

Studies on Pyrrhotite. III : Sintering of Pyrrhotite Cinder

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Studies on Pyrrhotite. III

Sintering of Pyrrhotite Cinder*

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Synopsis

The progress of sintering of pyrrhotite cinder during the process of roasting was studied by measuring the resistance of cinder to the penetration of a slender rod. The results showed that pyrrhotite cinder, in general, began to sinter at 250-350°C with a very high resistance to the penetration of a rod. The sulfate formed below 550°C, and the oxide formed above 550°C, both played a main part in the sintering process of cinder. In the range from the temperature at which the sintering began to about 400°C and in temperatures above 550°C, the resistance increased with the rise of temperature, whereas in the range from 400 to 550°C it decreased with the rise of temperature by the progress of the reaction of oxide formation due to "the first decreasing change in weight". It was also found that an addition of over 30 per cent of pyrite to pyrrhotite would enable to complete the roasting almost without the sintering of cinder.

I. Introduction

Though many studies⁽¹⁾ have been reported on the roasting reaction of pyrrhotite, this ore has, up to date, scarcely been considered as useful industrial resources. A main objection to the utilization of this ore is said to be its aptness to form hard clinkers by sintering, thereby the progress of the roasting reaction being obstructed and even the furnace being damaged. There have been, however, few studies on it, and so this sintering reaction and its mechanism have remained in the dark. For throwing some light on this problem, the present study has been undertaken.

II. Degree of sintering of pyrrhotite cinder

The degree of sintering of pyrrhotite cinder during the process of roasting cannot so easily be expressed as in the case of metal powders, because the former has not a homogeneous structure as in the case of sintered metal powders, but consists of three kinds of layers, namely, the outer reacted, the middle and the inner unreacted layers, as shown below. Therefore, in the case of pyrrhotite cinder, the degree of sintering cannot appropriately be expressed by means of a shrinkage in volume or of an electric resistance. The most important property of a sintered material is the mechanical strength, and, accordingly, it will be reasonable to express the degree of sintering in terms of the resistance to the penetration of a slender rod

* The 780 th report of the Research Institute for Iron, Steel and Other Metals.

(1) As outstanding works, we may mention

T. Ishiwara, K. Niwa and K. Koizumi, *Sci. Rep. RITU*, A3 (1951), 265; G.M. Schwab and J. Philinis, *J. Am. Chem. Soc.*, **69** (1947), 2588; M. Kameda, A. Yazawa and T. Kurosawa, *J. Min. Inst. Japan*, **68** (1952), 71; S. Yagi and K. Takagi, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **53** (1950), 371.

calculated by Eiterwein's formula⁽²⁾, as H. Mikashima and Y. Nakao⁽³⁾ have proceeded.

When a weight of R g is dropped at a height of h cm on the top of a slender rod weighing Q g and standing on the surface of the cinder, and this rod penetrates by τ cm into the cinder, the resistance of the cinder W g is derived and defined as follows:

The energy E inherent to the weight of mass R/g when it reaches the head of the rod of mass Q/g with the acquired velocity v will be expressed by

$$E = Rh \quad (1)$$

If the weight and the rod are both semi-elastic bodies, they will, for a time after the collision, move with a common velocity u . As total momentum does not change, v and u are connected with each other by

$$u = \frac{Rv}{(R+Q)} \quad (2)$$

Subsequent to the collision, the elasticity of the bodies induces them to recover the original positions and, consequently, to separate their centers of gravity from each other, till the perfect disappearance of the elastic deformation. If the coefficient of restitution is denoted by η , the velocities of the weight and the rod at this moment of initial separation, v_1 and v_2 , may be expressed respectively by

$$v_1 = u - \eta(v - u) = u(1 + \eta) - \eta v \quad (3)$$

and
$$v_2 = u + \eta u = u(1 + \eta) \quad (4)$$

Substituting (2) into (3) and (4),

$$v_1 = \frac{(R - \eta Q)v}{(R + Q)} \quad (5)$$

and
$$v_2 = \frac{(1 + \eta)Rv}{(R + Q)} \quad (6)$$

Then, the effective energy E_η of the semi-elastic bodies immediately after collision is given by

$$E_\eta = \frac{1}{2}R/gv_1^2 + \frac{1}{2}Q/gv_2^2,$$

which, by (5) and (6), may be rewritten as follows:

$$E_\eta = \frac{1}{2} \frac{v^2 R}{g(R+Q)} (R + \eta^2 Q) \quad (7)$$

As v is given by

$$v = \sqrt{2gh},$$

E_η may be rewritten as

$$E_\eta = \frac{Rh}{(R+Q)} (R + \eta^2 Q) \quad (8)$$

When the bodies are both perfectly rigid, $\eta=0$, and E_η becomes

$$E_\eta = \frac{R^2 h}{(R+Q)} \quad (9)$$

Now, if the rod penetrates into the sintered material by τ overcoming its resistance W , E_η may be expressed as

