Fluidized-Bed Roasting of Pyrite*

Motoo WATANABE and Akiichi KIGOSHI

The Research Institute of Mineral Dressing and Metallurgy

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Synopsis

For the purpose of getting a base as to thorough utilization of domestic pyrite which contains a small amount of cobalt, copper and zinc, the sulfatizing roasting process which is based upon the preferential sulfatization by fluidized-bed reactor which has a capacity of 5 kg per day was studied.

This paper describes the results of experiments, showing that it is useful to treat this kind of pyrite to produce water soluble sulfate of cobalt, copper and zinc while retaining most of iron in insoluble oxide from, and suggesting one of possibilities considered in treating the final reside after extraction.

Theoretical considerations are given on the gas composition and its distribution in the furnace, and the reacting temperature and the hold-up time of the solids in the furnace.

I. Introduction

Many domestic pyrite concentrates contain a small amount of cobalt, copper and zinc. Owing to the inability to maintain proper temperature and atmosphere by the furnacing equipment of the past, selective sulfatizing of the individual components in these ores has hardly been realized in actual practice. In the past few years a new type of equipment, the fluidized-bed roaster, has become available. It has revived interest in selective sulfatizing because of the ease with which the roasting conditions in the furnrce can be uniformed.

This paper describes the results of experiments carried out by the fluidized-bed reactor which has a capacity of 5 kg per day, and shows that it is useful in treating cobalt, copper and zinc bearing pyrite to produce water soluble sulfates of these metals while retaining most of iron in insoluble oxide form.

II. Experimental materials used

The experiments were carried out on the pyrite from Shimokawa Mine, Hokkaido, the particle size and the analysis of which are given in Table 1 and

Table 1. Particle size.

Size (mesh)	Content (%)
− 80 + 120	0.62
− 120 + 150	4.67
− 150 + 170	4.26
− 170 + 200	8.70
− 200 + 270	8.10
− 270 + 325	23.57
− 325	50.08

Table 2 respectively. Calculation from Table 2, the components of the concentrate are listed in Table 3.

Table 2. Chemical analysis of concentrate.

Element	Fe	Cu	Co	Zn	S
Content (%)	42.30	0.44	0.74	0.48	44.51

Table 3. Component of concentrate.

Compound	$FeS_{1.77}$	Cu_2S	CoS	ZnS	SiO_2
Content (%)	86.06	0.55	1.15	0.71	7.30

III. Preliminary considerations and tests

1. Fluidization of solids

When a fluid such as air is passed upward with increasing velocities through a loose mass of granular solid, several things will happen. First, the fluid percolates through the bed at extremely low velocities without agitating any individual particles. As the velocity continues to increase, the bed will expand until a point is reached at which a certain degree of freedom to move is imparted to the individual particle. As the velocity of the gas is further increased, the particles of solids begin to entrain overhead with the fluid and a relatively dilute suspension of solids and gas is formed above the liquidlike dense phase. As the gas velocity continues to increase, the relative concentration of the solids in the two phases becomes more nearly alike until a velocity is reached at which total entrainment of the solid is encountered and a single dilute suspension exists. The roasting procedure operated under such condition is called the fluidized-bed roasting. In this study the velecity required to form this single dilute suspension at the roasting temperature was determined by the results obtained at the room temperature. Glass tube 75 mm in inside diameter and 1 m in length placed vertically was used in this determination. The ore was supported on a perforated disk which was placed 20 cm from the bottom of the tube, as detailed later, and was fluidized by air inserted from the bottom of the tube which was connected with blower through a Oriffice plate. The top of the tube opened directly into two cyclones. Static pressures relative to atmospheric pressure and pressure drops across the fluidized-bed were read from the vertical manometers connected to pressure taps which are located at the top and the bottom of the tube. The experimental results are summarized in Fig. 1 by plotting ratio of L_f to L_c versus superficial velocities of air in the glass tube, where L_f is height of the fluidized-bed while L_c is that of the settled. It is seen from this that the same L_f/L_c ratio is obtained irrespective of the valur of L_c. Thus in observing the behavoir at room temperature, it was found that the best fluidizing condition was obtained when L_f/L_c ratio was equal to 2.1, at which seperficial air velocity requied was 15 cm/sec. Under this condition

a half of each charge which is so fine, almost -325 mesh, that entrained with the air could be seized by two cyclones. Comparing the pressure drops across the fluidized-bed at the operating temperatures which was employed by the equipment mentioned later to that obtained above, it was found that superficial velocity required in fluidizing at the roasting temperature is similar in all respects to that of room temperature equal to 15 cm/sec. Accordingly, it was evident from this basic consideration that the air flow rate could be determined by correcting the effect of the expansion of gas with which the superficial velocity would keep the constant value mentioned above.
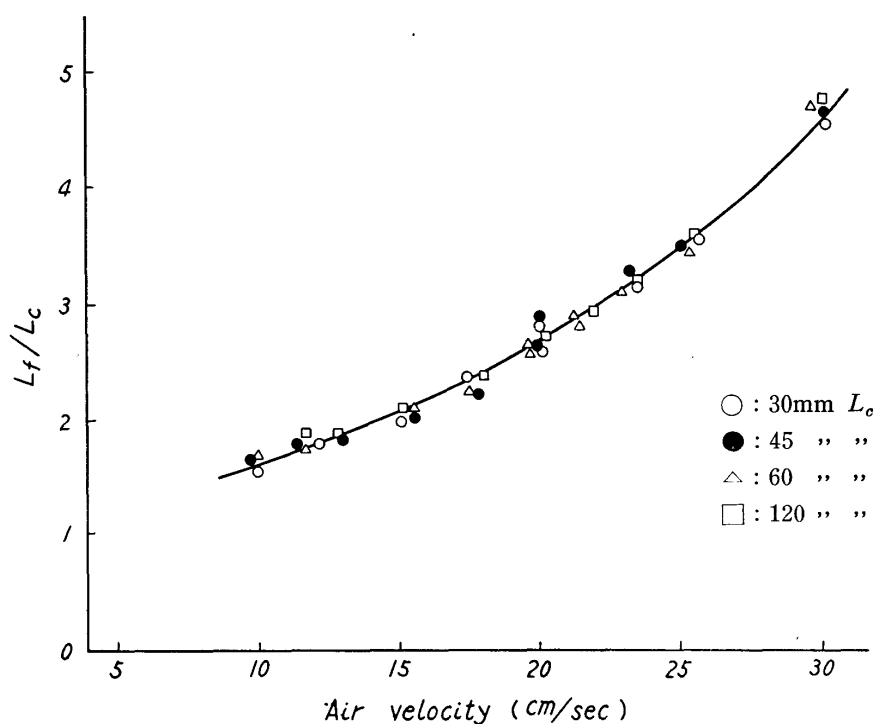

Fig. 1. Relation of L_f/L_c to superficial air velocity.

2. Preliminary oxidizing and sulfatizing tests

Some trials on preliminary oxidizing and sulfatizing roasting by boat were employed to determine the conditions desired for the fluidizing roasting. The experimental apparatus described by one[1] of the present writers was used. In this preliminary work, two kinds of samples which were seived into $-80+325$ and -325 mesh were tested because the dust carried over which entrained with air into the cyclone was almost -325 mesh. A silica boat, in which the sample was placed, was inserted in the reaction tube made from opaque silica, and heated outside by an electric resistance furnace which had been kept at a desired temperature. Under an abundant supply of air at the constant rate, the out-going gas containing sulfur dioxide gas was analysed. Then quantity of sulfur oxidezed from beginning to each time during the reaction can be calculated. On the assumption that the

(1) T. Isihara and A. Kigoshi, Bull. Res. Inst. Min. Dressing and Met., 9(1953), 177.

