Studies on Pyrrhotite. I : Combustibility of Pyrrhotite

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Combustibility of Pyrrhotite*

Masuteru MARUYAMA

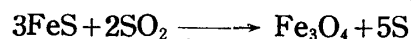*The Research Institute for Iron, Steel and Other Metals*
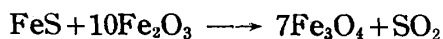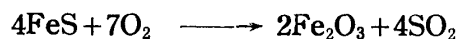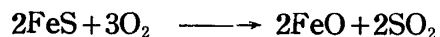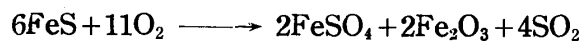
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Synopsis

In order to obtain a precise understanding of the combustibility of pyrrhotite, the roasting reaction rates and the relations between the roasting reactions and the roasting temperatures were investigated. It was found that pyrrhotite had a fairly low combustibility resulting from the low ignitibility, the slow reaction rate of oxide formation and the occurrence of the reaction of sulphate formation. The combustibility decreased with the increasing fineness of the ore particle. With increasing flow rate of air, the reaction rate of oxide formation increased, whereas the ignitibility decreased and, so, we cannot admit of any hasty decision whether the combustibility is improved by rapid air flow.

I. Introduction

Notwithstanding abundant deposits, pyrrhotites having the molecular formula Fe_nS_{n+1} ($n=5\sim16$) have not hitherto been utilized in industry as a source either of iron or of sulphur. This is presumed to be due mainly to the low combustibility. Here, the combustibility means the capacity of burning with its own heat of combustion. Many investigations on the roasting of pyrrhotite have been made, the leading work being carried out by T. Ishiwara, K. Niwa and K. Koizumi[1] and by S. Yagi and K. Takagi[2], but the accurate knowledge on the combustibility of the ore has not yet been obtained.

As seen in Table 1, the thermal properties of pyrrhotite are almost the same as those of pyrite, and, so, the low combustibility of the former does not result from its thermal properties. The roasting reaction of pyrrhotite is exceedingly complex and is conceivable in various ways, among which chief ones will be as follows:

$$6FeS + 11O_2 \longrightarrow 2FeSO_4 + 2Fe_2O_3 + 4SO_2$$
$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$
$$4FeS + 7O_2 \longrightarrow 2Fe_2O_3 + 4SO_2$$
$$FeS + 10Fe_2O_3 \longrightarrow 7Fe_3O_4 + SO_2$$
$$FeS + 9Fe_2O_3 \longrightarrow FeO + 6Fe_3O_4 + SO_2$$
$$3FeS + 2SO_2 \longrightarrow Fe_3O_4 + 5S$$

The combustibility of pyrrhotite is, therefore, considered to be associated closely with the above reactions and their reaction rates. Hence, the present

(1) T. Ishiwara, K. Niwa and K. Koizumi, Sci. Rep. RITU, A 3 (1951), 265.
(2) S. Yagi and K. Takagi, J. Chem. Soc. Japan, Ind. Chem. Sec. 53 (1950), 371; 54 (1951), 1, 3, 5.

research was carried out for the purpose of finding the relations between the combustibility and the above reactions or their reaction rates.

Table 1. Thermal properties of pyrrhotite and pyrite.

Ore	Molecular Formula	Specific Heat (cal/g°C)	Heat of Combustion (cal/g)
Pyrrhotite	Fe_nS_{n+1}	0.13～0.15	1,610
Pyrite	FeS_2	0.13～0.17	1,608

II. Experimental method

Pyrrhotites produced at the Ômine (Nara prefecture), the Kawayama (Yamaguchi prefecture) and the Akagane (Iwate prefecture) mines, and those produced artificially were used as the samples, and the roasting reaction of pyrites produced at the Hitachi mine in Ibaragi prefecture was compared with that of pyrrhotites. The chemical compositions of these ores are listed in Table 2.

Table 2. Chemical composition of ores.

Ore	Mine	Component							Molec. Formula
		Fe (%)	S (%)	Cu (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	SiO_2 (%)	
Pyrrhotite	Ômine	54.40	34.59	0.29	0.08	2.00	0.35	4.79	$Fe_{10}S_{11}$
	Kawayama	51.22	33.84	0.22	0.13	0.62	0.34	5.20	Fe_7S_8
	Akagane	53.52	33.90	0.23	0.51	2.88	0.35	7.97	$Fe_{10}S_{11}$
	Artificial	65.38	34.52	—	—	—	—	—	FeS
Pyrite	Hitachi	37.45	43.51	0.22	1.51	0.41	1.48	8.94	FeS_2

Each ore was crushed under 200 mesh and, further, in order to observe the effects of the fineness of ore particle, two kinds of fineness, 20～24 mesh and 48～50 mesh, were screened.

