Study on the Utilization of Pyrrhotite Principally Composed of Iron and Sulfur. IV : On the Direct Reduction of Roasting Gases with Cokes

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Study on the Utilization of Pyrrhotite Principally Composed of Iron and Sulfur. IV On the Direct Reduction of Roasting Gases with Cokes*

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Synopsis

1. Adopting the method to make the ratio of the contents of sulfur dioxide to those of oxygen in the course of roasting pyrrhotite equal to about same weight, the resulting roasting gases are introduced into the direct reducing furnace with coke, and the relations between the obtained yield of sulfurs and the reaction temperatures were found,

2. Even if the yield of sulfurs attained to only 70% and thereabout in the case of adopting 850°C as the reaction temperature, the ratio of carbon monoxide to sulfur dioxide in the produced gases became 2:1, and it was found that almost the entire amount of residual sulfur dioxide in the above reaction could be reduced to the simple sulfurs by application to those resulting mixed gases of the catalytical reducing method, reported in the previous paper (part 3).

3. Further, adopting 900°C as the direct reducing temperature described above, the yield of sulfurs in this reaction attained to 90%, but it was found that in this case, the ratio of sulfur dioxide to carbon monoxide became more than 4:1, and even in the case of applying the catalytic reduction, reported in part 3 of this paper, to the resulting mixed gases, carbon monoxide was tolerably lost.

I. Introduction

The authors set about these researches about ten years ago, to find a method for completely utilizing pyrrhotite, which is principally composed of iron and sulfur. Reports have already been submitted concerning fundamental researches to determine the efficient conditions for roasting,[1] conditions for making sulfuric acid

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* The 639th report of the Research Institute for Iron, Steel and Other Metals.

1) T.Ishiwara, K.Niwa and K. Koizumi, Sic. Rep. RITU, A 3 (1951),

from the roasting gases obtained in application of these conditions to the baby rotary furnace,[2] and the conditions for making a simple sulfur by means of catalytic reduction of the above roasting gases with blast furnace gases.[3] It was found that the residues obtained after roasting were sufficiently available for iron-making ; sulfuric acid could be smoothly prepared from roasting gases ; and a simple sulfur could be efficiently made from roasting gases by catalytic reduction with blast furnace gases.

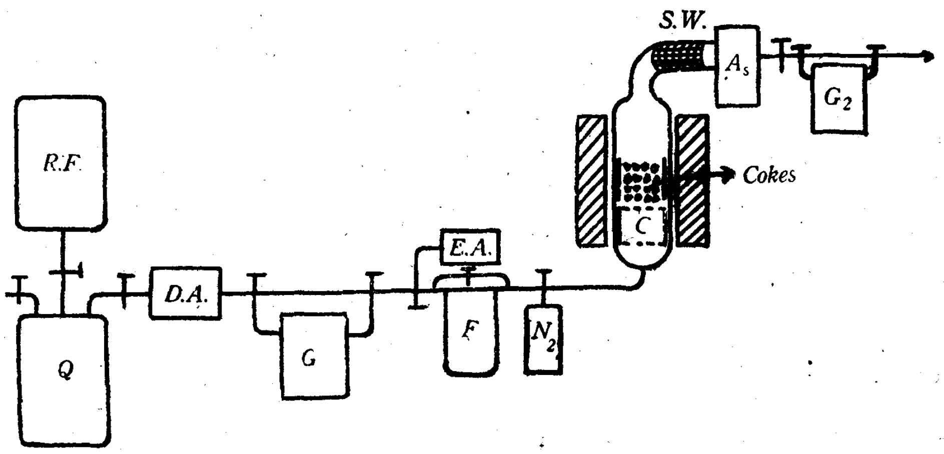
Thereafter, the present authors carried out researches to find the conditions, under which the sulfur dioxide was almost perfectly transformed into a simple sulfur by the catalytic reduction method described in the previous paper, (part 3) :-

"While a simple sulfur is made from roasting gases by reducing directly with cokes, the ratio of SO_2 : CO in the residual gases can be made to 1 : 2."

