

Study on the Utilization of Pyrrhotite Principally Composed of Iron and Sulfur. I : On the Roasting of Pyrrhotite

著者	ISHIWARA Torajiro, NIWA Kichizo, KOIZUMI Koichi
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	3
page range	265-276
year	1951
URL	http://hdl.handle.net/10097/26435

Study on the Utilization of Pyrrhotite Principally Composed of Iron and Sulfur. I On the Roasting of Pyrrhotite*

Torajirô ISHIWARA, Kichizô NIWA and Kôichi KOIZUMI

The Research Institute for Iron, Steel and Other Metals

(Received March 20, 1951)

Synopsis

Adopting the roasting process for the utilization of pyrrhotite, studies were made of the reciprocal relations among oxidation velocity, oxidation ratio, residual sulfurs in the cinders and production ratio of sulfur trioxide in roasting gases, under the several following conditions:—

- (1) Flow of air (cc/min/2 g): 100, 150, 300, 500 and 1000.
- (2) Mesh of ore: 150"~170", 48"~50", 20"~24", 14"~16", 9"~10" and 7"~8".
- (3) Roasting temperature (°C): 600, 650, 700, 800 and 900.
- (4) Roasting time: Below 200 min.

The most favourable conditions were confirmed as follows:—

1. The temperature range favourable for roasting is 700°~800°C.
2. In the range described above, sufficiently great oxidation ratios are obtained in the roasting time within one hour up to the mesh of 20"~24", even in case of 100 cc/min/2 g.
3. The cinders, roasted in such a condition as described above, contain residual sulfurs which have become under 0.2%, and are sufficiently available for iron-making.

I. Introduction

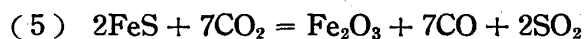
Pyrrhotites, having analyses ranging from Fe_5S_6 to $\text{Fe}_{16}\text{S}_{17}$, are found in abundance in all parts of Eastern Asia, but so far have not been utilized as a source of either iron ore or of sulfur, presumably because of the difficulty of their roasting, differing from the case of pyrites.

The recent demand for sulfide ores is, however, very great and the supply is nearing exhaustion, so the treatment of pyrrhotites, in place of pyrites, is considered to be a burning question. Thus, the present researches have been undertaken for the purpose of finding a perfect method for the utilization of pyrrhotite.

The following six cases principally were considered for utilization of sulfur contents in pyrrhotites:—

- (1) $\text{FeS} + \text{H}_2 = \text{Fe} + \text{H}_2\text{S}$
- (2) $3\text{FeS} + 4\text{H}_2\text{O} = 3\text{H}_2\text{S} + \text{Fe}_3\text{O}_4 + \text{H}_2$
- (3) $2\text{FeS} + \text{C} = \text{CS}_2 + 2\text{Fe}$
- (4) $\text{FeS} + 10\text{Fe}_2\text{O}_3 = 7\text{Fe}_3\text{O}_4 + \text{SO}_2$

* The 629th report of the Research Institute for Iron, Steel and Other Metals. This report was lectured at 12th general meeting of Japan Society of Metals in Toyama, in October, 1942.



Among possible methods the so-called "roasting process" (equation (6)) was chosen as most the familiar one and experiments were carried out as to the following points:—

- (1) the relations between oxidation velocity at each mesh of ore and each roasting temperature, and flow of air;
- (2) the relations among meshes of ore, roasting temperatures and oxidation velocity;
- (3) the relations between oxidation ratio at each mesh of ore and each roasting temperature, and roasting time;
- (4) the relations among residual sulfurs in the cinders, meshes of ore, and roasting temperatures;
- (5) the relations among production ratios of sulfur trioxide in roasting gases, meshes of ore, and roasting temperatures.

II. Experimental

1. Materials

The pyrrhotites used are produced at the Ômine mine in Nara prefecture. They have the analyses as follows:—

Fe: 56~61.5%; S: 34.2~38.2%; SiO₂: 0.36~1.78%; Al₂O₃: none;

MgO: trace~0.11%; CaO: none; Cu: trace~0.30%; As: trace; P: trace.

Crushing the ore described above, six kinds of meshes:

150"~170", 48"~50", 20"~24", 14"~16", 9"~10", and 7"~8", were chosen. Each kind was separately calcined for three hours in a vacuum at 900°C. Two grams of the materials thus obtained were adopted as the sample in each experiment.

2. Apparatus and Procedure

The scheme of apparatus used in these experiments is shown in Fig. 1. C is the

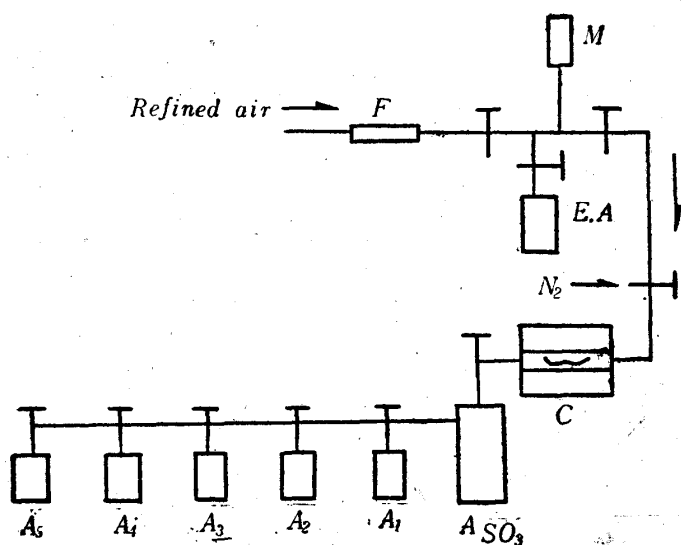


Fig. 1

electric furnace for roasting, A_{SO_3} is the absorbing apparatus for SO₃ only, and $A_1 \sim A_5$ are SO₂ absorbers, each of which contains 100 cc of 1.5% of hydrogen peroxide solution.

After introducing the boat, containing two grams of the samples described above, in the center of the roasting tube, C, which is evacuated to a vacuum of about 1/1000 mmHg, the furnace is gradually heated. Constancy of temperature having been

obtained, purified air is introduced. As soon as the pressure in the roasting tube attains to 1 atmosphere (this interval: 1~2 minutes), stopcock, A_{SO_3} , is opened, (when A_1 is previously turned towards the absorber), and then observing the reading of the flow-meter, F , a constant flow of pure air is passed. The gas thus coming out of the roasting tube consists mostly of SO_2 besides N_2 and contains a small quantity of SO_3 . SO_3 is absorbed into A_{SO_3} , and SO_2 is absorbed firstly into A_1 , then turning one stopcock after another, into A_2 to A_5 every constant time. After 200 minutes, in this manner, having finished roasting, the nitrogen is passed into the roasting tube in order to expel the residual sulfur dioxide.

