

2. Limit of Desulphurization of Liquid Pig Iron of Fe-C-S System with Solid Lime or Calcium Carbide

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Introduction

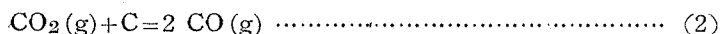
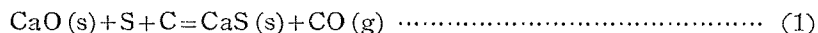
It is well known from the results of researches of many investigators¹⁾ that solid lime and calcium carbide are very effective desulphurizers for liquid pig iron. Recently, our attention was drawn to the fact that a new solid lime desulphurizing process—Kalling—Domnarfvet process²⁾—had been practiced in a blast furnace plant in Sweden for the last three years or so, and that S. D. Bamer and R. M. Hulme³⁾ obtained interesting results in the U. S. A. by desulphurizing cupola melt with solid calcium carbide fine powder on a semi-industrial scale.

The present writer⁴⁾ also studied the problem of the desulphurization of liquid pig iron with solid desulphurizers several years ago, and now intends to find the limit of the desulphurization of liquid pig iron of Fe-C-S system before he carries out his experiments on the same problem further.

Limit of Desulphurization of Liquid Pig Iron with Solid Lime

Suppose pig iron of Fe-C-S system and excess solid lime charged in a neutral crucible⁺⁾ are brought to equilibrium at about 1400°C. in a closed reaction chamber filled with nitrogen⁺⁺⁾ and carbon monoxide.

Principal reactions⁺⁺⁺⁾, which are expected to occur in the chamber, are assumed to be as follows:



Since the solubility of solid lime and the solid desulphurization product calcium sulphide in liquid iron and their mutual solubility are very low⁵⁾, the number of the degree of freedom of the equilibrium system should be 4,

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+) It means that the crucible is made of materials which are perfectly independent of the reactions in the reaction chamber.

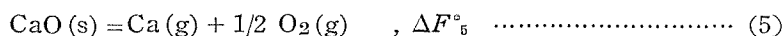
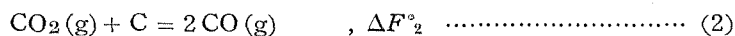
++) Nitrogen is assumed not to combine with other materials in the reaction chamber.

+++) Reaction (30) is ignored in this case.

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because in the present equilibrium system the number of phases is 4 and that of components, defined in the phase rule, is 6. Accordingly, we know that when temperature, total pressure^{+) and partial pressure of carbon monoxide are given, there exists a definite relation between the carbon content and the sulphur content of pig iron in a state of equilibrium.}

Now, when solid lime and calcium sulphide are assumed not to dissolve entirely into liquid pig iron and also to be entirely insoluble each toward the other, the change in standard free energy of the reaction (1), ΔF°_1 , can be determined by the algebraic addition of the change in standard free energy of the following reactions, $\Delta F^\circ_2 \sim \Delta F^\circ_6$:



Since $\Delta F^\circ_2 \sim \Delta F^\circ_6$ are known to be as follows:

$$\Delta F^\circ_2 = 29,550 - 28.24T \dots\dots\dots (7)^{6)}$$

$$\Delta F^\circ_3 = -66,560 + 20.15T \dots\dots\dots (8)^{7)}$$

$$\Delta F^\circ_4 = 31,520 - 5.27T \dots\dots\dots (9)^{8)}$$

$$\Delta F^\circ_5 = 192,000 - 49.10T \dots\dots\dots (10)^{9)}$$

$$\Delta F^\circ_6 = -169,600 + 47.40T \dots\dots\dots (11)^{10)}$$

we have

$$\Delta F^\circ_1 = 16,910 - 15.06T \dots\dots\dots (12)$$

from which it follows that:

$$\log K_1 = \log \frac{p_{\text{CO}}}{a_c a_s} = -\frac{3,696}{T} + 3.292 \dots\dots\dots (13)$$

where K_1 is the equilibrium constant of the reaction (1),

a_c the activity of carbon in pig iron, the product of the activity coefficient of carbon f_c and the weight pct of carbon [C%], and

a_s the activity of sulphur in pig iron, the product of the activity coefficient of sulphur f_s and the weight pct of sulphur [S%].

