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著者	ONO Kenji, KAMEDA Mitsuo, KANNO Hiroshi, IZUMI Nobuo
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A Research on the Treatment of Complex Sulphide Ores. III Selective Sulphatization Process*

Kenji ONO, Mitsuo KAMEDA, Hiroshi KANNO and Nobuo IZUMI

The Research Institute of Mineral Dressing and Metallurgy

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Synopsis

With the aim of recovering zinc, copper, lead, iron and sulphur from complex sulphide ores, the selective-sulphatization flotation process has been proposed by the Institute. Complex sulphide ores are treated with bulk flotation. The concentrate, after being reground, is subjected to the treatment of selective sulphatization. The object of the treatment lies in sulphatizing only the zinc and lead sulphides as far as possible, with minimum sulphatization of pyrite and chalcopyrite. In the treatment, the bulk concentrate is mixed with comparatively concentrated sulphuric acid, the mixture being kept at a temperature of around 150°C for one hour. The sulphatization product is leached out with water, and the resultant zinc sulphate solution can be electrolysed for zinc. On the other hand, chalcopyrite, pyrite, and lead sulphate can be recovered from the leach residue by application of differential flotation.

In the present report, the research on the selective sulphatization and the electrolytic recovery of zinc is given. First, to find out basic data for the treatment, a variety of sulphide minerals were subjected to the action of sulphuric acid of high concentration and the degree of sulphatization was examined. From the results, it was found that zinc minerals, including zinc blende and marmatite, galena, and pyrrhotite were readily sulphatized, while chalcopyrite and pyrite were almost unaffected. Second, the flotation concentrates from Hanaoka Mine, having the chemical composition as shown in Tables 2 and 4, were treated with the selective sulphatization. The representative result gave 97% of sulphatization percentage for zinc, while 3.6% and 2.0% for iron and copper, respectively. Optimum conditions for the tests were as follows: Concentration of H_2SO_4 , 60 vol%; solid-liquid ratio, 1:1; treating time, 1 hr and treating temperature, 150~160°C. The solution leached out from the sulphatization product was subjected to tests for production of zinc under the electrolysis process in usual practice and the cathode zinc of 99.97% purity, containing 0.024% of lead, 0.0046% of copper and 0.0029% cadmium, was obtained. Finally, similar tests were repeated on a larger scale and the good results were also obtained.

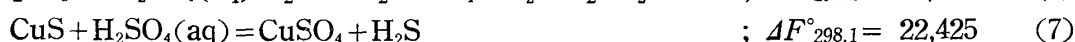
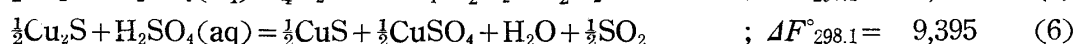
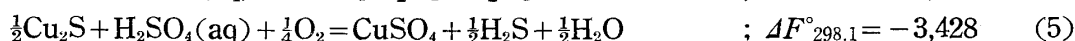
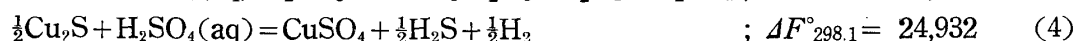
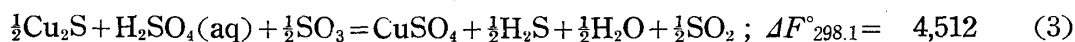
I. Introduction

The recovery of copper, zinc, sulphur etc. from complex sulphide ores is an important question for Japan so poor in natural resources. As one approach to the solution of this question, the Research Institute of Mineral Dressing and Metallurgy has proposed a process called "Selective-Sulphatization Flotation Process", as summarized in Report No. 1 of this series. The present report is to outline the results of the research and tests connected with the selective sulphatization and the electrolytic recovery of zinc, the phases of the process falling under the scope of the specialty of the authors.

* The 39th report of the Research Institute of Mineral Dressing and Metallurgy.

II. Outline of selective-sulphatization process

When sulphides of metal elements are subjected to the action of sulphuric acid of high concentration, lead and zinc sulphides are turned into comparatively water-soluble sulphates—a fact well known in analytical chemistry from olden days. The susceptibility of various metal sulphides to the reaction may be estimated from the following chemico-thermodynamical data⁽¹⁾:



Due to the lack of values for FeSO_4 and $\text{Fe}_2(\text{SO}_4)_3$, the values for pyrite and chalcopyrite cannot be calculated, but it may be readily understood that zinc and lead sulphides are easily sulphatized. However, these values do not show the velocity of the reaction. The selective-sulphatization process, as outlined in Report No. 1, consists in grinding down the complex sulphide ores, mix them with 60% sulphuric acid and heating the mixture to 130~170°C, and if it is possible to sulphatize only the galena and zinc blende in the ores, leaving chalcopyrite and pyrite intact, we may leach zinc out of the product of the reaction with water, and separate it from the residue of lead sulphate, chalcopyrite and pyrite, which can be treated by application of differential flotation.

The use of concentrated sulphuric acid in the process might be looked upon as a drawback in industrializing this method, but on reading a report of a similar process applied to zinc ores in USSR, cited in the Chemical Abstract⁽²⁾ for 1947, we took heart and proceeded to study the possible application of this process to complex sulphides.

III. Basic experiments on selective sulphatization

In the above mentioned report,⁽²⁾ no information is given on concrete numerical values, so we proceeded first to study the effect of sulphuric acid acting upon various metallic sulphides. The experimental apparatus was a simple one as illustrated in Fig. 1. The sulphatization vessel is of glass, the H_2S gas generated during the reaction being led into a water bottle, washed and discharged into the atmosphere as exhaust. As infiltration of air during the reaction into the sulphatizing vessel is not entirely free of harmful effects, as shown in reaction 5 mentioned above, this discharge of exhaust through water gives a welcome

(1) These data were calculated from the values involved in K. K. Kelley's "Contributions to the Data on Theoretical Metallurgy" (U. S. Bur. Min. Bull. 406 (1937)).

