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# A Research on the Treatment of Complex Sulphide Ores. IV

## Selective Flotation of Sulphatization Residue\*

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### Synopsis

In this report, the recoveries with selective flotation of chalcopyrite, pyrite and lead sulphate from the sulphatization residue of the bulk sulphide concentrate from the Hanaoka mine were dealt with.

The advantage of the process combining flotation with sulphatization, from the standpoint of flotation, may be considered to be as follows: (a) The liberation of minerals will be promoted chemically, (b) the surface of mineral grains will be cleaned, and (c) the separation of minerals in the residue will be easier than that in the original ore.

The samples of sulphatization residue containing 4.3 to 5.7% Cu, 14.5 to 20.0% Fe, 6.2 to 13.9% Pb, and 2.3 to 3.2% Zn, and of -150-mesh size, were subjected to tests.

The main problems in the selective flotation were the floatability of lead sulphate produced by sulphatization and the degree of regrinding necessary for the liberation of chalcopyrite from pyrite.

It was verified experimentally that the chemically pure lead sulphate was depressed at the pH of below 5.8 or above 6.2 when Aerofloat No. 25 was used as a collector and was floated at the pH of 8 to 9 when it was sulphidized with the predetermined quantity of sodium sulphide and potassium amyl xanthate was used as a collector.

The sulphatization temperature suitable for the separation of chalcopyrite and pyrite from lead sulphate from the standpoint of flotation was found to be 160° to 170°C in the temperature range of 130° to 170°C.

In the separation of chalcopyrite and pyrite from lead sulphate, the recoveries were 92.9% for Cu and 96.2% for Fe and the rejection was 83.5% for Pb with 0.1 kg/t of white camphor oil and 0.13 kg/t of Aerofloat No. 25 and at the pH of 6.

In the recovery of lead sulphate, the lead concentrate containing 36.7% Pb was obtained with the Pb recovery of 89.8% with 30 kg/t of sodium sulphide, 0.6 kg/t of white camphor oil and 1.0 kg/t of potassium amyl xanthate and at the pH of 9.2.

In the separation of chalcopyrite from pyrite, three stages of regrinding, one stage of roughing and two stages of scavenging were required to obtain the copper concentrate of 9.9% Cu with the Cu recovery of 95.2% and the pyrite concentrate of 41.4% Fe with the Fe recovery of 61.4% with 0.7 kg/t of white camphor oil, 0.8 kg/t of Aerofloat No. 25 and 60 kg/t of slaked lime and at the pH of 10.6.

The size of the flotation products was very minute when microscopically examined, namely, the bulk of -20 micron material was 72.5% for the copper concentrate, 74.8% for the lead concentrate, 40.2% for the pyrite concentrate, and 16.7% for the tailing.

The highest grade of concentrates obtained was relatively low, namely, 49.2% Pb for the lead concentrate, 11.7% Cu for the copper concentrate, and 41.4% Fe for the pyrite concentrate. It was, however, considered that a higher grade could not be obtained, because the degree of grinding of the sample was near the limit in flotation.

The overall recoveries in the selective sulphatization and flotation were 97% for zinc, 90% for copper, 77% for lead, and 58% for iron.

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\* The 43rd report of the Research Institute of Mineral Dressing and Metallurgy. The original report in Japanese was published in Bull. Res. Inst. Min. Dress. Met., 7 (1951), 31-42.

## I. Introduction

The present technic of differential flotation in dressing metallic sulphide ores owes much to the discovery of the efficacy of inorganic salts as selective flotation agents. It is not an overstatement to assert that the differential flotation of today has been given foundation by the inventions of Bradford, of Sheridan and Griswold, of Keller and others grappling with the same problem in the fruitful years of 1913 through 1924.<sup>(1)</sup> But recently, the demand for improved concentration and metal recovery, as well as higher selectivity in flotation has become ever more pressing, instilled by the necessity of processing lower grade or more refractory ores, efficient exploitation of metallic contents, and smelting of higher grade concentrate.

A study on "selective sulphatization-flotation"<sup>(2)</sup> for use in processing complex sulphide ores<sup>(3)</sup> is on foot at this institute. The process consists in a mode of application<sup>(4)</sup> of the Gromov and Derkachev's sulphatization process.<sup>(5)</sup> The feed is first floated to produce a bulk concentrate, which is reground and subjected to selective sulphatization, then separated into a solution of zinc sulphate and a residue, consisting of chalcopyrite, pyrite, lead sulphate, and a small amount of gangue, by washing with warm water and filtration. Zinc is recovered electrolytically from the solution and chalcopyrite, pyrite, and lead sulphate are separated from the residue by selective flotation.

This process shows the advantage in that (1) the sulphatization treatment chemically promotes the liberation of mineral grains; (2) the same treatment cleanses the surface of the mineral grains and helps the display of the floatability inherent to the mineral; (3) since sphalerite is eliminated by sulphatization and solution, the knotty problem of separating sphalerite and chalcopyrite is disposed of; (4) the sulphatization of galena into lead sulphate also facilitates its separation from chalcopyrite.

In this report, the outline of the results of test of selective flotation of the residues<sup>(6)</sup> obtained by the selective sulphatization of the so-called copper concentrate from the Hanaoka mine, Dowa Mining Co., Akita Prefecture, was described.

## II. Method of Testing

Two batches of residue obtained by grinding down to -150 mesh and sulpha-

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- (1) A. M. Gaudin, *Flotation*, (1932), 5-7.
  - (2) Kenji Ono, *Bull. Res. Inst. Min. Dress. Met.*, **7** (1951), 3-4; *Sci. Rep. RITU*, A **4** (1952), 486.
  - (3) Tsunehiko Takeuchi, *Bull. Res. Inst. Min. Dress. Met.*, **7** (1951), 5-18; *Sci. Rep. RITU*, A **4** (1952), 489.
  - (4) *Bull. Res. Inst. Min. Dress. Met.*, **4** (1948), 54; **5** (1949), No. 1, 74-5, 77, 78; **5** (1949), No. 2, 65, 70. *Mining Inst. of Japan, Technical Series, I* (1949), 19-26.
  - (5) B. V. Gromov, and D. I. Derkachev, *Tsvetnye Metal.*, **20** (1947), No. 1, 27-39; *C. A.*, **41** (1947), 5067a.
  - (6) Kenji Ono, Mitsuo Kameda, Hiroshi Kanno, and Nobuo Izumi, *Bull. Res. Inst. Min. Dress. Met.*, **7** (1951), 19-30; *Sci. Rep. RITU*, A **4** (1952), 506.

tizing the so-called copper concentrate from the Hanaoka mine were used as materials. Table 1 shows the results of analysis of the two samples. These samples, as shown, are chemically somewhat different in analytical values, Sample

Table 1. Chemical Analysis of Samples of Sulphatization Residue.

Sample	Cu (%)	Fe (%)	Pb (%)	Zn (%)
A	5.71	14.45	13.86	3.21
B	4.29	19.68	6.17	2.27

B being used in the main part of the experiment. Table 2 shows the distribution of particle size in Sample B. As shown, particles of  $-150 +270$  mesh size constitute 64.7% in weight of the total.

