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Study on the Utilization of Pyrrhotite Principally Composed of Iron and Sulfur. II
On Making Sulfuric Acid from the Roasting Gases of Pyrrhotite

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Synopsis

Considering the results obtained in the preceding paper, the pyrrhotite, mesh of which is 28″ ~ 32″, was roasted at 700° C using a baby rotary furnace, and from the roasting gases sulfuric acid was made by the contact process. Finally, the following results may be stated : —

1. As for our contact process for making sulfuric acid, the most favourable conditions are as follows : —
   (1) The sulfur dioxide concentration is 7~7·5 %.
   (2) The temperature of catalyser is about 440° C.
2. The pyrrhotite cinders, which are obtained in roasting 75 ~ 120 g. of ores (28″ ~ 32″) for 30 ~ 48 hours at 700° C in a baby rotary furnace, contain residual sulfurs, which amount to 0.2 ~ 0.4 %, and are sufficiently available for iron making.

I. Introduction

As the method of utilizing sulfur dioxide gas, obtained by the roasting process described in the previous paper, the following five kinds of process are considered :—

(1) $SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$

(2) $SO_2 + 2C \longrightarrow 2CO + S$

$SO_2 + 2CO \xrightarrow[\text{catalyser}]{} 2CO_2 + S$

(3) $3FeS + 2SO_2 \longrightarrow Fe_3O_4 + 5S$

(4) $SO_2 + 2NH_4OH \longrightarrow (NH_4)_2SO_3 + H_2O$

$3(NH_4)_2SO_3 + H_2O \longrightarrow 2(NH_4)_2SO_4 + S + 2NH_4OH$ (the NH_4OH formed is returned to the first step)

(5) $MnO_2 + SO_2 \longrightarrow MnSO_4 \begin{cases} \text{electrolysis} \longrightarrow Mn \\ + NH_4OH \longrightarrow (NH_4)_2SO_4 + Mn(OH)_2 \rightarrow Mn \end{cases}$

Among these processes, the method of sulfuric acid making by so-called contact process is adopted in an attempt to prepare sulfuric acid from roasting gases.

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* The 630 th report of the Research Institute for Iron, Steel and Other Metals.
This report was lectured at the 12 th general meeting of Japan Society of Metals in Toyama, in October, 1942.

II. Experimental

The scheme of apparatus used in these experiment is shown in fig. 1. R. K. is the baby rotary furnace, C is the electric furnace for the contact chamber, $F_1 \sim F_4$ are the flow-meters, G_1 and G_2 are the apparatus for gas analysis, $Q_1 \sim Q_3$ are the gas reservoirs, A_{SO_3} is the same absorbing apparatus for SO_3 only as in the previous paper, and $A_1 \sim A_3$ are SO_2 absorbers, each of which contains 1.5 % H_2O_2.

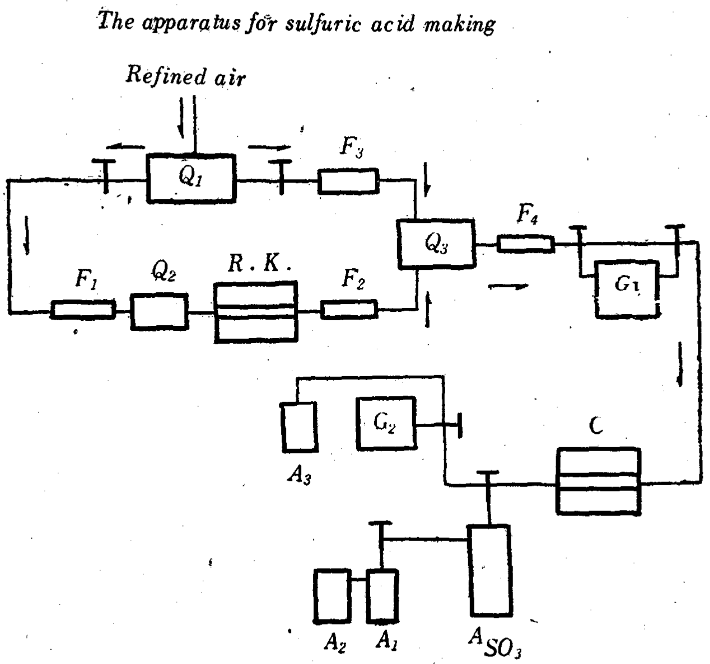

Fig. 1. $R. K.$: Bady rotary furnace
C : Electric furnace for catalytic chamber
F_1, F_2, F_3, and F_4 : Flow-meters
G_1 anl G_2 : Apparatus for gas analysis
Q_1, Q_2, and Q_3 : Gas reservoirs
A_{SO_3} : Absorbing apparatus for sulfur trioxide
A_1, A_2, and A_3 : SO_2-absorbers

