# On the Removal of Copper from Pyrites Cinder and the Roasting of Pyrites

AUTHOR(S):

NISHIHARA, Kiyokado; KONDO, Yoshio

# On the Removal of Copper from Pyrites Cinder and the Roasting of Pyrites

By

Kiyokado NISHIHARA and Yoshio KONDO

Department of Metallurgy

(Received April 22, 1952)

## 1. Introduction.

Japan reserves 150 million tons of pyrites, and, moreover, her pyrrhotite reserve is estimated at 60 million tons. Thus the resources of iron sulphide minerals in Japan are very abundant.

These pyrites and pyrrhotite are mainly used as raw material of sulphuric acid, and pyrites cinder, which is discharged from the roasters im sulphuric acid plants, contains 55–60% of Fe, if they are not roasted together with low-grade sulphide or sulphur ore such as MATSUO ore. At present, owing to the shortage of foreign iron ore in Japan, a large quantity of pyrites cinder is being used as iron ore. For instance, it was planned, in 1951, to use 500,000 tons of pyrites cinder as iron ore. Formerly, the low iron content of pyrites cinder, which was due to the mixed roasting of it with low-grade ore, or its high sulphur content, had prevented its limitless use as iron ore. But the prevention of the mixed roasting of it with low-grade ore and the development of the cinder sintering method of fine iron ore increased the mixing ratio of pyrites with iron ore.

Pyrites cinder contains about 0.4% of Cu, so that the content of copper in pig iron is high when the mixing ratio of pyrites cinder is increased, and such high copper pig iron cannot be used for steel-making. Therefore, the mixing ratio of pyrites cinder has been limited as yet. In order to increase the mixing ratio, copper in pyrites cinder must be removed as much as possible before it is charged to the blast furnace.

Methods of the removal of copper from pyrites cinder are:

a. copper in pyrites or pyrrhotite is separated by flotation or by magnetic separation, previously,

b. copper in pyrites cinder is removed by flotation,
c. copper in pyrites cinder is removed by leaching, and
d. copper in pyrites cinder is converted into chloride by chloridizing roasting and is leached (Ramèn process).

Of these processes, a. and b. require the grinding of ore or cinder, but by these methods it is in some cases impossible to increase the degree of separation above a limited value because of the state of copper in ore or cinder. In d., the separation of copper is most complete and its degree is about 90%, but a large quantity of salt is required in this process, and that is the reason for its not being adopted in Japan at present.

When pyrites cinder is used as iron ore, it is not always necessary to remove copper from it completely, but it is desirable to deal with a large quantity of pyrites cinder without using such troublesome methods as grinding or chloridizing roasting, to decrease the copper content economically to less than some limited amount.

In this study, from this point of view, the most suitable condition of leaching copper from pyrites cinder was searched out, and in that leaching condition, pyrites cinder obtained from many sulphuric acid plants were leached and their properties were examined. The results showed that the kind of a roaster and the operating condition of separate roaster affect evidently the degree of leaching copper from pyrites cinder. Therefore the relation between the operating condition of a roaster and the degree of leaching copper from pyrites cinder was investigated, and on the basis of the results obtained, operating conditions of a mechanical roaster to increase the degree of leaching copper from pyrites cinder were studied.

## 2. Determination of Conditions of Leaching Copper from Pyrites Cinder.

As mentioned in 1, we investigated the condition of leaching copper from pyrites cinder, in which soluble copper in pyrites cinder could be leached perfectly and most economically. The conditions for the experiments were as follows:

a sample of cinder is not ground, water or dilute sulphuric acid is used as the leaching solution, leaching is performed at the room temperature, and solutions are continuously stirred by hand or by the sample jar rotating on a pot mill (in the latter case the number of rotation of the sample jar is 120–125 r. p. m.).

The influences of concentration of acid, stirring time, and pulp density on the leaching degree of copper were examined.

i. Influence of concentration of acid.

Cinder of a rotary kiln of NISSHIN Chemical Co., cinder of a Herreshoff furnace of KONOSHIMA Chemical Co., and cinder of a Herreshoff furnace of HIROHATA Iron and Steel Works were used. Acid concentration of the leaching solution was varied to 0, 10 and 30 g/L of sulphuric acid, and the influence of acid concentration on the leaching degree was studied. Leaching conditions in this case: 2 g of a sample, and 100 cc. of the leaching solution were used; time of leaching was 2 hours, and stirring was performed by hand. After leaching and filtrating off, the residues were washed five times with water. By analyzing the copper in the filtrate, the leaching degree of copper was determined.

Results are shown in **Table 1.** As shown in the table, the leaching degree of copper scarcely increases with the increment of acid concentration. Therefore, it is found that water or the solution of 5 g/L sulphuric acid can leach all soluble copper from pyrites cinder.

**Table 1**

| | Sample I | | Sample II | | Sample III | | Sample IV | |
|---|---|---|---|---|---|---|---|---|
| Concentration of acid, g/L | Soluble Cu, % | Leaching Degree of Cu, % | Soluble Cu, % | Leaching Degree of Cu, % | Soluble Cu, % | Leaching Degree of Cu, % | Soluble Cu, % | Leaching Degree of Cu, % |
| 0 | | | | | 0.14 | 33.5 | 0.22 | 61.2 |
| 5 | 0.07 | 15.2 | 0.09 | 21.9 | 0.24 | 57.3 | 0.21 | 58.4 |
| 10 | 0.06 | 13.1 | 0.10 | 24.4 | 0.25 | 59.5 | 0.22 | 61.2 |
| 30 | 0.06 | 13.1 | 0.14 | 34.2 | 0.28 | 66.7 | 0.26 | 72.2 |

Sample I : Cinder of NISSHIN Chemical Co. (Cu 0.46%, S 3.51%)
Sample II : Cinder of BEFU Chemical Co. (Cu 0.41%, S 2.67%)
Sample III: Cinder of KONOSHIMA Chemical Co. (Cu 0.42%, S 2.41%)
Sample IV : Cinder of HIROHATA Iron and Steel Works (Cu 0.36%, S 0.75%)

ii. Influence of Stirring Time.

Cinder of KONOSHIMA Chemical Co., and cinder of HIROHATA Iron and Steel Works were used as samples, and the influence of stirring time on the leaching degree of copper was studied. Stirring was performed by the rotation of a sample jar. Leaching conditions in this case: 2 g of a sample, and 100 cc. of the 5 g/L sulphuric acid solution were used, and stirring time was varied to 2, 5, 10, 30 and 60 minutes. Results are shown in **Table 2.** It is found that the degree of leaching scarcely varies with the stirring time, and that, from this, a short stirring time of 2 to 5 minutes is enough to leach all soluble copper.

**Table 2**

| | Sample I | | Sample II | |
|---|---|---|---|---|
| stirring time, min. | Soluble Cu, % | Leaching Degree of Cu, % | Soluble Cu, % | Leaching Degree of Cu, % |
| 2 | 0.21 | 50.0 | 0.23 | 63.9 |
| 5 | 0.27 | 64.3 | 0.25 | 69.5 |
| 10 | 0.23 | 54.8 | 0.22 | 61.1 |
| 30 | 0.28 | 66.7 | 0.22 | 61.1 |
| 60 | 0.21 | 50.0 | 0.27 | 75.0 |

Sample I : Cinder of KONOSHIMA Chemical Co. (Cu 0.42%, S 2.41%)
Sample II: Cinder of HIROHATA Iron and Steel Works (Cu 0.36%, S 0.75%)

**iii.** Influence of Pulp Density.

The same samples as used in **ii** were also used in this experiment. The influence of pulp density in the leachihg process on the degree of leaching was studied. In this case, 5, 10, 20, 30, 50, 75 and 100 g of a sample and 100 cc. of the 5 g/L sulphuric acid solution were used. Stirring time was 5 minutes for the sample of KONOSHIMA and 2 minutes for that of HIROHATA. Results are tabulated in **Table 3.** From the Table, it is evident that pulp density in the leaching process does not affect the degree of leaching copper. But from our experiences, it can be anticipated that the treatment of cinder is easy when pulp density is about 30%.

