon and hydrogen, which serve us well in the case of oxides, are ineffective for producing metals by reduction with sulfides. The free energies of formation of both hydrogen sulfide and carbon disulfide are insufficiently negative for hydrogen or carbon to be useful reagents in reducing sulfide directly to metal .We could, of course, use a more expensive reducing agent, e.g., but two alternative strategies are possible.

(1)   One possible way is to convert a sulfide to an oxide through oxidation in air/ oxygen, following which the oxide can be reduced to metal.

(2)   For metals with low affinity for oxygen, smelting the sulfides to produce metals can be utilized (the use of Predominance Diagram, See Fig. 3 below).
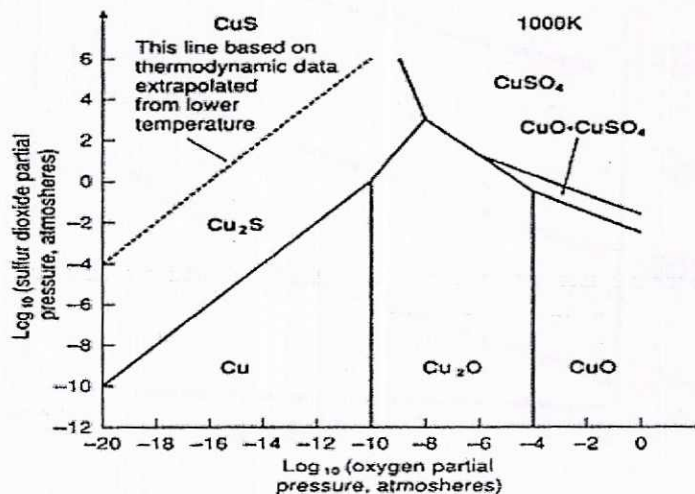

Fig. 3 : Predominance Diagram for the copper-oxygen-sulfur system

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Note that the differences between method 1 and 2 (aside from the differences in the affinity for oxygen between Pb and Cu) is that in method 2, the oxygen partial pressure must be kept low in order to produce SO_2 without forming copper oxide simultaneously.
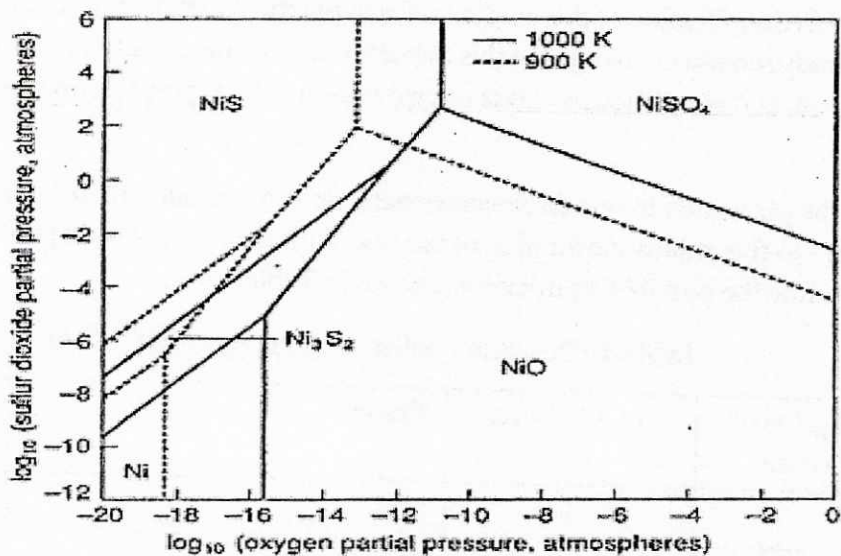

Fig.4 : Predominance Diagram for Nickel-Sulfur-Oxygen

Retort Smelting of Zinc and the System Zn-C-O

Traditional method of zinc production has been the batch reduction of zinc oxide (produced by roasting the naturally occurring zinc sulfide, sphalerite) using mixed-in coke particles in fireclay retorts.
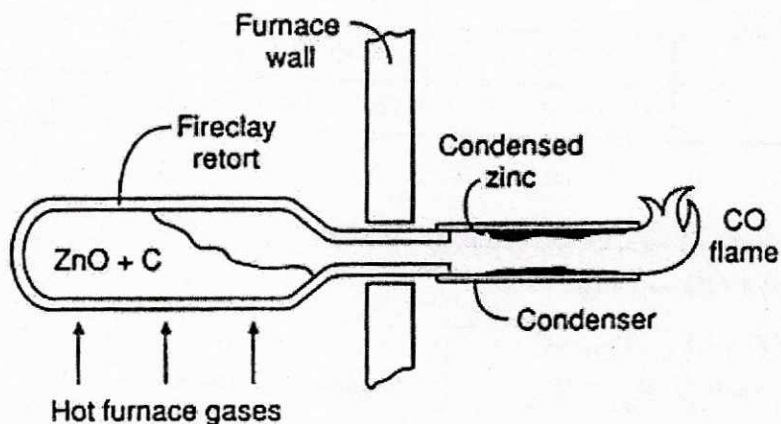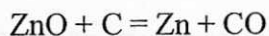

