

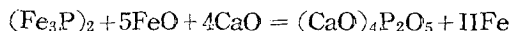
THE SAWAMURA LABORATORY

Head: Prof. Dr. Hiroshi Sawamura

I. On the Method of Manufacturing Low Phosphorus Pig Iron

By Hiroshi Sawamura

H. Sawamura¹⁾ first studied the equilibrium relation between the composition of the slag of $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}$ system and the content of phosphorus, carbon, silicon and manganese in molten pig iron. He assumed that pig iron can be dephosphorized under the following formula:



and, at a low temperature, e. g., 1300°C ., the apparent equilibrium constant of the above reaction is expressed after H. Schenck²⁾ as in the following:

$$\log K = \log \frac{(\sum P)}{(\sum \text{P}_2\text{O}_5)} \frac{(\text{FeO})^5}{(\sum \text{P}_2\text{O}_5)} \frac{(\text{CaO})^4}{(\sum \text{P}_2\text{O}_5)} + 0.060 (\sum \text{P}_2\text{O}_5) = -\frac{51800}{T} + 35.05$$

Where

K = apparent equilibrium constant

$(\sum P) = P$ in the pig iron in p.c.

(FeO) , (CaO) , $(\sum \text{P}_2\text{O}_5)$ = respectively free FeO, free CaO

and total P_2O_5 in the slag in p.c.

T = absolute temp.

The data³⁾ given by H. Schenck in his book were also adopted.

H. Sawamura and Ka Takumei⁴⁾ prepared the slag samples of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}$ system by melting the mixture consisting of lime, silica and FeO in a graphite crucible lined with alundum cement in nitrogen atmosphere. FeO used in this experiment was prepared by heating in vacuo the pure ferrous oxalate. The slag samples were contaminated with Al_2O_3 contained in the lining of the graphite crucible, and its content was from 2.5 to 39.4 p.c.

They were heated in an alumina tube in pure nitrogen current, and their melting points were measured by the naked eye through a glass plate fixed to an end of the heating tube. The results of the above-mentioned investigations made by H. Sawamura¹⁾ and H. Sawamura and Ka Takumei are summarized in Fig. I. The slag has the following composition:

$$(\sum \text{FeO}) + (\sum \text{SiO}_2) + (\sum \text{CaO}) = 89.74\%$$

$$(\sum \text{P}_2\text{O}_5) = 3.00\%$$

$$\text{neutral component} = 7.25\%$$

where $(\sum \text{FeO})$, $(\sum \text{SiO}_2)$, $(\sum \text{CaO})$ and $(\sum \text{P}_2\text{O}_5)$ are the total p.c. of the individual component in the slag.

In this figure, the curve M_1N_1 shows the composition of the slag in equilibrium with pig iron containing phosphorus of 0.01 p.c. . We can recognize that, if we want to manufacture pig iron containing phosphorus less than 0.01 p.c. with the slag under the above-mentioned condition, we must adopt the slag with the composition given in the area above the curve.

In the case pig iron contains phosphorus less than 0.03 p.c., the composition of the slag to be adopted is shown in the area above the curve M_2N_2 .

