On the Estimation of Commercial Values of Iron Ores

On the Estimation of Commercial Values of Iron Ores[*]

Tomimatu ISIHARA

The Research Institute of Mineral Dressing and Metallurgy

Synopsis

The commercial values of iron ores as the raw· materials for the production of low phosphorus pig iron by means of electric furnaces were estimated by the present writer from the metallurgical point of view. According to the custom in this country, hematite ore composed of 50% Fe, $A\%$ SiO_2, $B\%$ Al_2O_3, $a\%$ CaO, $b\%$ MgO, <0.3% S, and 0.02% P is taken as a standard iron ore. When the composition of commercial ore differs from that of the standard one, the smelters usually revise the price of commercial ore by their customary rules. To make this revision of price more scientific, the present investigation was undertaken. To make the matter simpler, some assumptions were made as follows :

(1) The ore is assumed to be smelted alone without mixing with any other ore, except manganesian ore.

(2) The basicity of slag $\{\%(CaO + MgO)/\%SiO_2\}$ is kept at 1.3.

(3) The content of FeO in slag is limited to 3.0.

(4) 4% SiO_2 in the ore will be reduced to Si and dissolved into the pig iron produced.

Then the commercial price of iron ores should be revised with regard to the content of iron, manganese, phosphorus and sulphur in the ores :

(1) A premiun or a reduction of

$$0.002F\{10\pm(0.33+0.018A-0.013B)\}$$
$$\pm(8.5+0.45A-0.35B)E\pm(1.41A-1.09B)D$$
$$\pm(14.63+0.78A-0.68)W\pm0.01\,(L+P+t)\pm0.05e$$

yen per ton of ore should be paid for each percent of iron on or off from 50.

(2) If the ore contains manganese, a premium of

$$0.033F_{mn}+0.002F(0.33+0.018A-0.013B)$$
$$+(1.41A-1.09B)D+(8.5+0.45A-0.35B)E$$
$$+(14.63+0.78A-0.6B)W+0.01(L+P+t)+0.05e$$

yen per ton of ore should be paid for each percent of manganese.

(3) If phosphorus content in the ore is below 0.02%, a premium of

$$0.016F(0.33+0.018A-0.013B)$$
$$+(11.28A-8.72B)D+(68.0+3.60A-2.80B)E$$
$$+(117.04+6.24A-4.8\,?)W+0.08(L+P+t)+0.40?$$

yen per ton of ore should be paid for each 0.005% below 0.02%.

(4) When the sulphur content in the ore is above 0.3%, up to 3.5% the maximum allowed, 500 yen or more per ton of ore should be deducted.

(5) If the ore is magnetite or limonite, it requires 150 or 120 kWH respectively more than hematite to produce one ton of pig iron.

Hence, the extra pay for electric power per ton of magnetite or limonite must be deducted from the price of corresponding hematite ores.

In these revision formulas, A is the silica content in percent in the ore, B the sum of CaO and MgO content in percent in the ore, D the price of 1 ton of limestone, e the cost of one kilogram of electrode, E the price of 1 kWH of electric power, F the price of one ton of standard iron ore, F_{mn} the price of one ton of 30% manganese ore, L the labour cost per ton of pig iron produced, P the repair cost per ton of pig iron, t the interest per ton of pig iron produced, and W the cost of water granulation of slag per ton of pig iron produced.

I. Correction for treating 1 ton of standard ore

Hewitt[1] has discussed the commercial values of iron ores as materials used for the production of steel in basic open hearth furnace and Unotoro[2] has give a suggestion for price estimation of iron ores upon computing the effects of the grade of iron ores on the quantity of the produced pig iron. It may be said that the price of iron ores is decided by their iron content, if other conditions are all alike, but from a metallurgical point of view, it must be pointed out that the price of iron ores cannot be calculated merely from any one factor only, since the quantity of the ore reserve, their chemical composition and physical condition as well as the kind of the pigs to be produced exert strong effect upon the equitable determination of their commercial values.

At present, the commercial custom in controling the price of iron ores envisages at the correction of standard price by a customary amount per percent of iron content deviating from the standard, which is set at 50% of iron content. This custom leads to many cases of dissatisfaction, on either party of the transaction, so that it a desideratum for the iron metallurgy to give a scientifically sound basis of price correction applicable to ores deviating from the standard composition. The problem is of special importance in Japan, where indigenous iron resources are poor, and much of the material must be imported from external parts. In the following, the author has described his proposal of more reasonable correction indices applicable to low phosphorus pig iron produced by electric furnaces.