(2) Haraguchi and Yoneta, *Tuchi to Kui no Kogaku*, 141 (Iwanami, Tokyo, 1951).

(3) H. Mikashima and Y. Nakao, *J. of Cast. Inst. of Japan*, 26 (1954), 347.

$$E\eta = (W - Q - R)\tau \quad (10)$$

From (9) and (10), the following formula may be obtained for W :

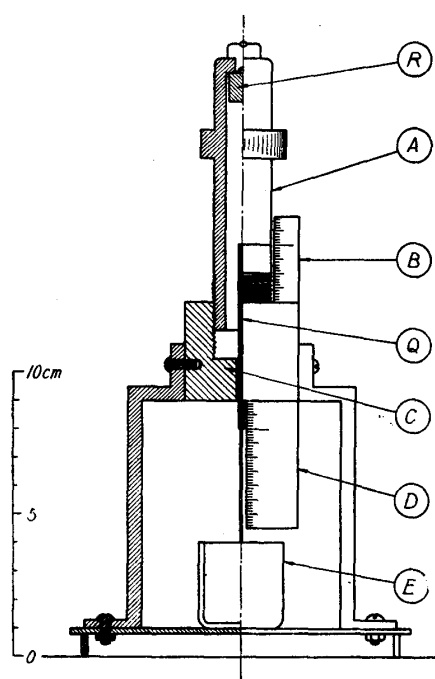
$$W = \frac{R^2 h}{\tau(R+Q)} + R + Q \quad (11)$$

In (11), R, Q and h are constants given by the experimental conditions, so W may easily be calculated, provided that τ is observed.

III. Experimental method

1. Apparatus for measuring the resistance to the penetration of a slender rod

Fig. 1 is the schematic diagram of the resistance meter. R is a weight and Q a slender rod, 3 mm in diameter at the upper half and 1 mm at the lower half, the lower end being rounded into hemisphere. When the boundary line between the upper and the lower halves of the rod is adjusted to the standard line of the scale D and the marked line of the guide pipe A to that of the scale B , the weight drawn up to the top of the guide pipe A keeps exactly the predetermined height of fall. Four guide pipes are put in, so that any one of the four kinds of heights, namely, 1, 5, 10 and 20 cm, may be available. The weights of the weight and the rod are 15.12 and 4.38 g respectively.



- A Guide pipe of weight
- B Scale
- C Guide pipe of slender rod
- D Scale
- E Quartz bucket
- R Weight
- Q Slender rod

Fig. 1. Schematic diagram of the resistance meter.

2. Experimental method

The ore ground into powder was placed in the transparent quartz bucket E , 15 mm in inner diameter and 30 mm in depth, which was suspended in an heating furnace kept at a fixed temperature, and was roasted in it for a fixed time under the air flow of 100 cc/min. When the roasting was completed, the bucket was immediately taken out of the furnace, and pouring N_2 gas on it, as K. Niwa and T. Wada⁽⁴⁾ had proceeded in their experiments, it was suddenly cooled in a Dewar vessel kept at the temperature of liquid air.

The cooled bucket containing now the roasted material was placed on the stage of the resistance meter, the rod was placed lightly on the material and the position of the boundary line of the upper and the lower halves of the rod was read on the scale D . Then, if the read position was not in line with the standard line of the scale D , say, was 0.20 cm below it, the guide pipe A was turned so that its marked line was lowered to 0.20 cm below the standard line on the scale B to adjust the distance of fall to the prescribed height with precision. Next, the weight was pulled up

(4) K. Niwa and T. Wada, Nippon-Kinzoku-Gakkai-shi (J. Japan Inst. Metals), 18 (1954), 1.

by a thread and let fall when the pull was stopped, to impinge upon the rod. Then, the height of the half-line of the rod was read on the scale D to measure the depth of penetration of the rod and the resistance of the sintered material was obtained from the formula (11).