(2) Gromov, B. V. and D. I. Derkachev: *Tsvetny Metal*, 20 (1947), No. 1 27—39; *Chem. Abstracts*, 24 (1947), No. 16, 5067.

sealing effect against intrusion of air. As sample, natural sulphide minerals as pure as obtainable, were used, ground down to the fineness of -15μ mesh. Sulphuric acid of 60 weight % concentration (specific gravity: 1.5) was added to

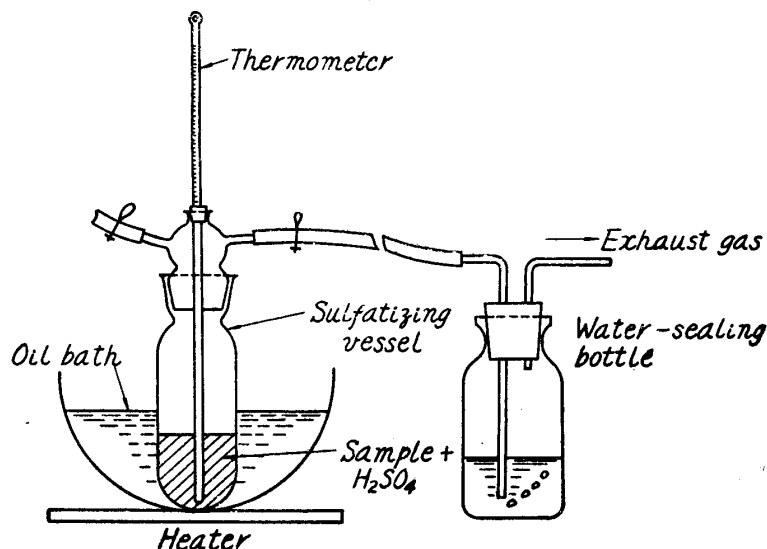


Fig. 1. Experimental apparatus on a smaller scale.

20~30 g of this mineral preparation, to the amount 1.5 times the theoretical requirement, and the mixture was heated in an oil bath, for one hour after the temperature was raised to the expected degree. After cooling down, the product of the reaction was leached in about 100 cc of water for one half to one hour, the metal content in the

solution assayed and the lixiviation percentage computed.

a) Zinc blende

As mentioned above, it is well to be expected that this mineral will be readily sulphatized, but it is of some interest how the marmatite type ores will react. The samples used were from Budô, Chichibu and Taishû Mines, each differing in iron content. The chemical composition is shown in Table 1.

Table 1. Chemical composition of zinc sulphides used.

Name of mines where samples were produced	Zn (%)	Fe (%)	Cu (%)	SiO ₂ (%)	S (%)
Budô	66.57	1.38	tr.	0.14	32.85
Chichibu	55.38	9.60	0.034	0.35	32.77
Taishû	54.91	12.03	none	0.42	33.53

At room temperature, no sign of reaction is patent, though a smell of hydrogen sulphide is detected. At 30°C, the gas begins to form bubbles, and at 85°C or so, the bulk of the mixture swells up to about three times. At 128°C, the rise in temperature is arrested, showing that heat is being absorbed. The product is a white solid, apparently a crystallization of zinc sulphate including water in excess.

The result is shown in Fig. 2. The percentage of sulphatization of zinc* is not high till the temperature rises to 120°C, but in the range of 130~170°C the percentage is 95% and over. Iron is reacted upon in a rate similar to zinc, so the marmatite type ores from Chichibu and Taishû Mines are susceptible to the treatment, but the presence of iron in quantity occasions some problems in the

* The zinc content was determined by means of volumetric determination with potassium ferrocyanide reported by Prof. Oka in Vol. 2, No. 5 of the present Reports.

purification of the solution for electrolysis.

b) Galena

The sample was taken from ores from Kamioka Mine, with the composition* of Pb 85.8%, S 13.7%, Fe 0.33% and Cu none, a comparatively pure specimen. At room temperature, some H₂S smell is detectable, but the bubbling is not so remarkable at higher temperature, and the end product remains in two layers of liquid and solid. Fig. 3 shows the result of assay for lead content present as lead sulphate, that is obtained quantitatively by lixiviation of the sulphatization product with 25% NaCH₃COO solution containing some acetic acid. Particles of -150 mesh yields only less than 40% of lead sulphatization, rising only very gradually up to 140°C. Between 150~170°C, the percentage rises rather sharply, but the maximum is 70%. The outward appearance of the product is a white powder, but some black galena is found remaining at the core. As lead sulphate is very difficult to dissolve in water, the lead sulphate, upon production, seems to tend to coat the galena particles, hindering the subsequent sulphatization. A similar test with the sample ground down to -270 mesh shows a similar curve of sulphatization percentage, but the percentage