**Table 3**

| | Sample I | | Sample II | |
|---|---|---|---|---|
| Pulp density, % | Soluble Cu, % | Leaching Degree of Cu, % | Soluble Cu, % | Leaching Degree of Cu, % |
| 4.8 | 0.21 | 50.0 | 0.24 | 66.7 |
| 9.1 | 0.18 | 42.8 | 0.26 | 72.2 |
| 16.7 | 0.23 | 54.8 | 0.28 | 77.8 |
| 23.1 | 0.20 | 47.6 | 0.27 | 75.0 |
| 33.3 | 0.24 | 57.1 | 0.28 | 77.8 |
| 42.8 | 0.20 | 47.6 | 0.26 | 72.2 |
| 50.0 | 0.20 | 47.6 | 0.24 | 66.7 |

Sample I : Cinder of KONOSHIMA Chemical Co. (Cu 0.42%, S 2.41%)
Sample II: Cinder of HIROHATA Iron and Steel Works (Cu 0.36%, S 0.75%)

Taking account of the results above-mentioned, we adopted the following leaching conditions in the tests of leaching copper from pyrites cinder described hereafter.

i. Size and quantity of cinder: More than 100 g of cinder in a roasted state (not ground) is used.
ii. Leaching solution: 5 g/L sulphuric acid solution.
iii. Leaching temperature: Room temperature.
iv. Pulp density: 33%.
v. Stirring: Vigorous stirring is performed.
vi. Washing after leaching: With water of which the weight is 1/5 of cinder, cinder is washed several times.

### 3. Relation between the Properties of Pyrites Cinder and the Leaching Degree of Copper.

Properties of pyrites cinder varies according to many conditions such as the roasting condintion, and so the leaching degree of copper, that is, the content of soluble copper in pyrites cinder, also varies remarkably. From this reason, we examined the influence of the contents of residual total sulphur, sulphide sulphur, sulphate sulphur, the magnetic property and other properties of pyrites cinder on the leaching degree of copper. In these experiments, pyrites cinder used was, almost in every case, cinder of pyrites mined at the YANAHARA mine that produces the largest tonnage of pyrites in Japan. (Cinder of pyrites of the YANAHARA mine contains about 0.4% of copper.)

i. Leaching degree of copper and the content of residual sulphur.

The relation between the degree of leaching copper from cinder and the content of residual sulphur in it is illustrated in **Fig. 1.** In this experiment, the method of leaching was the same as introduced in **2.** From **Fig. 1,** it is found that a tendency lies that in cinder of a high residual sulphur content, the leaching degree of copper is low.

It is desirable that the copper content in pyrites cinder is below 0.2% when it is used as raw material for iron manufacture. As shown in the figure, the degree of the leaching of copper reaches 50% in cinder of which the residual sulphur content is below 3%. In such pyrites cinder, the content of copper after leaching becomes less than 0.2%. It is also found that cinder of a rotary kiln shows in every case a lower leaching degree than that of a multiple-hearth roasting furnace.

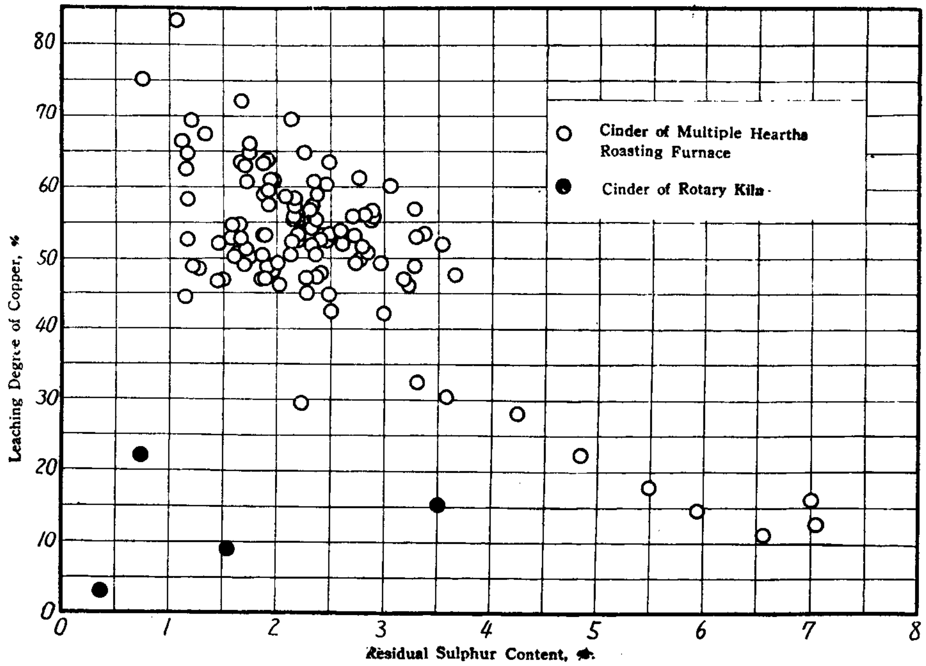


**Fig. 1.** Relation between Leaching Degree of Copper and Residual Sulphur Content in Pyrites Cinder.

**ii.** Leaching degree of copper and the content of sulphide sulphur.

The same as in **3, i,** the relation between the leaching degree of copper and the sulphide sulphur content in cinder is shown in **Fig. 2.** In this figure, the value of sulphide sulphur means the value of total residual sulphur minus the value of water soluble sulphur. As shown in the figure, the leaching degree of copper becomes lower when the sulphide sulphur content is higher. In order to decrease the content of copper in pyrites cinder after leaching to less than 0.2%, it is required to reduce the content of sulphide sulphur to less than 2.5%. In this figure also, cinder of a rotary kiln has a lower value of leaching degree of copper and it does not correspond to the sulphur content.

**iii.** Leaching degree of copper and the content of sulphate sulphur.

**Fig. 3** shows the relation between the degree of leaching copper from cinder and the content of sulphate sulphur in it. As shown in the figure, the content of sulphate sulphur is higher in cinder of a multiple-hearth roasting furnace than in cinder of a rotary kiln. The degree of leaching copper shows above 50% in cinder of which the sulphate sulphur content is more than 0.5%. n cinder of a multiple-hearth roasting furnace, the high residual sulphur