The roasting reactions were determined from the change in weight measured by thermo-balance and that in desulphurizing ratio given by the following formula:

$$R = (1 - \frac{w \cdot s}{W \cdot S}) \times 100,$$

where R is a desulphurizing ratio, W and w respectively the weights of raw ore and that of cinder, and S and s respectively the sulphur percentage of raw ore and that of cinder.

The apparatus used in the present experiments is shown in Fig. 1. The experimental methods are as follows:

1. Method by the changes in weight

 (i) Relations between the roasting temperatures and the roasting reactions

  Pt-crucible, 15 mm in diameter and 5 mm in depth, containing exactly 1000 mg of samples, is suspended at the right scale of the thermo-balance with a fine string of quartz and then is brought to the center of furnace (a). C-cock

having been closed and *A*- and *B*-cocks opened, purified air is introduced from
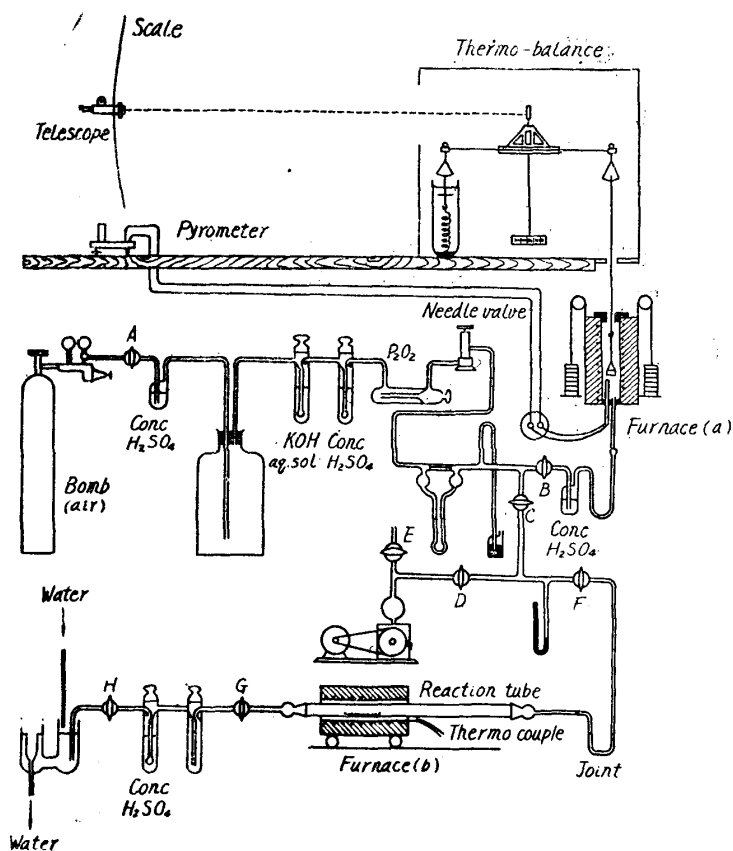the bomb into the furnace. After the constancy of flow rate of air has been
established, the furnace is
gradually heated to 800°C
at the rate of 2°C/min and
the changes in weight
during the oxidation of
sample can be obtained by
means of telescope with the
accuracy of 0.0225 g corre-
sponding to the reading 10
mm.

(ii) Roasting reaction
rates

The furnace is first
heated to the prescribed
temperature. After the
constancy of temperature
has been obtained, purified
air is introduced into the
furnace. After the con-
stancy of flow rate has been
obtained, Pt-crucible con-
taining samples is brought
to the center of furnace.

Fig. 1. Experimental apparatus.

2. Method by the changes in desulphurizing ratio

After introducing the porcelain boat containing about one gram of the sample
into the position between the center and the right end of the roasting tube
and setting the furnace in the position between the center and the left end of
the tube, *C*-cock is closed and then the tube is evacuated to the vacuum of
about 1/1000 mmHg, and the furnace is gradually heated to the prescribed
temperature. When the constancy of temperature has been obtained, *B*- and
D-cocks are closed, *C*-cock is opened and then purified air is introduced into the
tube. As soon as the pressure in it attains to 1 atmosphere, *G*-cock is opened
and purified air is passed through the tube. After the constancy of flow rate
has been obtained, the furnace is moved to the right and the boat is put in the
center of the furnace. After roasting, the tube is allowed to cool in vacuum
to room temperature and the residual sulphur in the cinder is analysed.