oxidizing of each particle proceeds centripetally from the surface, the quantity of sulfur oxidezed x is computed as follows:

$$x = 1 - \frac{r^3}{R^3} \qquad r = R(1-x)^{1/3},$$

where R and r is the radius of the particle and that of the unreacted respectively. The results obtained at 600°C are ahown in Fig. 2. The shape of these curves, except the point in which the curve is rather longer at the beginning and the end, can be seen to agree with those of the equation[2] by which the mechanism of roasting is explained as the rate of oxidation which is proportional to the diffusion velocity of oxygen in the oxide film which is formed on the surface of unreacted part during the oxidation. Thus it is seen that these two kinds of sample can be oxidized almost completely in seven minutes under abundant supply of air.
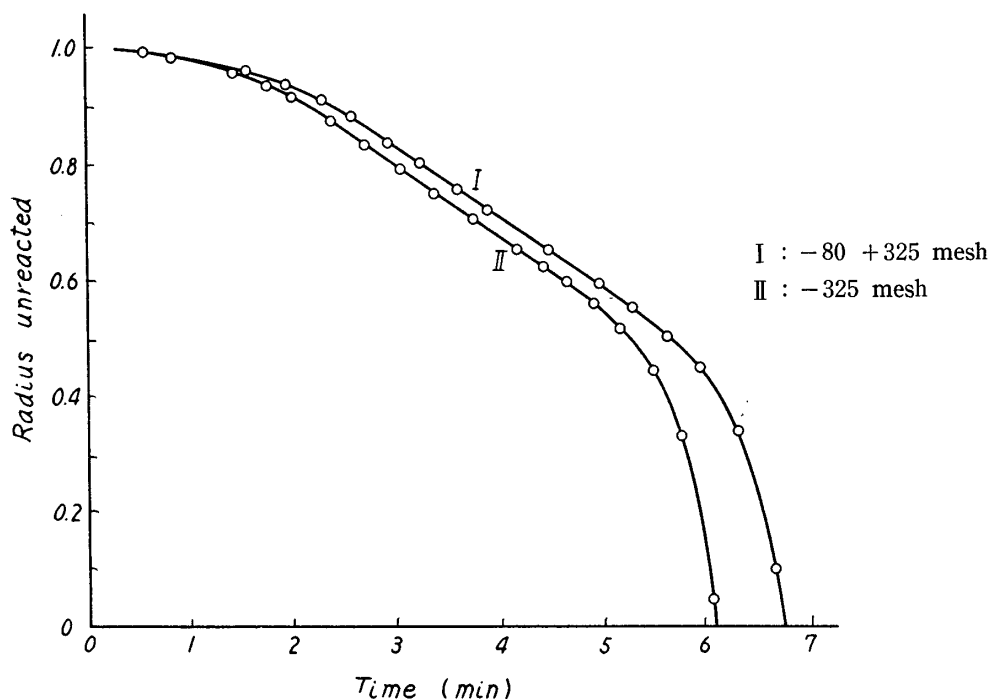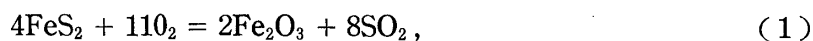

Fig. 2. Oxidizing of concentrates.

In roasting the sulfide materials, the basic reactions which will occur with the evolution of sulfur dioxide gas will be as follows:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2, \qquad (1)$$

$$2MS + 3O_2 = 2MO + 2SO_2. \qquad (2)$$

Sulfur dioxide gas thus issued will be converted to SO_3 by oxygen in excess air as follows:

$$2SO_2 + O_2 = 2SO_3. \qquad (3)$$

(2) Y. Ogawa, J. Min. Inst. Japan, **46** (1930), 515.

Eventually, the metal oxide formed by equation (2) could be converted to a sulfate form as follows:

$$MO + SO_3 = MSO_4,\qquad\qquad (4)$$

or
$$MS + 2O_2 = MSO_4.\qquad\qquad (5)$$

Whether the roasting proceeds according to equations (1) and (2) alone, or sulfatizing also has someting to do with it depends upon the relative stability of these sulfates at high temperature. As sulfates of cobalt, copper and zinc can exist stably at higher temperature and in more dilute atomsphere than those of iron, it must be possible from the theoretical point of view to produce sulfates of cobalt, copper, and zinc while retaining most of iron in oxide form. So the preliminary works by boat were next employed in sulfating manner in the current of mixed gas of sulfur dioxide, oxygen and nitrogen whose concentrations were 7.4, 10.9 and 81.7 per cent respectively. This composition was determined as follows: Stoichiometric relations between 1 gr of concentrate and gas are listed in Table 4.

Toble 4. Stoichiometric relations between 1 g concentrate and gas.

Equrtions	Air Required (cc)	O_2 in Air (cc)	SO_2 Issued (cc)	Total gas Issued (cc)	Volume change of gas (cc)
$4FeS_{1.77} + (3 + 4 \times 1.77)O_2 = 2Fe_2O_3 + 4 \times 1.77SO_2$	2,055.3	431.6	303.2	1,926.9	-128.3
$CoS + 2O_2 = CoSO_4$	27.0	5.7	—	21.3	$-\ 5.7$
$2Cu_2S + 5O_2 = 2CuSO_4 + 2CuO$	9.2	1.9	—	7.3	$-\ 1.9$
$2CuO + O_2 + 2SO_2 = 2CuSO_4$	1.8	0.4	-0.8	0.7	$-\ 1.2$
$ZnS + 2O_2 = ZnSO_4$	16.0	3.4	—	12.7	$-\ 3.4$
Total	2,109.3	443.0	302.4	1,968.8	-140.5

It is seen from this table that the air required for 1 gr of sample is 2109 cc, while the amount of gas evolution is 1969 cc containing 302 cc of sulfur dioxide. Accordingly, when the air flow is two times as great as the theoretical the concentration of sulfur dioxide in the reactor gas is

$$\frac{302}{1969 + 2109} \times 100 = 7.4 \ (\%),$$

and that of oxygen is

$$\frac{443}{1969 + 2109} \times 100 = 10.9 \ (\%),$$

and the remainder, 81.7 per cent is nitrogen. The experimental results at 600°C are summarized in Figs. 3 and 4. The full line shows the water solubility. When the consequent residue is leached by 1 % H_2SO_4, the part represented by dotted line which is considered to have been derived from oxides and basic sulfates of cobalt and copper is leached out. The final residue is considered to consist of Fe_2O_3, but a small amount of ferrites of cobalt and copper may be present. As shown in these figures, slight sulfatizing takes place in 20 minutes, while a considerable amount

of cobalt, copper and iron is leached out by dilute acid. Though sulfatizing takes place with the recovery of more than 90 per cent of the original cobalt and copper after 150 minutes, a very long time should be required for a complete sulfatizing of cobalt and copper.
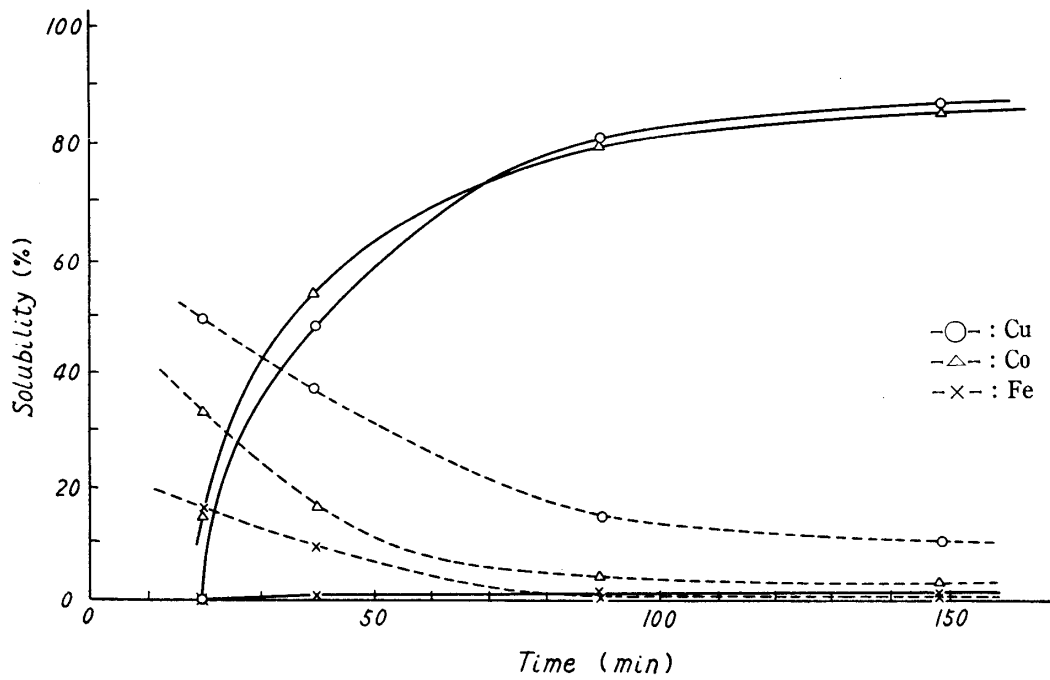
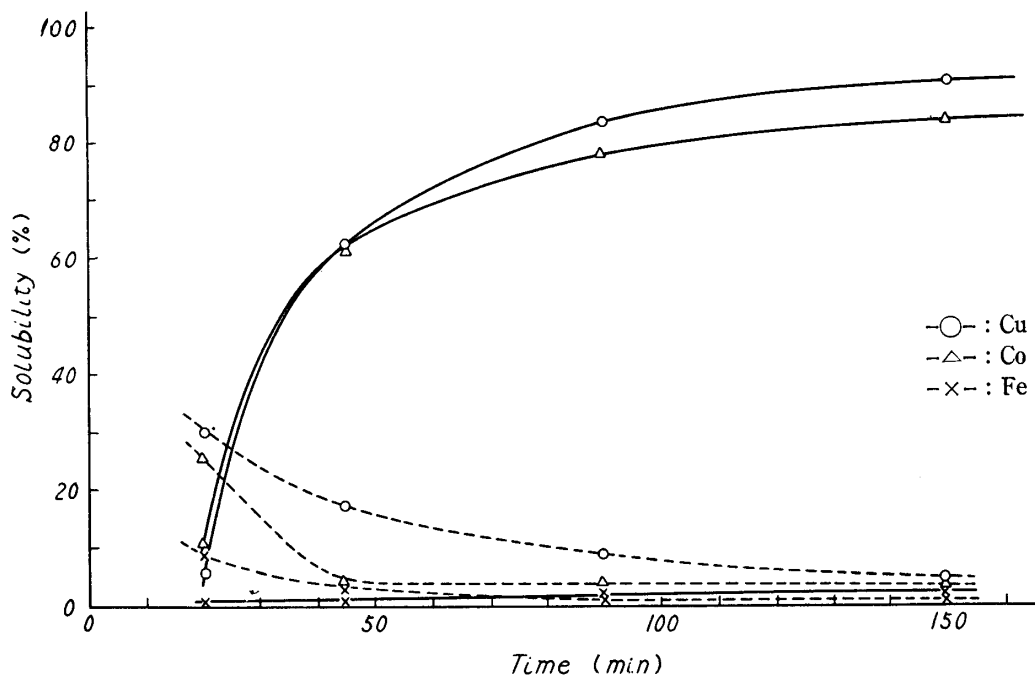Fig. 3. Sulfatizing of concentrate, −80+325 mesh.