Fig. 2 shows the relation between the depth of penetration and the resistance, when the weight was dropped at various heights. These values plot a hyperbola, and so the error in the calculated resistance tends to be magnified in the case of small depth of penetration. Therefore, comparatively accurate results can be obtained if a proper falling height of the weight was selected within the range of measurements indicated in Table 1, because of a considerable

Table 1. Useful resistance range of various measuring condition.

Measuring condition			Useful resistance range W , g
R , g	Q , g	h , cm	
15.12	4.38	1	20~ 60
"	"	5	40~150
"	"	10	60~250
"	"	20	100~400

depth of penetration. The cinder of pyrrhotite, however, did not always show the identical resistance to the penetration of a rod when the falling height was changed, and a constant relation cannot be detected between these values. Consequently, it was decided to use an identical condition as much as possible throughout the experiments, despite the fact that the result might contain some errors.

3. Samples used

The native pyrrhotite used in the present experiments was produced at the Akagane mine, Iwate prefecture, and the pyrite used for control was produced at the Hitachi mine in Ibaragi prefecture. The chemical compositions of these ores are shown in Table 2. For preparing the artificial pyrrhotites containing various

Table 2. Chemical composition of ores.

Ore	Mine	Component, %							Molecular formula
		Fe	S	Cu	Al_2O_3	CaO	MgO	SiO_2	
Pyrrhotite	Akagane	53.52	33.90	0.23	0.51	2.88	0.35	7.97	$Fe_{10}S_{11}$
Pyrite	Hitachi	37.45	43.51	0.22	1.51	0.41	1.48	8.94	FeS_2

percentages of sulfur, the method described in the last report⁽⁵⁾ was used.

(5) M. Maruyama, Sci. Rep. RITU, A6 (1954), 115.

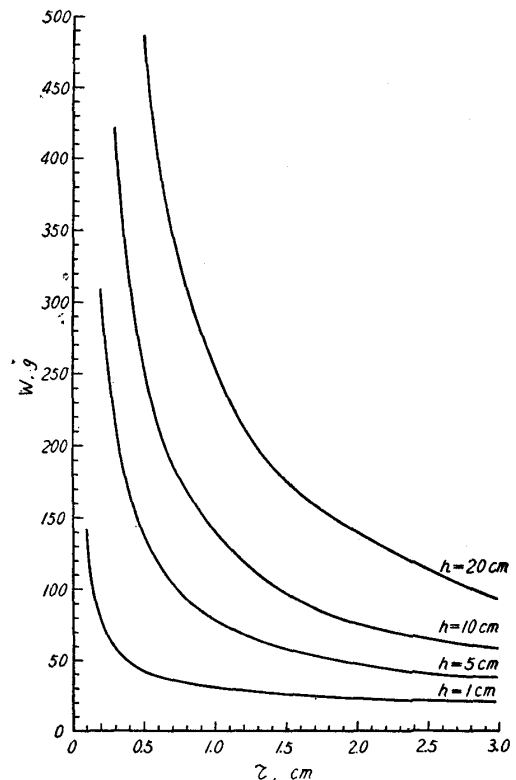


Fig. 2. Relation between W and τ when the weight was dropped from various heights.

IV. Experimental results and discussion

1. The relation between the resistance of pyrrhotite cinder to the penetration of a rod and the roasting temperature

To ascertain the temperature at which the sintering begins in the process of roasting pyrrhotite and to clarify the dependence of the intensity of sintering on the temperature, the resistance of native pyrrhotite powder of -200μ , which was roasted at various temperatures between 300 and 900°C for 10, 30 and 60 minutes was measured under the falling height of 5 cm in the case of roasting for 10 minutes, and of 20 cm in the case of the longer roasting.