III. Experimental results

1. Relation between roasting reaction and roasting temperature

The roasting reactions described above are generally classified into the re-
actions of sulphate formation and those of oxide formation. The former shows

the increase in weight and the latter the decrease, and so the change in weight taking place in the course of heating the sample from room temperature to 800°C at the heating rate of 2°C/min and the flow rate of 100 cc/min, was measured by means of a thermobalance, from which the relation between the roasting reaction and the roasting temperature was obtained.

Fig. 2 shows the heating curves of pyrrhotite produced at the Ômine mine and of pyrite. Both pyrrhotite and pyrite suddenly showed a remarkable decrease in weight, which shows the reactions of oxide formation, at about 405°C. In the case of pyrrhotite, however, this decrease was not greater than about 30 per cent of the total decrease, while, in the case of pyrite, it was about 80 per cent. Consequently, it might be said that the ignitibility of pyrrhotite would be considerably lower than that of pyrite. So, the present writer will provisionally name the above phenomenon of pyrrhotite "the first decreasing change in weight".

On the other hand, despite the occurrence of "the first decreasing change in weight", pyrrhotite was also apt to show the increasing change in weight, that is, the reaction of sulphate formation at temperatures below 550°C, while pyrite scarecely showed such an increase. These results would indicate that the occurrence of the reaction of sulphate formation might also be a main cause of the low ignitibility of pyrrhotite.

Similar characteristics were also observable in the ores produced at the Akagane and the Kawayama mines as shown in Fig. 3, the magnitude of the change being dependent on the kinds of ores. Among them, the ore produced at the Kawayama mine has comparatively greatly the excellent characteristics. It is, moreover, noteworthy that the heating curve of artificial pyrrhotite did not
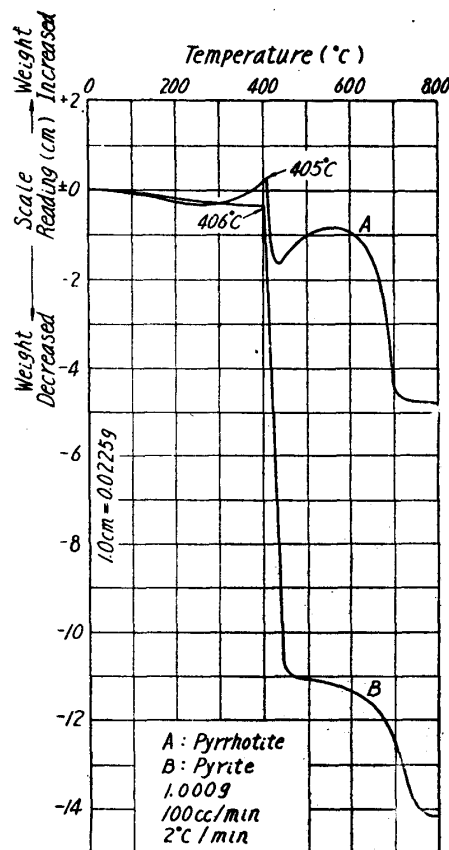

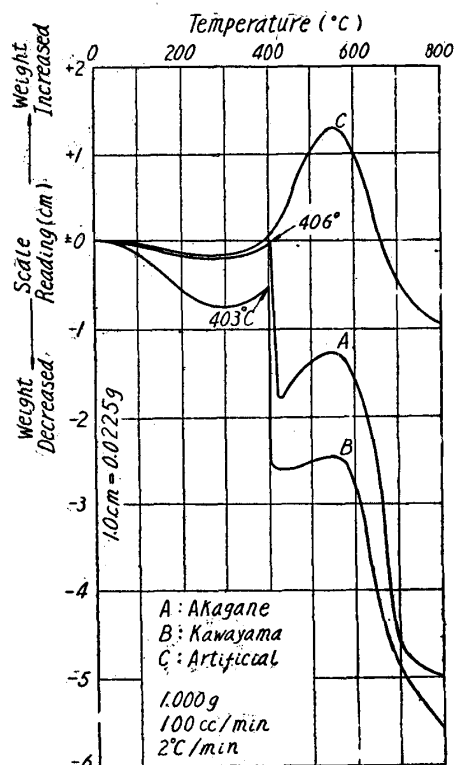Fig. 2. Heating curves of pyrrhotite and Pyrite.

Fig. 3. Heating curves of various pyrrhotites.