Table 2. Screen Analysis of Sample B.

Size (Mesh)	Weight (%)
$-150 +200$	40.65
$-200 +270$	24.07
$-270 +325$	8.13
$-325$	27.15
Total	100.00

For the test, a 50-g M. S. laboratory flotation cell of the Kyoto University type<sup>(7)</sup> was used. Chemicals in general use, such as white camphor oil<sup>(8)</sup> as a frother, potassium ethyl xanthate,<sup>(9)</sup> potassium amyl xanthate,<sup>(9)</sup> and Aerofloat No. 25<sup>(10)</sup> as collectors and sulphuric acid, caustic soda, slaked

lime and sodium sulphide<sup>(11)</sup> as modifiers, were used in preference.

The sulphatized residue contained chalcopyrite, pyrite, lead sulphate, and such gangue minerals as barite and quartz, as well as a small quantity of zinc mineral left over undissolved. Upon grinding the residue down to the fineness of  $-150$  mesh, we found that the degree of liberation of chalcopyrite from pyrite was not large enough,<sup>(3)</sup> but the liberation of chalcopyrite and pyrite from lead sulphate and gangue was comparatively good. So, in selective flotation, chalcopyrite and pyrite were first separated from lead sulphate and gangue, then the bulk concentrate was reground and chalcopyrite was separated from pyrite in the usual way, and lastly, lead sulphate was recovered from the gangue. In grinding samples, a 305-by 210-mm,  $\frac{1}{2}$ -hp batch ball mill was used. Six 5l-mm balls and twelve 24-mm balls, weighing 3.9 kg in total, were charged in the mill. 50 g of sample was loaded per test and dry grinding was applied throughout.

The problematic points in the above outlined selective flotation, we assumed,

(7) Gaichi Yamada, J. Mining Inst. Japan, **51** (1935), 467-75.

Kazuo Kanazawa, J. Mining Inst. Japan, **55** (1939), 18-37.

The specification of the cell is as follows: the agitating compartment,  $40 \times 40 \times 130$  mm; the frothing compartment,  $30 \times 80 \times 120$  mm; the amount of water added, 200cc; the impeller, with four blades,  $65^\circ$  in inclination, 10 mm in height, 36 mm in diameter, and with the speed of revolution of 2,600 per minute.

(8) The specific gravity, 0.998 ( $8^\circ\text{C}$ ); the per cent weight of fraction distilled, 2.74% below  $200^\circ\text{C}$ , 28.77% at  $200^\circ$  to  $210^\circ\text{C}$ , 56.85% at  $210^\circ$  to  $215^\circ\text{C}$ , 10.27% at  $215^\circ$  to  $220^\circ\text{C}$ , and 1.37% remaining. (Data by courtesy of Asst. Prof. Taro Yamasaki.)

(9) Sample by courtesy of the Nikko Heavy Chemical Industries Co.

(10) Sample from the American Cyanamid Co. by courtesy of Prof. Takanori Mayeda.

(11) Reagents of the extra pure grade.

lie in the floatability of the lead sulphate formed in the process of sulphatization, and the extent of regrinding necessary for the separation of chalcopyrite from pyrite.

### III. Past Studies on the Floatability of Lead Sulphate

Many studies on the floatability of anglesite have been published. Using oleic acid or a mixture of oleic acid and amyl alcohol as a collector and Sørensen's standard borate buffer solution, Talmud and Lubman<sup>(12)</sup> studied the effect of pH on the floatability of anglesite, and clarified that the floatability attained to the maximum when the pH was kept at 3. In the flotation of lead ores, DeVaney and Evans<sup>(13)</sup> found that when oxidized lead ores such as cerussite and anglesite were present, these were more readily turned into slime than galena, so that the use of chemicals commonly adapted to galena would result in the loss of 30% of lead content. To prevent this loss, they recommended the utilization of a concentrating table, the combined use of xanthate and cresylic acid, the use of sodium sulphide in the scavenging circuit and the retreatment by returning the froth containing oxidized ore into the roughing circuit. In his study on slime coating, del Giudice<sup>(14)</sup> discovered that the slime particles of calcite formed a coating on the surface of galena which had partially turned into lead sulphate by oxidation, and explained the phenomenon as caused by the lead carbonate, which had been formed by the reaction between lead sulphate and calcium carbonate, acting as a cementing material. Dean and some others<sup>(15)</sup> reported that the sulphidization of anglesite was promoted by the increase of sulphate ions in the pulp by the addition of sodium sulphate. In their study on the collection of anglesite by xanthate, Wark and Cox<sup>(16)</sup> reported as follows. The concentration of ethyl xanthate necessary for the induction of bubble contact on anglesite showed the minimum at the pH of 9.5 to 11, being 50 mg/l or less. The presence of sodium carbonate raised the required minimum of xanthate, but sodium sulphate had little effect till the concentration reached 300 mg/l. Sodium sulphide would activate anglesite and lower the minimum required concentration of ethyl xanthate. However, the effective concentration of sodium sulphide varied with the pH value, falling to the minimum at pH 6 to 10. Moreover, it acted as a depressing agent when present in excess, but the depressing action was not so strong against amyl xanthate as against ethyl xanthate. Sodium phosphate also activated anglesite, but the range of its effective concentration was narrower than that of sodium sulphide, the minimum concentration being

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(12) D. Talmud and N. M. Lubman, *Kolloid-Z.*, **50** (1930), 159-62.

(13) F. D. DeVaney and R. E. Evans, U. S. Bur. Mines, Rept. of Investigations, No. 3214 (1933), 1-9.

(14) G. R. M. del Giudice, *Trans. Am. Inst. Mining Met. Engrs., Milling Methods*, **112** (1934), 398-412.

(15) R. S. Dean and others, U. S. Bur. Mines, Rept. of Investigations, No. 3419 (1938), 1-80.

(16) I. W. M. Wark and A. B. Cox, *Trans. Am. Inst. Mining Met. Engrs., Milling Methods*, **134** (1939), 7-25.

