

# ON THE DRY METHOD FOR DECUPRIZATION OF PYRITE CINDERS

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## I. Introduction

Expansion of the Japanese iron and steel industry and increased consumption of imported ores has brought to the fore the problems of utilizing the pyrite cinders as the raw materials of ironmaking. The problem of eliminating their copper contents as much as possible, has become a matter of great importance to the national economy according to the fact that the pyrite cinders are high grade iron ores provided that their copper are reduced.

In recent years, there have been intensified efforts to eliminate copper in the pyrite cinders. Wet leaching method<sup>1)</sup> has been hitherto investigated sufficiently and has achieved some industrial application. The present method by the chlorination roasting consists essentially of passing the gas mixture of air and chlorine gas on the pyrite cinders at elevated temperature and proposes for the selective chlorination of copper oxide contained in them. Copper oxide is more easily chlorinated than iron oxide at the gas mixtures of low chlorine contents. Therefore, such treatment can eliminate much of the copper without appreciably increasing iron loss.

This paper presents the results of the study on the decuprization of pyrite cinders by the chlorinations roasting.

## II. Materials

The materials used are detailed below.

*Pyrite cinders:* Two kinds of pyrite cinders sieved below 100 mesh were used. Their chemical compositions in weight percentage are

A:	Fe	52.80%	Cu	0.320%
B:	Fe	55.06%	Cu	0.344%

*Gases:* Air by blower was washed by passing it through sodium hydroxide solution, sulfuric acid and then dried over phosphorous pentoxide.

Chlorine gas from tank was further purified by passing it through potassium permanganate solution, sulfuric acid and phosphorous pentoxide.

## III. Experimental procedure

Fig 1. is a schematic diagram of the experimental apparatus.

Purified gases of air and chlorine are led through the each flowmeters and

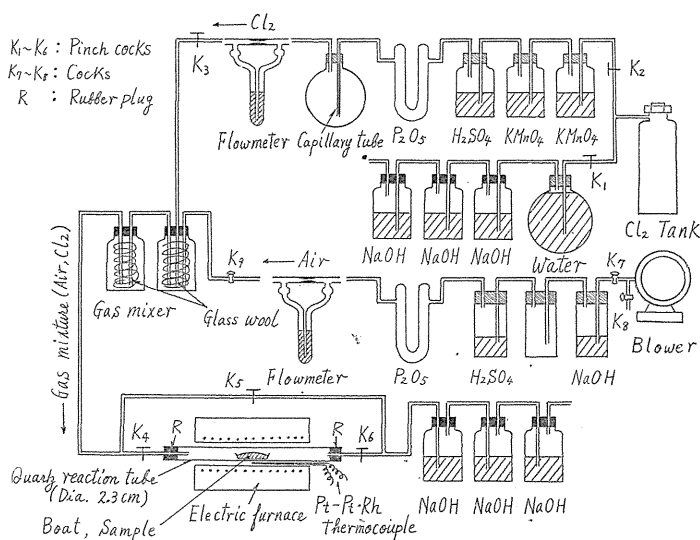


FIG. 1. Experimental apparatus.

mixed in the gas mixer. Chlorine in the exhaust gas is absorbed in sodium hydroxide solution.

After the cock  $K_4$  and  $K_6$  were closed, and the cock  $K_5$  was opened, the gas mixture was passed to the direction showed by the arrow in Fig. 1 and then the flow rates of the component gases were controlled by adjusting the pressure drops across the capillary flowmeters. Bringing the furnace to the desired temperature, 4.3 g of sample weighed in the porcelain boat was placed in the quartz reaction tube, and then the cock  $K_4$  and  $K_6$  were opened and the cock  $K_5$  was closed to introduce the gas mixture into reaction tube. Thus the measurement was started. After the complete of a run, the sample was analyzed for per cent copper and iron by the volumetric methods.

#### IV. Experimental results

The results of experiments for the sample A at 220 cc/min air flow rate are shown in Fig. 2 to Fig. 5.

As is shown in Fig. 2, the decuprization increases initially with increasing time of treatment, but after 1 to 2 hr. approximately the constant values are reached.