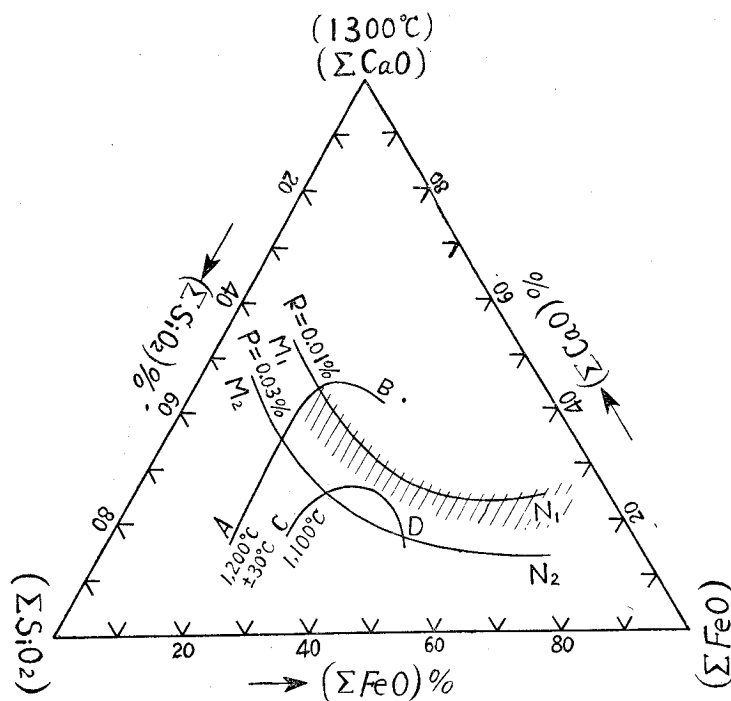


Fig. 1.

Curves AB and CD show the composition of the slag with the melting point of ca. 1200°C. and ca. 1100°C., respectively, and the melting point of the slag with the composition in the area of the former curve is higher than ca. 1200°C. and that of the slag with the composition in the area between the two curves is ca. 1100 and ca. 1200°C. .

The refining temperature must be kept as low as possible, because the higher the temperature, the greater becomes the amount of carbon which will be decarburized.

The conclusion was therefore, that the most proper composition of the slag for the manufacture of pig iron with phosphorus less than 0.02 p.c. is given in the hatched area in the figure.

H. Sawamura⁵⁾ carried out semi-industrial experiments in order to confirm the above-mentioned conclusion.

The Kenjiho pig iron was used as the raw material for these experiments, its composition being as follows:

$$C = 4.0\% \quad Si = 1.58\% \quad Mn = 1.55\% \quad S = 0.034\% \quad P = 0.254\%$$

The raw material was melted in a cupola furnace with the capacity of 500 Kg, and the cupola melt was charged into a special oil refining furnace with the capacity of ca. 300 Kg. The refining furnace was designed especially for the experiments as shown in Fig. 2. In the refining furnace the slag pool having the pre-determined composition was made at ca. 1400°C., into which the cupola melt at ca. 1350°C. was charged. Immediately the refining reaction occurred very violently, and the phosphorus content in the molten pig iron decreased rapidly. Twenty two refining experiments were carried out, and Fig. 3 shows an example of the change in the composition of pig iron and slag during the refining.

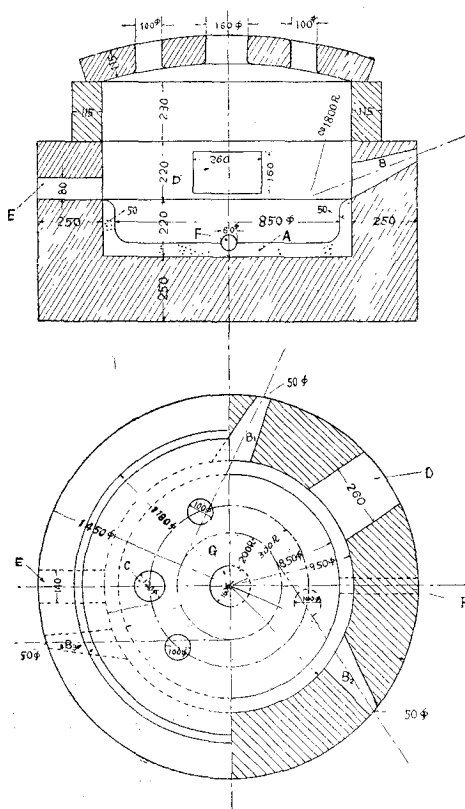


Fig. 2. (mm.)

- A: magnesia hearth B: oil burner holes
- C: Charging hole for molten pig.
- D: working door E: slag hole.
- F: tap hole G: charging hole for raw materials.

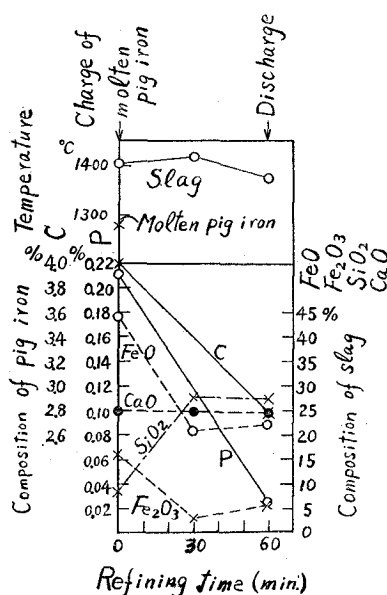


Fig. 3.