Fig. 4. Sulfatizing of concentrate, −325 mesh.

3. Hold-up time of particles in fluidized-bed

The hold-up time of charges in the blast furnace where the contents may come out layer by layer can be defined as W/w, where $W^{(3)}$ is the capacity of the furnace and $w^{(3)}$ is the feed rate. This concept may be meaningless, however, as far as the fluidized-bed is concerned; hence, the proper conception should be induced as follows :

In the fluidized-bed where the stationary stated is reached, if $M^{(4)}$ is the capacity of the fluidized-bed and Δm_i ($i = 1, 2, 3, \ldots\ldots, n, \ldots$)$^{(4)}$ is the feed rate per short time Δt_i, then the concentration of Δm_1 can be represented as

$$\frac{\Delta m_1}{M + \Delta m_1}\,,$$

because all of the Δm_1 is expected to disperse into the bed as soon as the insertion is made according to the character of the fluidized-bed. As Δm_1 is negliegibly small, then

$$\frac{\Delta m_1}{M}\,.$$

According to this feeding, the particle in a quantity identical to Δm_1 should be discharged. It follows that the quantity of Δm_1 contained in this dischrge is given by

$$\frac{(\Delta m_1)^2}{M}\,,$$

and Δm_1 remaining in the bed is

$$\Delta m_1 - \frac{(\Delta m_1)^2}{M}\,.$$

Accordingly, the quantity of Δm_1 discharged by the next charge, Δm_2, is

$$\frac{\Delta m_2}{M}\Big(\Delta m_1 - \frac{(\Delta m_1)^2}{M}\Big)\,.$$

Generally, by Δm_n

$$\frac{(\Delta m)^2}{M}\Big(1 - \frac{\Delta m}{M}\Big)^{n-1}$$

of Δm_1 is discharged, where $\Delta m = \Delta m_i$. Replacing Δm and n with the feed rate m and time $t^{(5)}$ respectevely, the above becomes

$$\frac{m^2}{M}\Big(1 - \frac{m}{M}\Big)^t\,. \tag{6}$$

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(3) Approximately speaking, this quantity may able to be measured in the unit of weight. Strictly speaking, however, changing in weight of the charge by the chemical reaction, conceptual unit which is disengaged to consider to be constant during the chemital reaction must be used.

(4) This values must be measured in a similar way as (3). Unit of weight, however, could be applied by simple correction as detailed later.

(5) When $\Delta t \to 0$, $n = 1$ at $t = 0$, accordingly $n - 1 = t$.

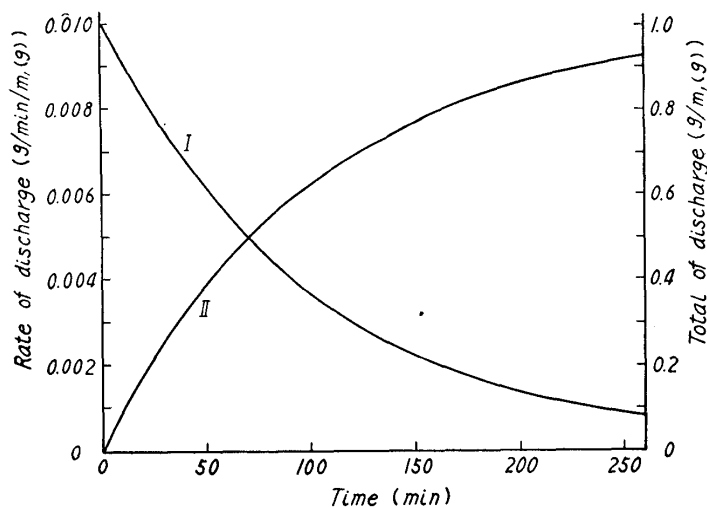An illustration of this formula in which m is equal to 1 and M equal to 100 is shown in Fig 5, curve I. This shape depends upon the m/M ratio. It is seen that the discharging rate of a definite charge is biggest at the time it is just feeded, and then decreases with the lapse of time. Accordingly, when the discharge is given for a certain period of time from the fluidized-bed under the stationary state, it appears that the curve I shows the relation between the hold-up time and the quantity of the particles consisting of the discharge, that is, the discharge is a jumble of the particles which have been subjected to various hold-up time. On the other hand, the relation between the solubility and time is shown in Fig. 3 and 4. Accordingly, quantitative relationships between the soluble and insoluble part of the calcine are to be illustrated in Fig. 6, in which Fig. 3
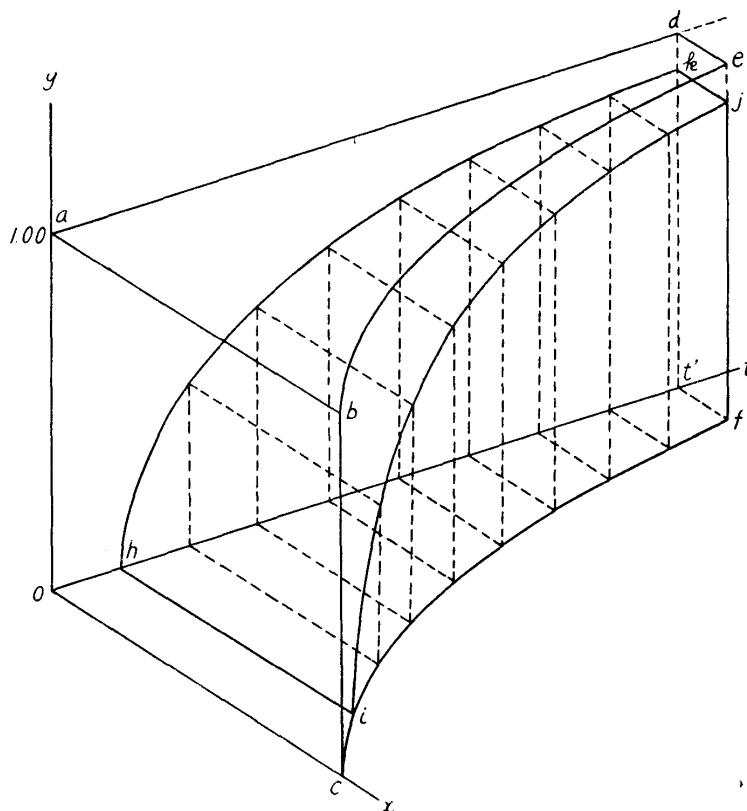