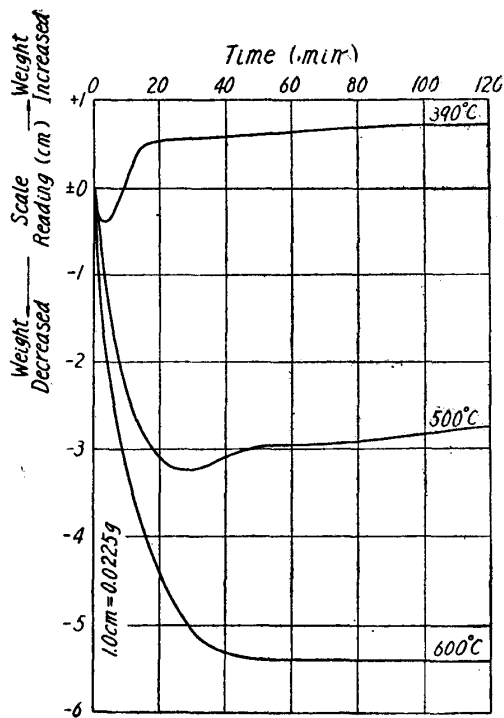show "the first decreasing change in weight". The differences in the character-

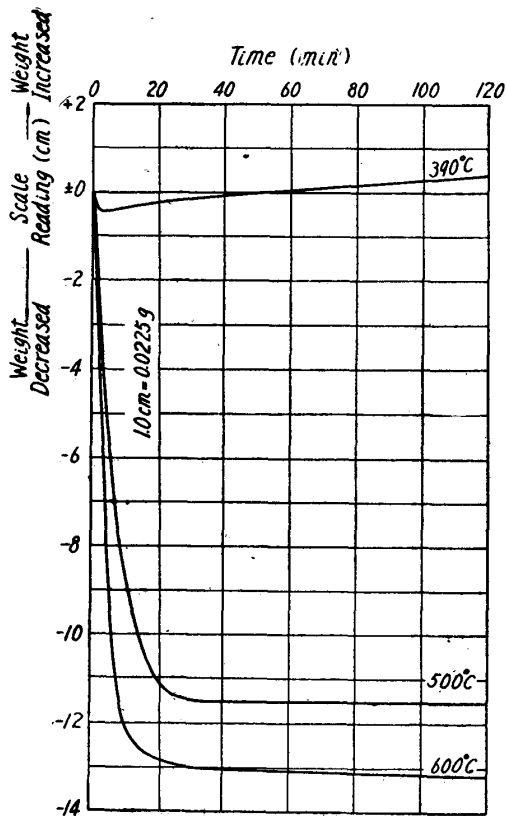Fig. 4. Reaction rates of pyrrhotite at 390°, 500° and 600°C.

Fig. 5. Reaction rates of pyrite at 390°, 500° and 600°C.

istics of these ores were presumed to be due to the difference in the value n in the molecular formula Fe_nS_{n+1}, as shown in Table 2.

2. Reaction rate of sulphate formation

Figs. 4 and 5 show respectively the change in weight of pyrrhotite (the Ômine mine) and that of pyrite, when roasted at 390°, 500° and 600°C with air flow at the rate of 100 cc/min. In the case of 390°C, pyrrhotite actively reacted with air to form sulphates at first, although the reaction rate dropped after 18 minutes, while the reaction of pyrite was very slight. In the case of 500°C, pyrrhotite reacted with air to form oxides at first, but its reaction rate was considerably slow; moreover, the reaction of sulphate formation took place after 30 minutes, leaving behind large amounts of unreacted ores. On the other hand, pyrite nearly finished all the reaction of oxide formation at a rapid rate. These results also made clear that the occurrence of the reaction of sulphate formation might be a main cause of the low ingnitibility of pyrrhotite, as mentioned above.

In order to observe the effects of the sulphates formed in cinders on the reaction rates of oxide formation, the sample, after roasting at 390°C for 2 hours, was re-roasted at 500°C for 2 hours and then at 600°C for 2 hours. The results obtained are shown in Fig. 6. In the first stage of the reaction at 500°C, the sample reacted with air to form sulphates, scanty as it was, and it took 4 minutes to commence the reaction of oxide formation. Furthermore, the maximum decrease in weight caused by the reaction of oxide formation was not more than two-third of that of the ore roasted directly at

500°C, and after 18 minutes, the reaction of sulphate formation took place again. In the case of 600°C, the time required to commence the reaction of oxide formation increased, and, furthermore, its reaction rate extremely dropped. It was, thus, found that the ignibility or the combustibility of pyrrhotite might be reduced by the sulphates formed in cinders.

3. Reaction rate of oxide formation

The reaction rates of oxide formation were determined from the change in desulphurizing ratio. For an example, the case of 700°C is shown in Fig. 7, in which A and B are the curves of pyrrhotite (the Ōmine mine) and pyrite respectively. As indicated in it, pyrrhotite had a slow reaction rate, taking about 2.5 times as much times that of pyrite to complete the reaction. The reaction rates were measured also at 600°, 800° and 900°C, but there was no difference between them. Consequently, the slow reaction rate of oxide formation seemed to be a cause of the low combustibility of pyrrhotite.