From these semi-industrial experiments, the fact was confirmed that pig iron containing phosphorus less than 0.02 p.c. and carbon more than 3 p.c. can be easily manufactured on a commercial scale from pig iron of common grade, if the refining temperature is properly kept and the composition of slag is kept as suggested by Fig. 1.

H. Sawamura, T. Mori and S. Sakurada⁶⁾ tried on a commercial scale to manufacture by the washing method low phosphorus pig iron of special grade with the following composition: C: $>3.2\%$ P: $<0.025\%$ Si $<2.5\%$ Mn: $>1.0\%$ S: $<0.025\%$ Cu: $<0.15\%$

The process of manufacture was same as in the case of semi-industrial experiments. A basic Héroult type electric furnace of 5 ton capacity was used as the refining furnace in these experiments. Raw pig iron was manufactured synthetically in an open low pit electric furnace with the capacity of ca. 2000 KW. at the rate of 3.5 ton per hr. Its carbon and phosphorus contents were as follows: C: 3.44~4.27%, P: 0.145~0.176%

The raw material of ca. 3.5 ton was tapped into a ladle and charged at ca. 1300°C. into the slag pool which was made beforehand in the refining furnace. Six refining experiments were carried out, and the conclusion was obtained that it is easy to manufacture on an industrial scale the low phosphorus pig iron in question, if the sulphur and copper contents of the raw material are adequately low. Its carbon, silicon and phosphorus contents were as follows: C $>3.8\%$, Si $<1.5\%$, P $\leq 0.5\%$

II. Research on the Method of the Chemical Briquetting of Cast Iron Turnings

By Hiroshi Sawamura and Masatoshi Tsuda

H. Sawamura and M. Tsuda⁷⁾ measured the cohesive force between the two pieces of cast iron specimen on their contact surface to solve the problem thoroughly, using the apparatus shown in Fig. 4.

A flat surface of the each cast iron specimen, 25 mm. in dia. and 10 and 20 mm. in thickness, was polished, and two pieces of the specimen were piled up in horizontal position as to bring their polished surface in contact. Various chemical reagents were interposed

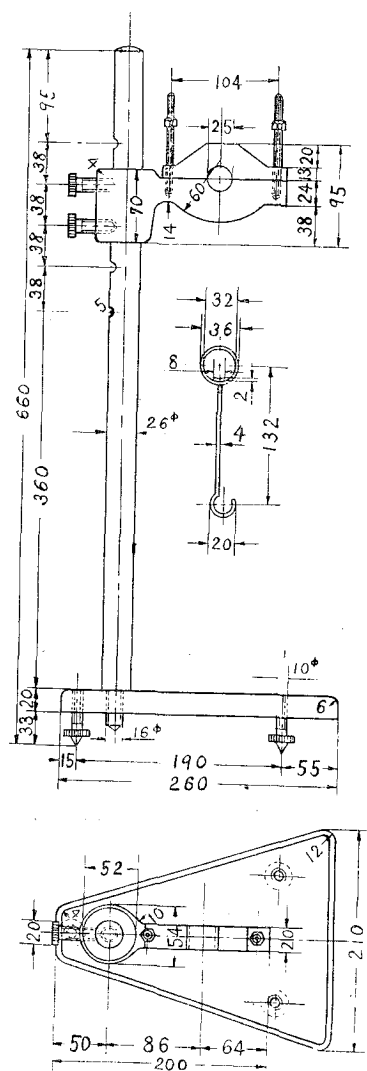


Fig. 4. (mm.)

between the piled specimens at the contact surface which were then kept still at room temperature. The cohesive force was measured at the pre-determined time from the instance when two specimens were piled. The result of the experiment is shown in Fig. 5.