Fig. 5 : Retort furnace for the reduction of zinc oxide to zinc.

Gases issuing from the neck of the retort pass through the furnace wall into a cooler condenser where zinc vapour is condensed and solidified

The reduction reaction is :
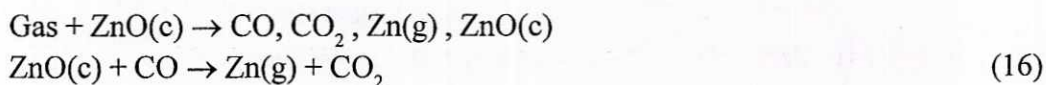
$ZnO + C = Zn + CO$

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Chemistry-of the system Zn-C-O underlies the industrial processes for retort smelting and blast furnace smelting of zinc (the Imperial Smelting Process). Thermochemical understanding of this system dates back to the study by C.G. Maier (USBM Bull 324, 1930), which is a comprehensive application of thermodynamics to practical metallurgy. The main conclusions from this study remain unchanged to this day, even though the quality of thermochemical data has improved, and simplified methods of calculation and graphical representation have been introduced.

Applying the phase rule to this three-component system, we find that the degrees of freedom, V, is equal to five minus the number of phases. With the four possible phases that can exist, we may outline the possible equilibria as shown in Table 1.

Table-1 : Possible Equilibria in the System Zn-C-O

Degrees of freedom	No. of phases	Phases	Symbol
4	1	Gas	IV
3	2	Gas + ZnO (c)	IIIA
3	2	Gas + C(c)	IIIB
3	2	Gas + Zn(l)	IIIC
2	3	Gas ZnO(c) + C(c)	IIA
2	3	Gas ZnO(c) + Zn(1)	IIB
2	3	Gas C(c) + Zn(1)	IIC
2	3	ZnO(c) + C(c) + Zn(1)	IID
1	4	Gas + ZnO(c) + C(c) + Zn(1)	I

IIIA.

$$Gas + ZnO(c) \rightarrow CO, CO_2, Zn(g), ZnO(c)$$
$$ZnO(c) + CO \rightarrow Zn(g) + CO_2 \tag{16}$$

$$\left.\begin{array}{l} K_1 = f_1(T) = P_{Zn} \cdot P_{CO2}/P_{CO} \\ R = 1.0 = P_{Zn}/(P_{CO} + 2P_{CO2}) \\ PT = P_{Zn} + P_{CO} + P_{CO2} = 1 \end{array}\right\} \text{3 equs. in 3 unknown}$$

$$\left.\begin{array}{l} P_{Zn} = 0.588 \\ P_{CO} = 0.236 \text{ for } T = \\ P_{CO2} = 0.176 \end{array}\right\} 1500 \text{ K}, P_T = 1, R = 1$$

IIIB.

$$Gas, C(c); CO, CO_2, Zn(g); C(c)$$
$$C(c) + CO_2 = 2CO \tag{17}$$

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$$K_2 = f_2(T) = P_{CO2}/P_{CO2}$$
$$R = 1.0 = P_{Zn}/(P_{CO} + 2P_{CO2})$$
$$P_T = P_{Zn} + P_{CO} + P_{CO2} = 1 \qquad P_{CO} = 0.4996$$
$$P_{CO2} = 0.0002$$

$\Rightarrow$ PZn = 0.5002   for 1500 K

Observed values for retort PZn = 0.5 , PCO = 0.49 , PCO_2 = 0.01

----------- closer to IIIB.