I

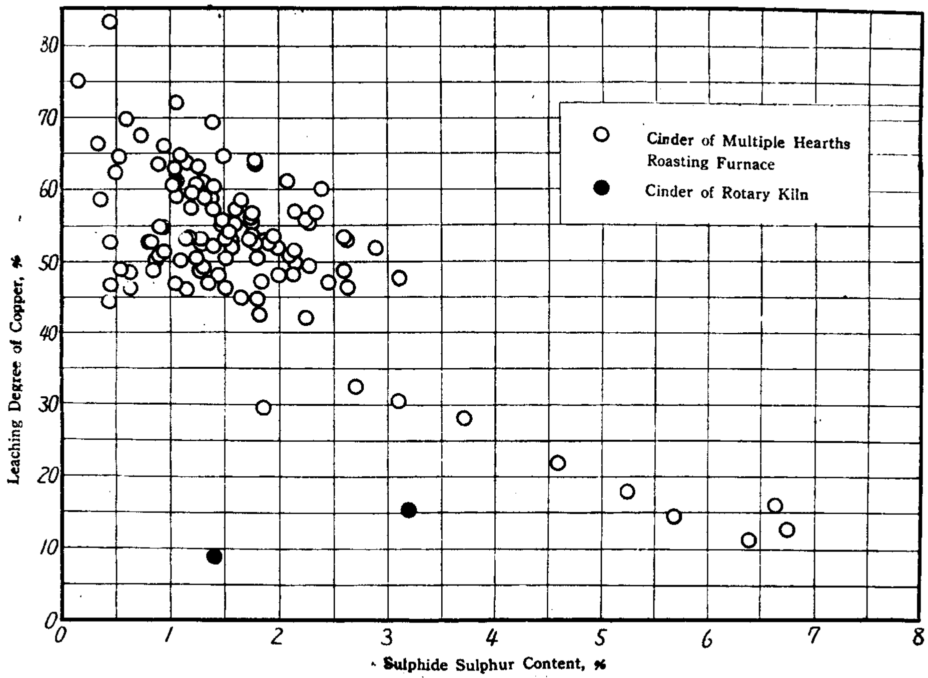


**Fig. 2.** Relation between Leaching Degree of Copper and Sulphur Content in Pyrites Cinder.

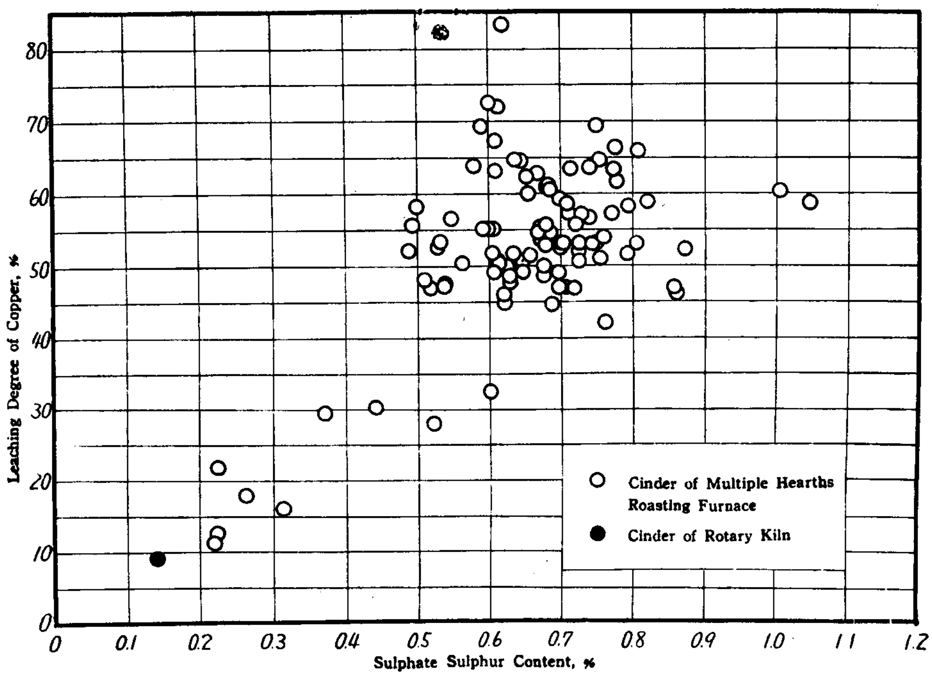


**Fig. 3.** Relation between Leaching Degree of Copper and Sulphate Sulphur Content in Pyrites Cinder.

content means the low sulphate sulphur content, and the latter has the value of about 0.7% when the residual sulphur content is below 3%.

As shown later, in the roasting of pyrites in a multiple-hearth roasting furnace, the sulphate sulphur content of cinder increases evidently when ore reaches the second or the third hearth from the lowest.

iv. Leaching degree of copper and the magnetic property of cinder.

The relation between the magnetic property of cinder and the leaching degree of copper was previously studied by MORIMUNE (1). In our study, several tests were made on this point and it was certified that the same tendency as noted by MORIMUNE existed. Results of the experiments are shown in **Table 4.** In this table, (A) shows the relation between the leaching degree of copper and the weight percentage of the magnetic part of cinder ground in an agate mortar. The magnetic separation was performed with a permanent magnet. The residual total sulphur content, and the sulphate sulphur content are also tabulated in it. The leaching degree of copper becomes higher and

**Table 4**

(A)

| Sample No. | Weight % of magnetic part | Weight % of non-magnetic part | Leaching Degree of copper, % | Residual total sulphur, % | Sulphate sulphur, % |
|---|---|---|---|---|---|
| H-6 | 99.0 | 1.0 | 11.1 | 6.56 | 0.22 |
| H-4 | 63.1 | 36.9 | 52.9 | 3.30 | 0.68 |
| H-7 | 52.9 | 47.1 | 29.4 | 2.23 | 0.37 |
| H-1 | 34.0 | 66.1 | 69.4 | 2.13 | 0.75 |
| H-9 | 24.6 | 75.4 | 58.2 | 2.16 | 0.50 |
| H-2 | 23.9 | 76.1 | 69.4 | 1.20 | 0.59 |
| H-8 | 22.7 | 77.3 | 63.2 | 1.88 | 0.61 |
| H-5 | 21.3 | 78.7 | 63.9 | 2.26 | 0.58 |
| H-3 | 12.2 | 87.9 | 83.3 | 1.07 | 0.62 |

(B)

| | Weigt percentage | Copper content, % | Leaching Degree of copper, % |
|---|---|---|---|
| Initial sample | 100 | 0.31 | 48.4 |
| Magnetic part | 29.7 | 0.35 | 28.5 |
| Non-magnetic part | 70.3 | 0.28 | 60.7 |

the residual total sulphur content becomes lower when weight percentage of the magnetic part gets smaller, excepting a few samples of a large magnetic part. In the case of these exceptional samples, the sulphate sulphur content is comparatively high, in spite of high percentage of the magnetic part.

The results of magnetic separation, the copper contents in the magnetic and non-magnetic parts and the leaching degree of copper in each part in the representative examples are shown in (B) of the same table. As shown in this table, the content of copper is higher in the magnetic part and lower in the non-magnetic part than in the initial sample. The leaching degree of copper is remarkably higher in the non-magnetic part, as compared with the magnetic part.

v. Other properties.

In general, red hematite colour appears in the pyrites cinder perfectly roasted, except a few examples. In such perfectly roasted pyrites cinder, the leaching degree of copper is high. On the other hand, pyrites cinder roasted imperfectly, which contains much residual sulphur, shows blackish colour and its leaching degree of copper is low. As to cinder of a multiple-hearth roasting furnace, the relations above-mentioned can be concluded, but as to cinder of a rotary kiln, in even the dead roasted one of a low residual sulphur content, its colour is blackish, and generally it has a low leaching degree of copper.

Of the section of a particle of cinder, circumferential part near the surface shows red hematite colour where the roasting is perfect, but in the center of the particle, as the roasting is imperfect, the colour is blackish. The center of cinder is remarkably magnetic compared with the circumferential part.

It is concluded from the results above-mentioned that pyrites cinder, especially cinder roasted in the multiple-hearth roasting furnace, shows the following properties:

| favorate cinder | unfavorate cinder |
|---|---|
| residual sulphur content is low, | residual sulphur content is high, |
| sulphate sulphur is above 0.5% | sulphate sulphur is below 0.5% |
| non-magnetic, | magnetic, |
| high leaching degree of copper. | low leaching degree of copper. |

## 4. Roasting of Pyrites Cinder.

As mentioned in the previous section, cinder imperfectly roasted shows a low leaching degree of copper. To increase the leaching degree of copper of such imperfectly roasted cinder, it is proper to roast it again at temperatures between 400°C and 600°C, that is, above the oxidation temperature of copper sulphide and below the formation temperature of copper ferrate. This fact is already explained by MORIMUNE. In this study also, the roasting was performed with three kinds of pyrites cinder of different residual sulphur contents, and the relation between the temperature or time of roasting and the degree of leaching copper from roasted products was inquired.