Iron ores in general use in foundries are hematite, magnetite and limonite. Sand iron is treated hereinunder as either fine magnetite or limonite and purple ores as hematite with high sulfur content. Among these, hematite is the best as material, while magnetite requires an additional 150 kWH[3] of electricity per ton of produced pigs due to its high conductivity and density, which interfere with the reduction process, and limonite 120 kWH more than hematite per ton of pigs, for the necessary reduction of its water content. This fact justifies a reduction of price of magnetite and limonite by the cost of 75 kWH and 60 kWH of electric power respectively from the price of hematite under similar conditions.

The following assumptions were made to simplify the concomitant conditions and expedite the calculation.

1. Ores are to be smelted unmixed by kinds, except ores containing manganese.

2. The basicity of slag is calculated as $\%(CaO+MgO)/\%SiO_2$, which is to be kept at 1.3 at the minimum.

(1) G. W. Hewitt, Blast Furnace Steel Plant, **27** (1930), 1234 ; Stahl u. Eisen, **60** (1940), 1818.

(2) S. Unotoro, Read at Yawata Iron Mfg Co.

(3) E. Haanel, Bur. Mines, U. S. A. **67** (1916), 8 ; A. J. Allmand and H. J. T. Ellingham, Applied Elec. Chem. (1924), 536.

3. The content of FeO in the slag is taken at 3.0%.

4. Coarse hematite ores of 50% iron content and having the underlisted chemical composition is taken as standard, 4% of the silica content being assumed to enter the pigs upon reduction to silicon.

Fe	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	S	P
50%	71.5%	A%	R%	a%	b%	<0.3%	<0.02%

Now, let B stand for $a+b$ and A_f for $A-4$

$$A_f + R + B = 100 - 4 - 71.5 = 24.5 ,$$

$$A_f = 24.5 - (R + B) .$$

The percentage X of free silica in A_f% to be translated into the slag by addition of flux is calculated thus:

$$X = A_f - B/1.3 = 24.5 - (R + B) - B/1.3 , \qquad \bullet$$

and the quantity of lime required for maintaining the basicity of slag at 1.3:

$$Y = \{24.5 - (R + B) - B/1.3\}1.3 = 1.3X .$$

So, if the quantity of slag generated from the ores in smelting one ton of iron ore is expressed by Z_1,

$$Z_1 = 10(1.3X + 24.5) + 10 \times 0.03(1.3X + 24.5)/0.97 ,$$

the value $10 \times 0.03(1.3X+24.5)/0.97$ in the above equation represents the quantity of FeO in the slag derived from the ore.

$$Z_1 = 13X + 245 + 0.403X + 7.595 \text{ kg} .$$

The limestone in common use contains 56% of CaO, but as it contains also 2.5% of silica, $2.5 \times 1.3 = 3.25$% of CaO does not act as flux and the available percentage of CaO is reduced to $56 - 3.25 = 52.75$%. If Y kg of lime is required for smelting one ton of iron ore, the required quantity of limestone amounts to $Y \times 100/52.75 \doteqdot 1.9Y$ kg. The slag produced by the addition of this amount of limestone, Z_2, is as follows:

$$Z_2 = 1.9Y(0.0325 + 0.025) + 1.9(0.0325 + 0.025) \times 0.03/0.97$$

$$= 0.109Y + 0.0032Y = 0.112Y = 0.149X .$$

In the next, manganese ore is added for the purpose of desulphurization and for manganese content. For economy, 60 kg of low content manganese ores of about Mn = 2.6% and $SiO_2 = 37$% composition is added per ton of produced pigs into the charge. This quantity corresponds to 30 kg of manganese ore per ton of iron ore. The quantity of slag attributable to the added manganese ore, Z_3, is calculated thus:

$$Z_3 = 30 \times 0.37 + 1.3 \times 30 \times 0.37 + 27.3(0.0325 + 0.025) + 28.66 \times 0.03/0.97$$