at pH 6.5 to 9, and the maximum being about 85 mg/l at pH 7. Wark and Sutherland<sup>(17)</sup> reported that mercaptobenzothiazole acted as a collector in alkaline pulp, but only at a considerably higher concentration. According to Pearson,<sup>(18)</sup> at the Halkyn mill, the feed contained some cerussite and sometimes a small quantity of anglesite, raising the lead content of oxidized lead ore to around 15% of the total. In order to recover this lead content, appropriate quantity of sodium sulphide was added at various stages in portions to prevent under- or overdose, and 64 to 70% of the lead content in the oxidized ore was successfully recovered, using thiocarbanilid and amyl xanthate as collectors and cresylic acid as a frother. Glembotskii<sup>(19)</sup> conducted a flotation test of anglesite, using sulphuric acid, sodium sulphate, fluoric acid, and sodium fluoride as depressing agents, and found that the depressing action was not great, owing to the high solubility of anglesite, and that the depressing action was dependent also on the nature of the electrolyte, sulphuric acid being more effective than sodium sulphate. He also tested the flotation of anglesite by addition of 1.0 kg/t of oleic acid and 0, 0.2, or 0.3 kg/t of sulphuric acid and obtained the corresponding lead sulphate recovery of 92, 48, or 28%, and concluded that the depression of flotation of minerals might be brought about by the decrease of ion concentration of minerals in the pulp by the addition of common ions.<sup>(20)</sup> According to Taggart<sup>(21)</sup> crude monoammonium phosphate was recommended for use with mercaptobenzothiazole. Data published by the Mineral Dressing Division of the American Cyanamid Co.<sup>(22)</sup> shows that anglesite is less susceptible to flotation than cerussite, and the best collectors are amyl xanthate and reagent No. 404.<sup>(23)</sup> When amyl xanthate is to be used as a collector, the most effective way is to add small amounts of amyl xanthate and sodium sulphide to each cell in frequent repetition. The reagent No. 404 may be used to advantage in combination with phosphates or phosphoric acid, and liquid Aerofloat or its combination with reagent No. 404, No. 301,<sup>(24)</sup> or amyl xanthate may be used for activated lead ores. Softening of pulp, by the addition of sodium carbonate and precipitation of calcium, iron, and zinc salts, will be effective. The optimum quantity of sodium sulphide should be decided by the lead acetate test. Copper sulphate has the effect of neutralizing the excessive basicity occasioned by sodium sulphide and helping flotation of

(17) I. W. Wark and K. L. Sutherland, *Trans. Am. Inst. Mining Met. Engrs., Milling Methods*, 134 (1939), 53-64.

(18) A. Pearson and the staffs of Huntington, Heberlein & Co., *Trans. Inst. Mining Met.*, 48 (1939), 769-773.

(19) V. A. Glembotskii, *Tsvetnaya Metal.*, 16 (1941), No. 16, 24-8; *C. A.*, 38 (1944), 6249.

(20) V. A. Glembotskii, *Tzvest. Akad. Nauk S. S. S. R., Otdel. Tekh. Nauk* (1948), 385-90; *C. A.*, 42 (1948), 6172.

(21) A. F. Taggart, *Handbook of Mineral Dressing*, (1945), 12-34.

(22) American Cyanamid Co., Mineral Dressing Division, *Mineral Dressing Notes*, No. 15 (1947). By courtesy of Mr. Teizo Matsuoka and the staffs of the Technical Division, Mining Association of Japan.

(23) Mercaptobenzothiazole according to H. J. Gisler, Denver Equipment Co., *Bull.*, No. RI-B.

(24) Sodium sec.-butyl xanthate according to A. F. Taggart, *Handbook of Mineral Dressing*, (1945), 12-08.

sulphidized lead ores. Given<sup>(25)</sup> announced the results of his study on the flotation of oxidized lead ores from the St. Anthony mine as follows. These ores consisted of cerussite, galena, anglesite, wulfenite, and pyromorphite and the lead content ranged between 3 and 5%. Oxidized ores were ground and floated in a separate system from that of sulphide ores. Sodium carbonate, American Cyanamid reagent No. 425,<sup>(23)</sup> and No. 301, Aerofloat No. 31, cresylic acid and sodium sulphide were used as flotation agents, of which sodium sulphide was added in small doses step by step. The pH value of the pulp was kept at 8.8 to 9.0 at the head of the rougher. The lead recovery reached 87.42%.

The above studies were sufficient to establish the floatability of anglesite in general, but it was thought necessary to ascertain whether such results were applicable in the selective flotation of lead sulphate artificially produced by sulphatization. As the particles of lead sulphate were comparatively fine, the majority being in the order of 10-micron size as shown in Table 9, the flotation test was conducted with chemical lead sulphate as the sample.

#### IV. Flotation Test of Lead Sulphate

As the sample, lead sulphate on the market was used.<sup>(26)</sup> The particle size was of 10-micron class in majority. Table 3 shows the distribution of particle size as determined by microscopic observation.

##### 1. Test with Potassium Ethyl Xanthate

Table 4 shows that, with 0.5 kg/t of white camphor oil as a frother, the increased addition of potassium ethyl xanthate over 0.05 kg/t, at which the lead sulphate recovery stands at 81.42%, has little effect in raising the recovery, which fluctuates between 81 and 84% at the outside. But a change in pH value by the addition of sulphuric acid and caustic soda is quite effectual, the recovery being the highest, at the pH range of 4 to 6,<sup>(27)</sup> and declining sharply to almost nil at the other pH ranges.

As the effect of ions of copper, iron and zinc coming from chalcopyrite, pyrite and undissolved sphalerite, present at the selective flotation of sulphatization residue, may not be excluded,

Table 3. Microscopic Sizing Analysis of Lead Sulphate.

Size (Micron)	Weight (%)
0—10	82.49
10—20	3.33
20—25	14.18
Total	100.00

Table 4. Effect of Addition of Potassium Ethyl Xanthate for Lead Sulphate Recovery.\*

Potassium Ethyl Xanthate (kg/t)	Lead Sulphate Recovery (%)
0	66.85
0.05	81.42
0.1	81.87
0.15	83.52
0.25	81.01
0.5	82.32

\* Test conditions: white camphor oil, 0.5 kg/t; pH, 4.0 to 4.4; temperature, 14.8 to 25.0°C; pulp density, 5%.

(25) E. V. Given, Eng. Mining J., 149 (1948), 88-90.

(26) Reagents of the chemically pure grade, manufactured by the Kanto Chemicals Co.

(27) The pH value of the tailing solution is indicated.

pure particles of these minerals, of -150 +200-mesh size, and in the amount corresponding to the calculated content of copper, iron and zinc in the normal sulphatization residue, that is, 6.2 g, 17.1 g, and 1.7 g respectively, were agitated for ten minutes with 200cc of distilled water in a 50-g flotation cell, and to the filtrate, 0.5 kg/t of white camphor oil and 0.05 kg/t of potassium ethyl xanthate were added and lead sulphate was floated therein under the varying pH values. The result, as shown in Fig. 1, indicates that each ion has the tendency to displace the curve of lead sulphate recovery to the side of higher pH value and that ions of copper and zinc have little effect on the maximum recovery, but ion of iron somewhat decreases the maximum recovery.

2. Test with Aerofloat No. 25

A similar test with Aerofloat No. 25 showed the result as given in Table 5,

Table 5. Effect of Addition of Aerofloat No. 25 for Lead Sulphate Recovery.\*

Aerofloat No. 25 (kg/t)	Lead Sulphate Recovery (%)
0	66.85
0.05	91.75
0.1	93.75
0.15	92.29
0.25	97.44
0.5	98.44

\* Test conditions : white camphor oil, 0.5 kg/t; pH, 5.8 to 6.0; temperature, 18.0 to 20.0°C; pulp density, 5%.

quite analogous to the result of the above test with potassium ethyl xanthate. But the highest lead sulphate recovery is seen at pH 5.8 to 6.2. As shown in Fig. 2, the copper and zinc ions have almost negligible effect on the recovery, but the iron ion has more remarkable effect on the recovery, than that in the case with potassium ethyl xanthate.