Samples used in this experiment are cinder of a Herreshoff furnace of HIROHATA Iron and Steel Works, cinder of a Herreshoff furnace of KONOSHIMA Chemical Co., and cinder of a rotary kiln of NISSHIN Chemical Co., each ground to the minus 48 mesh size. The sample put in a porcelain boat is inserted into a horizontal type resistance electric furnace previously kept at a definite temperature, and after the temperature of the boat reaches that of the furnace, the boat is kept at that temperature for a definite time. Then, the boat is taken out of the furnace, and cooled in a desiccator, and the leaching test is performed, of which leaching conditions are described previously in **2**. By analyzing copper in the leached solution, the degree of leaching copper from cinder is determined. Results are shown in **Fig. 4.** As shown in the figure, the leaching degree of copper increases in the samples roasted at 400°, 500° and 600°C, and the increasing rate becomes larger as cinder is roasted at higher temperatures. At the roasting temperatures of 500° and 600°C, the leaching degree of copper reaches a definite value after one hour of roasting, and even after a longer roasting time, it does not increases anymore. Nevertheless, at 700°C, the leaching degree of copper decreases. It is considered that this is caused by the formation of copper ferrate. With cinder of HIROHATA, the leaching degree of copper decreases even in a shorter time of roasting when it is roasted at 700°C, but with cinder of a higher residual sulphur content, such as of KONOSHIMA or of NISSHIN Chem. Co., when the roasting time is short, the the degree of leaching increases slightly and after a longer roasting time the leaching degree decreases.

It is considered from the experiments in **3** and **4**, that greater part of copper in pyrites cinder imperfectly roasted, especially roasted in a multiple-hearth roasting furnace, exists in the state of copper sulphide and because of this, the leaching degree is low; on the other hand, much of copper in cinder perfectly roasted is in the state of copper sulphate and its leaching degree is high.

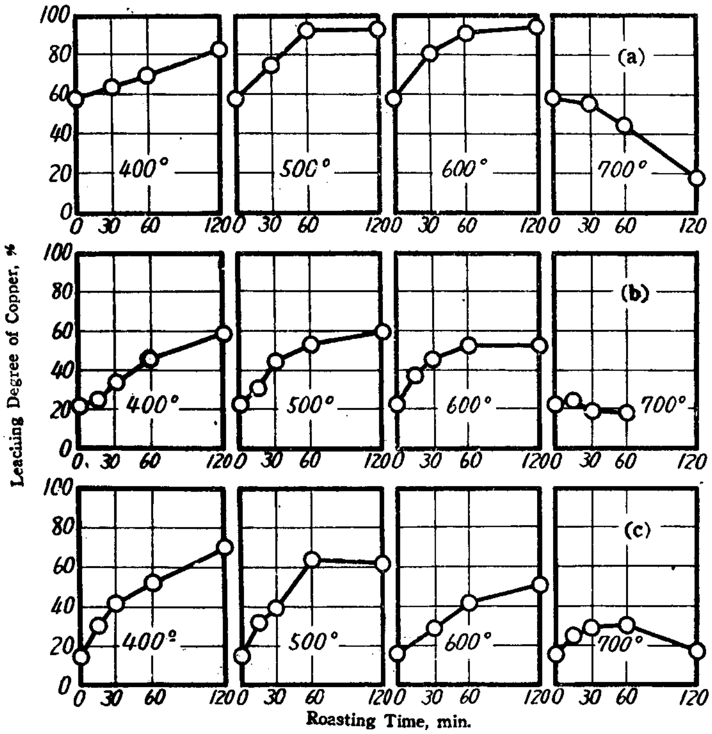


**Fig. 4.** Roasting of Cinder.

( a ): Cinder of HIROHATA Iron and Steel Works (Cu 0.36%, S 0.75%)
( b ): Cinder of KONOSHIMA Chemical Co. (Cu 0.42%, S 2.41%)
( c ): Cinder of NISSHIN Chemical Co. (Cinder of Rotary Kiln)(Cu 0.46%, S 3 .51%)

## 5. Relation between the Roasting Condition of Pyrites and the Leaching Degree of Copper.

As shown in the experiment of 4, the leaching degree of copper increases when pyrites cinder is roasted again in air at temperatures from 400° to 600°C. It is more convenient to roast pyrites perfectly and discharge trom the roasting furnace pyrites cinder, which has a high leaching degrees of copper and low residual sulphur, simultaneously.

About 85% of sulphuric acid plants in Japan are equipped with multiple-hearth roasting furnaces such as the Herreshoff furnace, for the purpose of roasting pyrites or elementary sulphur ore (2); therefore, in this study the roasting conditions of pyrites in the multiple-hearth roasting furnace were investigated. The roasting conditions of pyrites were pursued, in order to make it possible to decrease the residual sulphur content in pyrites cinder and increase the leaching degree of copper as much as possible. Moreover, when such roasting conditions were autually adopted, researches were made in point of whether the roasting capacity of the furnace could be increased or not.

i. Roasting furnaces which were used in investigation and the methods of investigation.

Roasting tests were performed in the Herreshoff furnace of 7 hearths, the Wedge furnace of 8 hearths and the Herreshoff furnace of 9 hearths. Types and dimensions of these furnaces are shown in **Table 5.**

**Table 5**

| Type | Herreshoff | Wedge | Herreshoff |
|---|---|---|---|
| Number of hearths | 7 (except drying hearth) | 8 (except drying hearth) | 9 (except drying hearth) |
| Diameter, m. | 5.42 | 5.94 | 5.94 |
| Height, m. | 5.62 | 7.16 | 8.16 |
| Area of total hearths, $m^2$. | 130 | 146 | 209 |
| Revolving velocity of arm, sec./rev. | 86, 75 and 67 | 168 | 124 and 144 |
| Number of teeth per arm | 14 and 16 | 6 | 12 |
| Size of air-hole | 200 mm. × 200 mm. | 200 mm. dia. | 200 mm. × 200 mm. |
| Number of air-hole | 6 | 12 | 6 |
| Normal capacity, t/d | 12.5 | 20 | 20 |
| Charging rate, t/d | 15[1)] | 19.2[2)] | 20[1)] |

1): Ore roasted is pyrite of YANAHARA mine.
2): Ore roasted is mixed ore composed of pyrite of YANAHRAA mine and iron concentrate of pyrrhotite of KAWAYAMA mine.

**Table 6**

| | YANAHARA ore | KAWAYAMA ore |
|---|---|---|
| Charging rate t/d | 12.0 | 7.2 |
| Mixing ratio % | 62.5 | 37.5 |

Total charging rate is 19.2 t/d.

The ore used in the test which was performed in the Herreshoff furnace of 7 hearths was pyrites of the YANAHARA mine crushed and screened with a 8 mm. sieve. In the test of the Wedge furnace of 8 hearths, the ore used was mixed ore composed of pyrites of the YANAHARA mine and iron concentrates of pyrrhotite of the KAWAYAMA mine, of which the mixing ratio is shown in **Table 6.** In the latter case, pyrites of the YANAHARA mine was crushed to the minus 6 mm. size and the moisture of pyrrhotite concentrate was 8.51%. In the test of the Herreshoff furnace of 9 hearths, pyrites of YANAHARA was crushed and screened with a 8 mm. sieve. The charging rate of pyrites is controlled by the adjustment of the length of a scraping knife which is situated upon the drying hearth and attached to the central shaft of the furnace. The quantity of ore is weighed and charged into a hopper above the furnace every two hours.