Fig. 5. Illust;ations of equations (6) and (7).
I ···eq. (6)
II ···eq. (7)

Fig. 6. Quantitative relation between soluble and insoluble parts.

or Fig. 4 is combined to the Fig. 5, curve I. In this fugure the curve cif corresponds to Fig. 5, curve I, and the curve *hk* corresponds to Fig. 3 or Fig. 4. From the illustrations, it can be seen that the volume enclosed by *aocbdt'fe* represents the total cobalt, copper and zinc contained in calcine, in which the lower section divided by *ijk* represents the soluble part and the upper section represents the part going into residue. Curve *hk* is innate to the character of the sample and its chemical reactions, but curve cif can be varied with m/M ratio. Since the inclination of this curve becomes loose with a decrease in the m/M ratio, the time required to constrict to zero becomes longer. Consequently, a considerably small m/M ratio is needed to get high solubility by extraction. Considering the relations mentioned above, in this study m/M is determined as 0.02, 0.008 and 0.004. Δm_1 which have been described in the above as the parts discharged during the time zero to t_1 can be calculated by an integration of equation (6) as follows:

$$W = \int_0^{t_1} \frac{m^2}{M}\left(1 - \frac{m}{M}\right)^t dt,$$

hence,

$$W = \frac{0.4343\, m^2}{M \log\left(1 - \frac{m}{M}\right)} \left\{(1 - \frac{m}{M})^t - 1\right\}. \tag{7}$$

This equation is illustrated in Fig. 5, curve II. In sampling for the extraction, which will described in later, the calcine in a bed in which the contents has almost been replaced by the calcine in the present condition must be treated. If R is the rate of replacement, then

$$R = \frac{W}{m} \times 100 \quad (\%),$$

where m is the feed rate. As seen earlier, the oxidation of the ore particle is almost finished in a few minutes, and the following change seems to be rather small. Then, in the calculation of these equations, M and W can be measured by the weight of calcine, and also by m that in oxidezed state. Therefore, by combining the two equations, the rate of the replacement is given by

$$R = \frac{43.43\, m'}{M \log\left(1 - \frac{m'}{M}\right)} \left\{(1 - \frac{m'}{M})^t - 1\right\}, \tag{8}$$

Table 5. Time required in replacing.

m/M	m'/M	$R\,(\%)$	$t\,(\text{hr})$
0.02	0.014	99.5	10.2
0.008	0.0056	,,	18.9
0.004	0.0028	,,	37.6
,,	,,	99.0	29.6
,,	,,	95.0	18.2
,,	,,	90.0	13.8
,,	,,	80.0	9.6
,,	,,	50.0	4.1

where m' is the value of m in the oxidized state, and experimentally m' is equal to $0.7\,m$. In order to reduce the error caused by lack of replacement as small as possible, R is fixed at 99.5 per cent in this study. The time required for 99.5 per cent of replacement under the condition where m/M is equal to 0.02, 0.008 and 0.004 calculated by the equation (8) is listed in Table 5.

IV.   Experimental apparatus and procedure

The experimental apparatus consists of a roating equipement and a control panel. The former has chiefly a roasting furnace, an electric heater, a blower and a feeder, and the later has the equipments required to observe and control all the roasting procedures. A sketch of experimental apparatus is shown in Fig. 7.
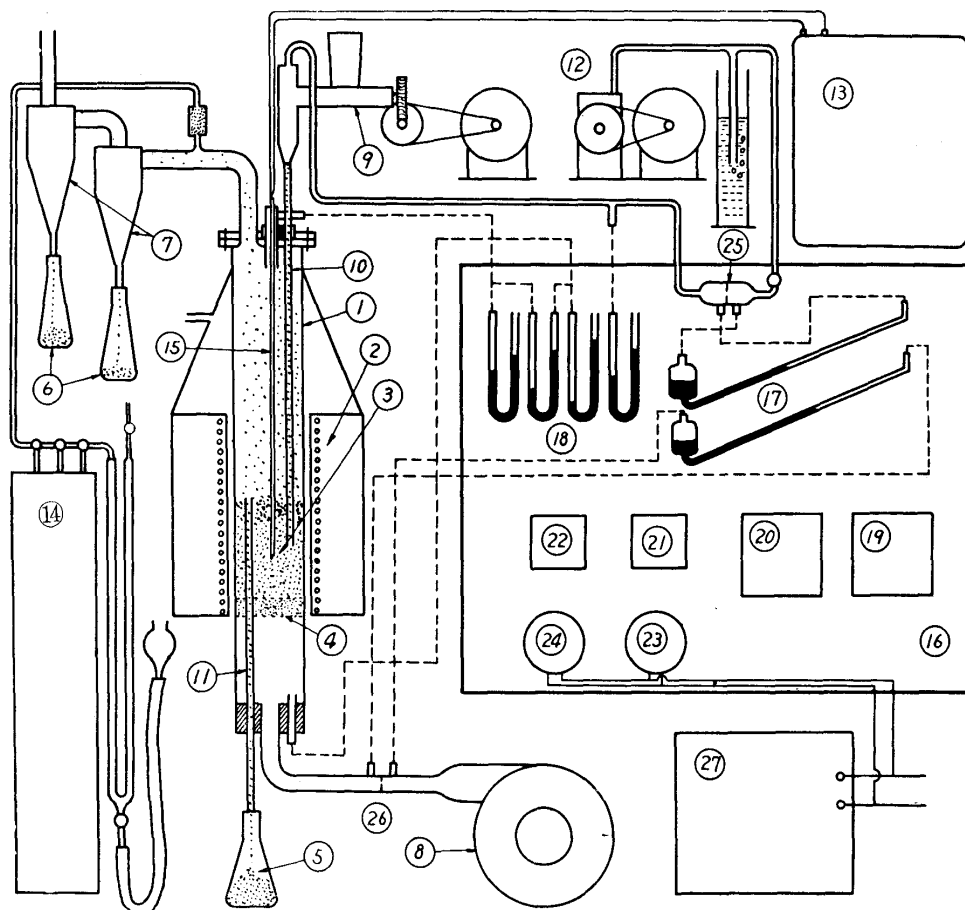
Fig. 7.   Experimental apparatus.

① Furnace	⑩ Feed pipe	⑲ Pyrometer
② Electric heater	⑪ Over flow pipe	⑳ Volt meter
③ Fluidized bed	⑫ Air pump	㉑ Ammeter (heater)
④ Supporting disk	⑬ Temp. controler	㉒ Ammeter (blower)
⑤ Over flow	⑭ Gas analyser	㉓ Transformer (blower)
⑥ Carry over	⑮ Thermocouple	㉔ Transformer (feeder)
⑦ Cyclone	⑯ Control panel	㉕ Oriffice
⑧ Blower	⑰ Flow meter	㉖ ,,
⑨ Feeder	⑱ Manometer	㉗ Transformer (heater)

The roasting furnace is made of SM tube 75 mm in inside diameter and 1 m in length. The top of the furnace is made of stainless steel, in which there are an exhaust pipe, a feed pipe, and a tap for measuring the temperature and the pressure. The bottom of the tube has the blowing pipe and an overflow pipe, and a tap for measuring the pressure. The perforated disk on which fragments of nichrome wire are heaped up is locate 15 cm from the bottom of the tube. The suppering bed thus formed is used for supporting the fluidizing bed and for distributing air. The overflow pipe is made of transparent silica, whose upper end coincides with the upper line of each fluidized-bed, while lower end is enclosed by a conical flask. The sample is charged through a feed pipe by means of a screw-feeder which is driven by the AC series motor. The feed rate of the sample can be regulated by controlling the voltage applied to the motor. For fear of the isolation of free fulfur from the pyrite in the feed pipe, air corresponding to ten per cent of total air is blown into the furnace with the sample by means of a rotary pump. The exhaust pipe opens to two cyclones. The air flow rate which is measured by an Oriffice meter is regulated at a desired point by controlling the voltage applied to the AC seiries motor which drives the fan.

A total charge of definite weight is inserted into the furnace, and is heated rapidly from outside by an electric heater, and when the point is reached where the temperature is 50°C lower than the desired point, the air begins to flow with increasing temperature. When it is confirmed by the reading of the manometers that the stable fluidized-bed has been formed, the feeding begins at the difinite rate. When the desired temperature is reached, this condition continues to maintain the time represented in Table 5. Thus the contents in the furnace are replaced by the calcine in the present condition. When these conditions are kept for more two houres, the overflow and the dust carried over are sampled, while sulfur dioxide and oxygen in the outgoing gas are analysed occasionally. The gas composition in each run is the average value. A calcine of about 2.5 g is used in each extraction after leaching, filtration and washing by water, and the residue undergoes the same treatment with 1% of sulfuric acid. Then the solubility of cobalt, copper, iron (in most studies zinc, too) is calculated by analysing these two kinds of solution and the final residue. The polarographic method[6] is used for analysis, in which pyridine and hydrochrolic acid for cobalt and copper, sodium citrate for iron and sodium tartrate for zinc are used as the supporting salt.