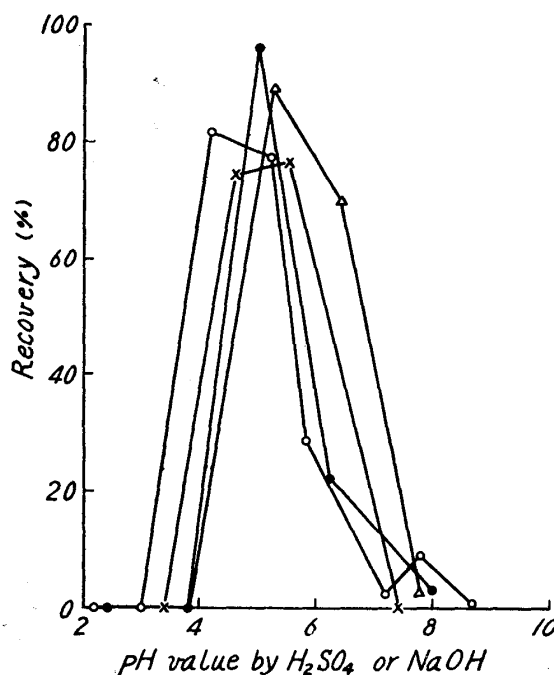


Fig. 1. Effect of pH Value and Metallic Ions for Lead Sulphate Recovery with Potassium Ethyl Xanthate. --o--: No ion --●--: Cu ion --△--: Zn ion --x--: Fe ion

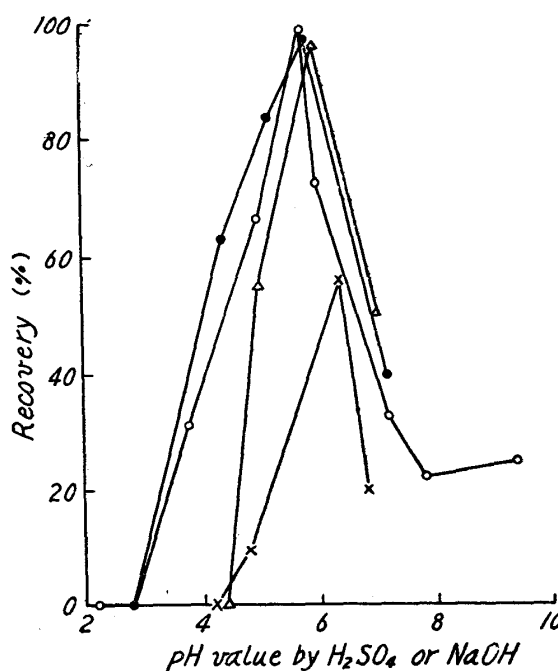


Fig. 2. Effect of pH Value and Metallic Ions for Lead Sulphate Recovery with Aerofloat No. 25. For notations see Fig. 1.



### 3. Test of Sulphidizing with Sodium Sulphide

Fig. 3 shows the result of flotation of lead sulphate, fully sulphidized with

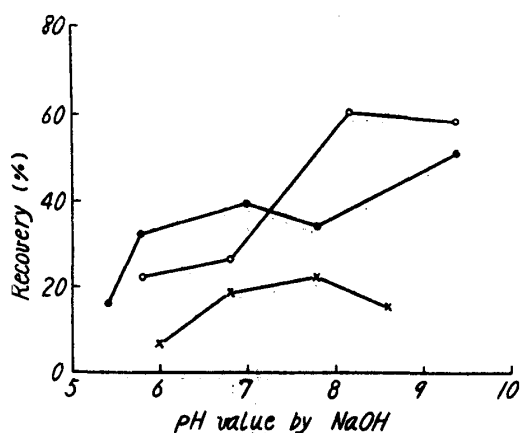


Fig. 3. Effect of pH Value and Some Collectors for the Recovery of Sulphidized Lead Sulphate.

—○—: KAmX —●—: Aerof. —×—: KEtX

sodium sulphide and separated by filtration, with 0.5 kg/t of white camphor oil as a frother and 0.1 kg/t of potassium ethyl xanthate, potassium amyl xanthate or Aerofloat No. 25 as a collector, and under varying pH values, by addition of caustic soda. Within the scope of test, the lead sulphate recovery is at the maximum at pH 8 to 9, when potassium amyl xanthate is used as a collector. When the amount of potassium amyl xanthate added is increased, the recovery rises to over 90% at 0.75 kg/t and to 96.7% at 1.0 kg/t.

### V. Separation of Copper and Iron Sulphides from Lead Sulphate

From the results of the fundamental tests described above, it may be reasoned that, to depress lead sulphate, Aerofloat No. 25 should be used as a collector and the pH value of the pulp be kept under 5.8 or above 6.2. However, we made

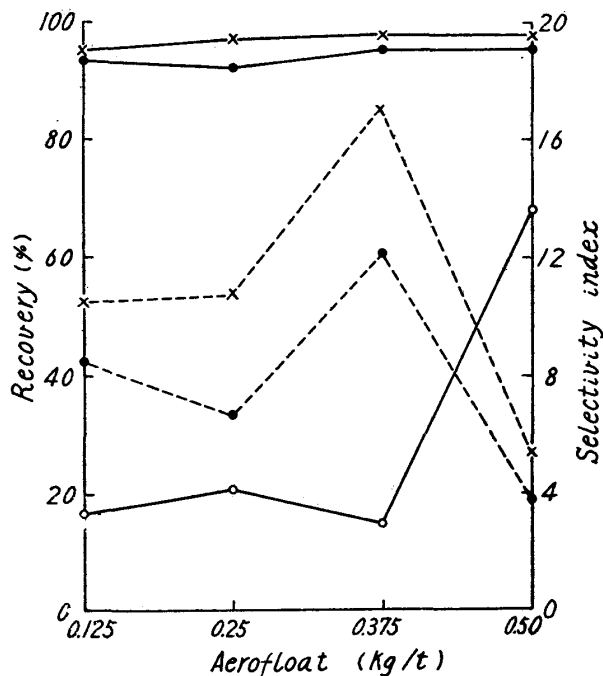


Fig. 4. Effect of Addition of Aerofloat No. 25 for Copper, Iron, and Lead Recoveries.

—×—: Fe recovery  
 —●—: Cu recovery  
 —○—: Pb recovery  
 - - - - : Fe-Pb selectivity index  
 - - - - : Cu-Pb selectivity index

further testing on the separation of copper and iron sulphides from lead sulphate, using potassium ethyl xanthate as a collector, to determine the effect of varying quantity of addition of white camphor oil, xanthate, and sodium silicate, as well as of the change in pH value and the temperature of sulphatization.