II. Experimental

1. Apparatus

The plan of the apparatus used in this work is shown in fig. 1. Q is the gas reservoir, into which the roasting gases, taken from the roasting furnace (baby



Q :	Gas reservoir	F :	Flow-meter
R.F. :	Regulating apparatus of gas-flows	C :	Porcelain reaction tube
		A_S :	Sulfur receiving tube
D.A. :	Drying apparatus of gas	S.W. :	Slag wool, (300°C)
G_1,G_1 :	Apparatus for gas analysis	E.A :	Evacuating apparatus

Fig. 1. The apparatus for sulfur-making by the reduction of roasting gases with cokes.

rotary furnace), have been previously introduced. R.F. is the apparatus, regulating flow of gas at constant velocity. F is the flow meter. C is the porcelain reaction tube (4 cm. in diameter), previously packed with about 80-30 grams of coke (7″-8″),

2) T.Ishiwara, K.Niwa and K.Koizumi, Sic. Rep. RITU, A 3 (1951).
3) T.Ishiwara, K.Niwa and T.Itô, Sci. Rep. RITU, A 3 (1951), 397.

which were heated to 950°C in vacuum in order to exclude volatile gases. As is the sulfur receiving tube. The corpuscles of sulfur are prevented from escaping by condensing in slag wool packed in S.W., which is heated to about 300°C.

2. Procedure

In the first place, the necessary weight of coke is introduced into C, which is evacuated, washed with nitrogen gas, and then is again evacuated, repeating this procedure two times. After oxygen has been excluded from this tube, it is gradually heated in vacuum ; constancy of temperature having been obtained, the mixed gases, the composition of which has been previously determined with G_1, are passed into C at a velocity of 50 c.c./min. In this case, the flow of gas is made constant with R.F., and the velocity is read with F. Observing the composition of mixed gases with G_1 from time to time in this way, the composition of gases coming from As is determined with G_2. At the end of experiment after constant time, the gases are changed into nitrogen, and moving the furnace up and down, the sulfurs adsorbed on the inner surface of reaction tube are expelled. The temperature having been lowered, As is removed from the apparatus, and the collected sulfurs are weighted. Thus, the yield of sulfur is estimated by comparing this weight with the theoretical value, calculated from the weight of gases used.

3. Preparation of solutions for gas analysis.

Orsat-apparatus is used for gas analysis in these experiments. The solutions used for gas analysis before reaction were as follows :-

Absorbing solution of SO_2	:	aqueous solution of 5N-NaOH.
That of O_2	:	sodium hyposulfite solution, added to potassium hydroxide solution.

The solutions used for gas analysis after reaction were as follows :-

Absorbing solution of SO_2	:	50% chromic acid solution.
That of CO_2	:	50% sodium hydroxide solution.
That of COS	:	potassium hydroxide solution (1 : 2), added with the same amount of alcohol.
That of O_2	:	alkaline sodium hyposulfite solution.
That of CO	:	ammoniacal cuprous chloride solution.

III. Rlesuts

Considering the experimental results obtained above (tables are omitted), the various relations are found among *the compositions of oxygen and sulfur dioxide in roasting gases, those of carbon monoxide, sulfur dioxide, oxygen and carbon dioxide in produced gases, the reaction temperature,* and *the yield of sulfurs.* The principals of these are shown as follows :-[4)]

4) (O_2) and (COS) in Produced gases show about 0-1% with almost no change, and have little influence on the other conditions.
Further,four kinds of experiments, in which the weight of coke was respectively 80 60, 45 and 30 grams, were carried out, but those four quantities gave the similar curves, so in this paper the case of 80 grams only was described as an example.

1. The relations between the composition of produced gases and that of roasting gases in each reaction temperature.

The relations between $(CO)/(SO_2)$ and $(O_2)_0/(SO_2)_0$ are shown in Fig. 2, where

	(CO) :	volume percentage	of CO in produced gases,
	(SO_2) :	that	of SO_2 in those gases,
	$(O_2)_0$:	that	of O_2 in roasting gases,
and	$(SO_2)_0$:	that	of SO_2 in those gases.