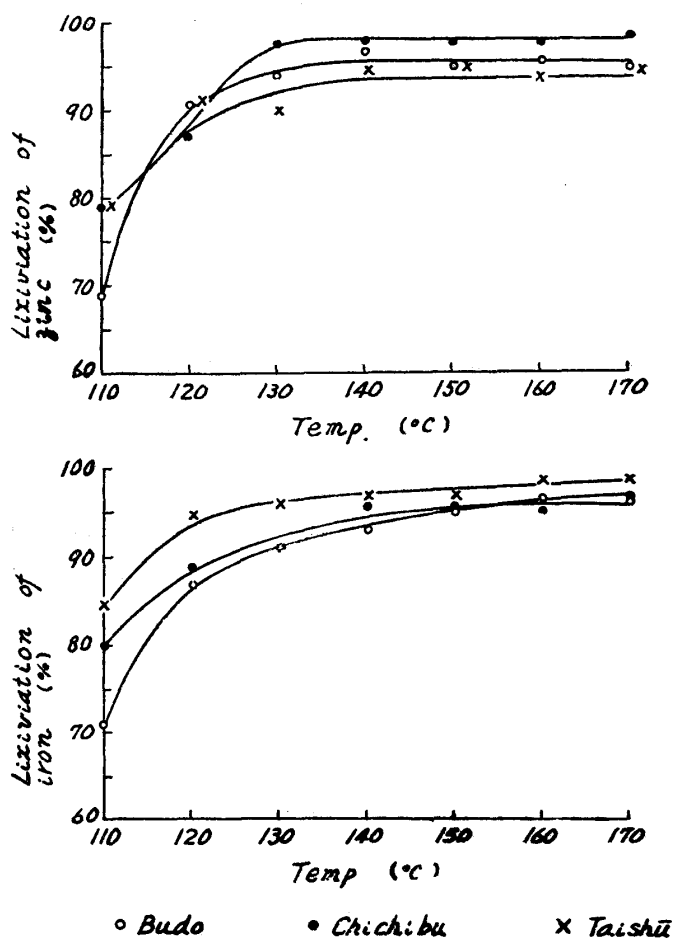


Fig. 2. Sulphatization of zinc blende and marmatite. Wt. of ore used: 30g, wt. of 60% H₂SO₄ used: 75g for Budo ore; 73g for Chichibu ore; 77g for Taishū ore.

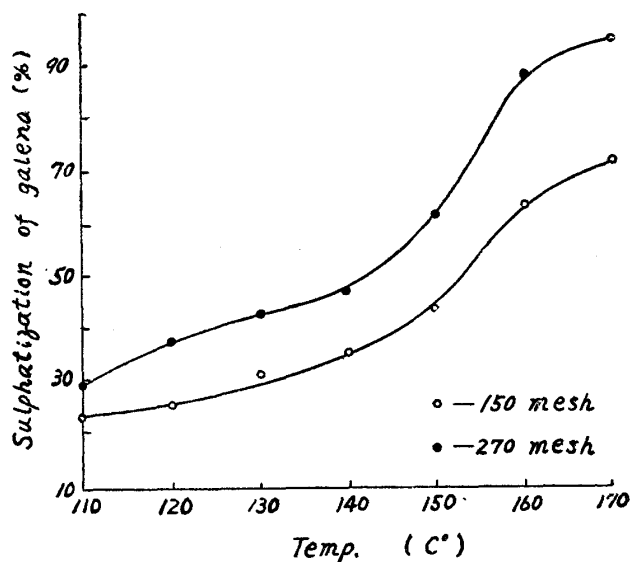


Fig. 3. Sulphatization of galena. Wt. of galena used: 20g, wt. of 60% H₂SO₄ used: 20g.

* The theoretical composition of galena is Pb, 86.6% and S, 13.4%.

rises to 90% at the temperature of 160~170°C. It is clear that the fineness of the particles affects the efficiency of sulphatization. An extension of reaction time to 2 hours with -150 mesh materials at the temperature of 160~170°C shows little effect.

c) Pyrrhotite

The sample, taken from Kuriki Mine product, was of Fe, 59.26%; S, 34.58% and

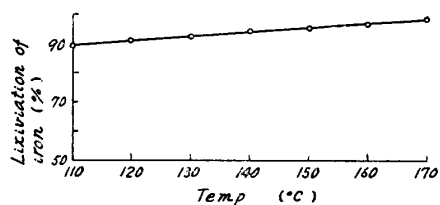


Fig. 4. Sulphatization of pyrrhotite.

Wt. of pyrrhotite used: 20g.
Wt. of 60% H₂SO₄ used: 26g.

Cu, none, in chemical composition. This sample showed active reaction, apparently reaching the optimum reaction rate at 90°C, and resulting in a solid of chocolate color. The result is shown in Fig. 4. At 110°C, the lixiviation percentage reaches 90%, which shows a tendency of rising with the rises in temperature.

d) Chalcopyrite

The sample, taken from Manzō Mine product, had a chemical composition* of Cu, 31.99%; Fe, 28.24% and S, 33.67%. Little reaction was produced, but at a

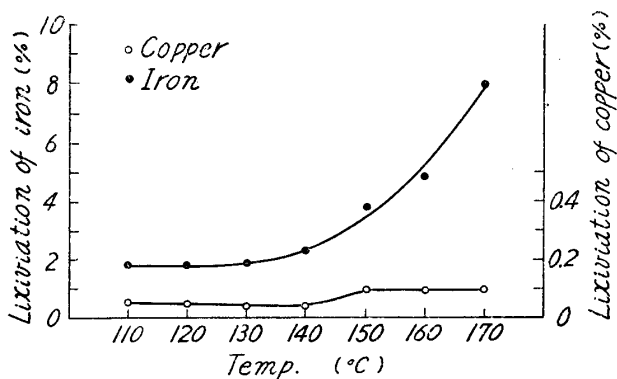


Fig. 5. Sulphatization of chalcopyrite.

Wt. of chalcopyrite used: 20g.
Wt. of 60% H₂SO₄: 40g.

temperature exceeding 140°C, some reaction became noticeable. The product of course remained in two layers of solid and liquid. The result is shown in Fig. 5. Cu is little affected, only less than 0.1% being transformed under 170°C, but iron is leached out to 2% up to 140°C and its lixiviation rises sharply with the rise of temperature above 150°C till it reaches the maximum of 8% at 170°C. Changing the air in the sulphatization

vessel into hydrogen sulphide brought about little change in the result.

e) Iron Pyrite

The sample, taken from Kamikita Mine product, showed the chemical composition** of Fe, 43.93% and S, 50.57%. The result is shown in Fig. 6. The change in temperature little affects the lixiviation rate, which remains in the range of 1~2% between 110°C and 170°C.