#### 1. Tests with Aerofloat No. 25

(i) Effect of varied amount of added Aerofloat

Fig. 4 shows the result of a flotation test, for examining the effect of varying amount of Aerofloat added, under the conditions: white camphor oil, 0.1 kg/t; Aerofloat No. 25, 0.13 to 0.5 kg/t; pH, 4.2 to 4.8; pulp density, 20%; temperature, 25.2 to 29.8°C; and flotation time, 10 to 15 min. Up to 0.38 kg/t of Aerofloat added, the recoveries of copper and

iron are high and the separation of lead is good, but when the quantity of Aerofloat is raised to 0.5 kg/t, the rejection of lead suddenly falls to 31.9%, no appreciable change being seen in the recoveries of copper and iron. This shows that, within the scope of the above test, the amount of Aerofloat added should be kept under 0.38 kg/t.

(ii) Effect of change in pH value by addition of sulphuric acid

Fig. 5 shows the result of a test, for examining the effect of change in pH value by addition of sulphuric acid, under the following conditions: white camphor oil, 0.1 kg/t; Aerofloat No. 25, 0.13 kg/t; pH, 2 to 6; pulp density, 20%; temperature, 27.0 to 32.0°C; and flotation time, 5 min. In the pH range of 2 to 3, the recoveries of copper and iron are 88.7 to 96.1% and the rejection of lead is 87.4 to 88.2%, and at the pH of 6, the recoveries of copper and iron are respectively 92.9 and 96.2% and the lead rejection is 83.5%, that is a remarkable success.

2. Test with Potassium Ethyl Xanthate

(i) Effect of varying amount of white camphor oil and of potassium ethyl xanthate

Fig. 6 shows the result of a test, for examining the effect of varying amount of white camphor oil and of potassium ethyl xanthate, under the conditions: white camphor oil, 0.1 to 0.5 kg/t; potassium ethyl xanthate, 0.025 to 0.13 kg/t; pH, 3.8 to 4.2; pulp density, 20%; temperature, 14.0 to 17.9°C; and flotation time, 5 to 15 min. When 0.5 kg/t of white camphor oil and 0.13 kg/t of potassium ethyl xanthate are added, the

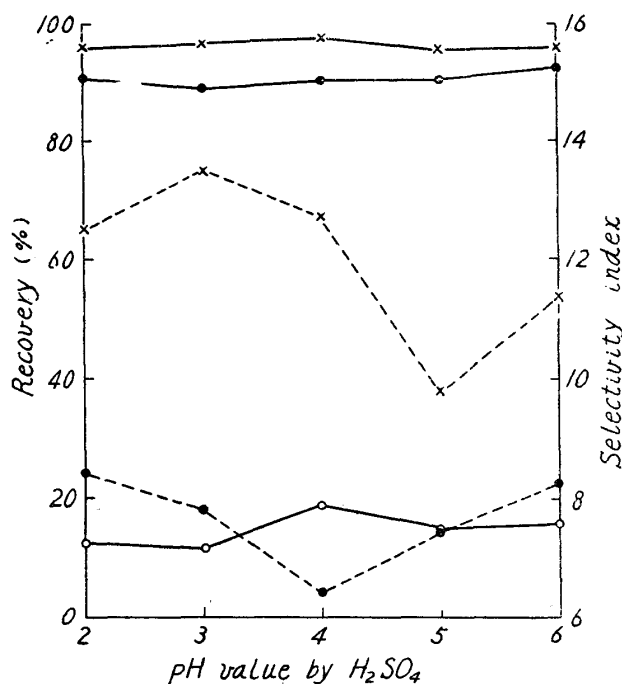


Fig. 5. Effect of pH Value for Copper, Iron, and Lead Recoveries with Aerofloat No. 25. For notations see Fig. 4.

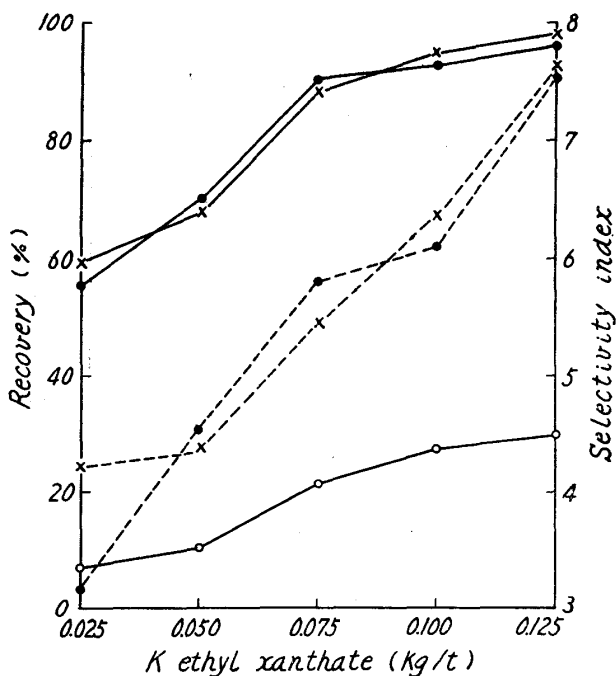


Fig. 6. Effect of Addition of Potassium Ethyl Xanthate for Copper, Iron, and Lead Recoveries. For notations see Fig. 4.

recoveries of copper and iron reaches 96.2 and 96.1% respectively, but the rejection of lead does not exceed 69.8%.

(ii) Effect of varying pH value by addition of sulphuric acid

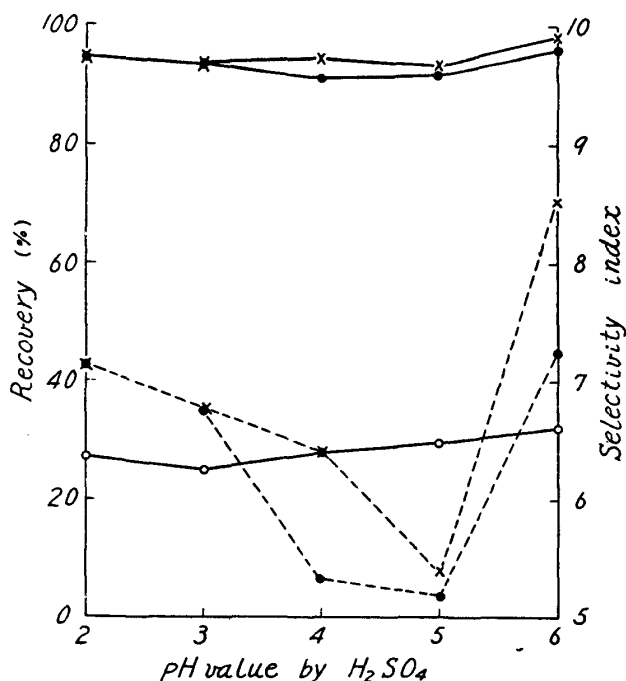


Fig. 7. Effect of pH Value for Copper, Iron, and Lead Recoveries with Potassium Ethyl Xanthate. For notation see Fig. 4.