The results are shown in Fig. 3. First, it is noticeable that the pyrrhotite cinder

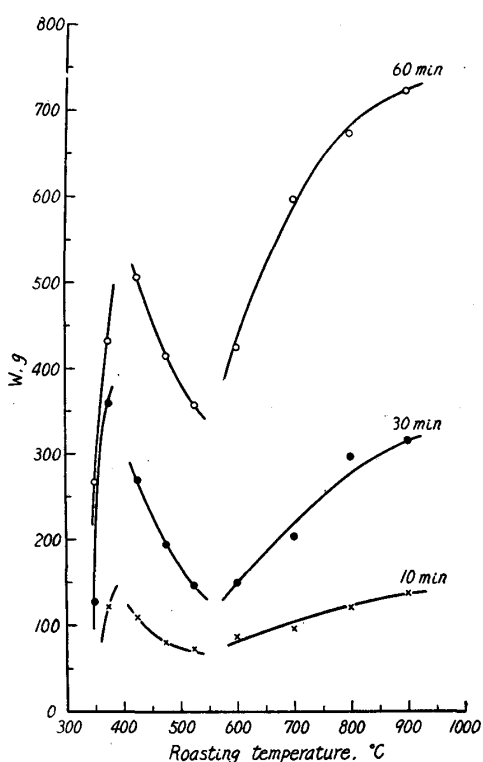


Fig. 3. Relation between the resistance of pyrrhotite cinder to the penetration of a rod and the roasting temperature.

begins to sinter at about 350°C, an unexpected low temperature. The relation between the resistance and temperature is clearly divided into three ranges. In the ranges of comparatively low temperature between the first sintering temperature and about 400°C and of high temperature above 550°C, the resistance increases with the rise of temperature, whereas in the range between 400 and 550°C the inverse relation holds, the resistance diminishing as the temperature rises. As shown in the above results, the resistance of pyrrhotite cinder is of a remarkably high level in any case, and it is especially notable that the magnitudes at such a relatively low temperature of about 400°C and at high temperatures from 800 to 900°C are nearly the same. This suggests the difficult technical problems encountered in the roasting process of pyrrhotite.

An examination of the structure of cinders showed that those roasted at temperatures lower than 400°C consisted of a dark-violet reacted layer and a gray unreacted layer, while in the case of the intermediate roasting temperature, 400~550°C, the reacted layer was divided into a thin dark-red outermost sublayer and an inner thick dark-brown sublayer. In the range of high temperature over 550°C, three thin sublayers were formed between the reacted and the unreacted layers, namely, dark-gray, dark-blue and violet sublayers. Of these layers and sublayers, the one showing the strongest resistance was, of course, the reacted layer; in the range of high temperature, however, the above-mentioned thin intermediate sublayers were also found sintered up to a high consistency and seemed to play a part in the high resistance shown in the cinder.

Fig. 4 shows the resistance of the unreacted layers of cinders roasted at various

temperatures, which was measured under the falling height of 1 cm. It is noticeable that the resistance of this layer is comparatively high when the roasting temperature is lower than 550°C. This layer will, therefore, be responsible for the high resistance shown in the cinder at low temperature roasting.

For the sake of contrast, the resistance of pyrite cinder was desirable, but it was found that the pyrite sinter was scarcely made under the above-mentioned experimental conditions. Upon continuing the roasting for 2 hours at various temperatures, it began to sinter only at 900°C and the resistance under the falling height of 5 cm was 125 g, a value lower than that of pyrrhotite roasted only for 10 minutes, evincing how easier pyrrhotite becomes sintered and how much more difficult it is to roast than pyrite.

2. Composition of sintered layers

As described above, the sintering of pyrrhotite cinder shows an extremely peculiar relation to the roasting temperature. To see this circumstance, the compositions of the layers formed in the sintered material, the contents of residual sulfur and sulfate sulfur were analysed. The method of analysis for these components was the same as that reported in the former paper⁽⁵⁾. The results of the analysis of the various layers found in cinders roasted for 60 minutes at 375, 475 and 700°C are shown in Table 3.

Table 3. Chemical composition of various layer of cinder.