4. Effect of fineness of ore particle on combustibility

The heating curves of three kinds of fineness, that is, 20~24, 48~50 and −200 mesh, were examined for the purpose of observing the effects of the fineness of particle. The heating curve of pyrrhotite is shown in Fig. 8 and that of pyrite in Fig. 9. In the latter, the effect was not so great, whereas in the former ores of 20~24 mesh and 48~50 mesh scarecely showed the decrease in weight at 405°C.

Next, the experiments were carried out to see the effect of the fineness of particle on the reaction rate of oxide formation. For an example, the case of 700°C is shown in Fig. 10. With increasing fineness, the reaction rate decreased and the residual sulphur in cinders increased. The
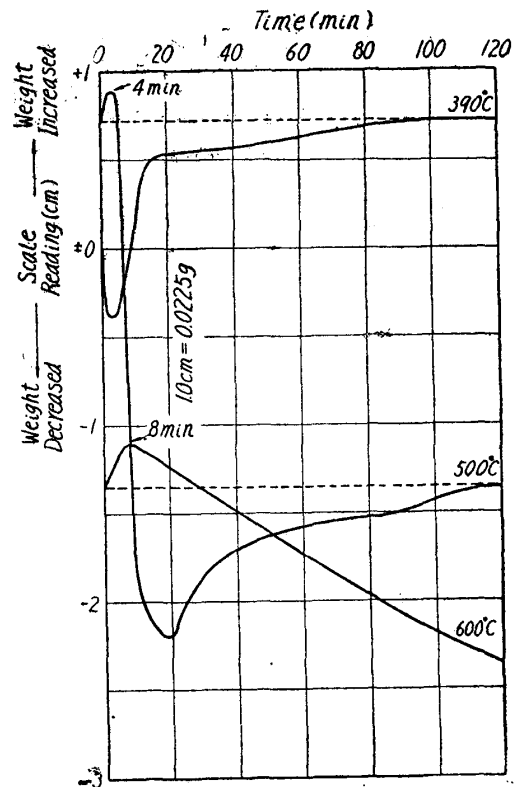

Fig. 6. Effect of sulphate formed in pyrrhotite particles on the reaction rate of oxide formation
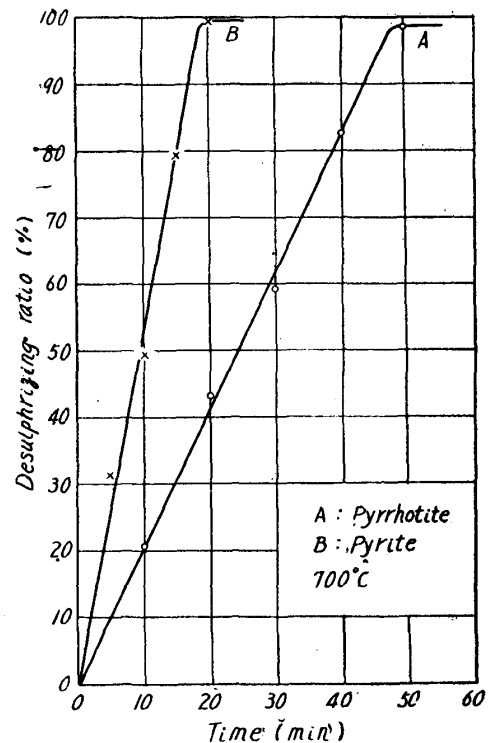

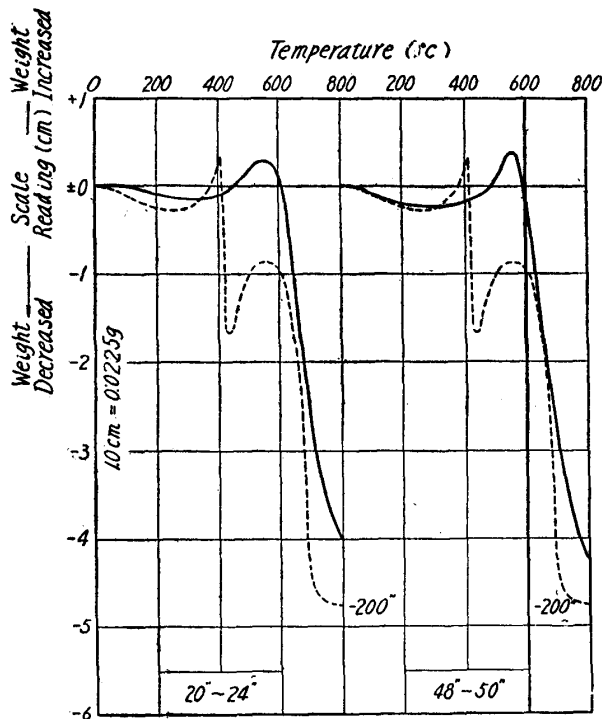Fig. 7. Reaction rates of oxide formation at 700°C.