$$= 29.54 \text{ kg}.$$

Again, 400 kg of coke of 80% fixed carbon, 20% of ash content, with 30% of SiO_2 content in the ash, is added per ton of produced pig iron as reducing and carbonizing agent, which represents 200 kg per ton of ore. The quantity of slag originating in this addition of carbon, Z_4, is calculated thus:

$$Z_4 = 200 \times 0.2 \times 0.3 + 1.3 \times 200 \times 0.2 \times 0.3 + 12 \times 1.3(0.0325 + 0.025)/0.5275$$

$$+ 28.64 \times 0.03/0.97 = 29.54 \text{ kg}.$$

50~80 kg of electrodes are consumed per ton of produced pigs, but as the

quantity is small, the quantity of slag produced in this way may be omitted in present calculation.

Accordingly, the total quantity of slag produced in the whole process of smelting one ton of standard ore, Z, is calculated as follows:

$$Z = Z_1 + Z_2 + Z_3 + Z_4$$
$$= 13X + 245 + 0.403X + 7.594 + 0.149X + 29.54 + 29.54 = 13.55X + 301.0 \text{ kg}$$
$$= 13.55 \times 24.5 - (R+B) - B/1.3 + 301.10 = 333.20 - 13.55R - 23.95B + 301.0 \text{ kg} .$$

Thus, in limit cases, 634 kg of slag is formed in smelting one ton of iron ore, or about 1.3 t of slag per ton of produced pig iron.

II. Correction for treating 1 ton of standard ores from different mines

Even when the iron content is equal to the standard, difference in ore deposit of origin usually accompanies difference in gangue, which in turn causes a variation in the required quantity of flux to obtain slag of standard composition, with consequent change in quantity of produced slag and the iron content lost in slag formation. This fact would result in change of smelting cost, which necessitates a correction in price determination. However, as the manganese ore and carbon as reducing agent is fed with the estimated quantity of pig iron in consideration, the quantity of slag generated by these agents may be assumed as undergoing no change. Now, let the chemical composition of the ore from a different deposit be represented as follows:

Fe	FeO	SiO$_2$	Al$_2$O$_3$	CaO	MgO	S	P
50%	71.5%	$A'\%$	$R'\%$	$a'\%$	$b'\%$	<0.3%	<0.02%

$$B' = a' + b' , \qquad A_f'' = A' - 4 ,$$
$$A_f' + R' + B' = 100 - 4 - 71.5 = 24.5 ,$$
$$24.5 - (R' + B') - B'/1.3 = X' .$$

In this case, the quantity of limestone Y' required per ton of ore for forming slag from X' units of free silica will be

$$Y' = 10 \times 1.3 \{24.5 - (R' + B') - B'/1.3\}/52.75 \text{ kg} ,$$
$$Y = 10 \times 1.3 \{24.5 - (R + B) - B/1.3\}/52.75 ,$$
$$Y - Y' = 10 \times 1.3 \{(R' - R) + (B' - B) + (B' - B)/1.3\}/52.75$$
$$= 0.25 \{(R' - R) + (B' - B) + (B' - B)/1.3\}$$
$$= 0.25 \{(R' - R) + (B' - B)\} + 0.19(B' - B)$$
$$= 0.25(R' - R) + 0.44(B' - B) = 10 \times 1.3(X - X') ,$$

and the iron content lost in $Y - Y'$ of slag will be

$$(\text{FeO}) = \{0.25(R' - R) + 0.44(B' - B)\}0.03/0.97$$
$$= 0.0075(R' - R) + 0.0132(B' - B) .$$

The difference in the quantity of slag formed by addition of limestone is calculated as follows:

$$(0.0325 + 0.025)Y' = 0.0575Y' ,$$
$$(0.0325 + 0.025) Y = 0.0575Y ,$$
$$0.0575(Y - Y') = 0.0575 \times 1.3(X - X')$$

$$= 0.0575 \times \{0.25(R'-R) + 0.44(B'-B)\}$$
$$= 0.014(R'-R) + 0.0253(B'-B) ,$$

and the loss in iron content as follows:

$$(FeO)' = \{0.014(R'-R) + 0.025(B'-B)\}0.03/0.97$$
$$= 0.00042(R'-R) + 0.00075(B'-B) .$$

Thus the difference from the results of calculation in 1 above is

$$(Y-Y') + 0.0075(R'-R) + 0.0132(B'-B)$$
$$+ 0.014(R'-R) + 0.0253(B'-B) + 0.00042(R'-R)$$
$$+ 0.00075(B'-B) = 0.265(R'-R) + 0.479(B'-B) ,$$

in which, the values of $(R'-R)$ and $(B'-B)$ are small and the correction may be omitted as well, but in very rare cases, necessity of such correction may possibly arise.