The accurate values of f_c have not been determined yet by direct measurement. J. Chipman¹¹⁾, however, found the relation between [C%] and f_c for iron of Fe-C system at 1540°C. by calculating from the value of the equilibrium constant of the reaction (2) and the observed equilibrium gas composition. According to K. Sano¹²⁾, the relation above mentioned is represented by the following equation:

$$f_c = 1 + 0.264 [\text{C}\%] - 0.046 [\text{C}\%]^2 + 0.042 [\text{C}\%]^3 \dots\dots\dots (14)$$

+) It is approximately equal to $p_{\text{N}_2} + p_{\text{CO}}$ and quantitatively almost independent of the equilibrium of the present system.

Though his results mean that f_c is independent of temperature, and not very accurate, they are adopted in the following calculation, since better data are not available at the present time.

Regarding f_s , we can find the accurate values in the research of J. P. Morris and R. C. Buehl⁽³⁾. The relation between $[C\%]$ and f_s determined at 1600°C. by them for pig iron of Fe-C-S system having a very low sulphur content, can be represented by the following equation:

$$f_s = 1 + 0.3875 [C\%] - 0.0750 [C\%]^2 + 0.0375 [C\%]^3 \quad \dots\dots\dots (15)$$

Since the results of their investigation show that the influence of temperature on f_s is very small, f_s as well as f_c is here assumed to be independent of temperature.

Then, combining Eqs. 13, 14 and 15, we have

$$\begin{aligned} \log \frac{[S\%]}{p_{co}} = & \left(\frac{3,696}{T} - 3.292 \right) - \left[\log \{1 + 0.264[C\%] - 0.046[C\%]^2 \right. \\ & + 0.042[C\%]^3 \} + \log \{1 + 0.3875[C\%] - 0.0750[C\%]^2 + 0.0375[C\%]^3 \} \\ & \left. + \log [C\%] \right] \quad \dots\dots\dots (16) \end{aligned}$$

Moreover, according to J. Chipman, R. M. Alfred and L. W. Gott⁽⁴⁾, the relation between temperature and the solubility of carbon in pure iron $[Cs\%]$ in a temperature range from about 1100°C. to about 2000°C. is represented as follows:

$$[Cs\%] = 0.6466 + 2.54 \times 10^{-3} T \quad \dots\dots\dots (17)$$

Accordingly, we can determine the relation among temperature, $[C\%]$ or $[Cs\%]$, and $[S\%]$ in pig iron in equilibrium at arbitrary p_{co} (atm) from Eqs. 16 and 17. The results of calculation are given in Table 1 and shown in Fig. 1.

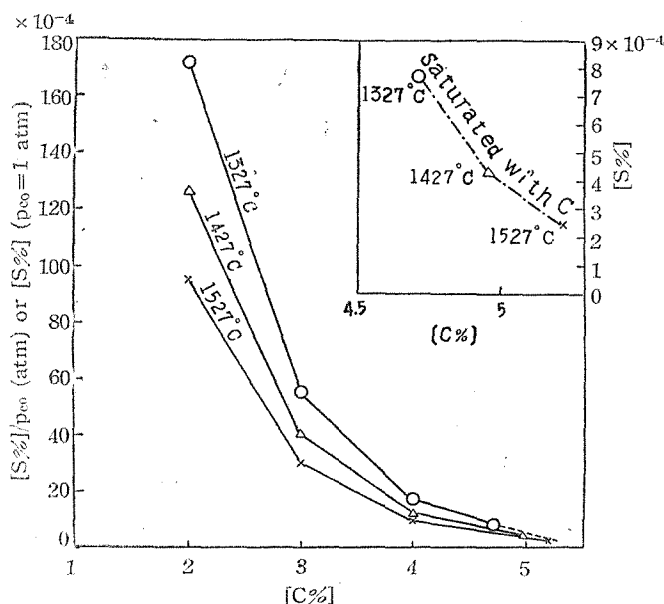


Fig. 1. Limit of desulphurization of pig iron with solid lime.