V. Experimental results

The experimental results are summarized in Tables 6, 7 and 8. In these tables, (1)-(5), (6)-(12), (13)-(15) and (16)-(17) are the results at 550°, 600°, 650° and 700°C respectively. In each run, the influences of the hold-up time by varying m/M ratio, and the gas composition by feeding ratio were observed. The desired feeding ratio which will be detailed in VI is to be obtained by varying the feed rate at the constant air flow rate while proper M must be chosen not to vary the m/M ratio.

(6) M. Shinagawa, *Polarographic method of analysis*, (1952), 175 ; 180 ; 204 ; 172.

Table 6. Experimental results, (I).

Exp. No.		1		2		3		4		5	
Roasting Temp.(°C)		550		550		550		550		550	
Feed Rate (g/min)		2.70		3.78		1.62		2.70		3.78	
m/M		0.020		0.020		0.008		0.008		0.008	
Replacing Time(hrs)		10		10		19		19		19	
α		0.5		0.7		0.3		0.5		0.7	
Gas concentration (%)	SO$_2$	7.6		8.0		4.4		7.8		10.3	
	O$_2$	11.4		9.0		14.6		10.9		6.8	
		Over flow	Carry over	Over flow	Carry over	Over flow	Carry over	Over flow	Carry over	Over flow	Carry over
Water Solubility (%)	Co	37.51	42.23	62.91	64.42	54.69	58.22	80.67	73.35	74.57	63.93
	Cu	16.12	22.82	50.15	38.84	52.21	66.44	88.67	80.74	64.17	62.86
	Zn	42.42	48.63			74.06	73.23	87.12	79.04	92.84	85.33
	Fe	0.70	1.90	1.34	2.99	3.59	7.29	2.48	10.23	2.04	7.74
Acid Solubilty (%)	Co	10.65	8.06	6.21	9.48	7.04	8.38	2.25	4.57	4.04	6.99
	Cu	47.09	44.63	30.73	16.61	12.69	11.45	3.20	6.37	20.80	19.05
	Zn	47.13	47.44			8.71	12.53	10.23	12.01	4.51	9.72
	Fe	4.40	4.41	2.46	4.21	5.55	6.16	1.66	4.96	1.64	4.34
Total Solubility (%)	Co	48.16	50.29	69.12	73.91	61.73	66.60	89.92	77.92	78.61	71.92
	Cu	63.21	67.45	80.88	55.45	64.90	77.90	91.87	87.11	84.97	81.91
	Zn	89.55	96.07			82.77	85.76	97.35	91.05	97.36	95.05
	Fe	5.10	6.32	3.80	7.21	9.14	13.45	4.14	15.20	3.68	12.08
Insolubility (%)	Co	51.83	49.71	30.88	26.09	39.27	33.40	17.08	22.08	21.39	29.08
	Cu	36.79	32.54	19.10	44.55	35.10	22.11	8.13	12.89	15.03	18.09
	Zn	10.45	3.93			17.23	14.21	2.65	8.95	2.64	4.95
	Fe	94.89	93.68	96.20	92.79	90.86	86.55	95.86	84.80	96.32	87.92

By comparing the results (1)-(5), it is seen that the water soluble cobalt, copper and zinc increases with decreasing m/M ratio; on the contrary, the acid soluble parts decreases, which is common to all temperatures experimented here. From the equilibrium points of view, lower temperature is better for sulfatizing, but considering the reaction velocity, rather high temperature is needed, and there must be mutual concession between them. By comparing (4), (9), (15) and (17) to know the influences of temperature alone, it is seen that the highest solubility of copper with overflow was obtained at 550°C, but nearly the same solubility of cobalt was obtained at 550° and 600°C, while that of iron at 550°C was two times as great as that at 600°C. Concerning the carryover, the highest solubility was obtained at 600°C, iron extracted being less than a half at 550°C though slightly more than that at 650° and 700°C. Accordingly, the best roasting temperature seems to be 600°C as far as range experimented is concerned.

As will be detailed in VI, various gas compositions are to be obtained by varying the feeding ratio. The influences of gas composition on the solubility can be seen by comparing (3), (4), (5), (8), (9) and (10). The maximum solubility of cobalt, copper and zinc was obtained by extraction in the case where the feeding ratio is equal to 0.5, followed by the case with 0.7 and 0.3 with little exceptions. Though the acid soluble part is smallest at 0.5, the total soluble component is largest at 0.5. Though the smallest solubility of iron is obtained at 0.7, the best feed rate

Table 7. Experimental result, (II).

6		7		8		9		10		11		12	
600		600		600		600		600		600		600	
2.54		3.56		1.52		2.54		3.56		2.54		2.54	
0.020		0.020		0.008		0.008		0.008		0.008		0.004	
10		10		19		19		19		37		48	
0.5		0.7		0.3		0.5		0.7		0.5		0.5	
6.0		8.4		4.9		7.1		11.5		6.6		7.2	
13.0		10.2		14.7		11.1		6.0		13.0		11.9	
Over flow	Carry over	Over flow	Carry over	Over flow	Carry over	Over flow	Carry over	Over flow	Carry over	Over flow	Carry over	Over flow	Carry over
57.34	51.03	58.62	53.68	64.17	58.33	79.43	74.39	70.31	60.70	79.98	76.15	83.16	77.70
51.18	28.27	40.51	57.14	63.50	71.37	72.34	84.82	59.16	54.89	79.59	81.40	86.19	82.89
47.32		69.87	67.13	74.25	71.75	90.84	81.53	84.66	75.87	85.32	68.46		
1.45	3.09	0.85	2.05	1.67	4.78	1.57	3.94	0.88	1.56	1.76	5.04	1.97	4.64
5.83	9.91	6.72	11.91	5.13	5.02	1.48	5.18	6.06	11.18	4.86	7.68	1.99	5.15
23.29	57.81	32.01	21.43	8.16	6.21	8.65	5.09	17.48	24.56	7.62	6.78	4.13	11.82
44.43		23.16	25.29	8.14	16.42	7.05	17.53	60.96	21.33	9.78	24.20		
2.40	4.84	1.95	3.68	1.60	3.19	0.99	3.25	0.94	2.86	1.43	4.13	1.41	3.98
63.27	60.94	65.34	65.59	69.30	63.35	80.91	79.57	76.37	71.88	84.84	83.83	85.15	82.85
74.47	86.08	73.72	78.57	71.66	77.58	80.99	89.91	76.65	79.54	87.21	88.18	90.32	94.17
91.75		93.03	92.42	82.39	88.17	97.89	99.06	95.62	97.20	95.10	92.66		
3.85	7.94	2.79	5.73	3.27	7.97	2.56	7.19	1.82	4.45	3.19	9.17	3.38	8.62
36.73	36.06	34.66	34.41	30.70	36.65	19.09	20.43	23.63	28.12	15.16	16.17	14.85	17.15
25.53	13.92	26.28	21.43	28.34	22.42	19.01	10.09	23.35	20.46	12.79	11.82	9.68	5.29
8.24		6.97	7.58	17.61	11.83	2.11	0.94	4.38	2.80	4.90	7.37		
96.15	92.06	97.20	94.27	96.73	92.03	77.44	92.81	98.18	95.55	96.80	90.83	96.62	91.38

seems to be 0.5 where the solubility of cobalt and copper to be maximum since its absolute value is very small.

If m/M ratio is reduced to as small as 0.004, then (11) is obtained at the same condition as (9), and if (11) is continued for 48 hrs. (12) is obtained. The ratio of weight overflow to carryover in (11) and (12) is 1 : 1.52 and 1 : 1.59 respectively. By comparing (9), (10) and (12) with one another, it is seen that better results can be obtained only by larger equipment in which m/M is smaller which is impossible with this small-scale equipment.