Fig. 8. Effect of fineness of particles on
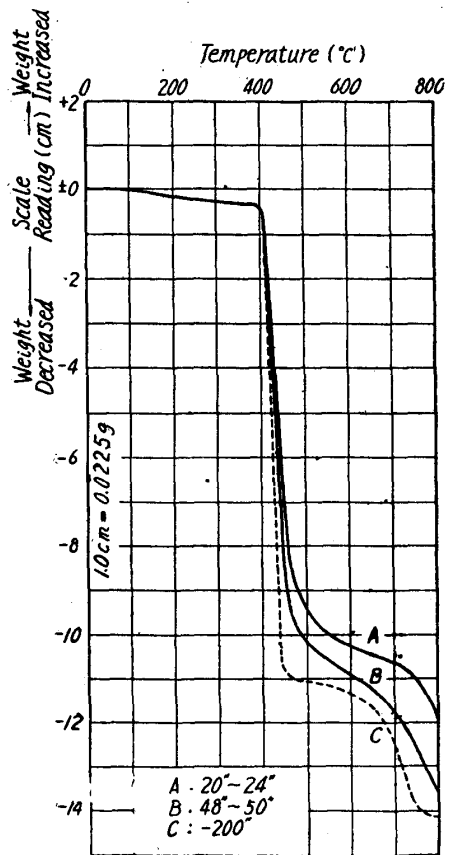the heating curve of pyrrhotite

Fig. 9. Effect of fineness of particles
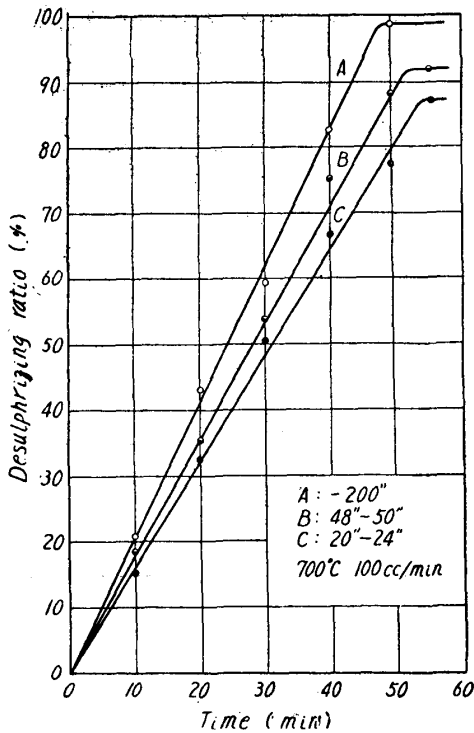on the Heating curve of pyrite.

Fig. 10. Effect of fineness of particles
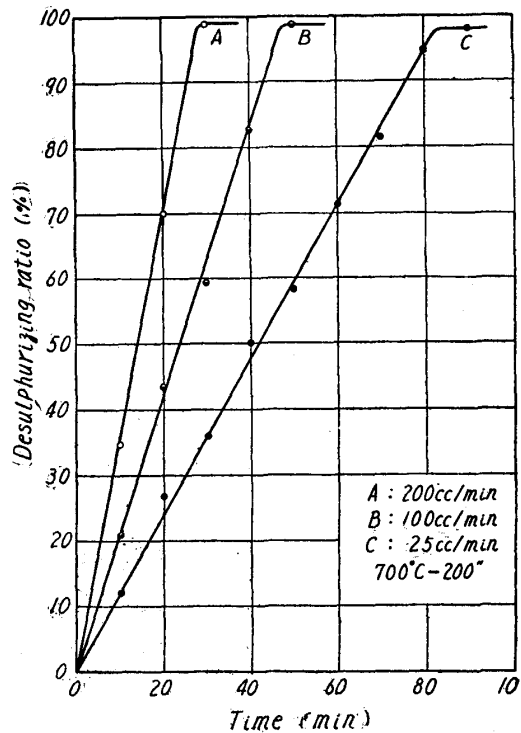on the   reaction   rate   of   oxide
formation

Fig. 11. Effect of flow rate of air on
the reaction rate of oxide formation

combustibility of pyrrhotite may, therefore, be reduced by increasing fineness, because of the lowering of both ignitibility and reaction rate of oxide formation.