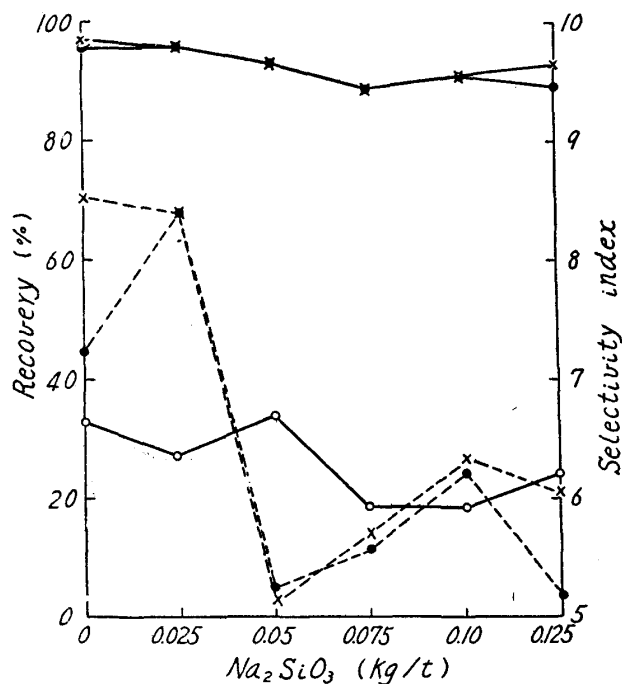


Fig. 8. Effect of Addition of Sodium Silicate for Copper, Iron, and Lead Recoveries with Potassium Ethyl Xanthate. For notations see Fig. 4.

Fig. 7 shows the result of a test, for examining the effect of varying pH value by addition of sulphuric acid, under the following conditions: white camphor oil, 0.4kg/t; potassium ethyl xanthate, 0.1kg/t; pH, 2 to 6; pulp density, 20%; temperature, 12.5 to 21.6°C; and flotation time, 10 to 30 min. As the pH value falls from 6 to 2, the recoveries of copper and iron decrease somewhat from 96.3 and 97.3% respectively, while the rejection of lead gradually rises from 66.9 to around 74%.

(iii) Effect of varying amount of sodium silicate

Fig. 8 shows the result of a test, for examining the effect of varying amount of sodium silicate, under the following conditions: white camphor oil, 0.4 kg/t; potassium ethyl xanthate, 0.1 kg/t; pH, 5.8 to 6.2; pulp density, 20%; temperature, 14.4 to 21.6°C; and flotation time, 20 to 40 min. When 0.075 kg/t of sodium silicate is added, the rejection of lead reaches the maximum of 81.2%, but the recoveries of copper and iron fall to 87.7 and 88.2% respectively, at the same time. Sodium silicate depresses the flotation of lead, but has the tendency to depress copper and iron as well.

(iv) Effect of change in temperature of sulphatization

According to the results of sulphatization test of galena, sometimes an unsulphatized core remains at the center of the particle,<sup>(6)</sup> which may be exposed by the peeling-off of the lead

sulphate shell when agitated in a flotation cell. Since the temperature of sulphatization is deemed to be a factor in determining the thickness of the lead sulphate shell, the test of the effect of the temperature of sulphatization on flotation was conducted.

Fig. 9 shows the result of a test under the following conditions: sulphatization temperature, 130 to 170°C; white camphor oil, 0.4 kg/t; potassium ethyl xanthate, 0.1 kg/t; pH, 3.8 to 4.2; pulp density, 20%; temperature of flotation, 12.5 to 17.2°C; and flotation time, 15 to 20 min. Within the scope of test, copper and iron exhibit no appreciable difference in grade as well as in recovery, but the rejection of lead is somewhat higher at higher temperatures, rising to 76.1% at 160°C and 75.3% at 170°C, while 92.8% of copper and 93.5% of iron being recovered. The result proved that the separation was rather appreciable at higher temperatures of sulphatization.

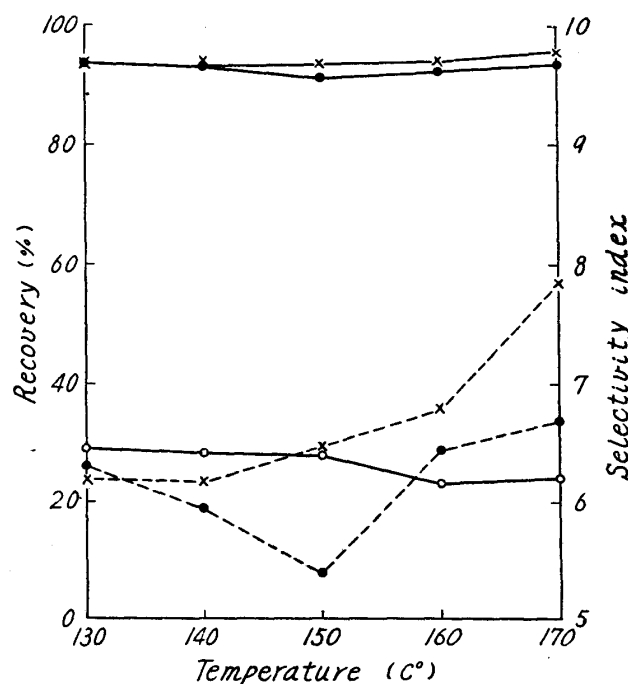


Fig. 9. Effect of Sulphatizing Temperature for Copper, Iron, and Lead Recoveries with Potassium Ethyl Xanthate. For notations see Fig. 4.

### 3. Results of Collective Copper-Iron Flotation

Table 6 shows the composite results of tests of collective flotation of copper and iron sulphides from lead sulphate under the following optimum conditions: white camphor oil, 0.1 kg/t; Aerofloat No. 25, 0.375 kg/t; conditioning, 5 min; flotation, 15 min; pulp density, 20%; temperature of flotation, 25.6 to 27.0°C; pH, 5.6 to 4.8. The results indicate that the recoveries are 96.21% for copper, and 98.01% for iron, and the rejection is 85.75% for lead.

Table 6. Composite Results of Collective Flotation of Copper and Iron Sulphides from Lead Sulphate.\*

Product	Weight		Grade (%)			Recovery (%)		
	(g)	(%)	Cu	Fe	Pb	Cu	Fe	Pb
Feed	45.10	100.00	3.95	21.89	7.88	100.00	100.00	100.00
Copper-iron concentrate	30.90	68.51	5.55	31.31	1.64	96.21	98.01	14.25
Lead tailing	14.20	31.49	0.48	1.38	21.46	3.79	1.99	85.75

\* Test conditions: white camphor oil, 0.1 kg/t; Aerofloat No. 25, 0.375 kg/t; conditioning, 5 min; flotation, 15 min; pulp density, 20%; temperature, 25.6 to 27.0°C; pH, 5.6 to 4.8.