Limit of Desulphurization of Liquid Pig Iron

Table 1. Results of Calculation from Eqs. 16 and 17.

Temperature (T)		1600 (1327°C.)	1700 (1427°C.)	1800 (1527°C.)
$\frac{[S\%]}{p_{co} \text{ (atm)}}$	{	2	172.3×10^{-4}	125.0×10^{-4}
		3	55.4 "	40.5 "
		4	17.6 "	12.9 "
		4.71 ^{a)}	7.8 "	—
		4.96 ^{b)}	—	4.3 "
		5.22 ^{c)}	—	—
				2.5 "

a)b)c) Maximum solubility of carbon in pure iron in weight pct at 1327°C., 1427°C. and 1527°C. respectively.

From these results the following facts are knowable:

(1) When solid lime exists in excess, the limit of the desulphurization of pig iron is independent of the amount of sulphur contained in iron before it is desulphurized.

(2) The limit of the desulphurization of pig iron with solid lime decreases as [C%] becomes higher when p_{co} and temperature are given. This tendency of decrease is shown by a curve similar to a hyperbola as expected from Eq. 13.

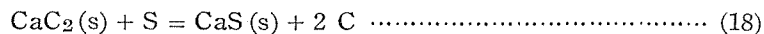
(3) The limit of the desulphurization of pig iron with solid lime decreases as temperature rises when p_{co} and [C%] are given.

(4) The limit of the desulphurization of pig iron with solid lime is in direct proportion to p_{co} when [C%] and temperature are given. Generally speaking, it is very low when p_{co} is less than one atmospheric pressure.

Limit of Desulphurization of Liquid Pig Iron with Solid Calcium Carbide

Suppose pig iron of Fe-C-S system and excess solid calcium carbide⁺⁾ charged in a neutral crucible are brought to equilibrium at about 1400°C. in a closed reaction chamber filled with nitrogen and carbon monoxide.

Now assume that, firstly, pig iron is desulphurized with solid calcium carbide after the following reaction:



and the other principal reaction in the chamber is the reaction (2)⁺⁺⁾, secondly, the solubility of calcium carbide and calcium sulphide in iron is very low, and thirdly, the mutual solubility of both materials is also very low.

According to the phase rule, the number of the degree of freedom of the present system should be 4, since the number of phases is 4 and that of

+) The melting point of calcium carbide is about 2300°C¹⁵⁾.

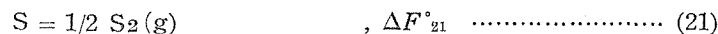
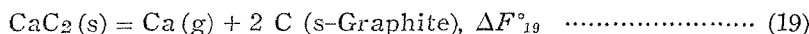
+ +) Reaction (30) is ignored in this case.

components is 6. Accordingly, the equilibrium of the system must be established when temperature, total pressure^{+) , p_{co} and either [C%] or [S%] are given. We know, moreover, that at given temperature there exists a definite practical relation between [C%] and [S%], from the following equation:}

$$K_2 = \frac{a_c^2}{a_s}$$

where K_2 is the equilibrium constant of the reaction (18).