5. Effect of flow rate of air on combustibility

The experiments were carried out with the ore (the Ômine mine) of 200 mesh at three kinds of flow rates of air, namely, 25, 100 and 200 cc/min. Fig. 11 shows an example of the effect of flow rate of air on the reaction rate of oxide formation observed at 700°C. According to it, the reaction rate of oxide formation decreases with decreasing flow rate of air. Furthermore, from the heating curve at 25 cc/min shown in Fig. 12 (a), it was found that the change in weight, especially "the first decreasing change in weight", decreased with decreasing flow rate. The combustibility seemed, therefore, to be improved by rapid flow rate. However, as seen in Fig. 12 (b) showing the

Fig. 12. Effects of flow rates of air on the heating curve of pyrrhotite.

heating curve measured at 200 cc/min, "the first decreasing change in weight" took place at two stages, namely, at 405° and 490°C. The change was, furthermore, small at 405°C and large at 490°C, and so the ignitibility might be reduced with increasing flow rate. This is presumed to be due to the fact that the reaction heat occurred are largely taken away by rapid flow rate of air. Considering the above results, it was not wise to admit of any hasty decision whether the combustibility could be improved by the increase in flow rate.
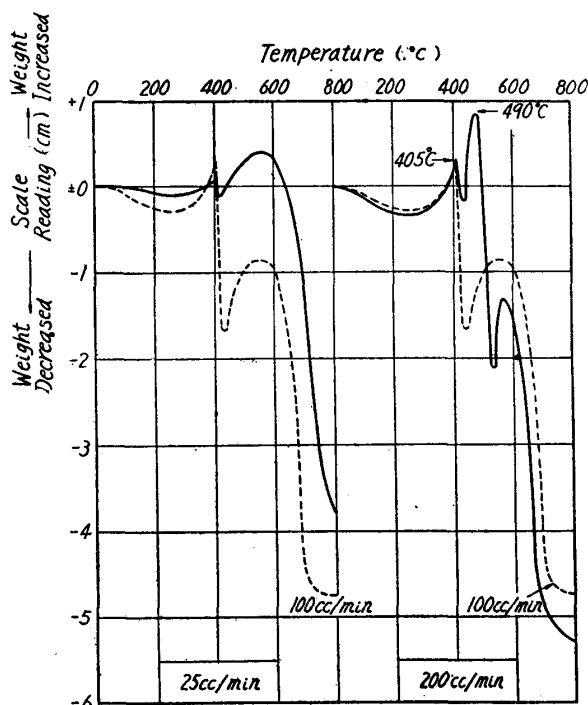
IV. Discussion

"The first decreasing change in weight" seen in the heating curves of native pyrrhotites is an anomalous phenomenon. It was also found by Mr. H. Saito[3], who had explained its mechanism as follows: the cintering of ore particles begins at 405°C, by which the reaction of sulphate formation is obstructed and only that of oxide formation goes on, and so the weight of particles remarkably decreases. The cintering phenomenon, however, may isolate many of unreacted particles from oxygen gas, and, accordingly, the reaction of oxide formation should be obstructed by it. Fig. 13 (by S. Yagi) and Fig. 14 (by H. Saito) show respectively the relation between the roasting temperature and the decrease of sulphur component in ore and that between the roasting temperature and the

(3) H. Saito, J. Min. Inst. Japan, **41** (1925), 726.

occurrence of SO_2 gas. From these figures, it will be seen that the reaction of oxide formation suddenly becomes vigorous at about 400°C. It is, however, hard to explain this fact by the cintering phenomenon.
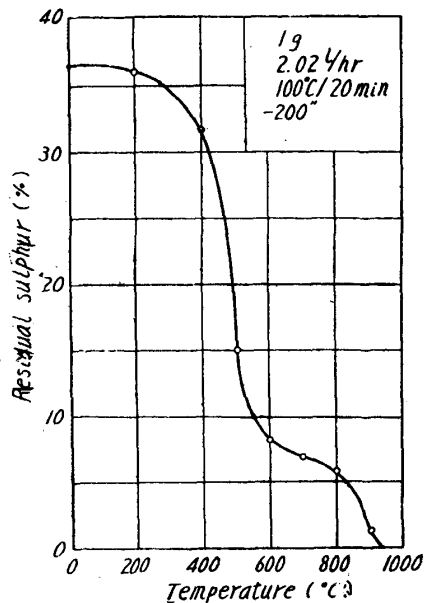