The roasting test, as a rule, continued 24 hours for each condition, and the sample of cinder was taken from the outside of the lowest hearth every four hours, and the sample of ore was taken from each roasting hearth 24 hours after the beginning of the test. They are cooled in a sealed vessel made of iron, and the total sulphur content and the water soluble sulphur content were analyzed. The test of leaching copper was performed with each sample and the contents of soluble copper and soluble iron were analyzed. The gas temperatures in the roasting hearths and the flue are measured every two hours with an alumel-chromel thermocouple which is inserted about 60 cm. into the furnace through the man-hole. The pressures of gas in the roasting hearths and the flue were also measured every two hours with an inclined manometer. The surface temperature of ore in the furnace was measured by an optical pyrometer occasionally. About 20 hours after the beginning of the roasting test, contents of $SO_2$ and $O_2$ in the flue gas and the gas in each hearth were measured with Reich's and Orsat's apparatus. One thing that can be regarded as a " lead " in the operation of the roasting furnace is " the boundary of the red heat zone ", that is, to inspect the extent of ore keeping dark red. In this experiment, the extent of dark red heat of ore at the instant of its being raked off by the teeth of the arm is defined as " the boundary of the red heat zone ", and it is respesented by the number of teeth counted from the end of the arm near the hole through which ore falls into the hearth. This boundary was measured every two hours from the beginning of the test.

ii. About the roasting test (the method of supplying air for combustion).

The following two methods of supplying air for combustion were tried in the roasting of pyrites or pyrrhotite in the multiple-hearth roasting furnace:

Method A; This is the formal method of the operation; air is supplied exclusively to the lowest hearth.

Method B: This is the method which was tried by the present authors; greater part of air is supplied to the third hearth from the lowest where ore still keeps dark red. In this method the quantity of air supplied to the lowest hearth is decreased to the amount necessary and sufficient for the combustion of ore present both in the second hearth from the lowest and in the lowest.

With each roasting furnace mentioned above, comparison of the two methods of operation was made in point of the contents of residual sulphur and sulphate sulphur, the leaching degree of copper of cinder, operating conditions and the roasting capacity of the furnace, and so forth.

**iii.** Results of the roasting tests.

**a.** Comparison of Methods A and B

With the Herreshoff furnace of seven hearths of which the charging rates are 15 t/d and 16.8 t/d, the following two operations were compared:

A. Air for combustion is supplied exclusively to the seventh hearth.

B. Greater part of air is supplied to the fifth hearth, and the quantity of air supplied to the seventh hearth is decreased to 1/8–1/10 compared with the instance of A.

Usually, with the multiple-hearth roasting furnace, air for combustion is supplied through the air-hole of the lowest hearth, but by this method the exact control of the quantity of air is made difficult, and so in this experiment, air is supplied through the windows, made where man-holes are in the fifth and seventh hearths, instead of the air-hole. That is to say, the doors of man-holes in the fifth and seventh hearths are removed and, instead of them, iron plates, each having a rectangular window of 100 mm. × 300 mm. in its center, are affixed to them as covers, and a shutter is put to each window in order to control its opening and closing. Air is supplied through these windows.

When the charging rate is increased, the lower limit of the dark red heat zone comes down, and even the ore in the lowest hearth gets in a state of dark red heat, and in this stage of operation, obstacles occur. So, in this test, by the control of the opening of the windows and by the control of the pressure of the fan exhausting $SO_2$ gas, the boundary of the red heat zone was adjusted.

The results of the test are shown in **Fig. 5.** As shown in this figure, in both cases of the charging rates of 15 t/d and 16.8 t/d, the residual sulphur content in cinder is lower in "B" than in "A" which is the formal method of operation. The content of soluble copper in pyrites cinder is somewhat increased in "B", compared with that in "A". But by the both methods of operation, fairly good results are brought about. The $SO_2$ content of flue gas scarcely changes, and the gas temperature is caused to go up 20–30 more degrees in the second and third hearths by the increment of the charging rate, in both methods. The surface temperature of ore also scarcely varies in both "A" and "B", while in "B" the temperature is somewhat lower. The distribution of the pressure of gas scarcely changes either in "A" or "B".

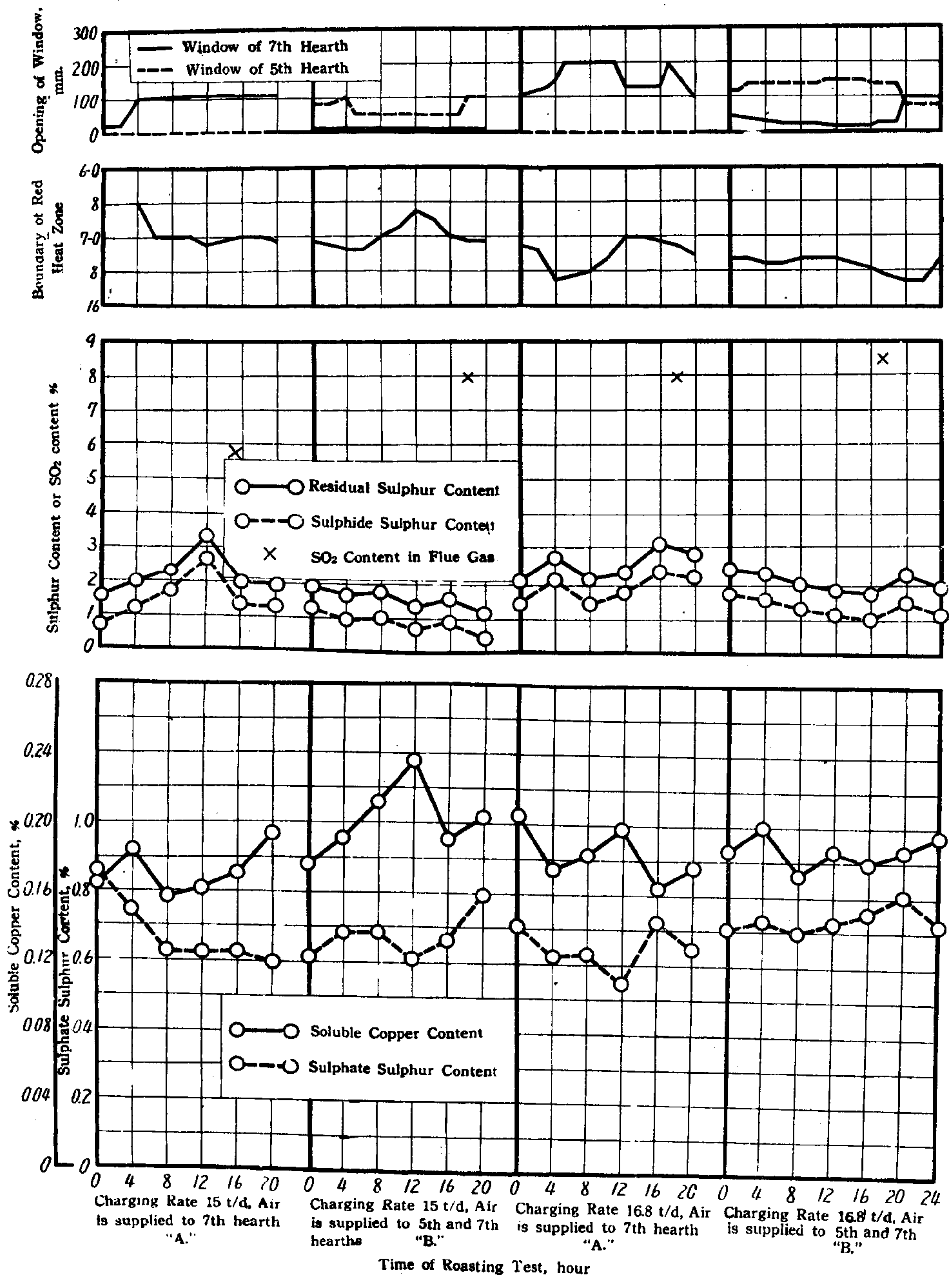


**Fig. 5.** Roasting Test of Seven Hearths Herreshoff Furnace.

Next, similar tests of roasting were performed with the Herreshoff furnace of nine hearths. Previously, the iron plates, through each of which a rectangular window of 150 mm. × 300 mm. was opened in the center, were attached to the man-holes of the seventh, eighth and ninth hearths, shutters having been affixed to them. The air for combustion was supplied through these windows and its quantity was controlled by adjusting these openings.