III. Correction due to change of iron content by 1%

One of the major aims of this report is to show how to correct the price of iron ores per one percent of increase or decrease in iron content of the ores. As ores from the same ore deposit may be assumed to contain gangues of similar composition, even in cases of different iron content, a change in iron content will accompany a corresponding change in the total quantity of gangue but the other conditions will remain the same. So, it may be assumed that the mutual ratio of SiO_2, Al_2O_3, CaO and MgO is not changed, the absolute quantity thereof only being subject to change.

The equivalent of 1% of iron content is 1.42% in FeO. Thus, a change of 1% in iron content means an inverse change of 1.42% in the quantity of gangue. That is,

$$\pm(SiO_2 + Al_2O_3 + CaO + MgO) = \pm 1.42 .$$

The above quantity of gangue, apportioned to the respective components as based on the calculations above, will be

$$SiO_2 = 1.42A/24.5 = 0.058A\% ,$$
$$Al_2O_3 = 1.42R/24.5 = 0.058R\% ,$$
$$CaO + MgO = 1.42B/24.5 = 0.058B\% ,$$

in which, the content of free silca is

$$0.058A - 0.058B/1.3 = 0.058(A - 0.77B)\% ,$$

and the quantity of limestone required to turn this quantity of free silica into slag is, per ton of ore,

$$10 \times 0.058 \times 1.3(A - 0.77B)/0.5275 = 1.41A - 1.0B \text{ kg} .$$

The cost therefor will be, when 1 kg of limestone costs ¥D,

$$(1.41A - 1.0B)D¥ . \tag{1}$$

The difference in the quantity of slag caused by a difference of 1% in iron content will be, per ton of ore,

$$10 \times 1.42 + 10 \times 0.058 \times 1.3(A - 0.77B) + \{1.42 + 0.754(A - 0.77B)\}0.031$$
$$= 14.63 + 0.78A - 0.6B \text{ kg} ,$$

in which equation, the term $\{14.2 + 0.754(A - 0.77B)\}$ 0.031 represents the quantity

of FeO entering the slag and lost. This quantity of FeO contains iron as follows:

$$\{14.2 + 0.754(A - 0.77B)\}0.031 \times 0.77 = 0.33 + 0.018A - 0.013B \text{ kg}.$$

The price of lost iron will be as follows, when the price of standard slag is taken at ¥F:

$$F(0.33 + 0.018A + 0.013B)/50 + 10¥. \qquad (2)$$

As the calories required for heating 1 kg of slag to fusion, including the decomposition and heating of limestone, stand at 500 KCal, the change in electric power consumed for the heating and fusion of slag corresponding to a change of 1% in iron content will be

$$(14.63 + 0.78A - 0.6B) \times 500 \times 4.19/3{,}600 = 8.49 + 0.45A - 0.35B \text{ kWH},$$

which, taking the price of power at ¥E per kWH, amounts to

$$(8.5 + 0.45A - 0.35B)E. \qquad (3)$$

As 50 kg of electrodes is consumed per ton of produced pig iron, the change in cost of electrodes occasioned by a change of 1% in iron content will be, per ton of ore, when the price of electrodes is ¥e per kg,

$$50e/50 \times 2 = e/2. \qquad (4)$$

Now, if the labor cost per ton of produced pig iron amounts to ¥L, the difference in labor cost caused by a difference of 1% in iron content will be, per ton of ore,

$$L/50 \times 2 = 0.01L¥. \qquad (5)$$

Taking the cost of water granulation of slag at ¥W per ton of produced pig iron, the change in cost of water granulation caused by change of 1% in iron content will be, per ton of ore,

$$(14.63 + 0.78A - 0.6B)W¥. \qquad (6)$$

Similarly, the change in maintenance and repair cost will be (P=maint. and repair cost per ton of pig iron from standard ore)

$$P/50 \times 2 = 0.01P¥, \qquad (7)$$

and the change in profit, (t=profit per ton of pig iron from standard ore)