Thus, the quantities of SO_3 and SO_2 produced every constant time are determined by titration of the solutions in the absorbers A_{SO_3} , $A_1 \sim A_5$, with normal solution of sodium hydroxide, using bromcresolblue as an indicator. Furthermore, taking out the boat at the end of experiment, the residual sulfurs in the roasting cinders are determined by chemical analysis.

III. Results

1. The relations between oxidation velocity of each mesh of ore and each roasting temperature, and flow of air

In the first place, the experiments were carried out as to each mesh previously described, at $700^\circ C$, with five kinds of air flow, that is, 100, 150, 300, 500, and 1000 cc/min, for the purpose of observing the effect of air flow.

For an example, the case of $150'' \sim 170''$ is shown in Fig. 2(a). The figures along each curve show the flow of air. As indicated in Fig. 2(a), the oxidation velocity increases generally with the flow of air. Furthermore, the relations between the time, in which the oxidation ratio of sulfur attains to 90%, and the flow of air are shown in Fig. 2 (b), for the purpose of minute observation of the fact described above. In the meshes from $150'' \sim 170''$ to $20'' \sim 24''$, the oxidation ratios are approximately proportional to the flow of air up to 500 cc/min, upwards of which the change of oxidation ratio with the flow of air is very slight. In the same range of meshes, generally, the effect of air flow becomes smaller with their increase. In the case of $14'' \sim 16''$ no change

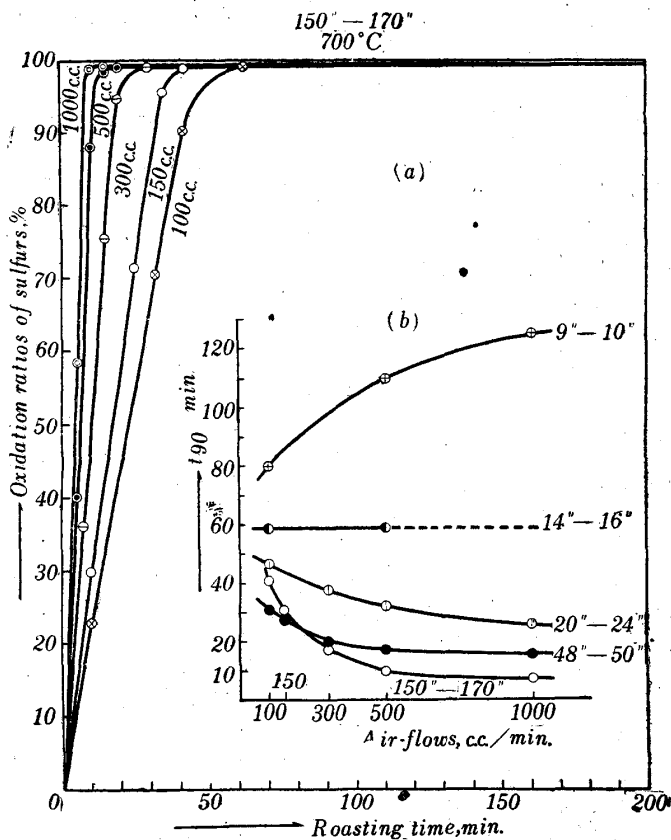


Fig. 2

of air flow becomes smaller with their increase. In the case of $14'' \sim 16''$ no change

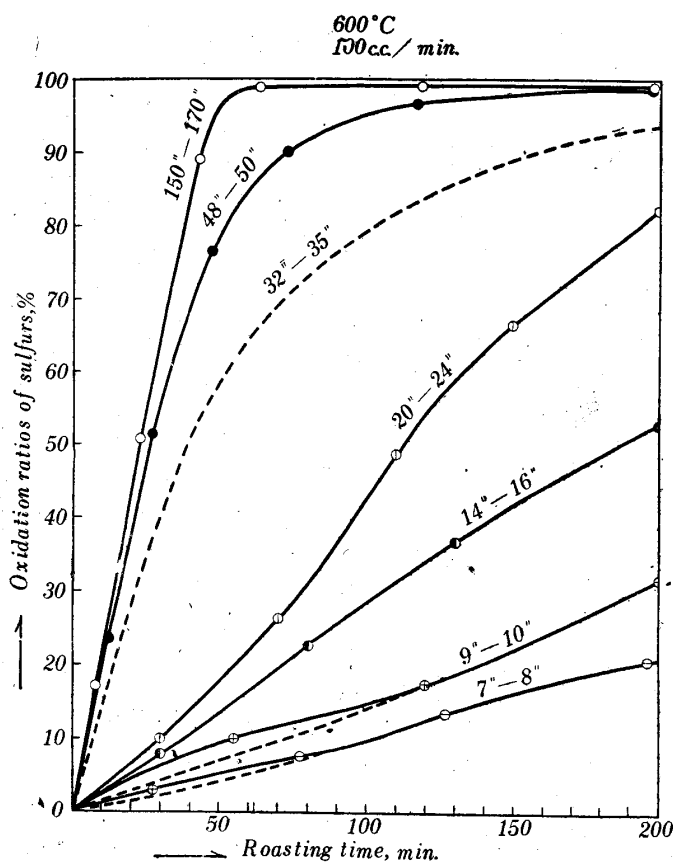


Fig. 3 (a)

