Title	An experimental study on the dressing methods of the mercury ore containing cinnabar and native mercury (I)
Author(s)	Terada, Rinpei
Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 8(3-1), 139-150
Issue Date	1950-12-20
Doc URL	http://hdl.handle.net/2115/37759
Type	bulletin (article)
File Information	8(3-1)_139-150.pdf

An Experimental Study on the Dressing Methods of the Mercury Ore containing Cinnabar and Native Mercury. (I)

Rinpei Terada

(Received Feb. 7, 1950.)

Foreword. The ITOMUKA Mercury Mine, Hokkaido, is the only one mine as the source of mercury in Japan at present. The ore of the mine contains cinnabar and native mercury which is the metallic mercury itself. The mercury content of the ore which is treated at the mill is about 0.4 per cent, of which about sixty per cent is from native mercury. Therefore, the recovery of the native mercury is very important.

There is no mercury mine in the world whose ore contains so much of native mercury. Consequently there is no writings concerning the recovery of the native mercury from the ore. This is the reason why I staited to study this problem.

At the dressing plant of the mine the pulp from the ball mill is treated in a collecting cone specially designed by the stuffs of the mine to get the native mercury. The native mercury passed over the cone is intended to be recovered by the flotation process which is adopted mainly to recover the cinnabar. The total recovery of the native mercury is about 70 per cent, 50 per cent in the cone and 20 per cent in the flotation circuit. The recovery of the cinnabar in the flotation circuit is about 75 per cent. So the total recovery of the mercury is 72 per cent. This result is very dissatisfactory.

Part. I

Coagulation of the Native Mercury in the Ore.

In the collecting cone of the native mercury which receives the pulp from the ball mill at the dressing plant of the mine the native mercury is coagulated and absorbed into the stock of mercury which is put in the cone at the beginning of the work. For a good coagulation the density of the feed pulp must be thin. So the ball mill discharge is diluted to about 18 per cent solid in the cone. The overflow from the cone is fed to the rake classifier in the grinding circuit, consequently the density of the pulp overflowed from the classifier is so thin that the flotaion process cannot be carried on effectively, unless there is some powerful thickening means between the classifier and the flotator, the pulp from the grinding circuit being the feed of the flotation circuit. This indicates that it is very practical if the native mercury is recovered in or after the flotation circuit either coagulated or floated. In these cases the effects of the flotation reagents on the coagulation of the native mercury is a very important question. Therefore, I started the study to examine the effect of the principal flotation reagents on the coagulation of the native mercury.

At the beginning of the work, a very small part of the pulp of the feed to the collecting cone was taken to be tested. But it is found that the content of the native mercury in this material was too small to detect any change in the pulp after treatment. Then, some sample of a high grade ore from the No. 1 level of the mine was taken and ground dry in a small ball mill for labolatory use. The mercury content of this sample is estimated to be 4 to 5 per cent in total. This rich ore is the material for the tests whose results are reported here.

There are two kinds of experiments; one at the laboratory of Itomuka Mine and the other at the laboratory of the Ore Preparation Division of the Fac. of Tech., the Hokkaido University. Principally there is no difference in the methods of testing in both cases except the fineness of the dry ground material for the test. At the mine the sample was ground to pass through 42 mesh screen, and at the University all through 150 mesh. By the sizing test followed by careful panning for each sized fraction it is ascertained that the parts coarser than 200 mesh in both cases contains no native mercury. Therefore, after the treatment described later any mercury found in the sized product larger than 200 mesh is the coagulated part of the original mercury.

50 g. of this ground material is taken for a test. The testing process is as follows;

(1) 200cc. of water is added to this material in a 500cc. Erlenmeyer's flask.

(2) The flask is shaked for 10 minutes by a hand as to draw an ellipse in a horizontal plane at the mine or for 120 minutes on the Ro-Tap shaking machine at the university. The effects of these two kinds of handling on the coagulation is of the same degree as stated later.

(3) The content in the flask is graded by the screens, 42 or 48, 60 or 65, 100, 150 and 200 mesh of the Tyler series.

(4) Each graded material is washed to drive out the rock particles and cinnabar by careful panning on a watch glass.

(5) The weight of mercury remained on the watch glass of each graded product is determined by a chemical balance.

By comparing the weights of mercury in each size larger than 200 mesh the effectiveness of each reagent can be decided; the mercury grains larger than 200 mesh being the product of the coagulation as above mentioned. The reagents tested are; lime, caustic soda, ethyl xanthate, butyl xanthate, amyl xanthate, pine oil, and New Float. The effect of the pulp density and shaking time are also tested.

The results are shown in the following figures. There are two figures on one plate, one is the result of sizing analysis of the coagulated mercury (horizontal axis the size in mesh, the vertical axis the weight in per cent in direct reading) and the other the total recovery of the coagulated mercury in per cent of the total mercury in the ore which is determined by the analytical method described later.

Fig. I. The effect of pulp density. This test is done by hand shaking. It shows that mercury is difficultly coagulated in a pulp denser than 30 per cent solid (Fig. Ib.) At the dressing mill of the mine the critical pulp density is said to be 18 per cent; as already stated this is far thiner than 30 per cent. The grade of the ore treated at the mine mill is very low compared with that of the sample tested, as noted before. It seems that the ore is poorer, the critical density for a good coagulation is thiner. Fig. Ia shows that the coagulated mercury grains unite in a mass very easily in this case.