## VI. Recovery of Lead Sulphate

From the results of the tests described in Par. IV above, it has been verified that sulphatization with sodium sulphide prior to flotation with potassium amyl xanthate is advantageous for efficient recovery of lead sulphate. However, it has also been demonstrated that overdose or underdose of sodium sulphide should be both avoided to gain good results, so the lead acetate test<sup>(22)</sup> was conducted for verifying the optimum amount of sodium sulphide required for the recovery of lead sulphate from the tailing of the collective copper-iron flotation tests outlined in Par. V above. The test showed that as much as 30 kg/t of sodium sulphide was required for best results. This fact is presumably caused by the extreme fineness of the lead sulphate particles. Moreover, it was ascertained that the pH of the pulp should be kept at 8 to 9 and 8 kg/t of caustic soda was required therefor.

The test was performed under the following conditions: white camphor oil, 0.6 kg/t; potassium amyl xanthate, 1.0 kg/t; caustic soda, 8 kg/t; pH, 9.2; pulp density, 17%; temperature, 21.0 to 27.2°C; conditioning, 10 min; and flotation, 45 min. The result of test is shown in Table 7. The grade was 21.5% Pb for the feed, 49.2% Pb for the concentrate, in which 51.4% of lead being recovered, and 27.4% Pb for the middling, in which 38.4% of lead being recovered. The composite grade and recovery for the concentrate and middling was 36.7 and 89.8% Pb respectively.

Table 7. Recovery of Lead Sulphate.\*

Product	Weight		Lead Content (%)	Lead Recovery (%)
	(g)	(%)		
Feed	33.70	100.00	21.46	100.00
Concentrate	7.55	22.40	49.22	89.76
Middling	10.15	30.12	27.35	
Tailing	16.00	47.48	4.63	10.24

\* Test conditions: white camphor oil, 0.6 kg/t; potassium amyl xanthate, 1.0 kg/t; caustic soda, 8 kg/t; sodium sulphide, 30 kg/t; conditioning, 10 min; flotation, 45 min; temperature, 27.2 to 21.0°C; pulp density, 17%.

## VII. Separation of Copper and Iron Sulphides

The collective copper-iron concentrate separated from lead sulphate in the tests described in Par. V consists mainly of chalcopyrite and pyrite. The ores from the Hanaoka mine are generally known for the low degree of liberation of mineral grains. For example, a case has been reported of the ore from the Nishi-kannondo pit showing the degree of liberation of chalcopyrite of 0% at -150 +200-mesh size, and 19% at -200 +270-mesh size.<sup>(2)</sup> The sample used for this test had been ground to -150-mesh size prior to sulphatization, but as may be seen from Table 9, both the copper and iron minerals are very small in size, the former being smaller than 20 microns and the latter around 20 microns

in majority. It was deemed imperative to liberate them by regrinding to accomplish the separation of copper and iron concentrates.

Table 8 shows the summary of the results of test for the separation of copper and iron sulphides. The collective copper-iron concentrate containing 5.61% Cu and 31.32% Fe was ground in a batch ball mill for one hour and floated for the first concentrate under the following conditions: white camphor oil, 0.4 kg/t; Aerofloat No. 25, 0.5 kg/t; slaked lime, 20 kg/t; pH, 11.6; pulp density, 20%; temperature, 20.8 to 27.0°C; conditioning, 10 min; and flotation 25 min. The first tailing was reground and retreated for the second concentrate under the conditions: white camphor oil, 0.2 kg/t; Aerofloat No. 25, 0.2 kg/t; slaked lime, 20 kg/t; pH, 9.8; pulp density, 20%; temperature, 24.0 to 25.2°C; conditioning, 10 min; and scavenging, 15 min. The second tailing was again reground and retreated for the third concentrate and the final tailing under the conditions: white camphor oil, 0.1 kg/t; Aerofloat No. 25, 0.1 kg/t; slaked lime, 20 kg/t; pH, 10.6; pulp density, 20%; temperature, 24.6 to 28.8°C; conditioning, 10 min; and scavenging, 10 min. The average copper content of the aggregate of the first to third concentrates was 9.9% with the copper recovery of 95.2%, but the copper content of the tailing did not fall under 0.6%. The iron content of the final tailing was 41.4% with the iron recovery of 61.4%.

Table 8. Separation of Chalcopyrite from Pyrite.\*

Product	Weight		Grade (%)		Recovery (%)	
	(g)	(%)	Cu	Fe	Cu	Fe
Feed	47.40	100.00	5.55	31.31	100.00	100.00
1st concentrate	15.35	32.38	11.70	19.80	68.21	20.48
2nd concentrate	5.49	11.58	8.25	24.11	17.20	8.92
3rd concentrate	4.57	9.65	5.61	30.02	9.74	9.24
Tailing	21.99	46.39	0.58	41.41	4.85	61.36
			9.86	22.57	95.15	38.64

\* Test conditions: white camphor oil, 0.7 kg/t; Aerofloat No. 25, 0.8 kg/t; slaked lime, 60 kg/t; conditioning, 30 min; flotation, 50 min; pulp density, 20%; temperature, 20.8 to 28.8°C; pH, 9.8 to 11.6.

### VIII. Size of Flotation Products

Throughout the tests described above, it was presumed that the degree of liberation of mineral grains played an important part in the efficiency of flotation process. For this reason, we undertook a microscopic analysis of the distribution of particle size in the products of the flotation tests. The results are presented in Table 9. It shows that the bulk of -20-micron material contained in the lead concentrate is 74.8%, and that in the copper concentrate, 72.5%, followed by 40.2% in the iron concentrate, and 16.7% in the tailing which is most coarse-grained.

In the above tests, the grade of concentrates was 49.2% Pb for the lead concentrate, corresponding to 72.1% of that of pure lead sulphate, 11.7% Cu for the copper concentrate, 33.8% of that of pure chalcopyrite, and 41.4% Fe for the iron

concentrate, 89.0% of pure pyrite. The grade of the concentrates was not so high in any case, but from the fact that particles under 5-micron size are very difficult to separate,<sup>(28)</sup> it may be assumed that the extent of grinding in the above tests is near the limit possible for flotation, and it seems difficult to hope for better separation.

Table 9. Microscopic Sizing Analysis of Flotation Products.

Size (Micron)	Weight (%)			
	Copper Concentrate	Iron Concentrate	Lead Concentrate	Tailing
0 — 10	31.79	2.61	44.28	2.77
10 — 20	40.74	37.61	30.52	13.89
20 — 50	27.47	59.78	25.20	25.00
50 — 74	—	—	—	27.78
74 —104	—	—	—	30.56
Total	100.00	100.00	100.00	100.00

### IX. Discussion of Results

Table 10 summarizes the results of selective flotation of sulphatization residues, the values for concentrates including those for middlings.

Table 10. Summary of Metallurgical Results of Selective Flotation of Sulphatization Residue.

Product	Weight (%)	Grade (%)			Recovery (%)		
		Cu	Fe	Pb	Cu	Fe	Pb
Feed	100.00	5.55	31.31	21.46	100.00	100.00	100.00
Copper concentrate	34.83	9.86	22.57	—	91.54	37.87	—
Iron concentrate	30.14	0.58	41.41	—	4.67	60.14	—
Lead concentrate	18.40	—	—	36.68	—	—	76.97
Tailing	16.63	—	—	4.63	—	—	8.78

Table 11 shows the summary of results of tests, including those of sulphatization.<sup>(6)</sup> It is therein indicated that the recovery of zinc is 97%, of copper, 90%, of lead, 77%, and of iron, 58%.