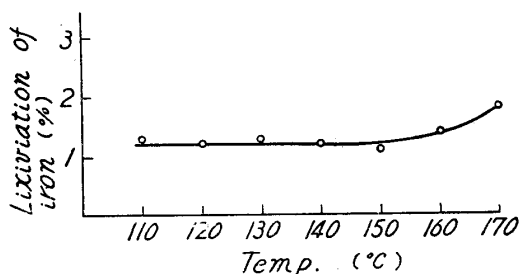


Fig. 6. Sulphatization of pyrite.

Wt. of pyrite used: 20g.
Wt. of 60% H₂SO₄ used: 25g.

In summarizing the results of the above tests, we find that zinc blende, marmatite,

* The theoretical chemical composition of chalcopyrite is Cu, 34.64%; Fe, 30.43% and S, 34.93%.

** The theoretical chemical composition of Pyrite is Fe, 46.55% and S, 53.45%.

galena and pyrrhotite are actively reacted upon by sulphuric acid, while chalcopyrite and iron pyrite show little reaction. Temperature factor comes into play especially by galena, the range between 150°C and 160°C being expected to be the optimum.

IV. Selective sulphatization of Hanaoka flotation concentrate

a) Effect of basic conditions

The sample was donated by Hanaoka Mine, and had the chemical composition as shown in Table 2. This sample was reground to -150 mesh before testing.

Table 2. Chemical and mineralogical composition of flotation concentrate from Hanaoka Mine (Sample I).

Name of chemical element	Wt. %	Name of component mineral	Mol. % *
Cu	3.86	Chalcopyrite	7.5
Fe	9.94	Pyrite	14.3
Zn	22.99	Zinc Blende	43.2
Pb	9.81	Galena	5.6
SiO ₂	11.91	Quartz	24.3
BaSO ₄	9.71	Barite	5.1
S	25.81		

* Mineralogical composition was calculated from the chemical composition by Prof. T. Takeuchi.

i) Effect of change in temperature

Using an apparatus similar to that illustrated in Fig. 1, the effect of temperature change was first tested under the following conditions: Sample, 30 g; H₂SO₄ of 60 vol% (68.5 wt%), 30 g; pulp density, 1:1 and lixiviation, 30 min. with 200 cc of water. During reaction, almost no H₂S smell was detected at room temperature, at 115°C or so, bubbles began to form and at 130°C, the reaction reached the climax, the bulk rising to around three times the original, and the surface had the appearance of dancing due to the bubbling. At this point, the rise in temperature came to a suspension for a time of about 10 min. Then the bubbles abated, the surface sank, and the temperature resumed to rise. The rise from room temperature to 150°C took 1 hr, to 160°C, 1 hr 10 min and to 170°C, 1 hr 20 min. The product was solid, which was readily dissolved into pulp in water. Analysis was made on the zinc, copper and iron contents in the solution filtered free of residual solid. The result is shown

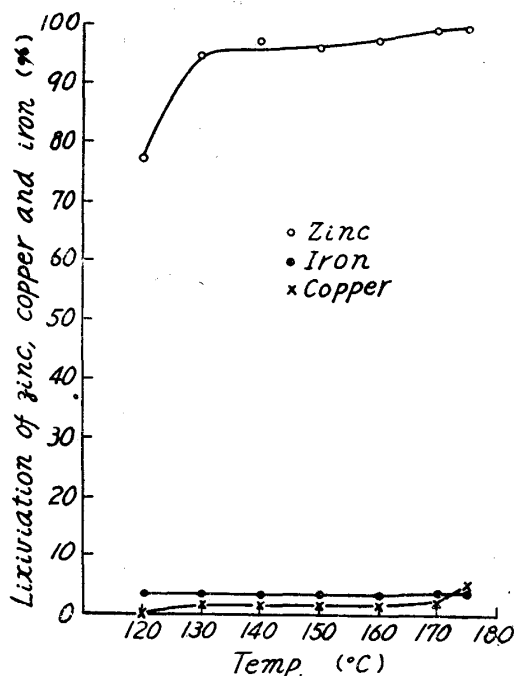


Fig. 7. Effect of temperature on sulphatization of concentrate from Hanaoka Mine. Concentration of H₂SO₄ used: 60(vol)%. Solid-liquid ratio: 1:1. Treating time: 1 hr.

in Fig. 7. The lixiviation percentage of zinc is low at 120°C, but at 130°C, it rises to 95%, rising still higher with the rise of temperature. The lixiviation of iron and copper remains low throughout the range, limited to 3.6~3.7% and 1.4~1.6% respectively. But as copper shows a tendency to rise sharply above 170°C in lixiviation percentage, a reaction temperature above 170°C should be avoided. On the other hand, a low temperature may cause imperfect reaction, so the temperature should be kept within the range of 150°C~160°C as standard process temperature. In processing in air, the lixiviation of copper tends to rise markedly at 150°C or above, perhaps due to the approximation of conditions to those of sulphatizing roasting process. Thus the entrance of air into the apparatus during the process should be kept down. The reaction itself generates a quantity of H_2S which drives off the air present, so a stoppage with a cock upon completed reaction is effective enough to keep out the air. The percentage of lead sulphate formation in the residue could not be determined with precision, due to imperfections in the qualitative analysis from lead sulphide, which could not be improved probably due to the presence of other elements. However, through rough analysis of the residue of 150°C, microscopic analysis and flotation test of residue, we came to the conclusion that nearly all of galena had been changed to lead sulphate. This is in discrepancy with the result of

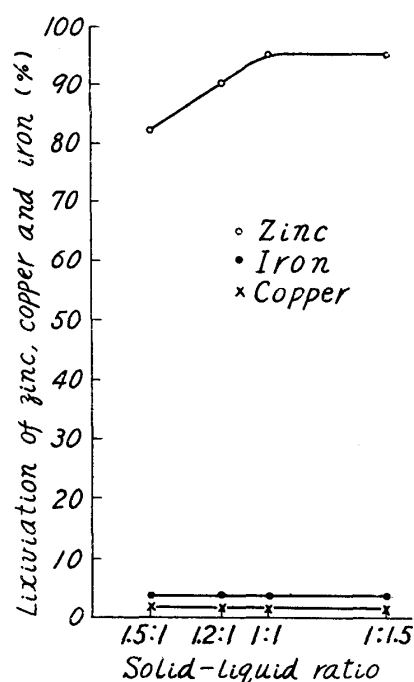


Fig. 8. Effect of solid-liquid ratio on sulphatization of concentrate from Hanaoka Mine.