$$t/50 \times 2 = 0.01t¥. \qquad (8)$$

Now the price of standard iron ore being ¥F per ton, the price of 1% of iron in it will be,

$$F/50 = 0.02F¥. \qquad (9)$$

Consequently, the price of iron ores should be subject to the following corrections per ton, per percent of change in iron content:

$$(9) \pm (1) \pm (2) \pm (3) \pm (4) \pm (5) \pm (6) \pm (7) \pm (8)$$

$$= 0.02F \pm (1.41A - 1.09B)D \pm (8.5 + 0.45A - 0.35B)E$$

$$\pm (0.33 + 0.18A - 0.93B) \times 0.002F \pm (14.63 + 0.78A - 0.6B)W$$

$$\pm 0.05e \pm 0.01L \pm 0.01P \pm 0.01t$$

$$= 0.002F\{10 \pm (0.33 + 0.018A - 0.013B)\} \pm (1.41A - 1.09B)D$$

$$\pm (8.5 + 0.45A - 0.35B)E \pm (14.63 + 0.78A - 0.6B)W$$

$$\pm 0.01(L + P + t) \pm 0.05 e ¥,$$

in which plus is applicable when the iron content is larger, and minus when

the iron content is smaller, than 50%.

IV. When the ores contain manganese

Manganese ores are added in smelting iron ores for the purpose of desulfurization and of obtaining the specified manganese content. The manganese ores used for these purposes are usually of the lowest permissible grade, to minimize the production cost of the pig iron. 60 kg of 26% manganese ores, containing 37% of SiO_2 is used per ton of produced pig iron, which amounts to 30 kg per ton of ore or only 3%. The atomic weight of iron and manganese being closely approximate, the error in calculation is almost in the allowable limit if the atomic weight of the two elements are treated as equivalent. Thus the above corrections due to change in percentage of iron content may be applied with the mere substitution of the price of manganese for the price of iron. When the price of 30% manganese ore per ton is taken at $¥F_{mn}$, the price of 1% of manganese in this ore will be

$$F_{mn}/30 = 0.033F_{mn} ¥ .$$

Accordingly, the following corrections will be required per 1% change in manganese content.

$$0.0033F_{mn} + (0.33 + 0.018A - 0.013B) \, 0.002F$$
$$+ (1.41A - 1.09B)D + (8.5 + 0.45A - 0.35B)E$$
$$+ (14.63 + 0.78A - 0.6B)W + 0.01 \, (L + P + t) + 0.05e \, ¥ .$$

V. When the phosphorus content is lower than 0.02%

The phosphorus content accompanying the flux, carboneous material and manganese ore used in smelting are assumed to enter into the slag in entirety, and also the phosphorus in the iron ore in part, in the form of $(CaO)_3P_2O_5$, the remainder of the latter being left in the produced pig iron in the form of Fe_3P. The dephosphorization reaction is represented as follows:

$$5(FeO) + 2[Fe_3P] + 3(CaO) = ((CaO)_3P_2O_5) + 11[Fe] ,$$
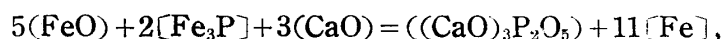
[ ] indicates the concentration in the molten iron and ( ) that in the slag. As [Fe] is nearly unit and constant, the equilibrium constant K_p in this case is calculated as

$$K_p = (FeO)^5(CaO)^3[\Sigma P]^2/((CaO)_3P_2O_5) ,$$

or

$$K'_p = (FeO)^5(CaO)^3[\Sigma P]/(P_2O_5) .$$

Schenck[4] gave the following experimental formula for this K'_p:

$$\log K_p' = -\frac{93,430}{T} + 53.747 .$$

This formula is cited in many books, but though it holds approximately at the temperature of 1,500°C, the $[\Sigma P]$ tends to rise sharply with higher temperature so that it soon exceeds the total quantity of the charged phosphorus by far. In consideration of such inadmissible results, the author proposes an

---

(4) H. Schenck, Phy. Chemie Eisenhüttenproz. I (1932), 261.