The following tests, similar to those with the Herreshoff furnace of seven hearths, were performed at the charging rates of 20 t/d and 22 t/d:

A: The same as in the formal method of operation, air is supplied exclusively to the lowest hearth.

B: Greater part of air is supplied to the seventh hearth and a limited quantity of air is supplied to the ninth hearth.

Comparisons were made of these two kinds of operations. In this test, the adjusting of the boundary of the red heat zone was carried out by the control of the opening of windows without controlling the pressure of the fan.

Results of the roasting tests are shown in **Fig. 6.** As shown in it, in both cases of the charging rates of 20 t/d and 22 t/d, by the method of "B" where the greater part of air for combustion is supplied to the seventh hearth, the residual sulphur content in cinder decreases, compared with that in "A". In more than eight hours from the beginning of the test, it decreases to below 2%. The soluble copper content also increases evidently more in "B" than in "A". With almost all samples of "B", the content of soluble copper is more than 0.175%. In the method of "A", at the normal charging rate of the furnace, that is, 20 t/d, the residual sulphur content shows the value of 2–3%. But by the increment of the charging rate up to 22 t/d, it increases remarkably, and due to this, the content of soluble copper in pyrites cinder is decreased. Contrary to this, in the method of "B", the content of residual sulphur is scarcely increased and the content of soluble copper is not decreased by the increment of the charging rate. The lower boundary of the red heat zone in the roasting furnace comes down remarkably and even in the lowest hearth ore is caused to appear dark red by the increment of the charging rate in the case of "A". But in "B", the increment of the charging rate does not effect transition of the boundary of the red heat zone. The maximum temperature in the furnace is increased a little by the increment of the charging rate in both cases of "A" and "B", difference between them being hardly noticeable. In "A", nevertheless, the lower boundary of the red heat zone comes down with the increment of the charge, and so the temperature of the lowest hearth goes up. The content of $SO_2$ in flue gas is 6–10%, and it is found that the maximum content

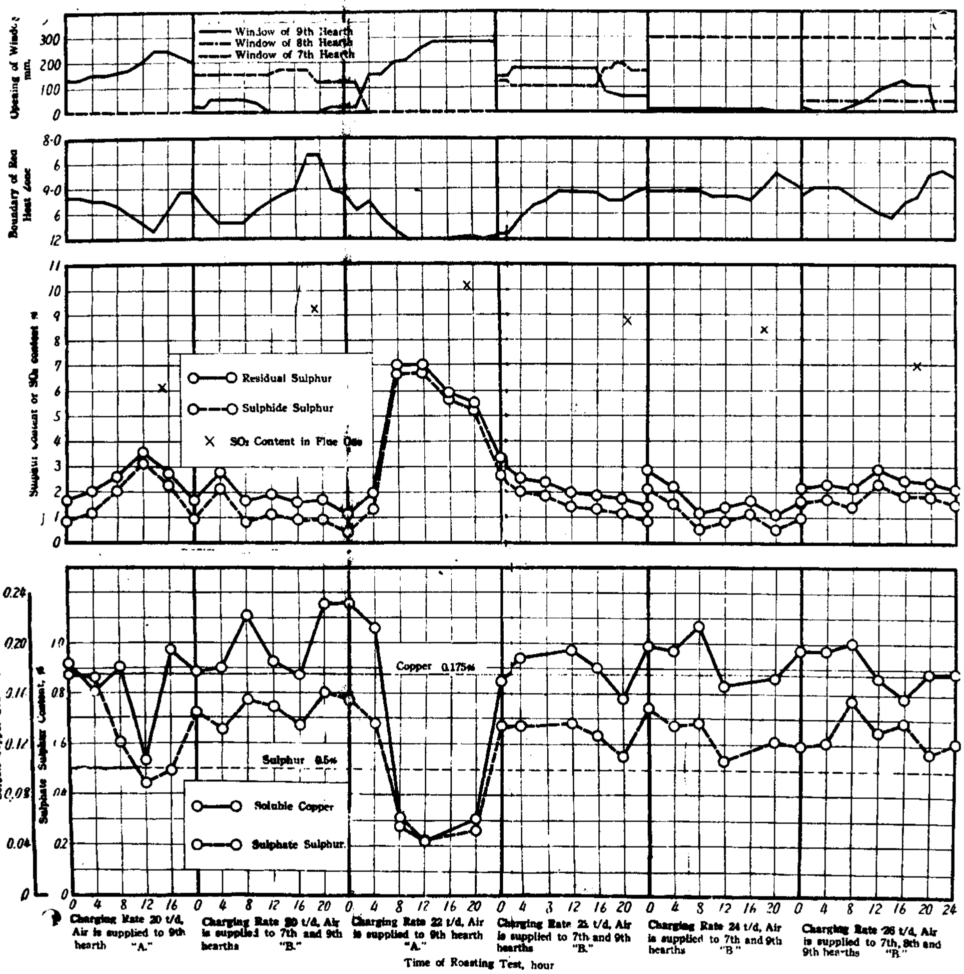


**Fig. 6.** Roasting Test of Nine Herreshoff Furnace.

is reached at the charging rate of 22 t/d and by the method "A", owing to the shortage of air supply. However, in "A" and "B", no remarkable difference can be found in this point. Also, in both cases, the formation of sintered cake could not be found throughout the test.

In the next stage, with the "B" method of air supply, the roasting tests were continued at the charging rates of 24 t/d and 26 t/d. In these cases, as shown in **Fig. 6**, the content of residual sulphur increases little, and is 2% even at the charging rate of 26 t/d. The content of soluble copper in cinder does not decrease and mostly shows the value more than 0.175%. From these facts, it becomes possible, by the use of the method "B", to increase the charging rate beyond the normal capacity of the roasting furnace. Any remarkable variations can not be found in the maximum temperature of the furnace, in the $SO_2$ content of flue gas, in the distribution of the pressure of gas in the furnace and in the formation of sintered cake.

**b.** Variation of the contents of sulphur and soluble copper in ore in the roasting furnace.

The authors tested the method of roasting which decreased the residual sulphur content as much as possible while increasing the content of soluble copper, and showed that this method was effective. Regarding the causes of these phenomena, the following consideration is given on a few examples from the point of the relation between the roasting condition and the contents of sulphur and soluble copper in ore in the hearths of the roasting furnace.