Table 11. Summary of Metallurgical Results of Selective Sulphatization-Flotation Process.

Product	Grade (%)				Recovery (%)			
	Cu	Fe	Pb	Zn	Cu	Fe	Pb	Zn
Zinc sulphate solution	0.03-0.08	0.11-0.33	—	5.70-6.57	1.69- 2.72	3.57- 3.67	—	96.86-97.91
Copper concentrate	9.86	22.57	—	—	89.99-89.05	36.51-36.48	—	—
Iron concentrate	0.58	41.41	—	—	4.59- 4.54	57.99-57.93	—	—
Lead concentrate	—	—	36.68	—	—	—	76.97	—
Tailing	—	—	4.63	—	—	—	8.78	—

(28) Jogoro Okada, Trans. Alumni Assoc., Department of Mining and Met., Kyoto Univ., 9 (1938), 669-92.

Table 12 shows the representative results of operation of selective flotation of complex ores from the Hanaoka<sup>(29)</sup> and Ikuno mines,<sup>(30)</sup> which seem to indicate the difficulty of selective flotation of such complex ores.

Table 12. Examples of Operation of Selective Flotation of Complex Sulphide Ores.<sup>(29)(30)</sup>

Mine	Grade of Concentrate (%)			Recovery (%)		
	Cu	Pb	Zn	Cu	Pb	Zn
Hanaoka mine	7.98	67.29	48.91	64.00	69.70	65.20
Ikuno mine	25.70	53.00	50.00	64.10	67.00	69.60

Table 13 is a summary of recent results of operation of flotation in Japan,<sup>(31)(32)</sup> in which the average values of recovery stand at 83% for copper, 73% for lead, 71% for zinc, and 58% for sulphur.

Table 13. Statistical Summary of Recent Results of Flotation Practice in Japan.<sup>(31)(32)</sup>

	Grade of Concentrate (%)				Recovery (%)			
	Cu	S	Pb	Zn	Cu	S	Pb	Zn
Maximum value	26.14	48.69	66.50	58.80	94.60	92.20	92.10	88.90
Minimum value	3.17	36.66	53.96	44.96	40.65	13.48	51.05	40.05
Average value	13.46	44.41	60.22	52.31	83.02	58.26	73.24	70.95
Number of data	22	21	9	9	21	23	9	9

The question whether the "selective sulphatization-flotation process" described above is economically more advantageous than the processes in common practice hitherto should be settled by the results of further basic and industrial tests.

### Summary

In this institute, the "selective sulphatization-flotation process" has been originated as a process for treating complex sulphide ores. This fourth report summarizes the results of tests for the recovery by selective flotation of copper, lead, and iron in the residues obtained by selective sulphatization of bulk sulphide concentrates from the Hanaoka mine, Akita Prefecture.

The general summary follows:

(1) The samples used were residues obtained by grinding, -150 mesh in size, and sulphatizing so-called copper concentrates from the Hanaoka mine. The

(29) Minoru Yagi, Paper read at the 3rd Meeting on Non-ferrous Metallurgy and Mineral Dressing Research, Research Institute of Mineral Dressing and Metallurgy. (Bull. Res. Inst. Min. Dress. Met., 5 (1949), No. 1, 76.)

(30) Konosuke Yamane, J. Mining Inst. Japan, 64 (1948), 227-47.

(31) Technical Committee on Mineral Dressing, Mining Inst. Japan, Flotation of Pyrite, (1950), Appendix 34-7.

(32) Technical Division, Mining Association of Japan, Flowsheet of Dressing and Cyanidation at the leading mines, (1950), 99-111.



grade of the residues was 4.3 to 5.7% Cu, 14.5 to 20.0% Fe, 6.2 to 13.9% Pb, and 2.3 to 3.2% Zn.

(2) The sulphatized residues consisted of chalcopyrite, pyrite, lead sulphate, a small admixture of gangue minerals as barite and quartz, and a residuum of undissolved zinc ore.

(3) By selective flotation, a bulk concentrate of chalcopyrite and pyrite was first floated, which was reground and then separated into chalcopyrite and pyrite, and finally lead sulphate was recovered from the gangue.

(4) The problems raised in these tests were the floatability of lead sulphate formed by sulphatization, and the degree of regrinding necessary for the separation of chalcopyrite from pyrite.

(5) For the elucidation of the floatability of lead sulphate, basic tests were conducted with pure lead sulphate, referring to existing literatures. It was ascertained that in depressing lead sulphate, Aerofloat No. 25 should be used as a collector and the pH value kept either below 5.8 or above 6.2, while in floating lead sulphate, the optimum amount of sodium sulphide, previously determined by the lead acetate test, should be used for sulphidizing, potassium amyl xanthate used as a collector, and the pH value kept at 8 to 9.

(6) Within the temperature range of 130 to 170°C in sulphatization, the selectivity of copper and iron to lead in flotation improved somewhat at 160 and 170°C.

(7) For the separation of copper and iron sulphides from lead sulphate, the commendable results of copper recovery of 92.9%, of iron recovery of 96.2%, and of lead rejection of 83.5% were obtained under the following conditions: white camphor oil, 0.1 kg/t; Aerofloat No. 25, 0.13 kg/t; pH, 6.

(8) For the recovery of lead sulphate, the results of lead content of 36.7%, and of lead recovery of 89.8% were obtained under the conditions: white camphor oil, 0.6 kg/t; potassium amyl xanthate, 1.0 kg/t; pH, 9.2.

(9) For the separation of bulk copper-iron concentrate, the results of copper content of 9.9%, with copper recovery of 95.2%, and of iron content of 41.4%, with iron recovery of 61.4%, were obtained by three stages of regrinding, one stage of roughing and two stages of scavenging under the conditions: white camphor oil, 0.7 kg/t; Aerofloat No. 25, 0.8 kg/t; slaked lime, 60 kg/t; pH, 9.8 to 11.6.

(10) The size of the flotation products was 74.8% of -20 microns for the lead concentrate, 72.5% of -20 microns for the copper concentrate, 40.2% of -20 microns for iron concentrate, and 83.3% of +20 microns for the tailing.

(11) The highest grade of concentrates was rather low, namely, 49.2% Pb for the lead concentrate, 11.7% Cu for the copper concentrate, and 41.4% Fe for the iron concentrate, but it was considered difficult to hope for higher grades, because of the permissible limit of grinding in flotation.

(12) The aggregate result throughout sulphatization and selective flotation was; the zinc recovery, 97%; the copper recovery, 90%; the lead recovery,

77%; the iron recovery, 58%.

(13) The advantages of this process may be mentioned: The liberation of minerals will be promoted chemically; the surface of mineral grains will be cleaned; sphalerite is dissolved and galena is converted into lead sulphate; the separation of copper, lead, zinc and iron is made easier.

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