Dephosphorisation of ferromanganese and the system Ba-P-O

The dephosphorization reaction under oxidizing conditions using BaO based fluxes may be represented as follows :

$$\frac{3}{2} BaO(s) + P(1\% Sol'') + \frac{5}{2} MnO(l) = \frac{5}{2} Mn(l) + Ba_{3/2}PO_4(s) \qquad (18)$$
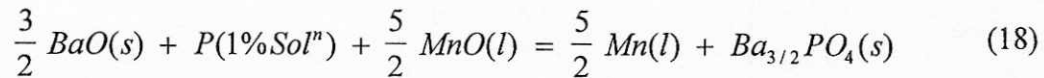
$$\Delta G^\circ = -136713 + 89.3TJ/mol \qquad (19)$$

The equilibrium constant (K) and the Henrian activity of phosphorus in the melt (h_p) for the above reaction can be expressed as :

$$K = \frac{a_{Mn(l)}^{5/2} \cdot a_{Ba_{3/2}PO_4}}{a_{BaO}^{3/2} \cdot h_P \cdot a_{MnO}^{5/2}} \qquad (20)$$

$$h_P = \frac{a_{Mn(l)}^{5/2} \cdot a_{Ba_{3/2}PO_4}}{a_{BaO}^{3/2} \cdot K \cdot a_{MnO}^{5/2}} \qquad (21)$$

Where ai is the Raoultian activity of component "i" and hP is the Henrian activity of the phosphorus dissolved in ferromanganese w .r .t.1% standard state. From the above expressions, to achieve a lower hp, the desirable conditions are :

-- Lower activity of the reaction product- $Ba_{3/2}PO_4$ in the slag (flux) phase
-- Lower activity of manganese in the Fe-Mn-C-P alloy
-- High activity of BaO in the slag phase
-- High activity of MnO in the slag phase

-- High value of K, which is possible at lower temperature since reactions are exothermic in nature.

The calculated value of K for equation (20) is 0.402 at 1673 K and 0.141 at 1873 K.

The role of different parameters as discussed above on the activity of phosphorus was examined with the help of predominance diagrams shown below in order to select most appropriate experimental conditions for selective removal of phosphorus.

The predominance area diagrams for Ba-P-O systems were constructed for standard states and non-standard states as shown in Fig.6 & Fig 7. The equilibrium Mn-MnO line that

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corresponds to the maximum equilibrium oxygen partial pressure for dephosphorization without loss of manganese has been superimposed on it. This figure identify the range of partial pressure of oxygen as shown by hatched area in (Fig 6 & Fig 7), under which oxidative dephosphorization is possible without loss of manganese.

As shown in Fig 5, the desirable conditions for dephosphorization are :

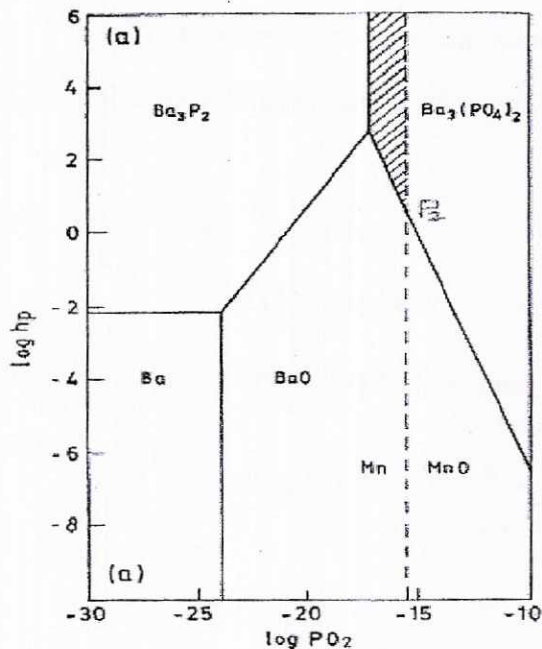aMn=0.3, (2) aMnO=0.5, (3) aBa$_3$(PO$_4$)$_2$=0.1, (4) Oxygen potential = 3.0X10-17 atm.

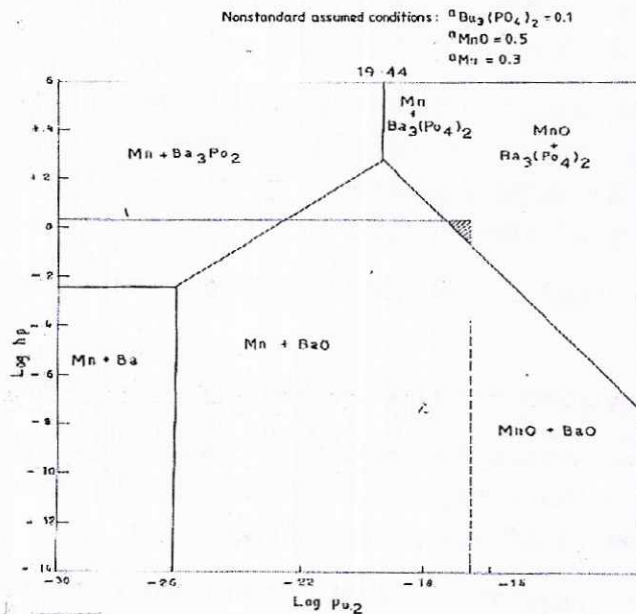Fig.6 : Predominance Area Diagram at 1673K for Ba-P-O System