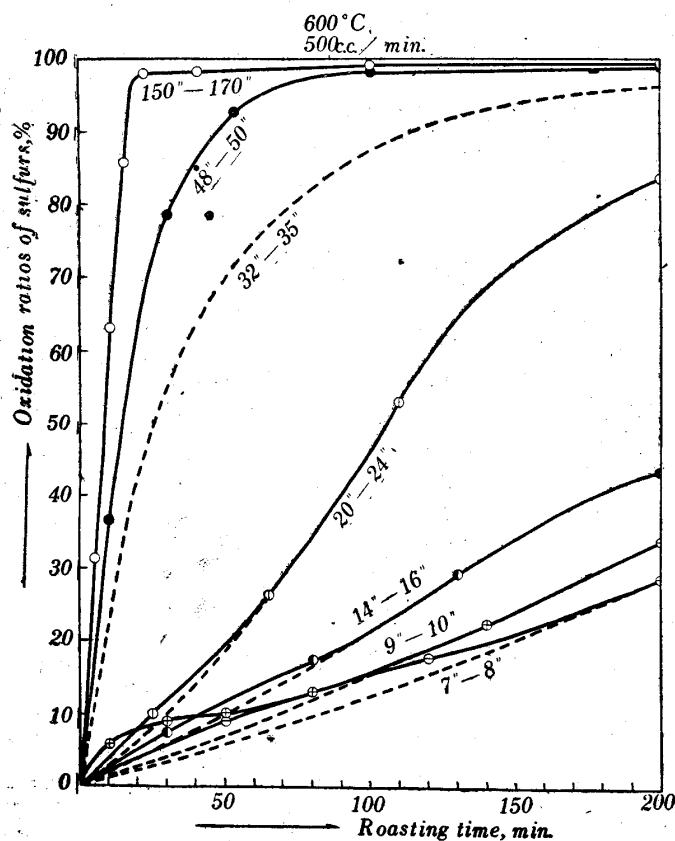


Fig. 3 (b)

with air flow is observed. This is presumed to be due to the fact that in the range of smaller grains the reaction to all surface is speedy, so the oxidation ratio depends on the air flow, while in the coarser ones the oxidation velocity is subject to the diffusion velocity of the gas in the surface oxidation layers. It is noticeable that in the case of 9''~10'' the oxidation velocity decreases with the increase of air flow. This is presumably due to the fact that in the coarser grain, such as 9''~10'', the temperature of surface reaction layer is lowered with the increase of air flow. Even in this case, above 500 cc/min, the change with air flow becomes smaller. Henceforth, adopting 100 and 500 (each cc/min) from among five kinds of flow described above, the experiments are continued.

2. The relations among meshes of ore, roasting temperatures and the oxidation velocity

Firstly, the case of 100 cc/min at 600°C is shown in Fig. 3(a). Only in the case of 150''~170'', does the oxidation ratio attain to 99% within 60 minutes. This percent is not obtained till 200 min in 48''~50'', and in larger meshes, the oxidation ratio is not sufficient even after 200 min. (In Fig. 3(a) the dotted line of 32''~35'' is the presumable curve estimated from the results on two meshes, 48''~50'' and 20''~24''.)

Secondly, the case of 500 cc/min

at the same temperature is shown in Fig. 3(b). In 150''~170'', the oxidation is mostly carried out at about 20 min and in 48''~50'', it is completed at about 100 min, but in larger meshes oxidation is not sufficient.

Thirdly, the case of 100 cc/min at 650°C:—Fig. 4(a)—. In 150''~170'' and 48''~50'', most of the oxidation is finished at 60 min, but in 20''~24'', oxidation is not sufficient even at 200 min, and in larger meshes, it did not occur.

Fourthly, the case of 500 cc/min at 650°C:—Fig. 4(b)—. In 150''~170'' and 48''~50'', most of the oxidation is finished at 20 min, but in 20''~24'', oxidation is not sufficient even at about 200 min, and in larger meshes, oxidation did not take place.

Next, the case of 100 cc/min at 700°C:—Fig. 5(a)—. In 150''~170'', 48''~50'' and 20''~24'', the oxidation is mostly completed at about 60 min, and in 14''~16'', it needs about 120 min., but in 9''~10'', it is not sufficient at 200 min, while in 7''~8'', it did not occur.

The case of 500 cc/min at 700°C:—Fig. 5(b)—. In 150''~170'', most of the oxidation is finished at about 15 min, in 48''~50'', it occurs at 25 min; in 20''~24'', at 60 min; in 14''~16'', at 120 min; and in the larger meshes than 9''~10'', oxidation is not finished even at 200 min.

The case of 100 cc/min at 800°C:—Fig. 6(a)—. In the meshes smaller than 20''~24'', the oxidation is mostly carried out

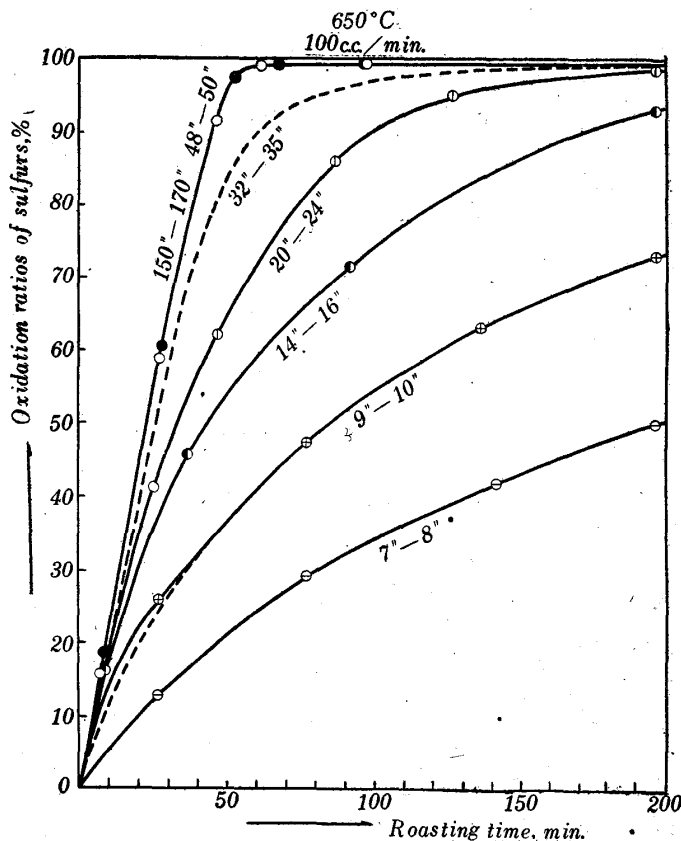


Fig. 4 (a)