In the first place, 75~110 g. of pyrrhotite, mesh of which is 28″ ~ 32″, are taken as roasting samples in R. K., and 75 ~ 120 g. (36~51 c.c.) of "Vanadium Catalyser", made by Japan Chemical Machine Making Co. Ltd., are introduced in G. Hereupon, R. K. is gradually heated. As soon as the temperature attains to 700° C, observing the scale reading of flow meter, a constant flow of air is introduced, and rotating the tube, contained samples, their roasting is carried out. The concentration of sulfur dioxide in the gas thus produced is determined by G_1. Eleven to twelve % sulfur dioxide, thus obtained, is diluted with air, added from the side of F_3, and the resulting gas is passed to C and then to A_3. In this case, 150 c.c./min. is selected for the total gas flow, which is ascertained with F_4.* The sulfur dioxide concentration is analysed by G_1 and G_2 from time to time. After the consistence of these concentrations, determined with these two analytical apparatus at the same time, have been ascertained, C is gradually heated. Constancy of temperature in C having been obtained, the direction of stopcock over A_{SO_3} is changed, to absorb sulfur trioxide in A_{SO_3}, and to absorb sulfur dioxide in A_1 and A_2. After one or two hours of this process, stopping the air flow, the stopcock over A_{SO_3} is shut. In this manner, the sulfur trioxide yields are estimated by titrating sulfur trioxide and dioxide, absorbed in A_{SO_3}, and A_1 plus A_2, respectively, with normal solution of sodium hydroxide.

* The flow of gas against 1 c.c. of catalyser amounts to 2.9 –4.2 c.c./min.

III. Results

1. The effect of sulfur dioxide concentration on sulfur trioxide yield.

Maintaining the temperature of catalyser constant at 450°C, the relation between sulfur dioxide concentration and sulfur trioxide yield was obtained, as is shown in fig. 2. The real line shows the experimental curve, while the dotted line shows the theoretical curve estimated from the equilibrium.

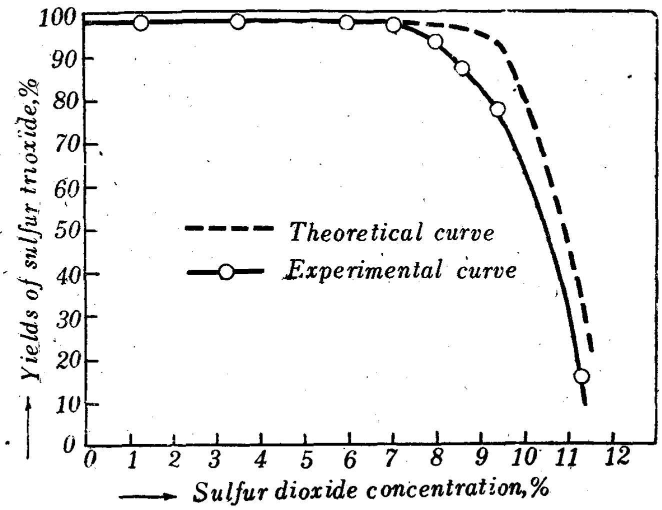

Fig. 2 The effect of sulfur dioxide concentrations. on the yields of sulfur trioxide.

As is seen in fig. 2, the experimental curve consists with the theoretical curve up to 7.5 % and the yield attains to 98 %. In case of higher concentrations, both curves turn their directions indicating lower sulfur trioxide yields with increase of the sulfur dioxide concentrations. Therefore, about 7~7.5 % is the most suitable for sulfuric acid making, as is theoretically considered.

2. The effect of the temperature of catalyser on the sulfur trioxide yield.

Maintaining the sulfur dioxide concentration constant at 7 %, the relation between the temperature of catalyser and the sulfur trioxide yield was obtained, as is shown in fig. 3. The real line shows the experimental curve and the dotted line the theoretical curve.

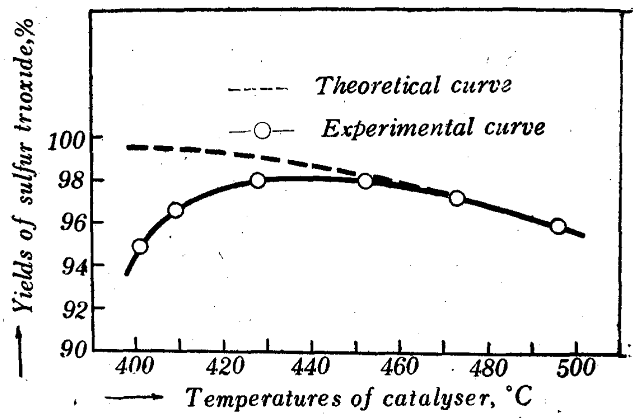

Fig. 3. The effect of the temperatures of catalyser on the yield of sulfur trioxide.

As is seen in fig. 3, the experimental curve departs from the theoretical curve below 450°C, and has maximum point at 430°~450° C in case of gas flow, 2.9~4.2 c.c./min./1 c.c. of catalyser.

3. Residual sulfurs in the roasting cinders of pyrrhotite.

Analysing the roasting cinders, obtained in rotary furnace, at the end of experiment, the residual sulfur amounts to 0.2~0.4 %, and it is ascertained that the roasting is sufficiently carried out in these experiments.

IV. Conclusion

From the experimental results described above, the following conclusions are gathered :—

1. The favourable conditions for sulfur trioxide making from roasting gases of pyrrhotite are as follows :—

Concentration of sulfur dioxide : 7 ~ 7.5 %.

Temperature of catalyser : about 440° C.

2. The pyrrhotite cinders, which are obtained in roasting 75~120 g. of ores (28~32 mesh) for 30~48 hours at 700° C in a baby rotary furnace, have residual sulfurs, which become 0.2~0.4 %, and can be used satisfactorily for iron making.

Summary

Considering the results obtained in the preceding paper, the pyrrhotite, mesh of which is 28″~32″, was roasted at 700° C using a baby rotary furnace, and from the roasting gases sulfuric acid was made by the contact process. Finally, the following results may be stated :—

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