Concentration of H_2SO_4 used: 60 (vol)%. Treating temperature: 150°C. Treating time: 1hr.

the basic test, a discrepancy perhaps due to the fineness of the galena particles in this test. Even if a small quantity of galena remains unchanged, the particles are completely surrounded by lead sulphate, and could be treated as lead sulphate particles in flotation process.

ii) Effect of solid-liquid ratio

The subject effect was tested under the conditions of temperature, 150°C; sample, 30 g; H_2SO_4 , 60 vol%; sulphatization time, 1 hr and lixiviation with 200 cc water for 30 min. The result is shown in Fig. 8. At the solid-liquid ratio of 1.5:1 to 1:1, the lixiviation percentage of zinc shows a rise, but between 1:1 and 1:1.5, no change is seen in the percentage, so that it is of no advantage to increase the ratio of liquid over 1:1. The lixiviation percentage of copper and iron shows no change throughout. On the assumption that all of the zinc blende and galena is turned into sulphates, and taking copper and iron not into calculation, the re-

quired theoretical quantity of the sulphuric acid would be 39.0 g against 100 g of concentrate. The quantity of sulphuric acid used in the test is then 1.17 times of the above theoretical quantity at 1.5:1 of solid-liquid ratio, 1.46 times

at 1.2:1, 1.75 times at 1:1, and 2.62 at 1:1.5.

iii) Effect of concentration of sulphuric acid

Fig. 9 shows the result of the test for the subject effect under the following conditions: temperature, 150°C; sample, 30 g.; solid-liquid ratio 1:1; sulphatization time, 1 hr. and lixiviation with 200 cc of water for 30 min. The concentration of H₂SO₄ is shown in vol%. The weight% of the acid used, calculated under specific gravity method, showed the equivalent value of 68.5 wt% for 60 vol%, 60 wt% for 50 vol% and 50 wt% for 40 vol%. The lixiviation percentage shows a slight rise with the higher concentrations, but the percentage is higher than 90% even with a 40% acid, in which case, the net volume of sulphuric acid is only 1.28 times of the theoretical value. Consequently, in collation with Fig. 8, it seems more advantageous to use diluted acid than to increase the pulp density, in economizing sulphuric acid. However, the use of dilute acid will cause a rise in the calorie required, due to the evaporation of water content in excess.

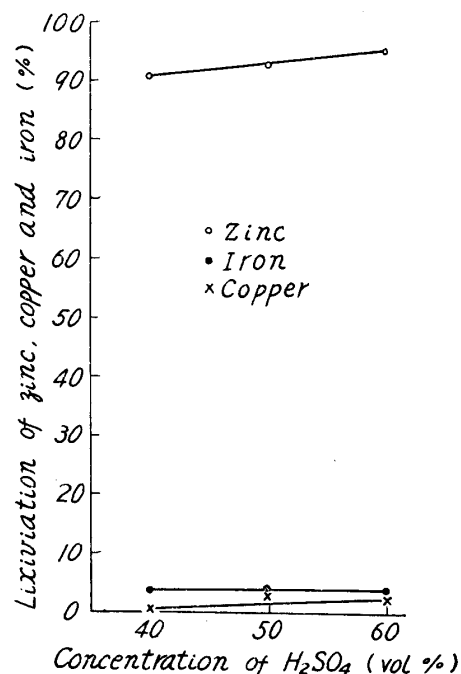


Fig. 9. Effect of sulphuric acid concentration on sulphatization of concentrate from Hanaoka Mine. Solid-liquid ratio: 1:1. Treating temperature: 150°C. Treating time: 1 hr.

Besides, the effect of change in treatment time was examined in this test, which revealed that one hour of holding time was sufficient for good results.

iv) When 100 g of sample was used

The above tests were all performed with 30 g of sample per test. Table 3 shows the result of a test with 100 g of sample, under the conditions of 60 vol% H₂SO₄, 100 g.; solid-liquid ratio, 1:1; treatment time, 1 hr. and lixiviation for 30 min. with 200 cc of water.

Table 3. Results of selective sulphatization treatment using 100 g of concentrate.

Treating temperature (°C)	Percentage extraction		
	Cu	Fe	Zn
130	2.72	3.61	97.05
140	1.76	3.57	97.91
150	2.27	3.67	97.09
"	1.69	3.62	97.05
"	2.00	3.62	96.86

The range of temperature was between 130°C and 150°C. It may be seen that the result is rather better than in all tests with 30 g of sample.

b) Test on a larger scale

The quantity of sample was increased to 0.6~0.8 kg and tests were conducted using opaque quartz crucible or Fe-Si autoclave type container under ordinary pressure. A large quantity of sample being required, a concentrate of chemical composition shown in Table 4 was used instead of the former sample.

Table 4. Chemical composition of concentrate used for larger scale treatment (Sample II).

Cu (%)	Fe (%)	Pb (%)	Zn (%)	SiO ₂ (%)	BaSO ₄ (%)	S (%)
3.29	14.73	4.23	17.14	13.22	8.30	25.79

Reaction of acid upon the copper and iron used in the packings and container not being excluded, the lixiviation of iron and copper showed a small increase over the values in the previous tests. 15 tests were conducted, the zinc solution being electrolysed and the residue being subjected to flotation tests. The representative results are as shown in Table. 5.

Table 5. Representative results of selective sulphatization treatment on a larger scale.