Fig.7 : Predominance Area Diagram for Ba-P-O and Mn-O system at 1573K

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Activity of Mn (aMn): High carbon helps in reducing the activity of carbon. It was found by Healy that aMn=0.3 is achievable for carbon saturated iron.
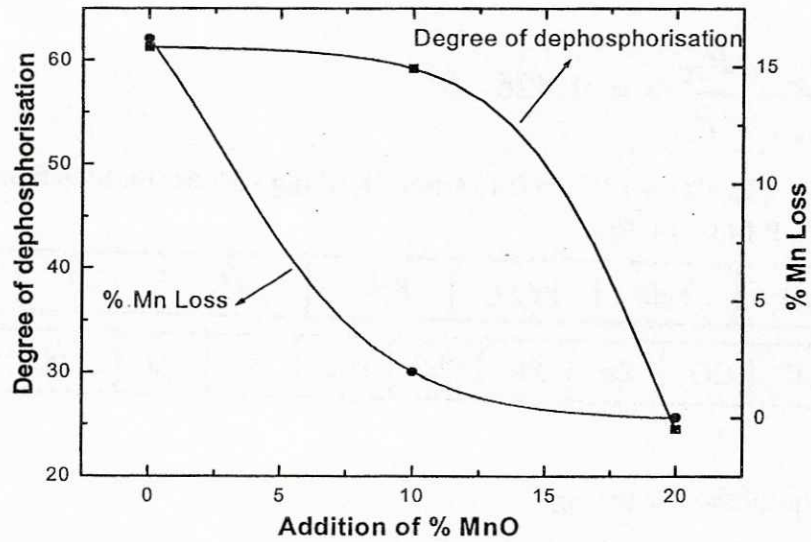

Fig. 8 : Variation of degree of dephosphorization & %Mn loss with Addition of % MnO in flux

Zinc Fuming from Lead Blast Furnace Slag and the system gas -slag system

This industrial process invloves reductive treatment of molten slag in a rectangular water-jacketed furnace. For Asarco's El-Paso Plant, the operating parameters are:

Slag treated : 120,000 tons slag/yr; Zn fumed:16000 t/yr.
Batch Process : 45 t slag, approx 120 min cycle.
Coal injection : 170 lbs/min, pulverized to 80% -200 mesh
Primary air : 5000 scfm
Secondary air : 11,000 scfm

Off gases combusted with leakage (tertiary) air above the bath.
ZnO fume captured in a baghouse; heat recovered in a steamboiler.
Tertiary air : 4200 cfm (est).

Slag analysis	Zn	Pb	S	SiO$_2$	CaO	MnO	MgO	FeO(tot)
Initial	13	1.4	1.7	23	18	1.6	1.6	31
Final	<2	-						

Coal analysis : 72% FC, 19% VM, 9.2% ash, (2.3% moisture)

Ultimate(dry) : 79.9%C, 4.3%, H, 1.7%N, 4.2% O, 0.9% S, 9.2% ash

Operating Temperature : 1150 -1300°C.

$(ZnO)\ (c) + CO = Zn(g) + CO_2,\ H = 192,500\ J$
At $1220^\circ C$,

$$K = \frac{P_{Zn}}{a_{ZnO}} \cdot \frac{P_{CO_2}}{P_{co}} = 0.426$$

At 15 mole % ZnO, $CO_2/CO = 1$, $PZn = 0.118$ atm. {Kellogg's Model for Slag Fuming (TMS-AIME, Sept, 1967, P 1439-1449)}

Slag		ZnO		FeO		Fe_3O_4		PbO		CaO		CaS		Other	
Gas	N_2	CO_2	CO_2	Zn	Pb	PbS	H_2S	S_2	SO_2	COS	H_2	H_2O			

Assumption :

Reduced gas in equilibrium with slag

Gas - slag interface capable of high mass -transfer rates.

Implies fastest possible rate of zinc fuming for a given input of fuel and air.

Fuming rate determined by the gas and fuel throughout rates and by the equilibrium constants of the reactions.

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