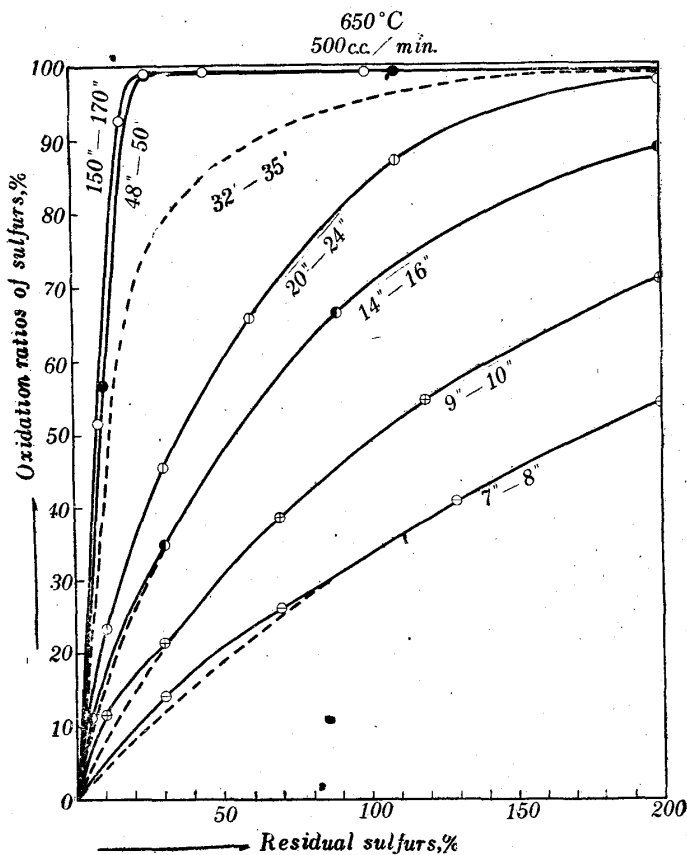


Fig. 4 (b)

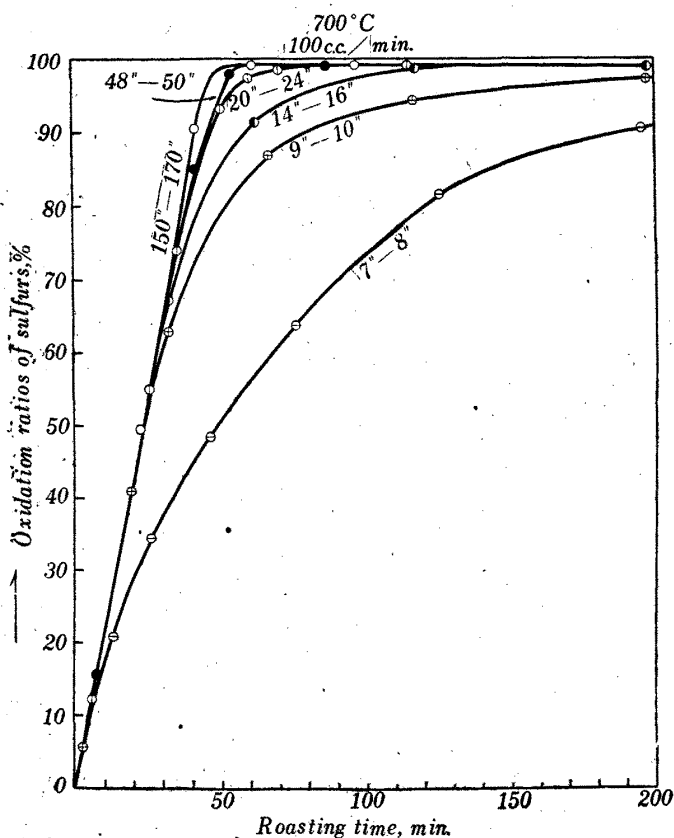


Fig. 5 (a)

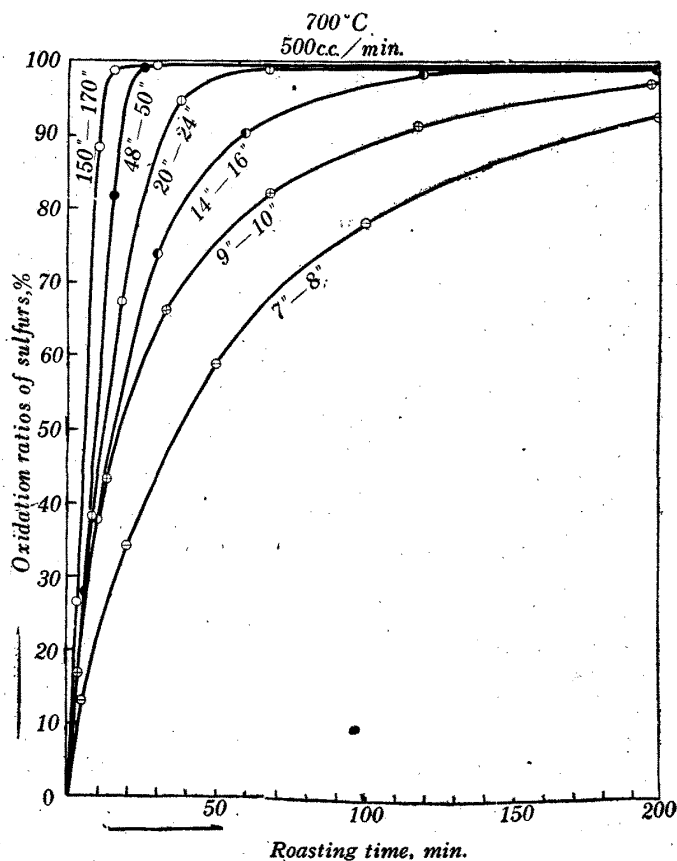


Fig. 5 (b)

at 60 min, in 14''~16'', it is complete at 90 min, and in 9''~10'', at 200 min, but in 7''~8'', it is not sufficient even at 200 min.

The case of 500 cc/min at 800°C:—Fig. 6 (b)—. In 150''~170'' and 48''~50'', most of the oxidation is finished at 20 min; in 20''~24'' and 14''~16'', 70 min is needed; in 9''~10'', 150 min; and in 7''~8'', 200 min.

The case of 100 cc/min at 900°C:—fig. 7 (a)—. In smaller meshes up to 20''~24'', the oxidation is mostly performed at 60 min; in 14''~16'', at 120 min, and in 9''~10'', 180 min. is needed, but in 7''~8'', oxidation does not occur even at 200 min.

The case of 500 cc/min. at 900°C;—Fig. 7 (b)—. In 150''~170'', the greater part of oxidation is finished at 20 min, and in 20''~24'', it is complete at 40 min; in 14''~16'', at 80 min, and in 9''~10'', 200 min is needed, but in 7''~8'', oxidation does not occur.

3. The relations between oxidation ratio of each mesh of ore, each respective roasting temperature, and roasting time

A comprehensive view of the relations among oxidation ratio, meshes of ore and roasting temperature at the same time, is obtained by cutting the oxidation ratio curves described above with perpendicular lines at 200, 120, 60, 30, and 15 min, as is shown in Fig. 8.