The influence of chlorine content on the elimination of copper and the loss of iron was measured with the chlorine contents between 2 and 9 pct.. From the results presented in Fig. 3, it is shown that the influence of chlorine content on the decuprization is small under these experimental conditions. On the other hand, some loss of iron occurs and the iron loss appears to increase in direct proportion to the chlorine content.

The measurements for various temperatures were carried out at the chlorine content and the treating time in the region where decuprization is approximately constant. As would be expected, the decuprization increases by raising the tem-

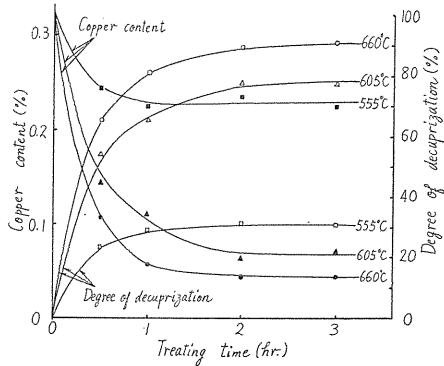


FIG. 2. Influence of treating time on decuprization at 4.55 pct. chlorine (Sample A).

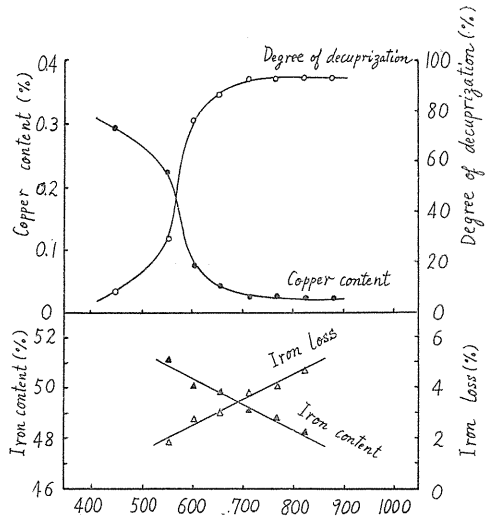


FIG. 4. Influence of treating temperature on decuprization and iron loss in 3 hr. treatment at 4.55 pct. chlorine (Sample A).

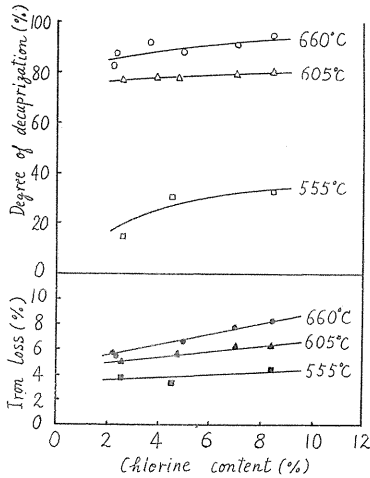


FIG. 3. Influence of chlorine content on degree of decuprization and iron loss in 3 hr. treatment (Sample A).

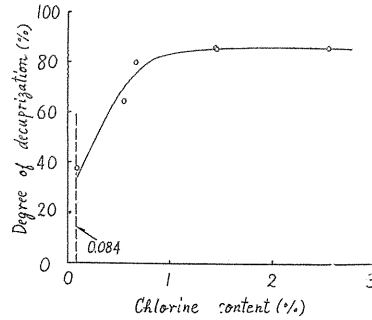


FIG. 5. Relation of degree of decuprization to chlorine content in 2 hr. treatment at 650°C (Sample A).

perature. The results are given in Fig. 4, which shows that when the temperature exceeds 500°C the decuprization becomes remarkable, at 700°C 91 pct. decuprization takes place and any further increase in the temperature has little practical influence on the elimination of copper.

The measurements with a much smaller chlorine contents were performed for the discussion of the decuprization process, which will be found in the later section. The data obtained are shown in Fig. 5.

In Fig. 6, Table 1 and Table 2 are shown the results of experiments for the sample *B* carried out under the condition of larger flow rates of air and lower chlorine contents, under which about the same decuprization as the above-mentioned results of the sample *A* and smaller iron loss may be expected.