Fig. 13. Relation between the roasting temperature and the residual sulphur (by S. Yagi)
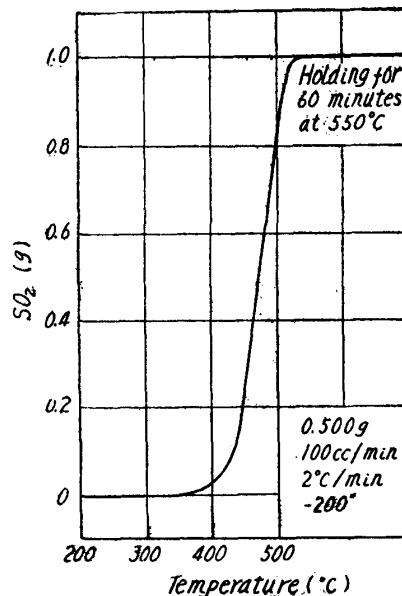

Fig. 14. Relation between the roasting temperature and the occurrence of SO_2 (by H. Saito)

Now, it is noteworthy that the temperature, at which "the first decreasing change in weight" occurs, accords with the ignition temperature of pyrite. From this fact, "the first decreasing change in weight" is presumed to be due to the decomposition and oxidation of pyrite components contained in native pyrrhotite. In fact, the crystals of pyrite are found in the structure of native pyrrhotite under microscope, and artificial ore containing no pyrite does not show "the first decreasing change in weight" in the heating curve.
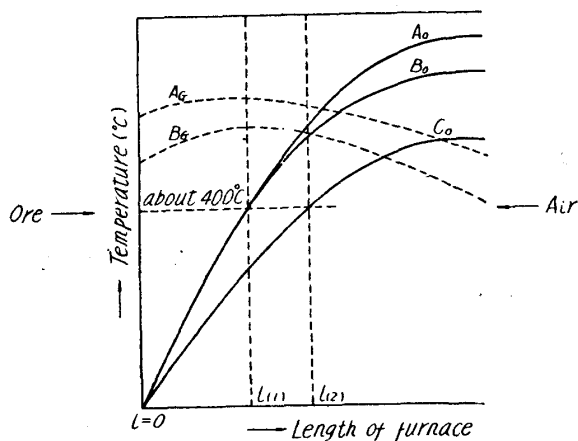

Fig. 15.

Basing on the results obtained above, the present writer will discuss whether pyrrhotite can successfully be roasted with the rotary kiln used generally as the roasting furnace of sulphide ores. Supposing that the temperatures of ores and gas in the furnace are distributed as indicated respectively by the curves A_0 and A_G in Fig. 15 when pyrite is roasted, let us consider the changes of temperature distribution caused by charging pyrrhotite in place of pyrite. As pyrrhotite has the same specific heat as pyrite, its temperature will rise along A_0-line to $l(1)$, at which it ignites. When the ignition once takes place, the temperature distribution of ore slips

out of A_0-line to B_0-line, because of the low ignitibility of pyrrhotite and its slow reaction rate of oxide formation. Accordingly, the temperature distribution of gas in the furnace also slips out of A_G-line to B_G-line of lower temperature side. Consequently, the rising rate of temperature of ores will decrease and the igniting position in the furnace transfers from $l(1)$ to $l(2)$, resulting in the broadening of the temperature range below 405°C as shown by C_0-line. In such a case, a large amount of sulphate is vigorously formed and the temperature distribution gets worse and worse. Thus, the roasting of pyrrhotites with rotary kiln is believed to be considerably difficult. Considering the results obtained and the discussion described above, it became eivdent that the following two points were essential to the investigation on the successful roasting method of pyrrhotite:

(1) to accelerate "the first decreasing change in weight" (or the reaction rate of oxide formation)

(2) to prevent ores from reacting with air to form sulphate.

The research in these points will be reported later on.

Summary

From the present experiments, it was found that pyrrhotite had a fairly low combustibility, resulting from the following facts:

(1) Pyrrhotite ignites at 405°C, but it forms oxides by halves and soon begins to form sulphates in the temperature range from 405 to 550°C, that is, the ignitibility may be considerably low.

(2) The reaction rate of oxide formation of pyrrhotite is considerably slower than that of pyrite.

(3) Sulphates formed in ore particles not only reduce the ignitibility, but also retard the reaction rate of oxide formation.

The combustibility gets worse than ever with increasing fineness of ore particle, because of the lowering of both ignitibility and reaction rate of oxide formation. With increasing flow rate of air, the reaction rate of oxide formation increases, while "the first decreasing change in weight" is divided into two stages, namely, at 405° and at a higher temperature, and the ignitibility may be reduced, and so it is not wise to admit of any hasty decision whether the combustibility is improved by rapid air flow.

Acknowledgement   •