Fig. 8 (a):—the case of 100

cc/min. In the range between 600° and 700°C, the oxidation ratios of sulfur in each mesh are fairly different from each other, but from 700° up to 900°C not much change with temperature is perceived. From Fig. 8 (a), the meshes, which are mostly oxidised within 60 min, are listed as follows:—

600° C: 150'' ~ 170''.

650° C: 150'' ~ 170'',

48'' ~ 50''.

700° C: 150'' ~ 170'',

48'' ~ 50'',

20'' ~ 24''.

800° C: 150'' ~ 170'',

48'' ~ 50'',

20'' ~ 24''.

900° C: 150'' ~ 170'',

48'' ~ 50'',

20'' ~ 24''.

On the other hand, in 14''~16'', oxidation usually needs 120 min. even above 700° C, and in 9''~10'', there is scarcely any oxidation at temperatures above 800° C for a roasting time of 200 min.

Next, the case of 500 c.c./min. is shown in fig. 8(b). From the shape of the curve there is observed much difference up to 700° C, but at 800° and 900° C it is not so much. In the coarser grains, the oxidation ratio is rather lower at 900° C. This is presumed to be due to the fact that the oxidation layer of magnetite grows in the surface of the grains and the diffusion velocity of the gas through this layer becomes smaller. From fig. 8(b), the meshes, which are mostly ox-

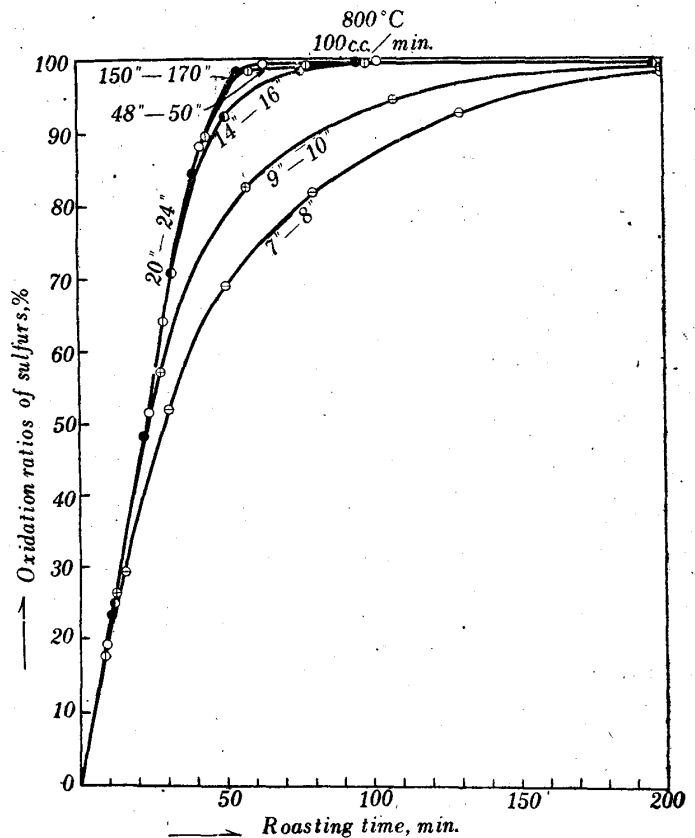


Fig. 6 (a)

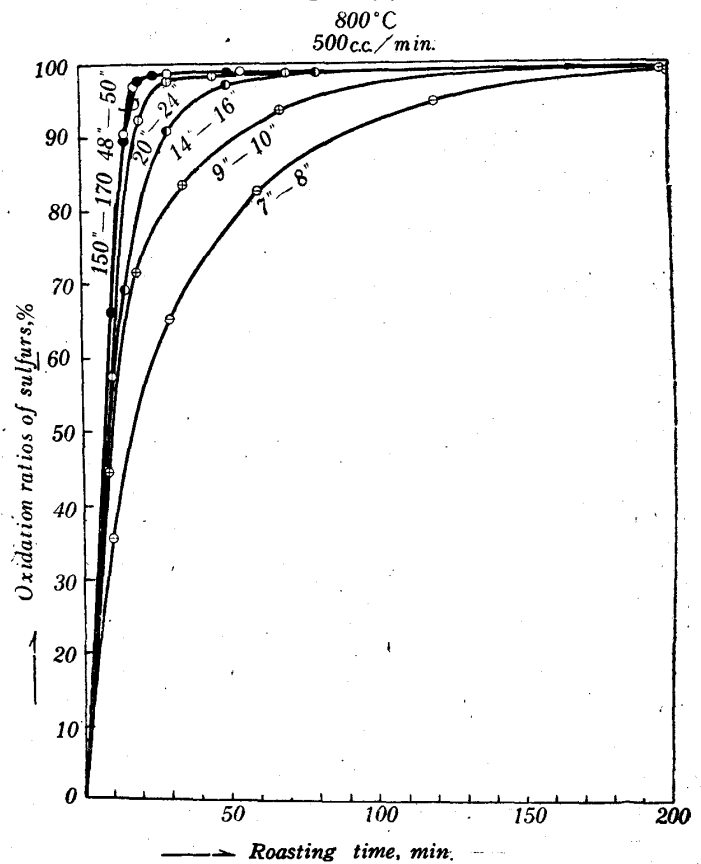


Fig. 6 (b)

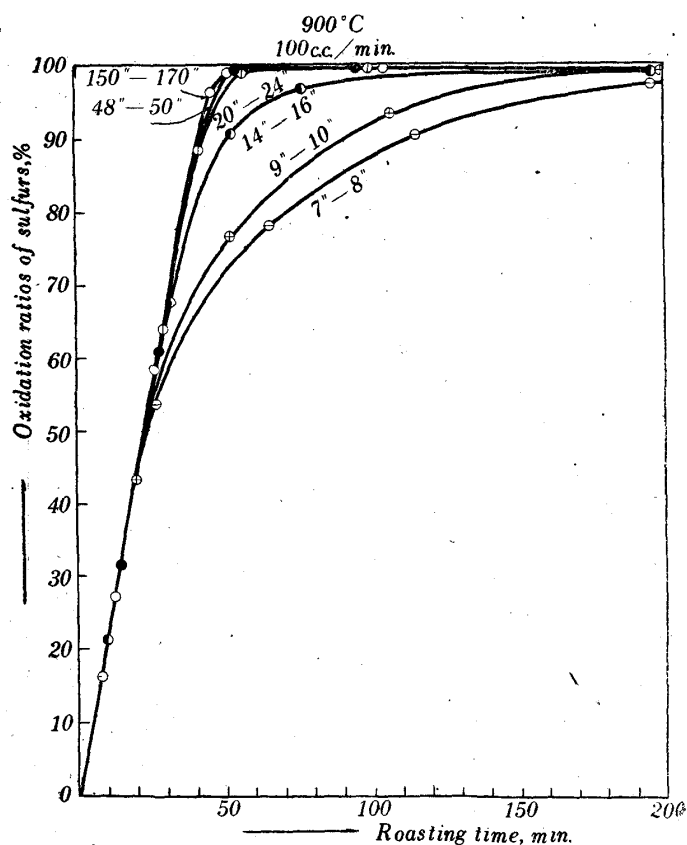


Fig. 7 (a)