Roasting temperature °C	Kind of layer	Residual sulphur %	Sulphate sulphur %	
375°	Reacted	27.85	2.45	
	Unreacted	32.27	0.077	
475°	Reacted	6.60	2.47	
	Unreacted	32.54	0.041	
800°	Reacted	0.374	trace	
	Middle {	I	28.82	"
		II	30.10	"
		III	31.51	"
Unreacted	33.00	"		

On comparing of the compositions of the reacted layers of cinders roasted at 375 and 475°C with each other, it was found that the reaction was not much progressed at 375°C, the content of residual sulfur being as yet very large, while at 475°C, the content of such sulfur fell to a far lower level; so there was a very conspicuous difference in the residual sulfur contents of the two layers. The content of sulfate sulfur, however, was little different, standing at around 2.5 per cent

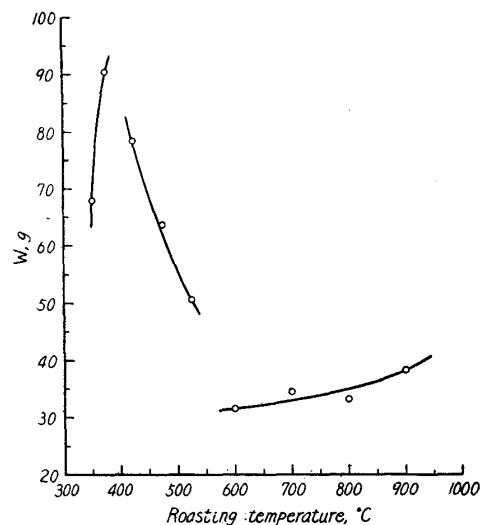


Fig. 4. Resistance of the unreacted layer of pyrrhotite cinder to the penetration of a rod.

in both cases. The resistances of cinders roasted at 375 and 475°C shown in Fig. 3 are 432 and 415 g respectively, showing a good correspondence with the change of sulfate sulfur content.

To ascertain this correspondence, the compositions of the reacted layers in samples roasted for 60 minutes at several temperatures between 300 and 900°C were examined, the results of which are shown in Fig. 5. In collation with Fig. 3, it

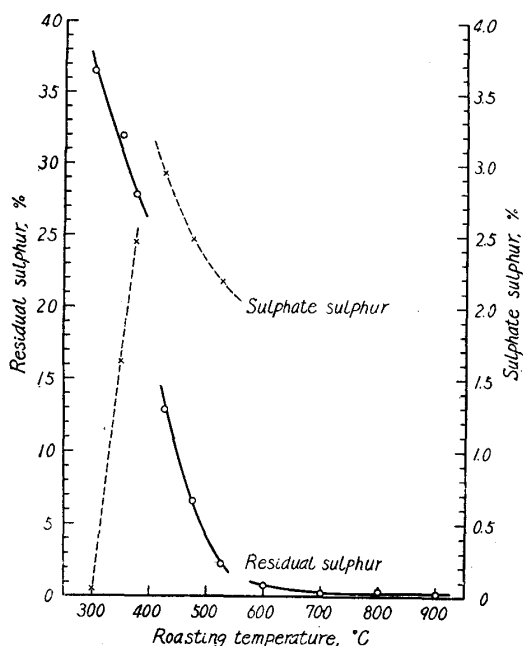


Fig. 5. Relation between the amounts of sulphate sulphur and residual sulphur of cinder and the roasting temperature

of about 90 g, but at 475°C it fell to 0.041 per cent and the resistance also dropped to 63 g, while at the high temperature of 800°C, the content became zero and the resistance was only 33g.

As seen in the sample roasted at 800°C, in the range of high temperature, the residual sulfur was very scarce and the sulfate was also negligible in the reacted layers. Therefore, in such a high temperature range, the high resistance of cinder must be attributed to the sintering of the formed oxides themselves. The composition of the intermediate layers showed that the content of residual sulfur therein was very high, being only a few per cent lower than that in raw ore. As no sulfate was found, the sintering of this layer might be deemed to be due neither to oxides nor to sulfates but to the eutectic of relatively low melting point, consisting of the formed oxide FeO and the unreacted sulfide FeS.

3. Effect of the size of ore particles on the sintering of cinder

The above-described experiments were carried out with minute powder of $-200''$, but in industrial practice, it is very difficult to grind ores to such an extremely small size and they always contain much coarser particles. So, for studying the sintering of coarser ore particles, those of $48-50''$ and $20-24''$ were roasted at various temperatures for 60 minutes and their resistances were measured.

was found that, though the relation was not so evident in the high temperature range, in the lower and the intermediate ranges the sulfate sulfur contents and the resistance showed a similar trend in their changes with the temperature. The sintering taking place in the lower temperature range must be attributed to the formed sulfates acting as a binder of ore particles. The remarkable decrease of residual sulfur in the intermediate range above 400°C is due probably to the progress of oxidizing reaction in "the first decreasing change in weight".