In Fig. 6 are shown the results investigated at 960 cc/min air flow rate varying the temperature between 500° and 980°C. The decuprization is about the same as for the sample A, but the iron loss is seen to be much smaller.

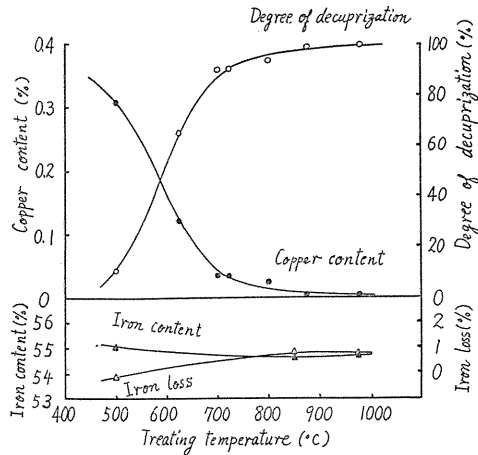


FIG. 6. Influence of treating temperature on decuprization and iron loss in 2 hr. treatment at 1.25 pct. chlorine (Sample B).

TABLE 1. Influence of Chlorine Content on Decuprization of Sample B in 2 hr. Treatment

Treating temperature (°C)	Flow rate of chlorine (cc/min)	Flow rate of air (cc/min)	Chlorine content (%)	Copper content (%)	Degree of decuprization (%)
800	5.5	1800	0.30	0.043	87.5
"	12.0	"	0.66	0.031	90.9
"	"	960	1.25	0.023	93.3
875	5.5	"	0.57	0.006	98.3
"	12.0	"	1.25	0.003	99.0
978	5.5	"	0.57	0.005	98.7
"	12.0	"	1.25	0.002	99.4

TABLE 2. Influence of Treating Time on Decuprization of Sample B at 950 C, 0.9 pct. Chlorine and 1060 cc/min Air Flow Rate

Treating time (min)	Copper content (%)	Degree of decuprization (%)
5	0.067	80.5
10	0.054	84.2
15	0.022	93.5
60	0.004	98.7

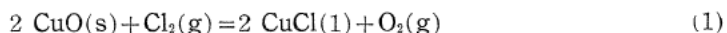
The results of Table 2 show that the rapid chlorination take place with the elimination of 80 pct. of the original copper after 5 min. treatment.

Despite the purely laboratory character of this work, it gives evidence of how the elimination of copper is affected by such factors as temperature, time and chlorine content.

#### V. Consideration for the decuprization process of the pyrite cinders

Since CuO is an important component of the pyrite cinders, the reaction of CuO with chlorine is of particular importance.

The experimental results on the chlorination reaction of CuO were described in the previous publication.<sup>2)</sup> The results of the study are as follows:



$$\Delta F^\circ = 6256.2 - 11.40 \text{ T ln T} + 4.33 \cdot 10^{-3} \text{ T}^2 - 0.14 \cdot 10^5 \text{ T}^{-1} + 56.0964 \text{ T} \quad (2)$$

The chlorine content of the gas mixture consisting of air and chlorine required for decuprization of the pyrite cinders will be appreciated from a consideration of the stoichiometric implication of the equation (1). The chlorine content required for this purpose is quite small and it is calculated to be 0.084 pct. chlorine at 650°C. The result calculated is shown in Fig. 5.

On the other hand, chlorination reaction rate of CuO has been found to be very fast. This result is good agreement with the rapid chlorination of Table 2.

#### VI. Summary

A relatively simple method for the decuprization of the pyrite cinders has been studied.

The method consists of roasting the pyrite cinders with air containing chlorine gas of low content at 700° to 1000°C. In this manner, 90 pct. or more of copper has been eliminated without much increasing iron loss.

Then, though several points remain to be explored, the decuprization process based on only the chlorination reaction of CuO has been considered.

#### References

- 1) Section Report of Japan Institute of Metals, No. 15, p. 29, 1954.
- 2) K. Sano and K. Okajima: J. Iron Steel Inst. Japan, 44, 859, (1958).