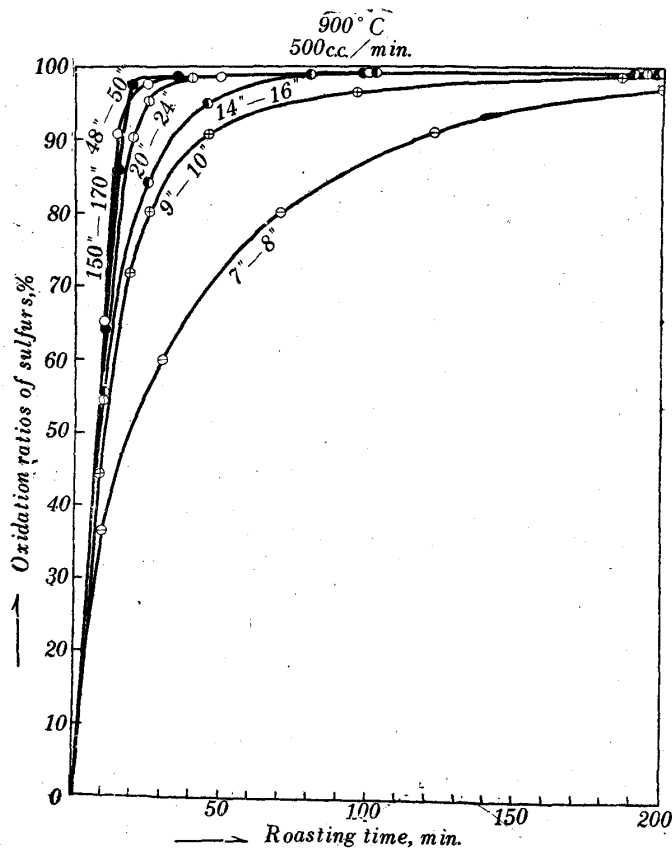


Fig. 7 (b)

idised within 60 min., are selected as follows:—

600°C: 150'' ~ 170''.

650°C: 150'' ~ 170'',

48'' ~ 50''.

700°C: 150'' ~ 170'',

48'' ~ 50'',

20'' ~ 24''.

800°C: 150'' ~ 170'',

48'' ~ 50'',

20'' ~ 24'',

14'' ~ 16''.

900°C: 150'' ~ 170'',

48'' ~ 50'',

20'' ~ 24'',

14'' ~ 16''.

The difference from the case of 100 c.c./min. is the addition of 14''~16'' to the sizes oxidised at 800° and 900° C. In 9''~10'', the oxidation usually needs 120 min. at 800° C, and in 7''~8'', it does not occur within even 200 min. at 800° C. In these two meshes, the oxidation ratios become lower at 900° C, presumably due to the same cause as described above.

4. The relations among residual sulfurs in the cinders, meshes of ore, and roasting temperatures

The relations among residual sulfurs in the cinders, meshes of ore, and roasting temperatures were obtained, as was shown in fig. 9. In each mesh, the mean value of air flows between 100 and 500 c.c./min. was adopted. As is seen in fig. 9, in the cases of 600°C, the quantities of residual sulfurs become much more in the meshes above 20''~24'' than in smaller ones, and

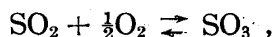
especially, in 7''~8'', such residuum amounts to 25%. At 650°C, it becomes considerably less, but in 14''~16'', it is again much more. At 700°C, it decreases tolerably, that is, within 0.2% up to 14''~16''. At 800°C~900°C, the residual sulfurs decrease 0.2% up to 9''~10''. In the case of 7''~8'', they are above 0.5% at all temperatures observed, and in this case, they become fairly more at 900° than at 800°C.

In short, the tendency of the oxidation ratio curves, described in the former section, is also confirmed from the results obtained here.

5. The relations among production ratios of sulfur trioxide in roasting gases, meshes of ore, and roasting temperatures

These relations are shown in fig. 10.

Generally, considering from the following equilibrium:—



$\Delta F > 0$ above 780°C, and therefore, sulfur trioxide should not be produced, while, as is seen in fig. 10, it is produced at 800° and 900°C. This result is presumably due to the production at the low temperature part of the wall in the roasting tube. In this case, the higher the temperature is, the harder this production becomes as a matter of course.

On the whole, the larger the meshes, the more the production ratio of sulfur becomes. This is presumed to be due to the fact that the larger the meshes are, the more the concentration of sulfur dioxide is diluted and then the resultant excess of oxygen becomes favourable for the production of