The composition of the final residue from (11) and (12) is shown in Table 9. These final residues are some what magnetic. Though the intensity of magnetisation of the residue of carryover was almost uniform, the residue of overflow can be divided into two parts whose magnetism is relatively strong and weak. The analysis of the residue of overflow which is divided in magnetic field of about 1,000 örsted is shown in Table 10. As will be seen from this cobalt, copper and sulfur tends to concentrate into the magnetic part. Though ferrites can be considered as the magnetic compounds of these metals, they are expected to decompose under the conditions described[7],[8] here. The X-ray analysis made by the methods of Debye-Scherrer with the residue and artificial ferrite is shown in Photo. Though

(7) Y. Umezu and S. Suzuki, J. Min. Inst. Japan, **70** (1954), 151.
(8) Y. Umezu and S. Suzuki, J. Min. Inst. Japan, **70** (1954), 559.

Table 8. Experimental results, (III).

Exp. No.		13		14		15		16		17	
Roasting Temp.(°C)		650		650		650		700		700	
Feed Rate (g/min)		2.40		3.36		2.40		2.30		2.30	
m/M		0.020		0.020		0.008		0.020		0.008	
Replacing Time(hrs)		10		10		19		10		19	
α		0.5		0.7		0.5		0.5		0.5	
Gas Concentration (%)	SO₂	8.0		8.6		7.3		7.8		7.9	
	O₂	9.8		9.6		11.5		10.9		10.5	
		Over flow	Carry over	Over flow	Carry over	Over flow	Carry over	Over flow	Carry over	Over flow	Carry over
Water Solubility (%)	Co	38.49	49.45	42.03	48.09	72.41	64.41	38.22	49.25	30.50	41.93
	Cu	39.92	63.29	38.84	63.40	67.51	69.17	22.94	54.28	25.53	48.41
	Zn	45.29		48.57	50.00	78.25	85.10	68.00		66.70	75.81
	Fe	0.73	3.16	0.78	2.52	1.08	3.11	0.42	3.15	0.32	2.05
Acid Solubility (%)	Co	8.45	7.96	5.72	11.92	5.00	4.00	6.51	3.94	7.70	6.00
	Cu	14.86	3.60	15.63	16.23	7.28	4.85	18.58	5.41	11.43	6.35
	Zn	44.46		43.43	41.76	17.90	10.61	24.70		21.78	15.03
	Fe	1.63	3.65	1.63	4.99	0.87	2.72	0.99	2.62	0.71	2.33
Total Soulbility (%)	Co	46.93	57.41	47.75	60.01	77.41	68.41	44.71	53.19	38.20	47.94
	Cu	54.78	69.69	54.48	79.63	74.79	74.03	41.52	59.69	36.96	54.76
	Zn	89.75		92.03	91.76	96.15	95.72	92.70		88.47	93.54
	Fe	2.36	6.82	2.42	7.51	1.95	5.83	1.41	5.76	1.03	4.38
Insolubility (%)	Co	53.06	42.59	52.25	39.99	22.59	31.59	55.27	46.81	61.80	52.06
	Cu	45.22	30.34	45.52	20.36	25.21	25.97	58.48	40.31	63.04	45.24
	Zn	10.25		7.97	8.24	3.85	4.28	7.29		11.25	6.46
	Fe	97.64	93.18	97.58	92.49	98.05	94.17	98.59	94.23	98.97	95.62

Table 9. Compositions of final residues.

Exp. No.		Co (%)	Cu (%)	Fe (%)	S (%)	SiO₂(%)
11	Over flow	0.1741	0.0969	53.15	0.2057	13.40
	Carry over	0.2288	0.0730	51.09	0.458	9.38
12	Over flow	0.1812	0.0812	53.36	0.1610	13.12
	Carry over	0.1968	0.0301	52.41	0.347	10.59

Table 10. Analaysis of the residue divided in magnetic field.

Exp. No.		Wt (%)	Co (%)	Cu (%)	Fe (%)	S (%)	SiO₂(%)
11	Magnetic	25.92	0.3193	0.1816	60.30	0.3548	10.88
	Non-magnetic	74.08	0.1233	0.0673	50.74	0.1535	14.28
12	Magnetic	22.02	0.3337	0.1878	56.80	0.2578	9.63
	Non-magnetic	77.98	0.1381	0.0511	52.39	0.1337	14.15

it was feared that accurate diffraction lines could not be obtained because of a small content of cobalt and copper, ferrite cannot be recognized in these lines. The behaviour of sulfur cannot be understood even if the ferrits is considered. Cobalt and copper may be recovered by utilizing this sroperty.

From Table 7 it is seen that there is slight difference in the solubility of

overflow and carryover with respects to cobalt and copper. It is considered to be due to the fact[9] that even the particle which must be carried away in gas stream as it is fine will be held up in the fluidized-bed for almost the same number of hours as large particles. If there is no difference in hold-up time, no remarkable difference is to be expected in the amount reacted, as seen in Figs. 3 and 4. A slight difference in acid solubility of overflow and carryover, however, may be due to the fact that some of very fine ore particles will be carried away in gas stream after relatively short hold-up time.
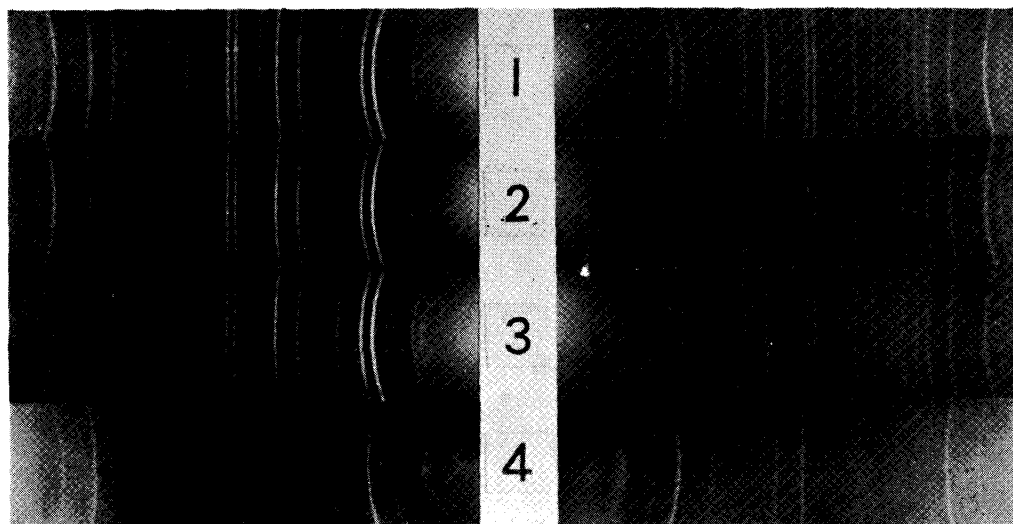
Photos. 1–4. X-ray powder photographs of final residue and ferrite.
1 : magnetic residue
2 : non-magnetic residue
3 : residue from carry over
4 : artificial ferrite

VI. Discussions of experimental results

1. Relation between feeding ratio and composition of outgoing gas
    The feeding ratio, α, is defined as

$$\alpha = f/F, \tag{9}$$

where f is the actual feed rate and F is a theoretical feed rate which is equivalent to the present air flow rate. If V_{air} is the theoretical volume of air required for a certain amount of ore concentrate while the volume of sulfur dioxide in the outgoing gas is V_{SO_2} and change in gas volume with the chemical reaction is V_0, then a partial pressure of sulfure dioxide, p_{SO_2}, in the outgoing gas passing the bed whose feeding ratio is α may be written in the form

$$p_{SO_2} = \frac{\bar{r} V_{SO_2}}{\dfrac{V_{air}}{\alpha} - \bar{r} V} \quad (atm.), \tag{10}$$

where $\bar{r}$ is the fraction of sulfur oxidized versus total sulfur. As it is seen from

(9) M. Leva, Chem. Eng. Prog., **47** (1951), 39.