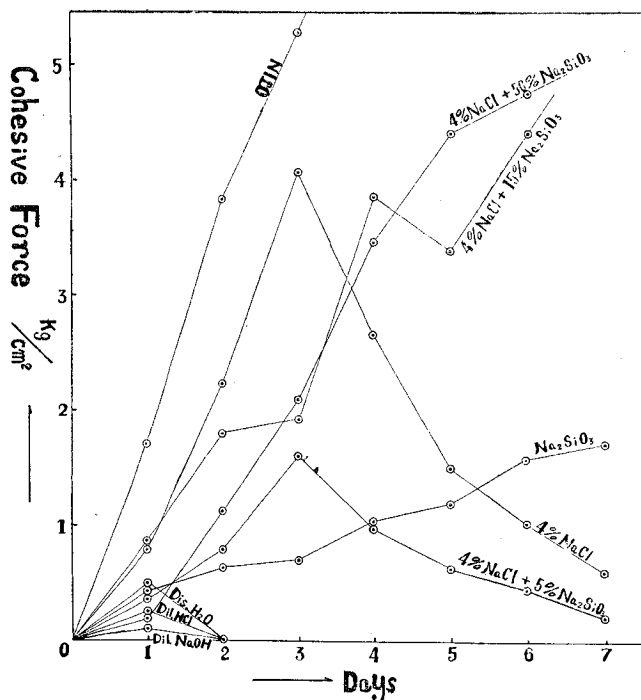
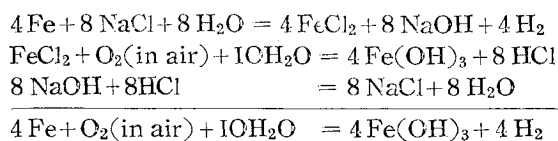


Fig. 5.

It was confirmed that (1) "OJIN" (the waste liquor in pulp factory) is the most effective reagent among the reagents the authors adopted; (2) 4 p.c. NaCl solution, almost same as sea water, is also effective, but the maximum point is shown on the cohesive force-time curve after three days.

The reason why the piled specimens wetted with the NaCl solution cohere tightly each other is the formation of $\text{Fe}(\text{OH})_3$ between the specimens as shown in the following:



NaCl in this case acts as a catalyzer. The formation of $\text{Fe}(\text{OH})_3$ proceeds from the periphery of the contact surface towards its centre, because the air, necessary for the formation of $\text{Fe}(\text{OH})_3$, is more accessible to the former than to the latter. As the reactions proceed, the amount of the reaction product $\text{Fe}(\text{OH})_3$ increases,

resulting in the increase of cohesive force. However, as the amount of $\text{Fe}(\text{OH})_3$ becomes too much and H_2 , generated at the inner part at the contact surface, can not escape outward through $\text{Fe}(\text{OH})_3$ formed at its periphery, the compound will be broken by the pressure of H_2 accumulated in the inner part of the contact surface resulting in the decrease of cohesive force between the piled specimens.

The cohesive force of the piled specimens were also measured after they were heated at various temperatures, and the fact was confirmed that (1) when the piled specimens are heated at a low temperature such as 200°C . the strong cohesive force caused by using "OJIN" becomes so weak that it is not worth mentioning, (2) the cohesive force caused by using 4p.c. NaCl solution does not decrease even at a higher temperature such as 600°C . but becomes almost negligible at 800°C .

3. On the Influence of TiO_2 in Slag upon the Graphitic Structure of Gray Cast Iron

By Hiroshi Sawamura and Masatoshi Tsuda

H. Sawamura found that, when molten cast iron is cast in a sand mould after it is kept in contact with molten slag containing TiO_2 in high p.c., the graphitic structure in the casting takes a so-called eutectic form.

H. Sawamura and M. Tsuda are continuing to make further research into this phenomenon in details, and the results will be published in the near future.

- 1) Sui-Yo-Kaishi, **11**, 83 (1942).
- 2) H. Schenck: Physikalische Chemie der Eisenhüttenprozesse. II, 152.
- 3) *Ibid*, 21~32.
- 4) Tetsu-To-Hagane, **29**, 307 (1943).
- 5) Not yet published.
- 6) Tetsu-To-Hagane, **36**, 4 (1950).
- 7) Imono, **20**, 2 (1948).