Under the assumption that solid calcium carbide and calcium sulphide do not entirely dissolve in iron, and also that they are insoluble each toward the other, we can determine easily the change in standard free energy of the reaction (18), ΔF_{18}° , from that of the following reactions, $\Delta F_{19}^\circ \sim \Delta F_{22}^\circ$:



Since $\Delta F_{19}^\circ \sim \Delta F_{22}^\circ$ are known to be as follows:

$$\Delta F_{19}^\circ = 59,800 - 21.60 T \dots\dots\dots (23)^{16)}$$

$$\Delta F_{20}^\circ = 17,800 - 24.20 T \dots\dots\dots (24)^{17)}$$

$$\Delta F_{21}^\circ = 31,520 - 5.27 T \dots\dots\dots (25)^{18)}$$

$$\Delta F_{22}^\circ = -169,600 + 47.40 T \dots\dots\dots (26)^{19)}$$

we have

$$\Delta F_{18}^\circ = -60,480 - 3.67 T \dots\dots\dots (27)$$

and

$$\log K_2 = \log \frac{a_c^2}{a_s} = \frac{13,220}{T} + 0.802 \dots\dots\dots (28)$$

Assuming that both f_c and f_s are independent of temperature as in the previous case, we have the following equation from Eqs. 14, 15 and 28:

$$\begin{aligned} \log [\text{S}\%] &= 2 \left[\log \{1 + 0.264 [\text{C}\%] - 0.046 [\text{C}\%]^2 + 0.042 [\text{C}\%]^3\} + \log [\text{C}\%] \right] \\ &\quad - \log \{1 + 0.3875 [\text{C}\%] - 0.0750 [\text{C}\%]^2 + 0.0375 [\text{C}\%]^3\} \\ &\quad - \left(\frac{13,220}{T} + 0.802 \right) \dots\dots\dots (29) \end{aligned}$$

The relation among temperature, [C%] or [C_s%], and [S%] of pig iron in equilibrium can be found from Eqs. 17 and 29. The results of calculation are given in Table 2 and shown in Fig. 2.

From these results the following facts are knowable:

(1) When solid calcium carbide exists in excess, the limit of the desulphurization of pig iron is independent of the amount of sulphur contained

+) It is approximately equal to $p_{N_2} + p_{co}$ and quantitatively almost independent of the equilibrium of the present system.

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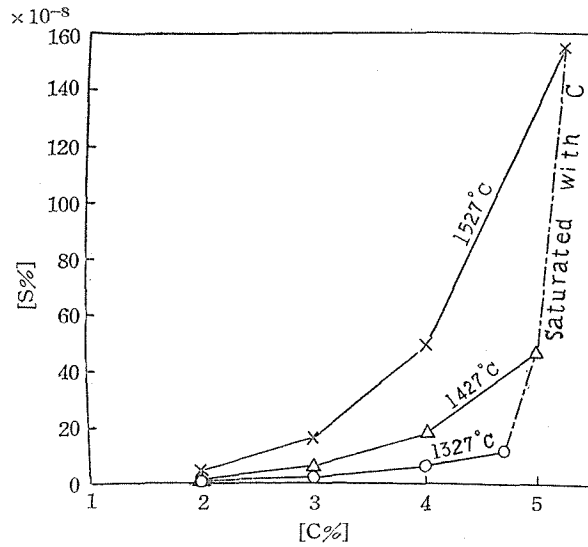


Fig. 2. Limit of desulphurization of pig iron with solid calcium carbide.

Table 2. Results of Calculation from Eqs. 17 and 29.

Temperature (T°)			1600 (1327°C.)	1700 (1427°C.)	1800 (1527°C.)
[S%]	[C%]	2	0.5×10^{-8}	1.7×10^{-8}	4.5×10^{-8}
		3	2.0 "	6.0 "	16.2 "
		4	6.0 "	18.3 "	49.4 "
		4.71 ^{a)}	11.8 "	—	—
		4.96 ^{b)}	—	46.1 "	—
		5.22 ^{c)}	—	—	155.4 "

a)b)c) Maximum solubility of carbon in pure iron in weight pct at 1327°C., 1427°C. and 1527°C. respectively.

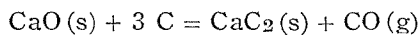
in iron before it is desulphurized.