A relation similar to the above, also existed in the case of the unreacted layers. At 375°C, there was the minute content of 0.077 per cent of sulfate sulfur in the unreacted layer which showed a resistance

As shown in Fig. 6, in the case of coarse particles, the resistance of cinder fell very markedly and so the sintering is of little consideration in such materials. The temperature-resistance relation in this case was also divided into three ranges. In the intermediate range, however, the resistance increased with the rise of temperature contrary to the case of fine particles. As given in the first report⁽⁶⁾, the heating curve of coarse particles scarcely showed "the first decreasing change in weight", that is, the reaction of oxide formation was not active in this range, but only the reaction of sulfate formation went on actively with the rise of temperature. Therefore, in the case of coarse particle, the sintering of cinder should become harder with the rise of roasting temperature, which coincides fairly with the experimental results.

The curve of resistance shows a discontinuity at about 400°C, and so it is presumable that "the first decreasing change in weight" slightly appears though not seen in the heating curve. At any rate, it can be seen from this curve that the ignitibility and the combustibility of coarse ore particles are low, and, accordingly, such ore particles should be avoided as possible in the roasting operation of pyrrhotite, notwithstanding the weak sintering.

4. Rate of sintering

Figs. 7 and 8 show respectively the relations of the resistance and the thickness of the reacted layers versus time. From these figures it will be seen that the resistance is much larger at 350°C, at which the reacted layer was well developed, than at any other temperature, and that it is larger at 475°C than at 600°C, the reacted layer being thicker at the former than at the latter. Therefore, it may be assumed that the thickness of the reacted layer plays an important role in the resistance of cinder.

The marked development of the reacted layer in low temperature range, exemplified by the sample roasted at 375°C, may be due presumably to a high rate of di-

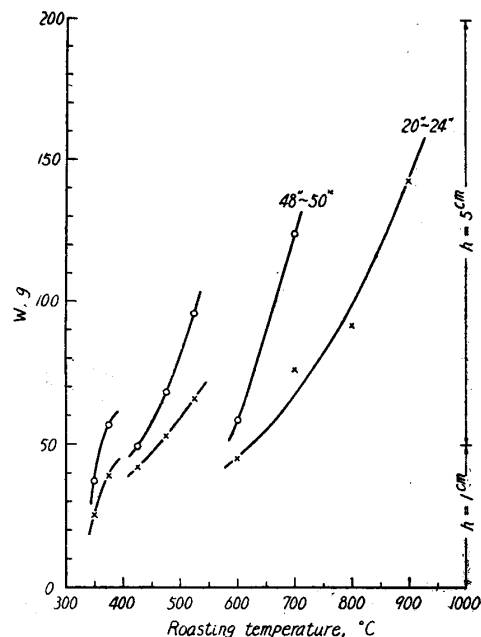


Fig. 6. Resistance of cinder of coarse pyrrhotite grain to the penetration of a rod.

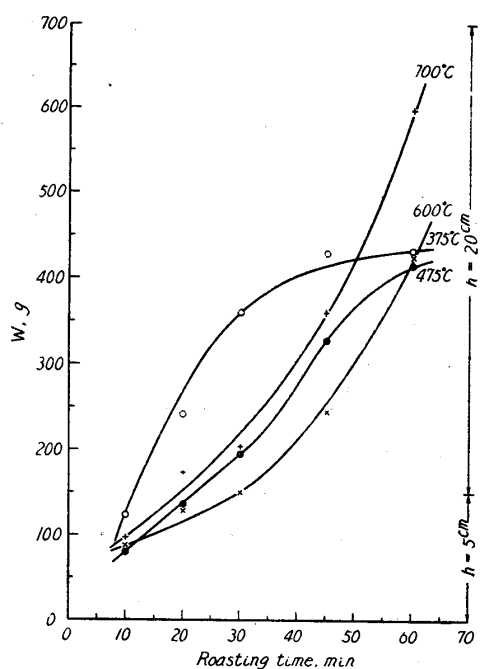


Fig. 7. Relation between the resistance of cinder to the penetration of a rod and the roasting time.

(6) M. Maruyama, Sci. Rep. RITU, A5 (1953), 208.

ffusion of oxygen gas through the pores of the pile of ore powders, occasioned by the low evolution of SO_2 gas due to the weakness of the reaction of oxide formation.