**Fig.** 7 shows the comparison between "A", which is the formal method, and "B", in which the greater part of air is supplied to the sixth hearth, with

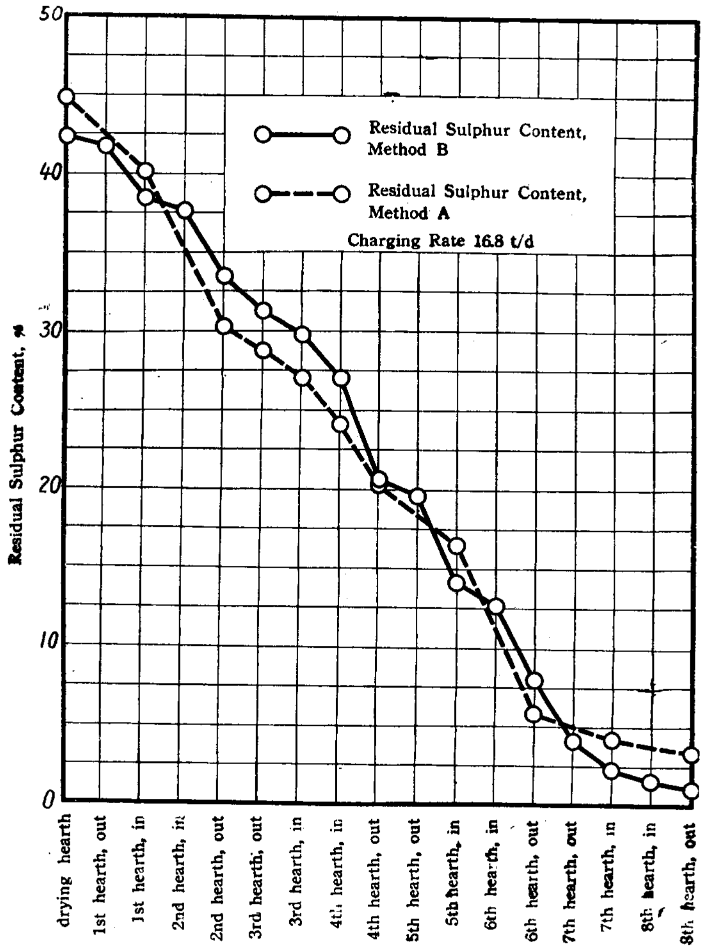


**Fig. 7.** Roasting Test of Eight Hearths Wedge Furnace.

the Wedge furnace of eight hearths. Any remarkable difference between "A" and "B" can not be found in the content of sulphur in ore present in hearths up to the sixth from the drying hearth. However, in "B", the decrement of the sulphur content appears in the seventh and eighth hearths as yet. This fact shows that oxidation continues in these hearths.

In the roasting of pyrites or mixed ore of pyrites and pyrrhotite in a multiple-hearth roasting furnace, the supply of air to the lowest hearth cools the ore in lower hearths of the furnace. On the other hand, the particle of ore increases thickness of its oxide layer on its surface going down the roasting furnace, and so, its rate of oxidation and the quantity of heat produced in unit time decreases. Due to this, by cooling with air, the temperature of the particle of ore at last goes down to less than its oxidatipn temperature, and oxidation is interrupted and, in spite of the presence of an unroasted kernel in the particle, ore is discharged as it is from the furnace. On the contrary, when the greater part of air is supplied to the upper hearths and the quantity of air supplied to the lowest hearth is decreased as in "B", the cooling of ore by air in the lower part of the furnace decreases, and even in the stage of a thickened oxide layer on the surface of ore and a decreased quantity of heat produced in unit time, the particle keeps a temperature above its oxidation temperature longer than in "A", and accordingly oxidation continues longer. In **Fig. 7** (curve B), on account of this, the decrement of the sulphur content is observed in the seventh and eighth hearths. It is evident that this has a favorable effect on the decrement of residual sulphur and the increment of the leaching degree of copper in pyrites cinder.

**Fig. 8** shows the influence of the methods of air supply on the contents of total sulphur, sulphate sulphur, soluble copper and soluble iron in the ore, at the charging rate of 22 t/d of the Herreshoff furnace of nine hearths. As evident in this figure, any difference in the sulphur content is hardly found in hearths up to the fifth from the drying hearth in the both methods of operation, but in the "B" method, the content of sulphur decreases remarkably below the sixth hearth, compared with the case of "A", and it is already about 2% in the eighth hearth. That is, in the method "B", the rate of oxidation of ore is accelerated and the roasting furnace of nine hearths functions the same as the roasting furnace of eight hearths or of seven hearths. And in the method of "B", from the sixth hearth downward, where the sulphur content remarkably decreases, the content of sulphate sulphur increases, and the contents of soluble copper and soluble iron also increase simultaneously. On the contrary, in "A" method, the lower boundary of the red heat zone comes

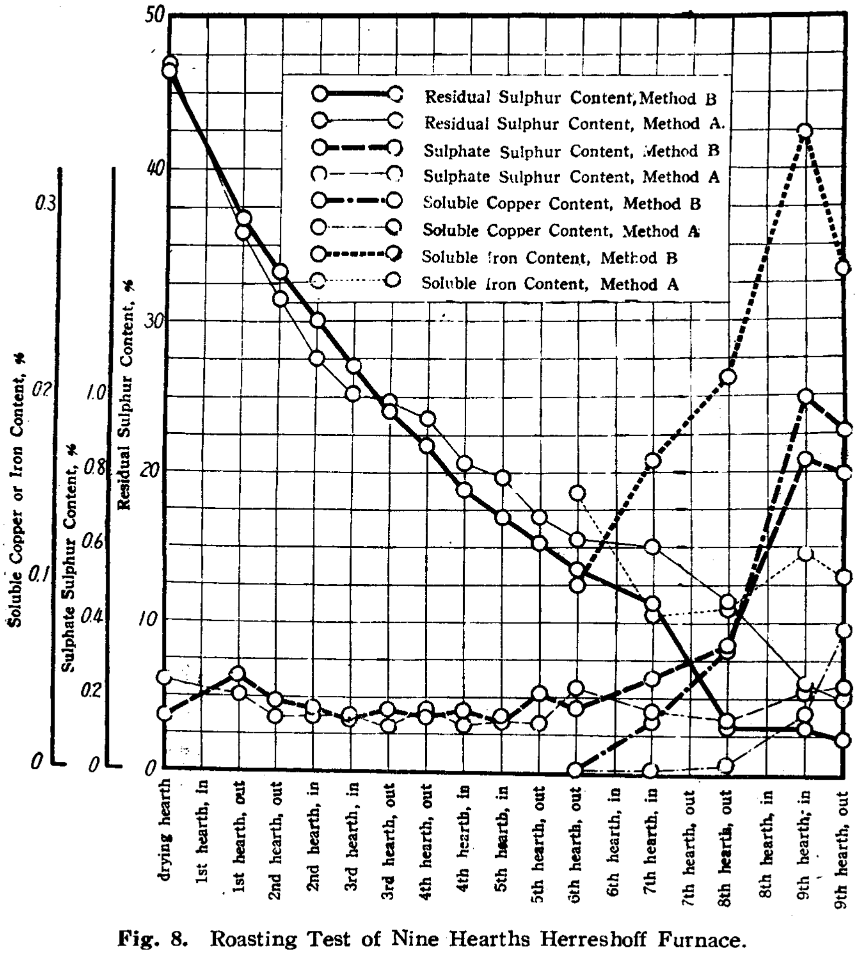


**Fig. 8.** Roasting Test of Nine Hearths Herreshoff Furnace.
(Charging Rate 22 t/d)

down, and the content of residual sulphur does not decrease comparatively even below the sixth hearth and the content of sulphate sulphur scarcely increases even on the outside of the ninth hearth. The content of soluble copper little increases below the eighth hearth.