Weight of sample Kg	Concentration of sulphuric acid Wt.%	Solid : liquid ratio	Temperature °C	Apparent electric power Kwh/kg	Percentage extraction		
					Cu	Fe	Zn
0.6	70	1 : 1	150~160	3.95	3.92	5.59	97.37
0.7	70	1 : 1	150~155	3.20	2.93	5.00	94.80
0.8	60	1 : 1	150~165	5.6	6.10	5.70	95.89
0.8	70	1 : 1	150~165	3.17	4.90	5.35	94.55

V. Electrolysis of solution from selective sulphatization process for zinc

a) Composition of samples

Two kinds of sample were used, being somewhat different in chemical composition as shown Table 6.

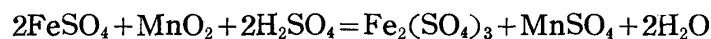
Table 6. Chemical composition of leach solutions resulting from selective sulphatization treatment.

Name of chemical element	Leach solution from Sample I	Leach Solution from sample II
Zn (g/l)	60.42	70.30
Cu (g/l)	0.2695	0.7665
Cd (g/l)	0.2188	0.329
Mn (g/l)	0.200	0.238
Total Fe (g/l)	1.139	3.338
Fe ⁺⁺ (g/l)	0.6317	2.950
As (g/l)	0.00148	0.0015
Bi (g/l)	0.00133	0.00023
Ni (g/l)	0.002	tr.
Co (g/l)	tr.	tr.
Sb (g/l)	tr.	tr.
Cl' (g/l)	0.0014	0.0023
Free H ₂ SO ₄ (g/l)	74.24	181.3

The contents of Cu, Cd, As, Bi, Ni, Co, Sb and Cl', elements harmful to the processing, were negligible, but the presence of a rather large quantity of iron raised some trouble.

b) Oxidation of ferrous sulphate by manganese dioxide.

Firstly, the effects of quantity of MnO_2 present, length of time and change of temperature were tested with sample 1. As the permissible limit of Fe^{++} content in electrolyte is set at 20 mg/l., the terminus of oxidation was fixed at the point where the Fe^{++} content fell below 20 mg/l. The equation for the process is assumed as follows:



The theoretical quantity of MnO_2 required in the reaction, calculated from the above equation, is 0.493 g/l for sample I and 2.28 g/l for sample II.

250 cc of sample I was heated in a water bath, stirred by a flow of air (about 0.4 l/min.), to which MnO_2 , ground into fine powder in an agate mortar, was added and shaken, then the heating under air agitation was resumed.

As the reaction was not satisfactory at the temperature of 60°C, the experiments were made at a temperature of 90°C. Fig. 10 shows the time required for the Fe^{++} content to fall below 20 mg/l. The quantity of used MnO_2 is given in the percentage of the theoretical quantity of MnO_2 required.

The result shows that an increase in the added MnO_2 quantity shortens the time of oxidation. With 200% of MnO_2 , a reaction time of 2½ hours is adequate.

The test with sample II was conducted under the conditions of quantity of solution, 1 l per test; MnO_2 , 200% of theoretical quantity (4.5~4.8 g/l); reaction time 2.5 hrs; temperature, 90°C and air agitation at the rate of 0.8~1.4 l/min. The residual Fe^{++} was determined by titrating 10 cc of solution taken from the test liquor with $KMnO_4$ solution at 10 min, 30 min and 1 hr after the initiation of the test, then at every 30 min. The result is shown in Fig. 11. It is seen that 95% and 98% of Fe^{++} is oxidized in 10 and 30 min. of time, respectively, after addition of MnO_2 , and the goal is reached in 2.5 hrs. The straight line in Fig. 11 shows the values in the reaction test by mere air agitation, without addition of MnO_2 , which shows that the rate of oxidation decreases in straight proportion with the lapse of time. 50 mg/l of Fe^{++} is oxidized in 1 hr and a complete oxidation is expected to take around 70 hrs. MnO_2 should be ground finely just before use, as large grains are hard to dissolve, some remaining in

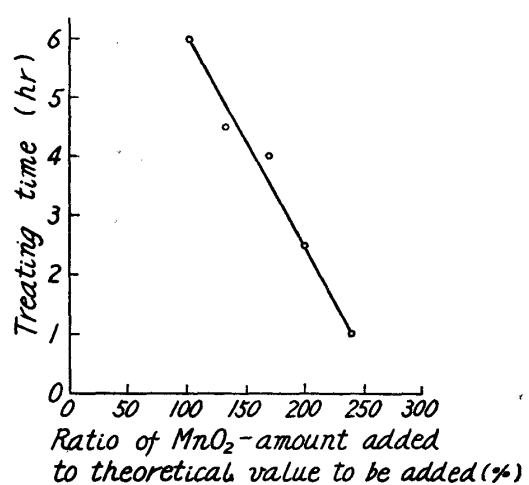


Fig. 10. Relation between amount of MnO_2 added and treating time required for oxidizing ferrous ions into ferric ions up to concentration of below 20 g/l Fe^{++} .
Solution used: Leach solution from sample I. Treating temperature: 90°C. Rate of air agitation: about 0.4 l/min.

the original shape throughout the process. The somewhat worse values in Fig. 11 apparently show the case where the use of MnO_2 was in an improper way.

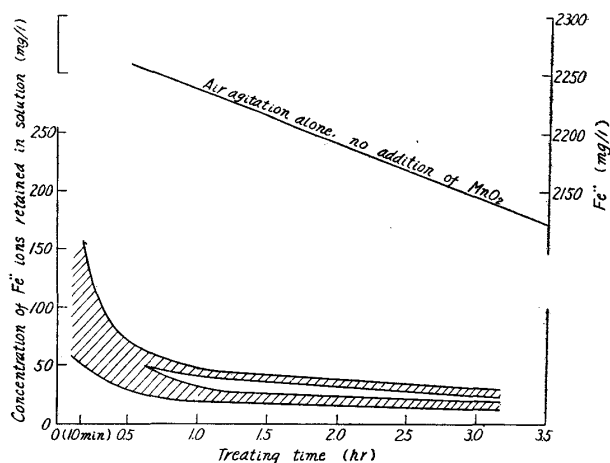


Fig. 11. Change in concentration of Fe^{2+} ions retained in solution due to process of treating time.