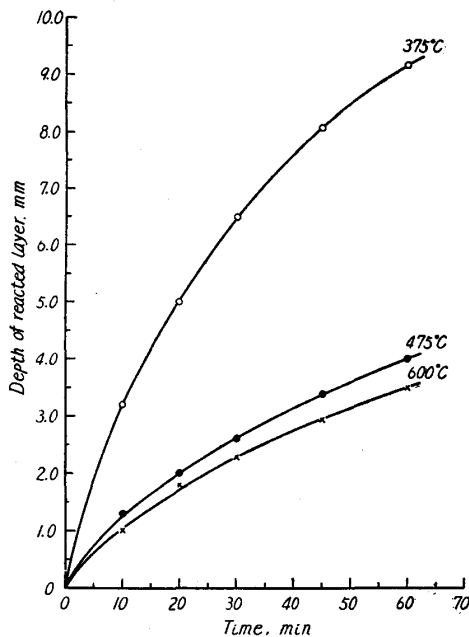


Fig. 8. Relation between the depth of reacted layer and the roasting time

increase with the rise of temperature, resulting in the increase of the thickness of the reacted layer, but in the actual measurement, the thickness was almost constant up to 900°C . This will be due perhaps to the fact that, in the high temperature range, the rapid progress of the sintering of the formed oxides causes a lowering of the total volume of pore. Therefore, the sintering must be taken into consideration in calculating the precise roasting reaction rate of pyrrhotite powder.

5. Sintering of FeS_n cinder

In the last report, it was clarified that the n -value of FeS_n was closely related with its combustibility. Consequently, it may be surmised that the n -value stands in some relation with the sintering of cinder. So, three kinds of FeS_n with 1.01, 1.08 and 1.14 of n were prepared by the same method as described in the last report. The ores were ground down to $-200''$ and roasted at various temperatures between 200 and 900°C for 30 minutes, and their resistances were measured under the falling height of 20cm.

Fig. 9 shows the results obtained. The resistance of $\text{FeS}_{1.14}$, the mixed crystal with high sulfur content, changed in the same way as in native pyrrhotite, that is, the temperature-resistance relation was divided into three ranges. In $\text{FeS}_{1.01}$ and $\text{FeS}_{1.08}$, both being a solid solution, the resistance increased parabolically from the onset of sintering up to 550°C without the discontinuity at about 400°C . As seen from the heating curve of FeS_n , it may be due to the absence of "the first decreasing change in weight".

The relation between the resistance and the n -value was not clear in the range of temperature above 550°C , but in the range below 550°C , the first sintering

On the contrary, in the intermediate temperature range, in which "the first decreasing change in weight" takes place, and in the high temperature range, in which only the reaction of oxide formation progresses, the diffusion of oxygen gas will be much retarded with detriment to the development of the reacted layer. The experimental results clearly prove it. In spite of the unchanged correlation with the thickness of the reacted layer, the rises of resistance at 375 and 475°C are strongly slow, accompanying the progress of the reaction, in comparison with that at high temperature. This probably means that the rate of sintering under the presence of sulfate is considerably slower than that of oxide.

In the range of high temperature, the rate of diffusion of oxygen gas should theoretically

temperature transferred below 250°C with a slight increase in resistance, as κ -value was lowered.

In the last report, it was emphasised in the roasting of pyrrhotite to use ores of mixed crystal with high sulfur content, instead of those composed of solid solution, which was endorsed from the present experiment on the sintering of cinder.

6. Roasting of the mixture of pyrrhotite and pyrite

In the above experiments, it was shown that pyrite cinder showed no strong tendency to the sintering. So, in roasting the mixture of pyrrhotite and pyrite, the sintering of cinder was studied.

The results of the experiments with the roasting time of 30 minutes are shown in Fig. 8, in which the mixing ratio is denoted by $P_y/(P_r + P_y)$, P_r and P_y being the weights of pyrrhotite and pyrite, respectively. The figure shows that, whenever the mixing ratio of pyrite exceeds 30 per cent, the sintering is remarkably diminished at any temperature, showing a good effect of mixing pyrite. Especially, it is of importance that this effect is large in the ranges of low and intermediate temperatures below 550°C. It is, therefore, evident that such a mixture may be roasted under the same practical conditions as pyrite.