At the charging rates of 24 t/d and 26 t/d by the roasting method of "B", the same tendencies as above are recognized in the contents of total sulphur, sulphate sulphur, soluble copper and soluble iron. That is, the content of sulphate sulphur in cinder is above 0.5% and the degree of leaching copper from cinder is above 50%, as shown in **Fig. 9** and **10.**

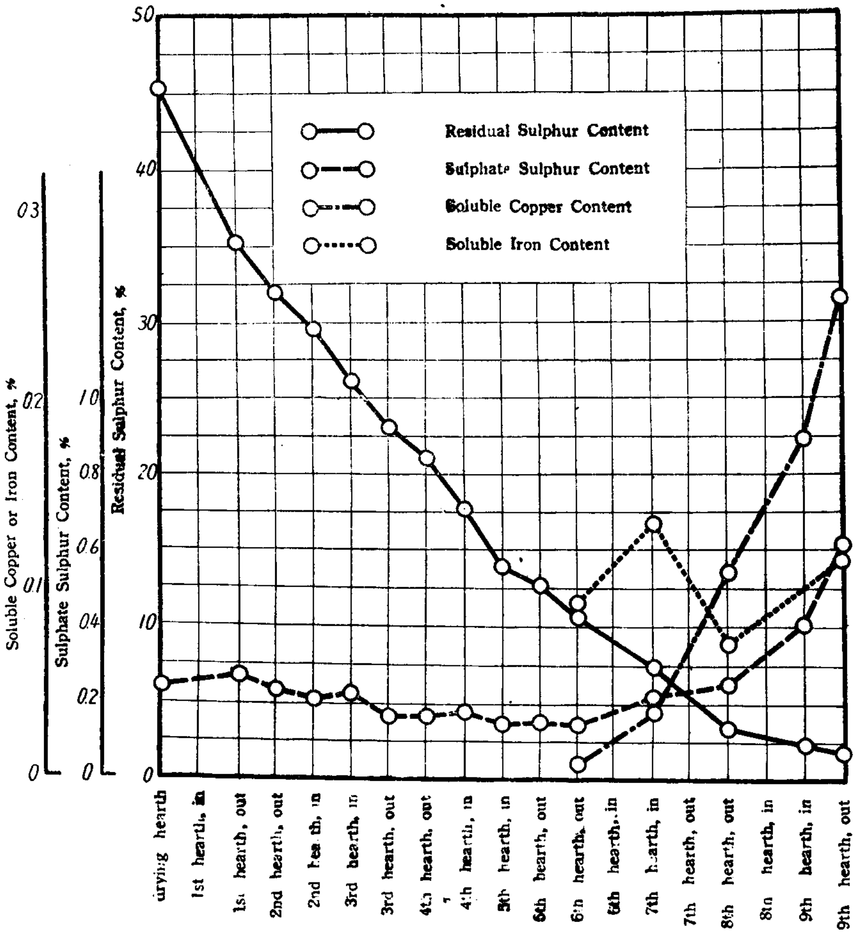


**Fig. 9.** Roasting Test of Nine Hearth Herreshoff Furnace.
(Charging Rate 24t/d, Air is supplied to 7th and 9th hearth)

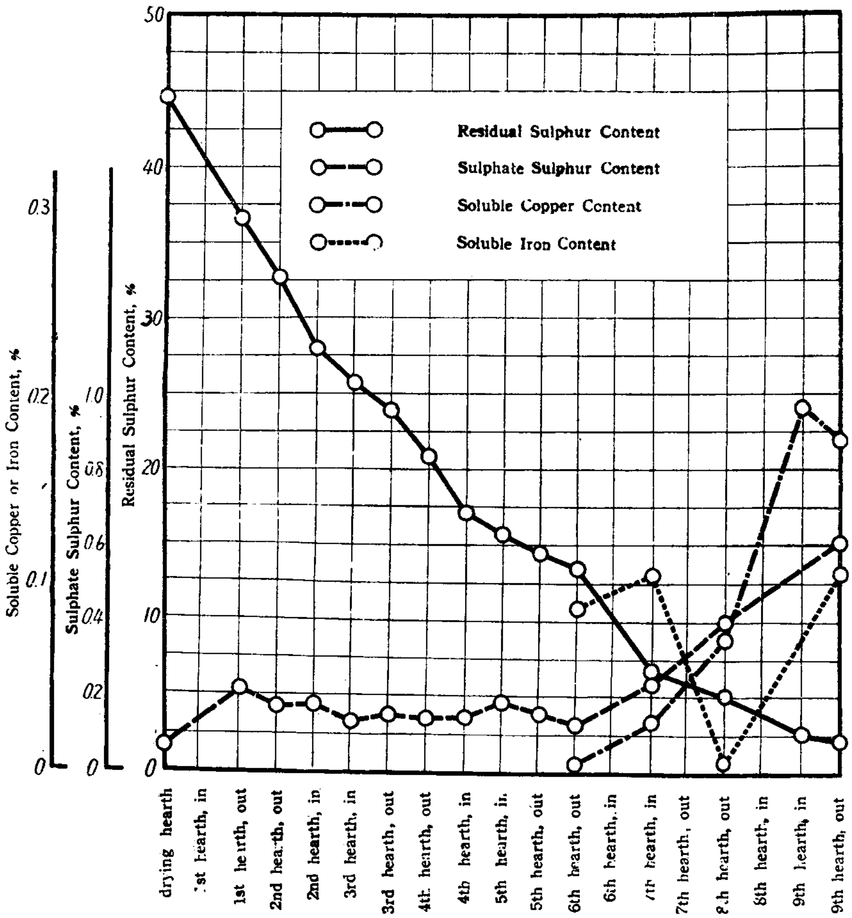


**Fig. 10.** Roasting Test of Nine Hearth Herreshoff Furnace.
(Charging Rate 26 t/d, Air is supplied to 7th and 9th hearth)

## 6. Conclusion

Studies were made on the methods of leaching copper from pyrites cinder and the method of increasing the leaching degree of copper, and the following results were obtained.

1. Soluble copper in pyrites cinder is able to be leached in the following conditions of leaching:

i. Size of cinder: not ground but in a roastes state.
ii. Leaching solution: 5 g/L sulphuric acid solution.
iii. Temperature of leaching: room temperature.
iv. Pulp density: 30%.

v. Stirring: vigorously performed.
vi. Time of stirring: 5 minutes.
vii. Washing after stirring: With water of which the weight is 1/5 of cinder, several times carried out.

2. The leaching degree of copper decreases when the residual sulphur content and the sulphide sulphur content are high in cinder. The leaching degree of copper is high in cinder of a high sulphate sulphur content. Magnetic or blackish pyrites cinder shows a low leaching degree. As to cinder of pyrites of the YANAHARA mine (containing about 0.4% of copper), when the content of residual sulphur is below 3% and the content of sulphate sulphur is above 0.5%, the leaching degree of copper shows above 50%.

3. Roasting of pyrites cinder in air at 400° to 600°C increases the leaching degree of copper while the roasting above 700°C decreases it.

4. In the roasting of pyrites in a multiple-hearth furnace, when the greater part of air is supplied to upper hearths instead of the lowest hearth, and the quantity of air supplied to the lowest hearth is decreased to 1/8 or 1/10, the residual sulphur content of pyrites cinder decreases and the leaching degree of copper increases. Moreover, by this method of operation, the capacity of the roasting furnace can be increased beyond its normal capacity. In this method of operation, the $SO_2$ content of flue gas is almost the same as in the formal method of operation and the formation of sintered cake does not increase, as compared with the case of the formal method. Any obstacles can not be found in the operation by this method of the roasting furnace.

In the execution of this study, continuous and great assistance has been given by HIROHATA Iron and Steel Works of FUJI Iron and Steel Co. Ltd., HIBI Refinery of KAMIOKA Mining Co. Ltd. and BEFU Chemical Co. Ltd.. Here, we express our heartful gratitude to these companies for their assistance. Moreover, this study has been performed with the cooperation of the members of our laboratory. We also express our gratitude to them.

Parts of this study were completed thanks to the financial support of the Ministry of Education.

**References:**

1) T. MORIMUNE: Tetsu to Hagane, **27**, No. 1, (1921), 1.
2) T. OHARA: Kagaku-Kogyo, **2**, No. 3, (1951), 248.