Solution used: Leach solution from sample II.
Treating temperature: 90°C . Amount of MnO_2 used: 200% of theoretical value. Rate of air agitation: 0.8~1.4 l/min.

complete solution of the dose. As zinc oxide was limited in its effect to raising the pH value up to about 4.6, $\text{Ca}(\text{OH})_2$ was added, also in small separate doses, to bring the pH value up to 5.4~5.6. With sample I, the representative result

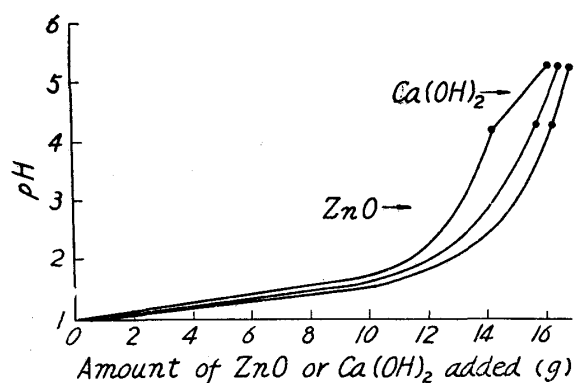


Fig. 12. Change in pH value due to increasing amounts of ZnO and there after added $\text{Ca}(\text{OH})_2$.
Solution used: Leach solution from sample I (250cc). Treating temperature: 90°C .

g to 250 cc of sample I and of 5~10 g/l to sample II.

Filtration of 250 cc of sample I presented little difficulty, but the presence of an amount of iron in sample II caused considerable difficulty* in filtering it. In unwashed precipitate, a considerable quantity of ZnO or $\text{Zn}(\text{OH})_2$ was found,

The above tests confirms that the temperature should be 90°C and the quantity of MnO_2 200% of the theoretical value, for optimum results. Presence of some free sulphuric acid is desirable and MnO_2 is best used in the state of fine powder freshly ground.

c) Proper pH value and filtration in precipitation process of $\text{Fe}(\text{OH})_3$

Zinc oxide as neutralizing agent was added in repeated small doses to the resultant solution kept at the temperature of test. The pH value of the solution was determined with pH testing paper after each

complete solution of the dose. As zinc oxide was limited in its effect to raising the pH value up to about 4.6, $\text{Ca}(\text{OH})_2$ was added, also in small separate doses, to bring the pH value up to 5.4~5.6. With sample I, the representative result is as shown in Fig. 12. The curve represents the change under a temperature of 90°C . Under a temperature of 60°C , the pH value showed a sharp rise when the added quantity of ZnO came up to 14~15 g. The added quantity of ZnO has been to the amount of a little over 100% to something more than 150% of the theoretical value required, being 15~16 g for 250 cc of sample I and 140~150 g/l for sample II. $\text{Ca}(\text{OH})_2$ was added to the amount of 0.7~1.0

* From the separate experiment made thereafter by the authors, it is found that whole or partially replacement of zinc oxide with lime milk, though enlarging the volume of the precipitate, may facilitate markedly the filtration of the solution containing remarkable quantity of iron.

and it must be born in mind that when the solution is cooled, Zn(OH)_2 tends to precipitate around the pH value of 5.6.

d) Elimination of copper and cadmium

Zinc powder in the approximate quantity equivalent to the quantity of copper and cadmium in the solution was added on two occasions during the test, that is, at first, 0.2~0.5 g to sample I and 1.0~1.6 g to sample II, and next, 0.2 g to the former and 0.5~1.0 g to the latter. The time of 1 hr was allowed per each addition, the temperature being kept at 60°C for sample I and at 90°C for sample II. Copper was assumed to be precipitated nearly completely at the first addition and cadmium at the second. The elimination worked almost to perfection, only under 2 mg/l of copper and 0.5 mg/l of cadmium remaining in sample II after treatment. In temperature, 90°C was preferable to 60°C, and adequate agitation was deemed indispensable.

e) Electrolysis for zinc

The two samples, after going through the above described treatments, were subjected to experimental electrolysis. The conditions adopted in Magdeburg process were followed in general features. In the purified solution, the presence of manganese was rather large, due to the use of relatively large amount of MnO_2 as oxidizer, but as is well known, this metal had little harmful effect in electrolysis.

i) Electrolysis of sample I

Conditions were as follows: Zn content, 60 g/l; free H_2SO_4 , 160 g/l; anode, 1% Ag-Pb plate; cathode, 99.99% Al plate; room temperature (10°C); area of electrode, 28.80 cm^2 ; electrode distance, 3.7 cm; current density, 3.75 amp/dm^2 and time of treatment, 3 hrs.

5 tests were made under these conditions. Good result was obtained at average voltage of 3.145 V and current efficiency of 94.2%, the appearance of cathode deposit being excellent, and the grade* of the produced zinc was of 99.97% purity, containing 0.024% of Pb, 0.0046% of Cu and 0.0029% of Cd.

ii) Electrolysis of sample II

The test was of a larger scale than in i) above. Solution was obtained by 15 purification processes of 1 l each. Its chemical composition was as shown in Table 7.

Table 7. Chemical composition of purified solution (from sample II) used for electrolysis of zinc.

Zn (g/l)	Cu (mg/l)	Cd (mg/l)	Mn (mg/l)	Fe (mg/l)	Cl' (mg/l)	As (mg/l)	Bi (mg/l)
108.5	2	<0.5	997.9	4.5	1.2	0.5	<0.13

As shown above, impurities were extremely small, except manganese, which did not detract from the purity of the solution for electrolysis, as cases are

* The grade of the produced zinc was determined by polarograph analysis at Hosokura Mine. The authors appreciate it very much.

known of refineries producing zinc of 99.99% grade from solutions containing more than 5g/l of manganese.