Table 9 that the residual sulfur in the final residue is very little, $\bar{r}$ may apploximately equal to one as far as the usual gas composition is concerned. Thus the partial pressure of sulfur dioxide with given α can be calculated by equation (10) and Table 4. The relation between partial pressure of sulfur dioxide and oxygen is expressed by the equation in Table 4

$$p_{SO_2} = \frac{302}{1969} - \frac{302}{1969 \times 0.2099} \, p_{O_2} ,$$

hence,

$$p_{SO_2} = 0.1536 - 0.732 \, p_{O_2} . \tag{11}$$

If this is substituted in equation (10), then the corresponding partial pressure of oxygen can be calculated. The partial pressure of sulfur dioxide and that of corresponding oxygen are plotted against α in Fig. 8, where dotted line shows the
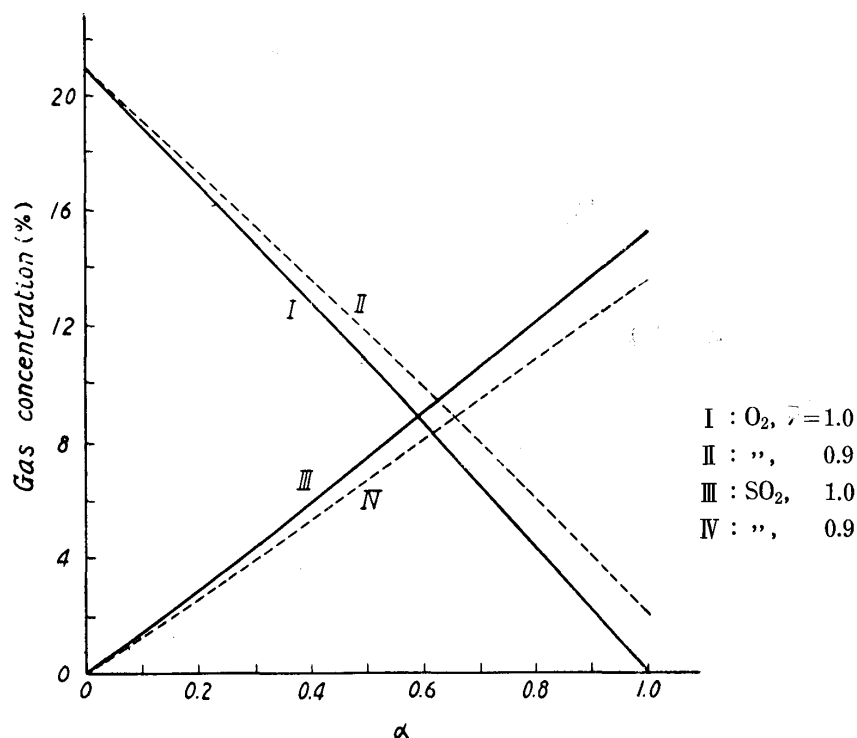

Fig. 8. Relation of feeding ratio to partial pressure of sulfur dioxide and oxygen.

case where $\bar{r}$ is equal to 0.9. It is seen that the partial pressure of sulfur dioxide increases with α, whereas that of oxygen decreases. In Table 11 the experimental results obtained with α which is equal to 0.3 and 0.5 agree well with the calculated values. The case when α is equal to 0.7, however, differ somewhat from the calculated value except (5) and (10). This may be considered as to be due to the following facts. In the case where α is equal to 0.5 and 0.3, there will be more chances for the ore particles to contact with upgoing gas than in the case of 0.7. As seen in Tables 6 and 7, it is clear from the comparison of m/M ratio that hold-up time of (5) and (10) is longer than the cases (2), (7) and (14). Accordingly,

$\bar{r}$ can be assumed to be one in (5) and (10), while in (2), (7) and (14) the experimental results approximately agree with the value $\bar{r}$ which is equal to 0.8. By comparing (2), (7) and (14) with one another, it is seen that the partial pressure of sulfur dioxide increases with increasing temperature among them because $\bar{r}$ follows the reaction velocity which increases with temperature.

Table 11. Comparing of experimantal results and
the calculated as to gas compositions.

Exp. No.	α	SO_2 (%)	O_2 (%)
Calc. ($\bar{r}=1.0$)	0.3	4.4	15.0
3	,,	4.4	14.6
8	,,	4.9	14.7
Calc. ($\bar{r}=1.0$)	0.5	7.4	10.8
1	,,	7.6	11.4
4	,,	7.8	10.9
6	,,	6.0	13.0
9	,,	7.1	11.1
11	,,	6.6	13.0
12	,,	7.2	11.9
13	,,	8.0	9.8
15	,,	7.3	11.5
16	,,	7.8	10.5
17	,,	7.9	10.5
Calc. ($\bar{r}=1.0$)	0.7	10.5	6.0
Calc. ($\bar{r}=0.9$)	,,	9.4	8.1
Calc. ($\bar{r}=0.8$)	,,	8.3	9.7
2	,,	8.0	9.0
5	,,	10.3	6.8
7	,,	8.4	10.2
10	,,	11.5	6.0
14	,,	8.6	9.6

2. Gas distribution on the fluidized-bed

If air is inserted at the rate of G per minute upward into the fluidized-bed whose height is h and sectional area is S, the particles are so accelerated with air stream and repulsed one another that the probability of existence of each particle may be considered to be constant all over the bed. Air passes upward through these particles losing its oxygen and at the same time increasing sulfur dioxide, and leaves the bed from its upper end at which gas composition is the same as mentioned in 1). Therefore, it seems that partial presure of oxygen is to be highest at the lower end of the bed and decreases with the increase of its height while that of sulfur dioxide has an opposite distribution. From the foregoing statements, the gas distribution can be calculated on an assumption as follows :

The amount of sulfur dioxide formed is proportional to the oxidation velocity of sulfide, which is also proportional to the diffusion velocity of oxygen in the oxide film formed as mentioned earlier. Accordingly, if p is the partial pressure of oxygen contacting with ore particle and p_e is that at the equilibrium, then

$$v = K' \ (p - p_e),$$

where v is the oxidation velocity and K' is a constant. If N is the number of ore particle per unit volume, then the consumption velocity of oxygen is v, which may

be given as

$$v = K''N(p - p_e).$$

Hence, if the pressure difference of oxygen across the horizontal thin layer dh, is dp, then

$$-Gdp = SK''N(p - p_e)dh,$$

where Gdp means the volume of oxygen which decreases within dh, assuming that the air is to be heated instantly up to the reaction temperature as soon as it is introduced into the bed and the change in the gas volume by the cheminal reaction is to be neglected. If K is given by

$$K = SK''N/G,$$

then the above equation can be writte in a simple form

$$-dp = K(p - p_e)dh,$$

and the integrations are readily carried out, with the result

$$p = p_e + e^{-Kh}A,$$

where A is the integration constant. When h is equal to zero, p is equal to the

I : p_{O_2}
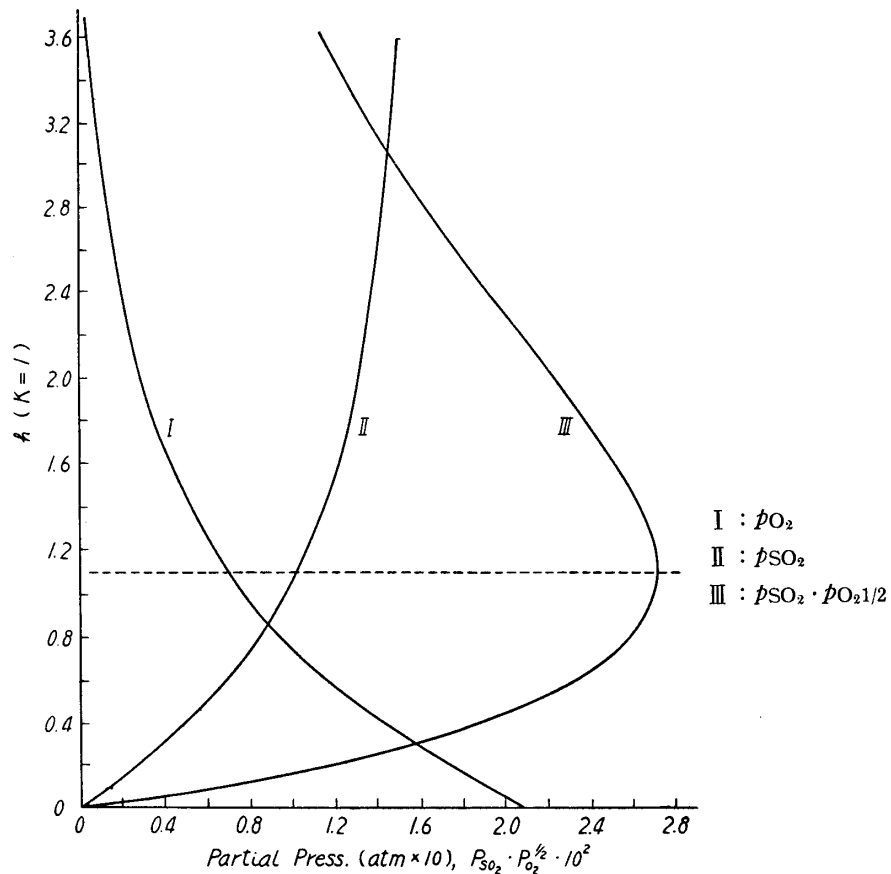II : p_{SO_2}
III : $p_{SO_2} \cdot p_{O_2}1/2$

Fig. 9. Typcal distribution of SO_2 and O_2 in bed, I, II, Sulfatization product, III.

oxygen partial pressure of the atmosphere $p_{O_2}^0$, A is given as follows:

$$A = p_{O_2}^0 - p_e .$$

If the partial pressure of oxygen at h is written p_{O_2}, then

$$p_{O_2} = p_e + (p_{O_2}^0 - p_e) e^{-Kh} .$$

As the value of p_e is negliegibly small, then the above equation is simplified as follows:

$$p_{O_2} = p_{O_2}^0 e^{-Kh} \text{ (atm)} . \tag{12}$$

By inserting this in equation (11), the partial pressure of sulfur dioxide can be written as follows:

$$p_{SO_2} = 0.1536 - 0.732 p_{O_2}^0 e^{-Kh} . \tag{13}$$

According to equations (12) and (13), the gas distribution in the fluidizedbed can be calculated by analysing outgoing gas or a given point in the bed. Typical examples are illustrated in Fig. 9, curve I and II.