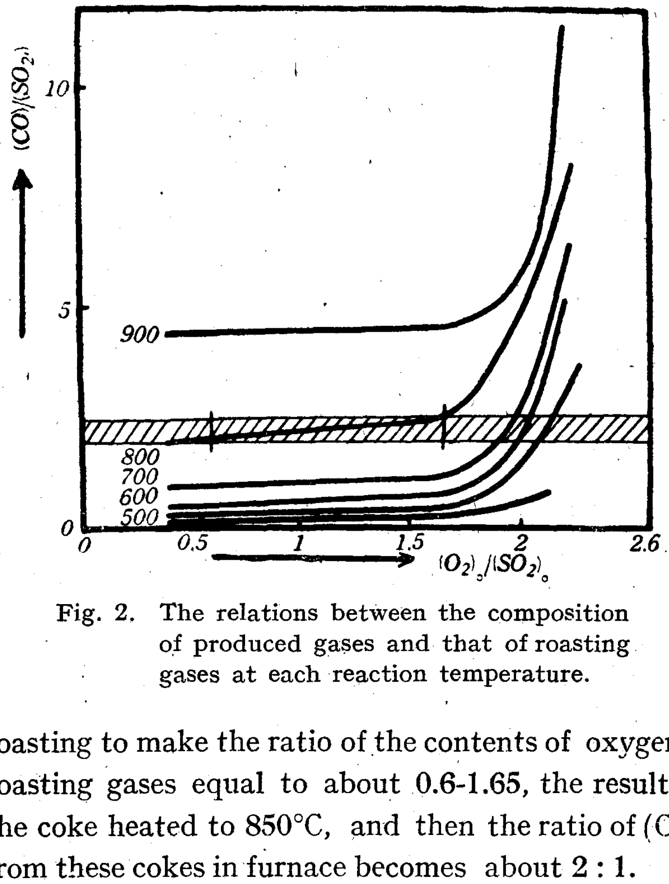


Fig. 2. The relations between the composition of produced gases and that of roasting gases at each reaction temperature.

As is seen in Fig. 2, the ratio of $(CO)/(SO_2)$ increases with elevation of temperature, and at the same temperature, the more the ratio of $(O_2)_0/(SO_2)_0$, that is, the greater the content of oxygen in roasting gases is, the larger the ratios of $(CO)/(SO_2)$ become.

From this figure, the conditions, under which the ratio of $(CO)/(SO_2)$ attains to 2:1, were found as follows :–

The temperature : 850°C

$(O_2)_0/(SO_2)_0$: 0.6-1.65

In other words, regulating the blow in the course of roasting to make the ratio of the contents of oxygen to those of sulfur dioxide in roasting gases equal to about 0.6-1.65, the resulting mixed gases are passed over the coke heated to 850°C, and then the ratio of $(CO)/(SO_2)$ in the gases produced from these cokes in furnace becomes about 2 : 1. Therefore, applying the method described in the previous paper (Part 3) to these resulting gases, which are introduced into the catalytic chamber[5], a simple sulfur can be efficiently made from the above produced gases.

2. The relations between the yield of produced sulfurs and the ocmposition of roasting gases at various temperatures.

These relations are shown in fig. 3. As is seen in this figure, the yield of sulfurs increases with elevation of temperature. In the case of constant temperature, the yield of sulfurs increases with the decrease of oxygen contents in roasting gases at 850°C, but there is no change between them at 900°C.

In the conditions found in Fig. 2, the yield of sulfurs is 75-65%, and when

5) In this case it is better that $(CO)/(SO_2) \geqslant 2$.

$(O_2)_0/(SO_2)_0=1$, it becomes 70%.

3. The relations between the yield of sulfurs and temperatures.

Considering the effect of temperatures on the mean yields of sulfurs over the whole range of the ratios of $(O_2)_0/(SO_2)_0$, observed, Fig. 4 is obtained. The yield of sulfurs attains to about 70% at 850°C, and applying the method of catalytic reaction, described in the previous paper (Part 3), to the residual mixed gases as the second stage, a simple sulfur is prepared.

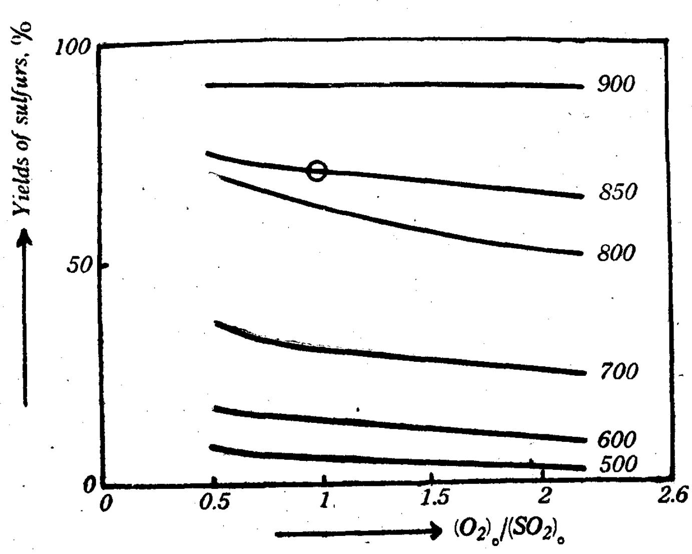


Fig. 3. The relations between the yields of produced sulfurs and compositions of roasting gases.