(2) The limit of the desulphurization of pig iron with solid calcium carbide decreases as [C%] becomes lower at given temperature. This tendency of decrease is shown by a curve similar to a parabola as expected from Eq. 28.

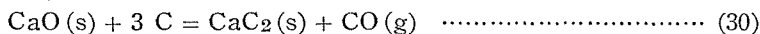
(3) The limit of the desulphurization of pig iron with solid calcium carbide decreases as the temperature lowers at a given [C%].

(4) Generally speaking, the limit of the desulphurization of pig iron with solid calcium carbide is considerably low.

Equilibrium of Reaction



In the previous two cases, the desulphurization of pig iron has been discussed ignoring the following reaction:



The above reaction, however, should be taken into consideration in the both cases where the reactions (1) and (18) are assumed to occur in the reaction chamber.

According to O. Ruff and E. Förster²⁰⁾, the mutual solid solubility of lime and calcium carbide is considered to be very low at temperature below 1640°C. Assuming that the both solid desulphurizers are entirely insoluble each toward the other, the change in standard free energy of the reaction (30), ΔF°_{30} , can be found from that of the reactions (1) and (18), represented by Eqs. 12 and 27, as given in the following equation:

$$\Delta F^\circ_{30} = 77,390 - 11.39 T \quad \dots\dots\dots (31)$$

Accordingly, we have

$$\log K_3 = \log \frac{p_{\text{co}}}{a_c^3} = - \frac{16,916}{T} + 2.490 \quad \dots\dots\dots (32)$$

where K_3 is the equilibrium constant of the reaction (30). When Eq. 32 is combined with Eq. 14, the result is:

$$\begin{aligned} \log p_{\text{co}} = & \left(- \frac{16,916}{T} + 2.490 \right) + 3 \left[\log \{ 1 + 0.264 [\text{C}\%] \right. \\ & \left. - 0.046 [\text{C}\%]^2 + 0.042 [\text{C}\%]^3 \} + \log [\text{C}\%] \right] \quad \dots\dots\dots (33) \end{aligned}$$

The relation among temperature, $[\text{C}\%]$ or $[\text{C}_s\%]$, and p_{co} of the present equilibrium system can be determined from Eqs. 17 and 33.

The same relation can also be found by the proper combination of values given in Tables 1 and 2, since it should be a condition for the simultaneous equilibrium of the reactions (1) and (18).

The results of calculation by the latter method are given in Table 3 and shown in Fig. 3, which teaches us that, when temperature is given, the reaction (30) proceeds to the left side in the field above the curve A-B where the existence of solid calcium carbide is not allowed, and the same reaction proceeds in a reverse direction in the field below the curve A-B where the existence of solid lime is not allowed.

From the new point of view above expounded, the treating of the limit of the desulphurization of pig iron obtained in the previous two cases will be revised as follows:

It is recognized that the conditions, represented by the field above the curve A-B in Fig. 3, are necessary for the desulphurization of pig iron by

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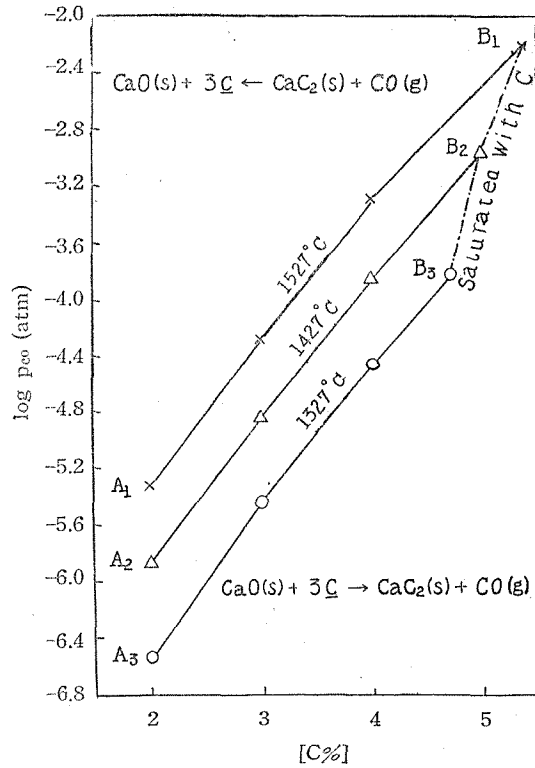


Fig. 3. Equilibrium condition of reaction $\text{CaO(s)} + 3\text{C} = \text{CaC}_2\text{(s)} + \text{CO(g)}$.