Summary

The above results may be summarized as follows:

- (1) Pyrrhotite particles were very apt to sinter in the course of roasting, native ores beginning to sinter at about 350°C.
- (2) The temperature at which sintering began varied according to the sulfur content of pyrrhotite. It transferred below 250°C when the sulfur content lowered and the n -value in the molecular formula FeS_n approached 1.
- (3) The relation of resistance of pyrrhotite cinder versus roasting temperature was divided into three ranges. The resistance rose rapidly from the temperature

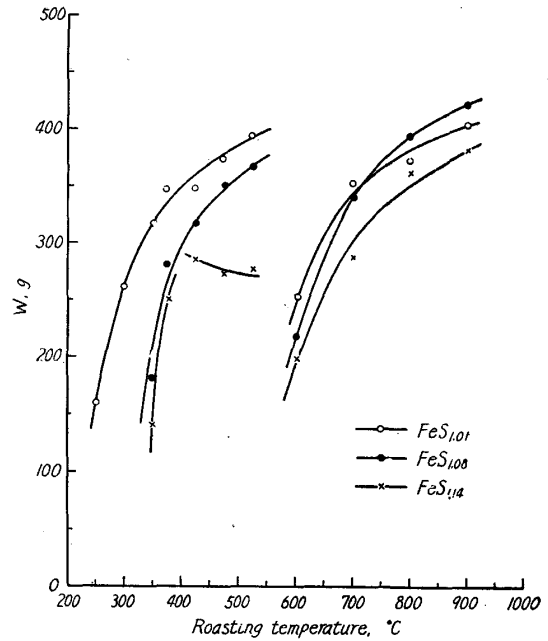


Fig. 9. Resistance of cinder of FeS_n to the penetration of a rod.

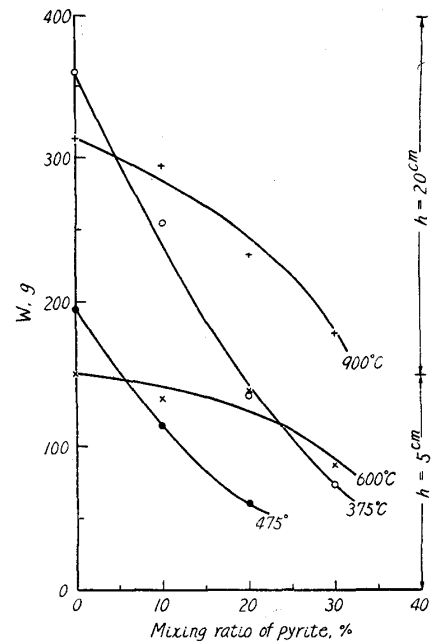


Fig. 10. Resistance of cinder of mixture of pyrrhotite and pyrite to the penetration of a rod.

of first sintering up to about 400°C and fell with the rise of temperature above 400°C but rose again above 550°C.

(4) In the lower and intermediate temperature ranges, the sintering of cinder might be attributable to the formed sulfate acting as a binder of ore particles.

(5) The temporary lowering of the resistance of cinder in the intermediate range of 400~550°C was caused by the decreasing of the formed sulfates resulting from the progress of the reaction of oxide formation in "the first decreasing change in weight".

(6) The high resistance of cinder appearing in the high temperature range was due mainly to the sintering of the formed oxides themselves, and partly to the formation of eutectic of formed FeO and the unreacted FeS.

(7) Ores in which the n -values of FeS_n were lower than 1.12, being solid solutions, showed continual increase of resistance from the temperature of the beginning of sintering up to 550°C, without showing discontinuity at about 400°C.

(8) At the outset of the roasting reaction, the thickness of the reacted layer was one of the chief factors for high resistance.

(9) The progress of sintering due to the formed sulfate was slower than that due to the formed oxide. Consequently, with the progress of the reaction, the resistance in the lower and the intermediate temperature ranges became lower than that in the high temperature range.

(10) As the size of ore particle became coarse, the sintering of cinder remarkably fell. Though divided into three temperature ranges, the resistance did not drop as in the case of fine powder, but kept on the rising with temperature in the intermediate range.

(11) An addition of over 30 per cent of pyrite to pyrrhotite would enable the completing almost without the sintering of cinder.

Acknowledgement

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