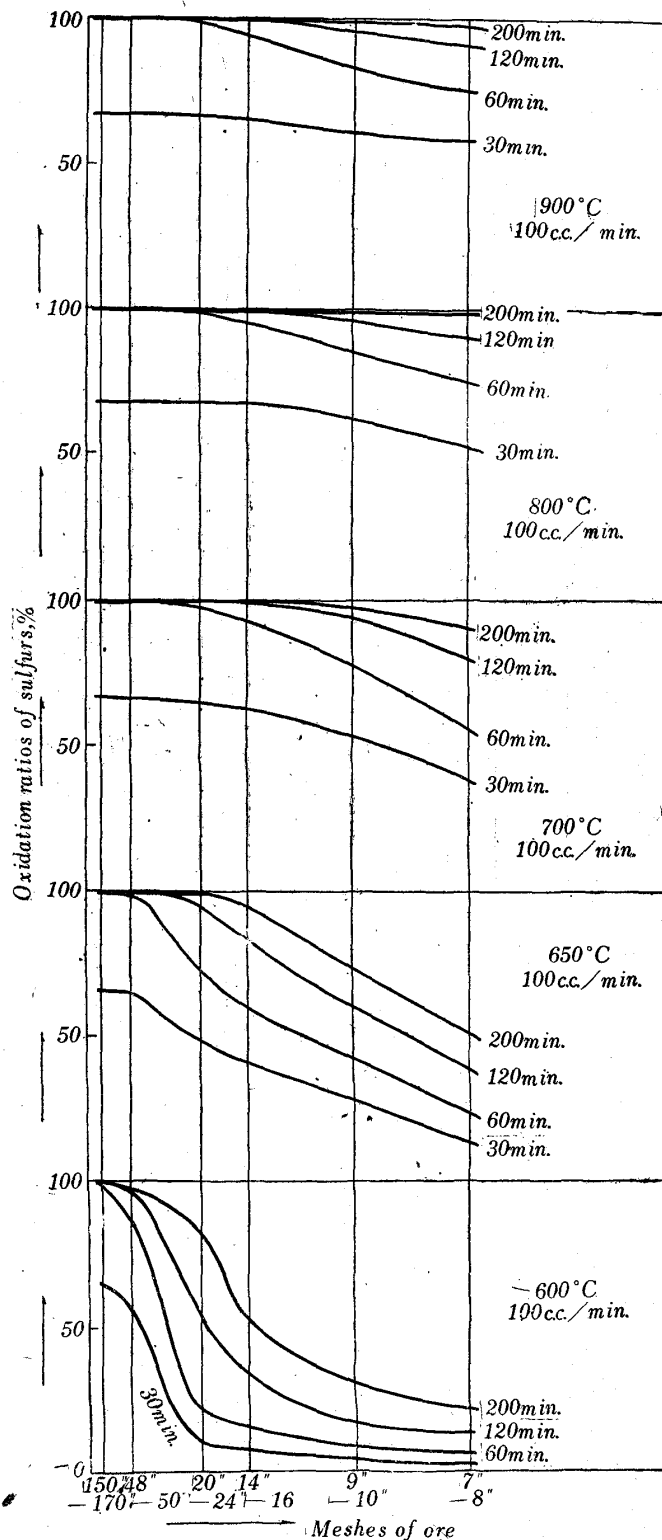


Fig. 8 (a).

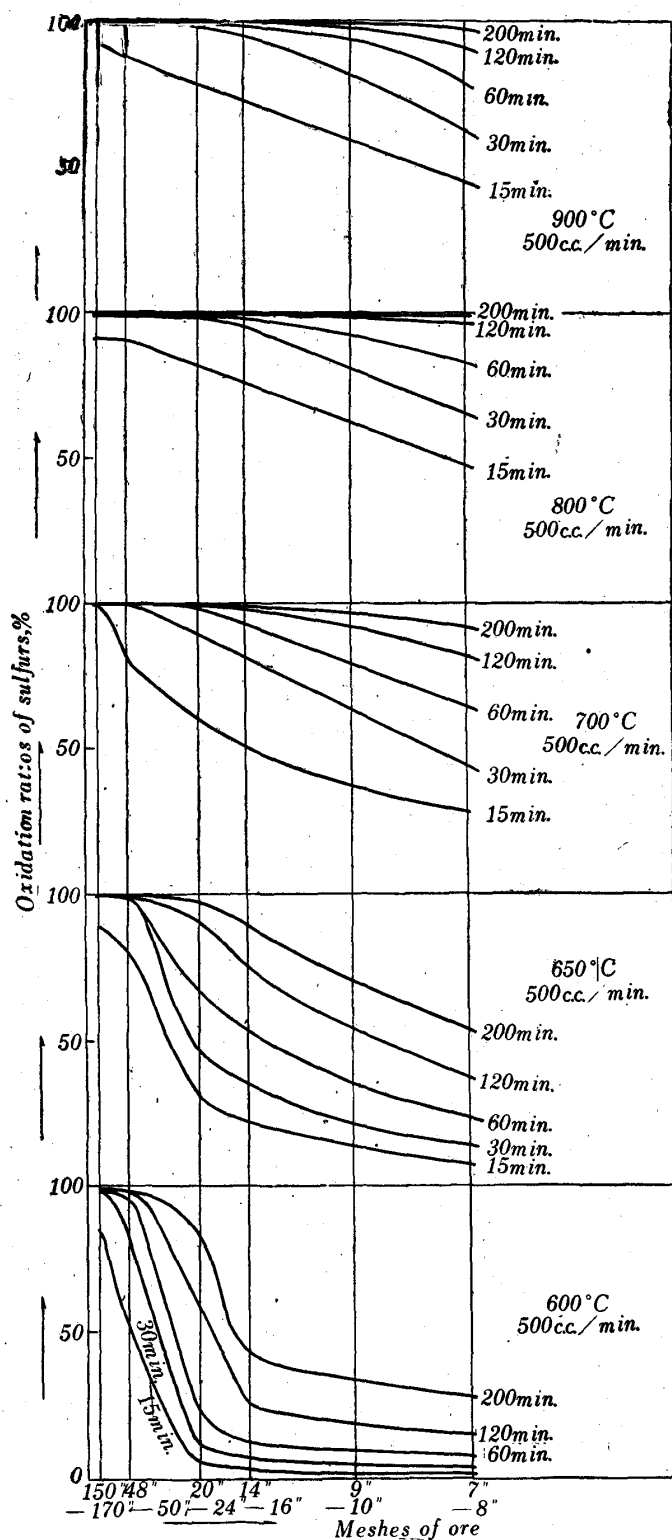


Fig. 8 (b).

with the decrease of meshes. The fall in the right side of the maximum point is presumed to be due to the fact that the concentration of sulfur dioxide is too high in this case.

sulfur trioxide.