Table 3. Results of Calculation from Tables 1 and 2.

Temperature (T)		1600 (1327°C.)	1700 (1427°C.)	1800 (1527°C.)
$\log f_{co} \text{ (atm)}$	[C%]			
	2	-6.537	-5.870	-5.326
	3	-5.442	-4.829	-4.276
	4	-4.467	-3.848	-3.293
	4.71 ^{a)}	-3.820	-	-
	4.96 ^{b)}	-	-2.970	-
	5.22 ^{c)}	-	-	-2.206

a)b)c) Maximum solubility of carbon in pure iron in weight pct at 1327°C., 1427°C. and 1527°C. respectively.

the action only of solid lime, and those represented by the field below the curve A-B, are necessary for the desulphurization by the action only of calcium carbide.

At given temperature and $[C\%]$, the limit of the desulphurization of pig iron should be given by the equilibrium $[S\%]$ determined from the reaction (1) when p_{co} is kept more than the pressure represented by the curve A-B

in Fig. 3 even in the use of solid calcium carbide as a desulphurizer. It should be given by the equilibrium $[S\%]$ determined from the reaction (18) when p_{co} is kept less than the pressure represented by the curve A-B even in the use of solid lime as a desulphurizer. Accordingly, the minimum value of the limit of the desulphurization of pig iron occurring after the reaction (1) should be the equilibrium $[S\%]$ corresponding to the curve A-B in Fig. 3, i. e., the limit of the desulphurization which occurs after the reaction (18) at the same temperature. In other words, it is impossible to bring the limit of the desulphurization of pig iron after the reaction (1) to a level lower than the equilibrium $[S\%]$ determined from the reaction (18) at given temperature and $[C\%]$, though p_{co} in the system is extremely reduced.

Summary

(1) The limit of the desulphurization of pig iron of Fe-C-S system with solid lime or calcium carbide has been determined by thermodynamical calculations under the following probable assumptions:

a) The desulphurization with solid lime occurs only after the reaction $\text{CaO(s)} + \underline{\text{S}} + \underline{\text{C}} = \text{CaS(s)} + \text{CO(g)}$. It occurs only after the reaction $\text{CaC}_2\text{(s)} + \underline{\text{S}} = \text{CaS(s)} + 2 \underline{\text{C}}$ when pig iron is treated with solid calcium carbide.

b) Both lime or calcium carbide and the desulphurization product calcium sulphide do not entirely dissolve into pig iron. These materials have no mutual solubility.

c) The relation between f_c and f_s in pig iron and its $[C\%]$ is independent of temperature in a range from about 1300°C. to about 1600°C.

d) All the equations of the change in standard free energy adopted in the present paper are accurately applicable to any temperature in a range from about 1300°C. to about 1600°C.

(2) Assuming that solid lime and calcium carbide are entirely insoluble each toward the other, the equilibrium conditions have been determined for the reaction $\text{CaO(s)} + 3 \underline{\text{C}} = \text{CaC}_2\text{(s)} + \text{CO(g)}$. The results obtained in the previous two cases have been examined with a new consideration, resulting in the conclusion that, at given temperature and $[C\%]$, the limit of the desulphurization of pig iron with solid lime is generally larger than that in the case where pig iron is treated with solid calcium carbide, and its minimum value is equal to the limit of the desulphurization with solid calcium carbide.

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