3. Effect of the feeding ratio on sulfatizing

The basic principles concerning sulfatizing roasting should be considered from the general equations:

$$SO_2 + \frac{1}{2} O_2 = SO_3, p_{SO_2} \cdot p_{O_2}^{1/2} \cdot K = p_{SO_3} . \tag{14}$$
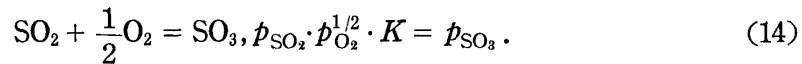
Considering the content of cobalt and copper, as so little amounts of sulfur trioxide participate in sulfatizing in this experiment, the partial pressure of oxygen and sulfur dioxide from equations (12) and (13) may be inserted in equatin (14) directly as followr:

$$p_{SO_2} \cdot p_{O_2}^{1/2} = p_{O_2}^{1/2} e^{-(1/2)Kh} (0.1536 - 0.732 p_{O_2}^0 e^{-Kh}) . \tag{15}$$

An illustration of this formula is given in Fig. 9, curve III. Considering the character of the fluidized-bed, its sulfatizing ability is considered to be proportional to the area enclosed by the ordinate and the curve III because the same chance is given to all the particles to travel across all over the bed. This area S, for the height h, is given by equation (15) as follows:

$$S = \int_0^h \left\{ p_{O_2}^{\frac{1}{2}} e^{-(\frac{1}{2})Kh} (0.1536 - 0.732 p_{O_2}^0 e^{-Kh}) \right\} dh ,$$

hence,

$$S = \frac{0.3072}{K} \left\{ p_{O_2}^{\frac{1}{2}} e^{-(\frac{1}{2})Kh} (1.5882 p_{O_2}^0 e^{-Kh} - 1) + 0.3054 \right\} . \tag{16}$$

If the total height of fluidized-bed is L_f, then the partial pressure of oxygen C_{Lf} at L_f or in the outgoing gas is given as follows:

$$C_{Lf} = p_{O_2}^0 e^{-Kh} . \tag{17}$$

It is seen from above equation that C_{Lf} is given by K when L_f is constant. Hence, if the partial pressure of oxygen in the atmosphere, the character of ore particle and the condition of the reaction are constant, K is not a constant but a variable depening on the feeding ratio. Accordingly, (17) is revised as

$$C_{Lf} = p^{\circ}_{O_2} e^{-XL_f}, \tag{17'}$$

and hence, from equation (16),

$$S = \frac{0.3072}{X} \left\{ C^{1/2}_{Lf}(1.5882\,C_{Lf} - 1) + 0.3054 \right\}. \tag{16'}$$

The insertion of given values less than 0.2099 in C_{Lf} of the equation (16') and (17'), the maximum S is obtained at the point where the partial pressure of sulfur dioxide and corresponding oxygen are 13.2 and 3.0 per cent respectively. It is seen from Fig. 9 and equatin (10) that this gas composition corresponds to the case where the feeding ratio is 0.87. As seen earlier in V the maximum solubility by extraction cannot be obtained at α which is equal to 0.7 but 0.5 without any exceptions. This experimental tendency seems to be contrary to that described above. Two reasons may be considered: a) the distribution of gas may be disturbed by the motion of the particles and consequently may be considerably uniform, b) greater amount of oxygen than that represented by equation (14) is to be needed.

Since the violent motion of particles in the bed, a) seems to be probable. In this case distribution of gas may deviate from that represented by equations (12) and (13), and in an excessive case, it may be assumed that the range where the equation (13) can be applied is only within a limitted narrow height near the bottom of bed while in the most part of bed it may be almost uniform. Hence, according to the reason together with equatiin (14) and Fig. 9, it seems that the maximum sulfatizing will be obtained where the partial pressure of sulfur dioxide is 0.102 and that of corresponding oxygen at 0.070. This composition corresponds to the condition α equal to 0.66, which differs also from the experimental results.

Though being short of details, b) can be understood by the intermediate products such as basic sulfate or oxide during sulfatizing seen is earlier (III and IV). In the same manner the introduction of equation (16') and the insertion of indexes equal to 1, 3/2 and 2 in the partial pressure of oxygen will give

$$S_1 = \frac{0.1536}{X} \left\{ C_{Lf}(2.382\,C_{Lf} - 1) + 0.1049 \right\}, \tag{18}$$

$$S_{3/2} = \frac{0.1024}{X} \left\{ C^{3/2}_{Lf}(2.858 C_{Lf} - 1) + 0.0385 \right\}, \tag{19}$$

$$S_2 = \frac{0.0768}{X} \left\{ C^{2}_{Lf}(3.176 C_{Lf} - 1) + 0.01469 \right\}. \tag{20}$$

The values of α which give the maximum to these S are calculate in the same manner as in equation (16'), and the relation between the indexes and α is shown in Fig. 10. It is seen from this that the apparent velocity of aggregative sulfatiz-

ing may be proportional to $p_{SO_2} \cdot p_{O_2}^2$ because the condition where α equal to 0.5 corresponds to the case where the index of the partial pressure of oxygen is about two. The relation between an index of partial pressure of oxygen and α when the product of the partial pressure of oxygen and that of corresponding sulfur dioxide becomes maximum is shown in Fig. 10, curve II. According to this, when it is assumed as in a), it seems that the apparent velocity may be proportional to $p_{SO_2} \cdot p_{O_2}^{1\sim2}$. Consequently, it is seen that when fluidized technique is applied to sulfatizing roasting an abundant supply of oxygen must to be indispensable to effective sulfatizing.
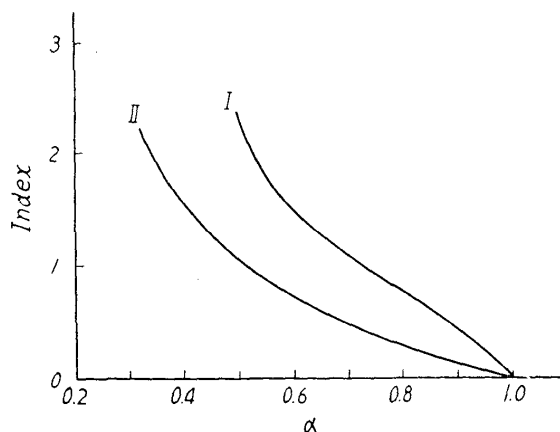

Fig. 10. Relation of index to feeding ratio.

I : Theoretical distribution
II : Uniformed distribution

Summary

For the purpose of getting a base for a thorough utilization of cobalt, copper and zinc bearing pyrite, the sulfatizing roasting process which is based upon the preferential sulfatizing by means of fluidized-bed was studied. According to the experimental results obtained by the fluidized-bed reactor which has a capacity of 5 kg ore per day, it was found that the most suitable roasting temperature for this precess, as far as the range studied here is concerened, was 600°C, and 83~85 and 90~95 per cent of cobalt and copper was extracted respectively by water and dilute acid, while iron was retained in insoluble oxide form, and air required was two times as great as the thohretical. The solubility of cobalt and copper should increase by reducing m/M ratio with a large equipment. The content of copper in the final residue was low enough to be utilized as a material for iron making. By magnetic separation the residue from the overflow could be divided into magnetic and non-magnetic part, and in the former part copper, cobalt and sulfur was concentrated. Accordingly, these components coule be recovered by means of a appropriate method.