Next, comparing the case of 100 c.c./min. with that of 500 c.c./min, the production ratios of sulfur trioxide are generally larger in the latter case than in the former one. This is presumably due to the presence of the excess of oxygen favourable to the production of sulfur trioxide. Both cases consist in the existence of maximum values between 650° and 700° C in the meshes above $20''\sim 24''$, but in the case of 100 c.c./min., this maximum point exists at about 650° C, while, on the contrary, in 500 c.c./min., it does so at about 700° C. This is presumed to be due to its transition to the higher temperature side, owing to the excess of oxygen. In both cases also, the inclination from 600° to the above maximum point becomes larger with the increase of grain size. This is obviously due to the marked increase of the absolute quantity of sulfur dioxide produced. Furthermore, the tendency of the transition of maximum point to the lower temperature side with the decrease of meshes follows since the favourable concentration to produce sulfur trioxide is gradually changed to the lower temperature part, owing to the increase of production ratio of sulfur dioxide

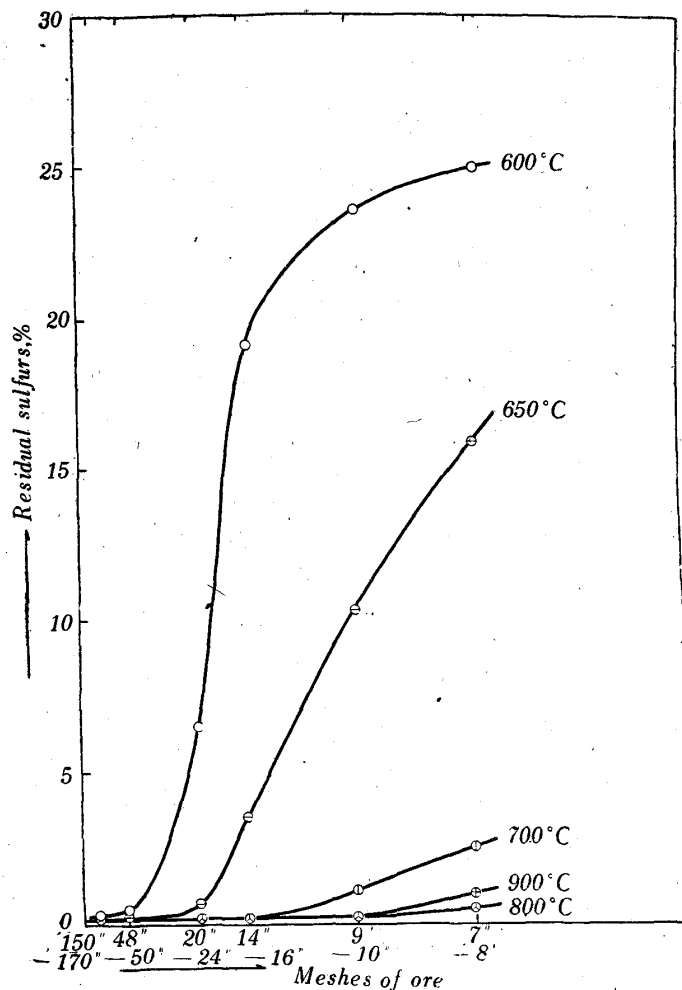


Fig. 9.

IV. Conclusion

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

1. The temperature range favourable for roasting is 700°~800° C. In this range, sufficiently great oxidation ratios are obtained in the roasting time within one hour up to the meshes of 20''~24''. In the case of air flow of 500 c.c./min./2g., the meshes up to 14''~16'' can be similarly used. 9''~10'' can also be oxidized in 2 hours.

2. The cinders, of each mesh, roasted in such a way as described above, contain residual sulfurs, which have become under 0.2 %, and are sufficiently available for iron-making.

3. For the purpose of lowering the production ratio of sulfur trioxide, it is better that the air flow is not excessive and the roasting temperature is brought near 800° C. The lower temperature part of the reaction chamber may be decreased even to 700° C.

Summary

Adopting the roasting process for the utilization of pyrrhotite, studies were made of the reciprocal relations among oxidation velocity, oxidation ratio, residual sulfurs

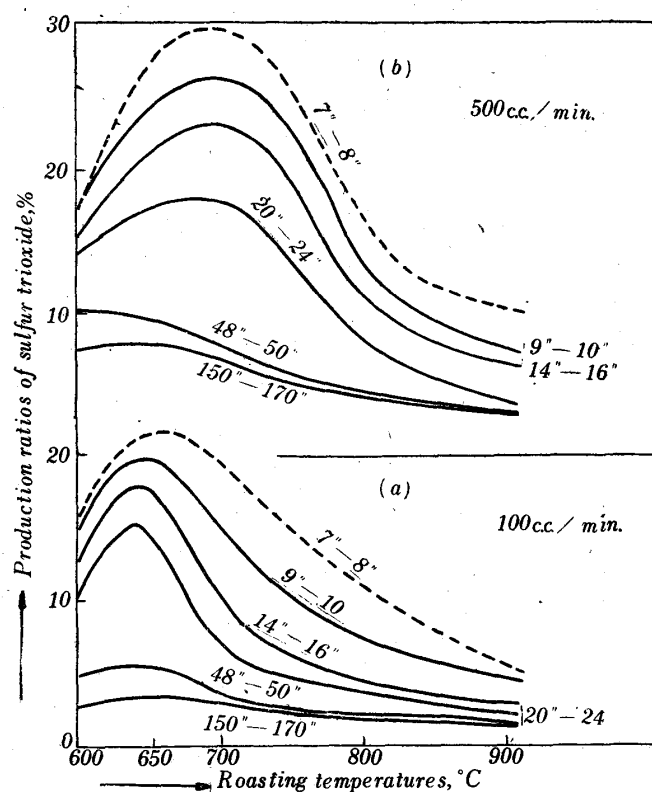


Fig. 10.

in the cinders and production ratio of sulfur trioxide in roasting gases, under the several following conditions:—

- (1) Flow of air (c.c./min./2 g.): 100, 150, 300, 500 and 1000.
- (2) Mesh of ore: 150'' ~ 170'', 48'' ~ 50'', 20'' ~ 24'', 14'' ~ 16'', 9'' ~ 10'', and 7'' ~ 8''.
- (3) Roasting temperature (°C): 600, 650, 700, 800 and 900.
- (4) Roasting time: Below 200 min.

The most favourable conditions were confirmed as follows:—

1. The temperature range favourable for roasting is 700°~800°C.
2. In the range described above, sufficiently great oxidation ratios are obtained in the roasting time within one hour up to the mesh of 20''~24'', even in case of 100 c.c./min./2 g.
3. The cinders, roasted in such a condition as described above, contain residual sulfurs which have become under 0.2%, and are sufficiently available for iron-making.

The authors wish to express their gratitude to the late Mr. Y. Inada, Bachelor of Engineering, who was engaged in preliminary experiments of this study, and to Mr. M. Tayama for his work on the analysis of samples and cinders, and to the Japan Steel Tube Co. Ltd. for their presentation of samples of pyrrhotite.

Further, the Scientific Research Grant from the Educational Department covered the greater part of the expenses of this work, and it is a pleasure for the authors to take this opportunity of expressing their hearty thanks.