amendment as follows, based on the actual results of low phosphorus pig iron production in electric furnaces:

$$\log K'_p = -27{,}610/T + 18.633 \,.$$

By application of this formula, when one of the terms $[P]$ or (P_2O_5) is known, the other may be readily calculated. However, the (CaO) and (FeO) in the dephosphorizing reaction being free compounds, the concentration of the former may be calculated from the chemical analysis values according to the following equation:

$$(\textstyle\sum CaO) = (CaO) + (CaO)(SiO_2)/2D_{CaO \cdot SiO_2} + (CaO)_{P_2O_5} + (CaO)_{Al_2O_3}$$
$$= (CaO) + (CaO)(SiO_2)/2D_{CaO \cdot SiO_2} + 1.2P_2O_5 + 0.83Al_2O_3 \,.$$

$D_{CaO \cdot SiO_2}$ in the above equation stands for the equilibrium constant of thermal dissociation of $CaO \cdot SiO_2$, which, according to Schenck,[5] is computed as follows:

$$\log D_{CaO \cdot SiO_2} = \log (CaO)(SiO_2)/CaO \cdot SiO_2 = -\frac{3{,}186}{T} + 2.61 \,.$$

The concetration of free FeO is given by the following experimental formula:

$$(\textstyle\sum FeO) = (FeO) + (FeO)_{SiO_2}$$
$$= (FeO) + (FeO)^2(SiO_2)/3D_{(FeO)^2 \cdot SiO_2}$$

The term $D_{(FeO)^2 \cdot SiO_2}$ represents the thermal dissociation equilibrium constant of $(FeO)^2 \cdot SiO_2$, which is given by Schenck[6] as follows:

$$\log D_{(FeO)^2 \cdot SiO_2} = \log \frac{(FeO)^2(SiO_2)}{3D_{(FeO)^2 \cdot SiO_2}} = -\frac{11{,}230}{T} + 7.76 \,.$$

The values of $[P]$ or $(\textstyle\sum P_2O_5)$ can be obtained by measuring the concentration of CaO or FeO in the slag from standard ore and substituting it in the equation of $\log K_p'$ given above. By a slag of the basicity taken as standard in this calculation, the values of 0.022% and 0.037% were given for $[P]$ and (P_2O_5) respectively, under the working temperature of 1,500°C.

Now, let slag ratio (sr) stand for the ratio of the quantity of the slag to that of the produced pig iron, and the term dephosphorizing ratio (dr) indicate the ratio of the percentage of phosphorus in the slag to that of phosphorus in the produced pig iron, and the total dephosphorization stands under the following relation:

$$\mathrm{sr} \times \mathrm{dr} = \mathrm{sr} \times \frac{(\textstyle\sum P)}{[\textstyle\sum P]} \,.$$

If the basicity and the FeO content of the slag is kept constant and the operation completed under a fixed temperature, the value of dephosphorizing ratio, or $(\textstyle\sum P)/[\textstyle\sum P]$ remains constant, so that the dephosphorization depends on the slag ratio.

Suppose the content of phosphorus in the ore decreased by 0.005%, the total decrease per ton of ore becomes $1{,}000 \times 0.00005 = 0.05$ kg. Under a constant temperature and a constant dephosphorization ratio, the slag ratio must be so adjusted that the phosphorus content in the produced pig iron is maintained

(5) H. Schenck, Ibid. II (1934), 29.
(6) H. Schenck, Ibid. II (1934), 25.

at 0.022%. As 0.037% of $(\sum P_2O_5)$ is equivalent to 0.0244% of $(\sum P)$, the quantity of slag may be decreased by $0.05 \div 0.000244 = 204$ kg, that is the slag ratio may be reduced by 0.204 to assure production of low phosphorus pig iron. As 204/28 is about 8, this decrease in phosphorus content is similar to an increase of 8% of iron content in its effect, so that the price of the ore should be adjusted as follows per 0.005% of reduction of phosphorus content:

$$0.016F\,(0.33 \times 0.018A - 0.013B) + (11.28A + 8.72B)D + (68.0 + 3.60A - 2.8B)E$$
$$+ (117.04 + 6.24A - 4.8B)\,W + 0.08\,(L + P + t\,) + 0.40\,e\,¥\,.$$

This is of course only of mathematical interest, as it is almost impossible to adapt the slag ratio to a desired value in practice, when the chemical composition of the ore and its basicity is fixed, and cheap, phosphorous carbon materials used to balance the low phosphorus content. The cases of treating low phosphorus ores mixed with ores of higher phosphorus content are not considered in this peport.