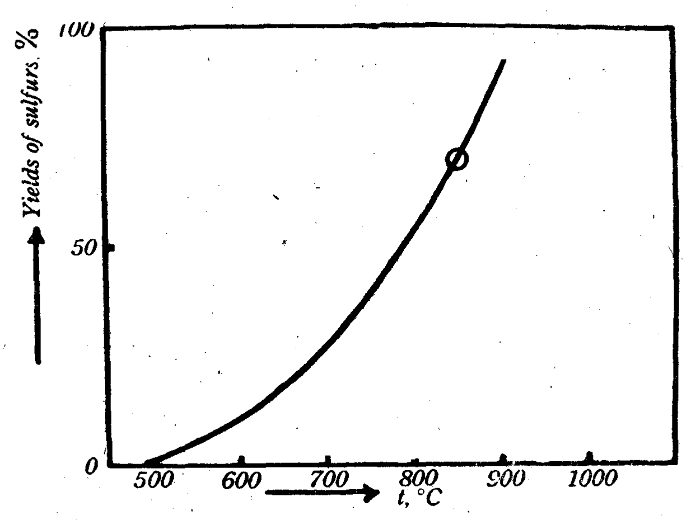


Fig. 4. The relations between the yields of sulfurs and temperatures.

IV. Conclusions

1. Regulating the blow in the course of roasting pyrrhotite to make the ratio of the contents of oxygen to those of sulfur dioxide in roasting gases equal to about 0.6-1.65, that is, to the same weight and its vicinity, the resulting gases are passed to the directly reducing furnace with coke heated to about 850°C as the second stage, and then the yield of sulfurs attains to 70%. Further, in this case, the ratio of carbon monoxide to sulfur dioxide in the gases, produced from these cokes furnace, becomes about 2 : 1. Thus, applying the method described in the previous paper (Part 3) to these resulting gases, which are reduced catalytically, as the third stage, almost the entire amount of residual sulfur dioxide can be reduced to simple sulfurs.

2. From the experimental results obtained above, the yield of sulfurs attains

to 90% by the direct reduction alone with cokes at 900°C, but in this case, the ratio of sulfur dioxide to carbon monoxide in the produced gases becomes far larger than 1 : 2, and then the produced carbon monoxide comes to be lost considering higher temperature. In order to prevent this loss, a process to supply the shortage of pure sulfur dioxide is necessary before the catalytic reduction has been carried out as third stage. This procedure requires a complicated apparatus.

At the same time, even if the yield of sulfurs decreases to 70% at 850°C by the direct reduction as the second stage, the ratio of carbon monoxide to sulfur dioxide in the produced gases becomes 2 : 1, and then it is advisable that applying the third stage of catalytic reduction to these produced gases, so as to reduce almost the whole amount of residual sulfur dioxide in the above second stage of reaction to simple sulfurs.

3. However, it must be noted that the cost of the above third stage of catalytic reduction is too high. Though ten percent of sulfur dioxide is lost, it may be better way that the whole process be ended with performance of the above second stage of reaction alone. But even in this case, some disadvantage is expected on the point of studying the treatment of 10% residual sulfurs.

Summary

1. Adopting the method to make the ratio of the contents of sulfur dioxide to those of oxygen in the course of roasting pyrrhotite equal to about same weight, the resulting roasting gases are introduced into the direct reducing furnace with coke, and the relations between the obtained yield of sulfurs and the reaction temperatures were found.

2. Even if the yield of sulfurs attained to only 70% and thereabout in the case of adopting 850°C as the reaction temperature, the ratio of carbon monoxide to sulfur dioxide in the produced gases became 2 : 1, and it was found that almost the entire amount of residual sulfur dioxide in the above reaction could be reduced to the simple sulfurs by application to those resulting mixed gases of the catalytical reducing method, reported in the previous paper (Part 3).

3. Further, adopting 900°C as the direct reducing temperature described above, the yield of sulfurs in this reaction attained to 90%, but it was found that in this case, the ratio of sulfur dioxide to carbon monoxide became more than 4 : 1, and even in the case of applying the catalytic reduction, reported in part 3 of this paper, to the resulting mixed gases, carbon monoxide was tolerably lost.

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