The conditions of the test were as follows: Electrolyte quantity, 10l; Zn content, 60 g/l; free H_2SO_4 , 160 g/l; anode, pure lead plates electrolysed in $MnSO_4$ solution before use, to give a cover of MnO_2 film; area of electrodes, 20 cm \times 10 cm—3 plates (1 of 3 plates used on both sides and 2 on one side each); cathodes, 99.9% Al; area of cathodes, 20 cm \times 10 cm—2 plates (2 plates used on both sides); electrode distance, 4 cm; room temperature (around 30°C); current density, 7.5 amp/dm²; electrolysed for 4 hrs with addition of 0.5 g/l of gelatin in two installments.

As the result, the voltage in the bath changed in a range of 3.56 V—3.39 V, the current efficiency standing at 85.0%, and 170.00 g of zinc was produced, of 99.845% purity, containing 0.123% of Pb, 0.003% of Cu, 0.001% of Fe and 0.025% of Cd. The rather high content of lead was apparently due to the use of pure lead anodes.

Summary

The subject of this report is a link in the selective-sulphatization flotation process proposed by this Institute for treatment of complex sulphide ores, that is, the selective sulphatizing and the electrolysis parts of the process. The sulphatization aims at sulphatizing only the zinc and lead sulphides as far as possible, with minimum sulphatization of copper and iron sulphides, by treating the complex concentrates with comparatively concentrated sulphuric acid at a temperature of around 150°C. The product of sulphatization can be leached out with water, and the zinc sulphate solution electrolysed for production of zinc.

The results of the tests may be summarized as follows:

(a) Basic tests on selective sulphatization

A variety of sulphide minerals, ground down to -150 mesh, were treated with 60% H_2SO_4 in quantity of 1.5 times of the theoretical value, at a temperature range of 110~170°C, for one hour. On examining the degree of sulphatization, it was found that zinc minerals, galena and pyrrhotite were readily sulphatized, while chalcopyrite and pyrite were almost unaffected.

(1) Zinc minerals, both of zinc blende and marmatite types, were readily sulphatized, the lixiviation percentage of both zinc and iron reaching 95%, at a temperature above 130°C. Galena also reacted actively, but a film of insoluble lead sulphate produced during the reaction seemed to cover the remaining particles and retard the progress of the reaction. When galena was ground down very finely and the temperature was kept sufficiently high, it was almost completely sulphatized. Pyrrhotite was also sulphatized quite readily.

(2) Iron pyrite was scarcely sulphatized. The lixiviation percentage of iron remained at less than 2.0% throughout the range of temperature. Chalcopyrite was also hard to be sulphatized, but at higher temperature, the sulphatization of iron tended to rise. At 150°C, the lixiviation percentages of copper and iron

stood at 0.1% and 3.8% respectively.

(b) Tests on Hanaoka flotation concentrates.

(1) First, the effects of temperature change, pulp density and sulphuric acid concentration were tested with 30 g of sample per test. A rise of temperature to 130°C brought about the maximum vigor in reaction, when the lixiviation percentage of zinc came up to 95%, which rose with a further rise in temperature. Lixiviation of iron and copper remained at 3.5% and 1.5% respectively. A change in solid-liquid ratio from 1.5:1 to 1:1 accompanied an increase in lixiviation of zinc, but further change from 1:1 to 1:1.5 was without effect. Tests with various concentrations of sulphuric acid from 40~60 vol% revealed that the zinc lixiviation rose with a rise in acid concentration, but even with 40 vol% acid, a lixiviation percentage of 90% was realized, so that it seemed more advantageous to use diluted acid than to increase the pulp density, in economizing sulphuric acid. But a dilute concentration of H_2SO_4 caused an increase in the required calorie for maintenance of optimum temperature, due to the evaporation of more water. Iron and copper lixiviation was little affected by a change in acid concentration.

(2) Next, more substantial tests were made with 100 g of sample per test. Test conditions were: Concentration of H_2SO_4 , 60 vol%; solid-liquid ratio, 1:1; treatment time, 1 hr. The result obtained were almost analogous with the above tests, the lixiviation percentage of zinc coming up to 97%, while that of iron and copper remained at 3.6% and 2.0% respectively, at 150°C.

(3) Finally, similar tests on a larger scale were made, with 0.6~0.8 kg of sample per test and using opaque quartz or Fe-Si containers in unpressured autoclave-type apparatus. The representative results showed a zinc recovery percentage similar to the preceding tests, but the lixiviation of iron and copper somewhat increased, apparently due to defects in the container.

(c) Electrolysis for zinc of leached solution from selective sulphatization process

Two samples of leached solutions were subjected to tests for production of zinc under the electrolysis process in usual practice. The solutions were richer in iron content than the solutions commonly used in such processes.

(1) For oxidation of Fe^{2+} , 200% of the theoretical quantity of MnO_2 , 90°C in temperature and $2\frac{1}{2}$ hours of treatment under air agitation gave the desired results. For neutralising the solution, zinc oxide was added to bring up the pH value to 4.6 and then slaked lime was superadded to obtain a pH value of 5.6. $Fe(OH)_3$ was filtered off, which operation became difficult when the iron content was too large. Copper and cadmium were nearly completely eliminated by addition of powdered zinc.

(2) The purified solution was electrolysed in general compliance with standard Magdeburg process. The conditions were: Free H_2SO_4 , 160 g/l; Zn, 60 g/l; anode, 1% Ag-Pb; cathode, pure Al; room temperature; current density, 3.75 amp/dm²; electrode distance 3.7 cm and average voltage, 3.15 V. The result showed a

current efficiency of 94.2%, and production of zinc containing 0.024% of lead, 0.0046% of copper and 0.0029% of cadmium at the cathode. Similar tests were repeated on a larger scale.

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