VI. When the sulfur content in ores stand between 0.35% and 3.5%

It is well known fact that a part of the total sulfur content in the charge volatilizes before the melting zone is reached and removed as sulfurous acid gas in the vicinity of the furnace top. The desulfurization proper is effected by the transfer of FeS into the slag, where it becomes stabilized by reacting with the free CaO and MnO therein into CaS and MnS, thus:

$$[FeS] + (CaO) \rightleftarrows (FeO) + (CaS)\,,$$
$$[FeS] + (MnO) \rightleftarrows (FeO) + (MnS)\,.$$
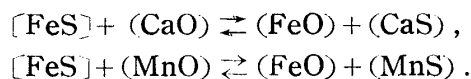
This reaction has been studied by many investigators, reports by Chipman,[7] Rivet,[8] Matoba and Unotoro[9] and Sano[10] deserving special mention. Schenck[11] has given the following formula for the desulfurizing reaction of CaO:

$$\log K_{CaS} = \log\,(CaS)(FeO)/[FeS](CaO) = -1{,}400/T - 0.65\,,$$

and for that by manganese, $([Mn] + [FeS] \rightleftarrows [Fe] + (MnS))$

$$\log K_{MnS} = \log\,[Mn][S]/(S)_{Mn} = -3{,}840/T + 1.17\,.$$

Matoba premised $K_{Mn} = [S][Mn]$ and deduced

$$\log K_{Mn} = \log\,[S][Mn] = -970/T - 0.106\,,$$

while Sano gave the following on the same reaction:

$$\log K_{Mn} = \log\,[Mn][FeS] = -5{,}269.945/T - 3.696\,.$$

It may be that a true equilibrium is not reached in practical operation due to the impurities coexisting in pig iron, but it must be pointed out that the above formulae do not hold on actual verification, especially under high

(7) J. Grant ; J. Chipman ; J. Metals, **189** (1951), 319.
(8) J. G. Rivet, J. Iron Steel Inst. 21 (1951), 25.
(9) S. Matoba ; T. Unotoro, Tetsu to Hagane (in Japanese), **33** (1944), 65.
(10) K. Sano, Denkiseiko (in Japanese), **22** (1951), 80.
(11) H. Schenck, Phy. Chemie Eisenhüttenproz. **II** (1934), 167.

temperatures. The following slight variation of Matoba's formula gives somewhat better results:

$$\log K_{\mathrm{Mn}} = -970/T + 0.90.$$

Upon combining the two formulae of desulfurization reaction above, we get:

$$(\mathrm{CaS}) = [\mathrm{FeS}]K_{\mathrm{CaS}}/(\mathrm{FeO}) = (\mathrm{CaO})K_{\mathrm{Mn}}K_{\mathrm{CaS}}/(\mathrm{FeO})[\mathrm{Mn}].$$

A computation according to this formula leads to a value of 0.38% (S) at 1,500°C, when the slag is kept at the standard basicity and [S] at 0.02%, which value well agrees with the results of actual operation.

The total desulfurization depends on the following relation between the slag ratio (sr) and desulfurization ratio (dr), that is (S)/[S]:

$$\mathrm{sr} \times \mathrm{dr} = \{(\mathrm{S})/[\mathrm{S}]\} \times \mathrm{sr} .$$

The desulfurization ratio is constant when the basicity of the slag and the operating temperature are kept constant, according to the foregoing theory and formulae, so that the slag ratio must be augmented, if the sulfur content of the ore is high and the sulfur content in the produced pig iron is desired to be kept at the standard percentage. However, the same limiting conditions apply here as with phosphorus, described above, so that it is economically practicable only by ores of sulfur content not exceeding 0.3%, to process by increasing the slag ratio up to 1.4, with the standard basicity of the slag unchanged. But if the sulfur content of the ore exceeds 0.3%, it is economically sounder to proceed with the smelting, after reducing the sulfur content to within 0.3% by preliminary roasting. Thus if the ore has a sulfur content of above 0.3%, its price should be reduced by the cost of roasting. The exact cost of roasting differs from foundry to foundry according to the local conditions, but in common practice, the cost per ton of ore roughly approximates ¥500.