Fig. 2. The effect of solid lime. Fig. 2b indicates that solid lime is very harmful. 0.05g. of lime to 50g. of the ore (Ikg. of lime per I ton of ore) hinders markedly the coagulation of the mercury. This can be attributed to the anionic charge on the mercury grains in water and cationic charge on the lime particles. The mercury grains can be very easily covered by the lime particle—slime coating—, and the coagulation is hindered.

Fig. 3. The effect of the soluble part of lime. At the beginning of this test a saturated solution of lime is prepared, and at each test a known amount of this solution is added to the water as indicated in following table ; Comparing the figures 2b and 3b, reffering pH value, it is clearly ascertained that nevertheless solid lime hinders strongly the coagulation, the soluble part of the lime has little effect on the coagulation of mercury.

No. of test	Amount of sat. sol. of lime	Amount of water
1	0	200 cc.
2	50 cc.	150 cc.
3	100 cc.	100 cc.
4	150 cc.	50 cc.
5	200 cc.	0

Fig. 4. The effect of caustic soda. It has no serious effect, but the size characteristics of the coagulants is different from the foregoings. The second large grains are predominant indicating that the unification of the coagulants is hindered by this reagent.

Fig. 5. The effect of ethyl - xanthate.

Fig. 6. The effect of butyl - xanthate.

Fig. 7. The effect of amyl - xanthate.

Fig. 8. The effect of "New Float."

These figures show that these flotation reagents have no serious effect on the coagulation when the amount of it is limitted in the range of ordinally amount used in the flotation practice. The order of the effectiveness is seemed to be parallel to the strength of the reagent as a collector.

Fig. 9. The effect of pine oil. It hinders the coagulation with an amouut of 150g. per ton of ore. The amount of pine oil used in the ordinary case of flotation is much smaller than 130g. So the pine oil can be considered to have no serious effect on the coagulation of mercury in the flotation circuit.

Fig. 10. The effect of time of mechanical shaking by "Ro-Tap" Fig. 10b shows that in 90 minutes the amount of coagulated mercury reaches 83 per cent of the original, in next 30 minutes it increases only 1 per cent, and the maximum coagulation is practically 88 per cent.

Fig. 1b shows that by hand shaking 85 per cent coagulation is reached in 10 minutes, when the pulp density is 20 per cent which is the pulp density in the tests throughout. From these facts the shaking time was chosen 10 minutes in hand saking and 120 minutes in mechanical shaking.

Conclusion.

From these results it can be concluded that the native mercury is coagulated in the flotator when the reagents for flotation are used carefully not to exceed the critical amount against the coagulation of mercury. In this case lime is prohibbited.

If the coagulated grains of mercury are collected in any fixed corner in the flotator, mercury can be separated as one concentrate product of the dressing work. The coagulated mercury grains escaped from the flotator can be catched by a shaking table. In this respect the application of the "Gri-Con Mill" which is invented by Prof. Dr. T. Takakuwa and has four dressing activities in one machine; grinding by ball mill action, classifying by spitzkasten, jigging by mechanical jig and flotation; is very interesting.

The results of the studies on flotation and tabling of this ore will be reported in Part III.

Fig. 1. The Effect of Pulp Density.

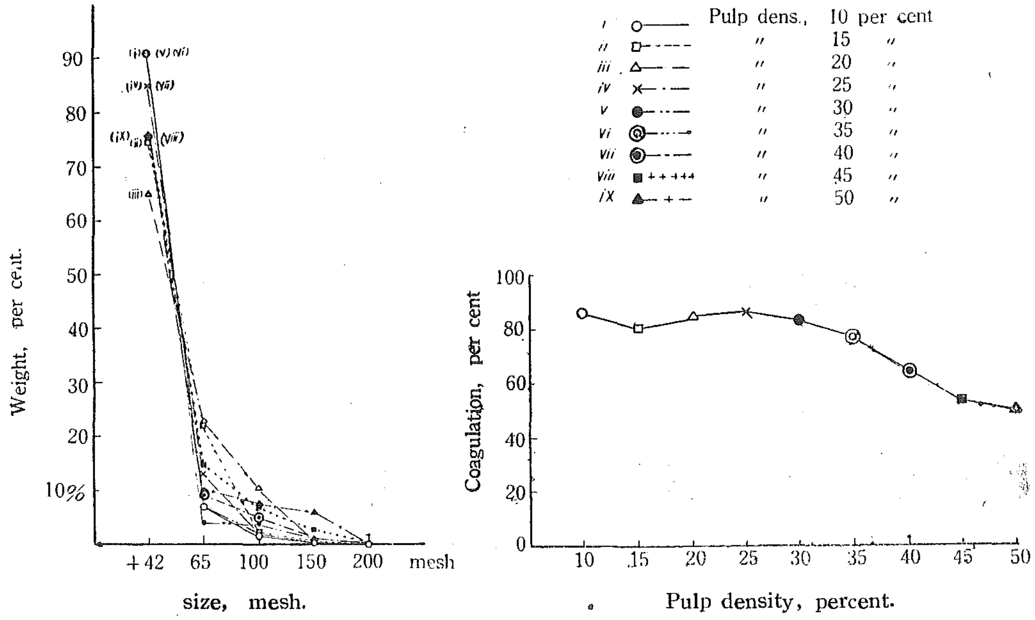


Fig. 1a **Fig. 1b**

Fig. 2. The Effect of Solid Lime.

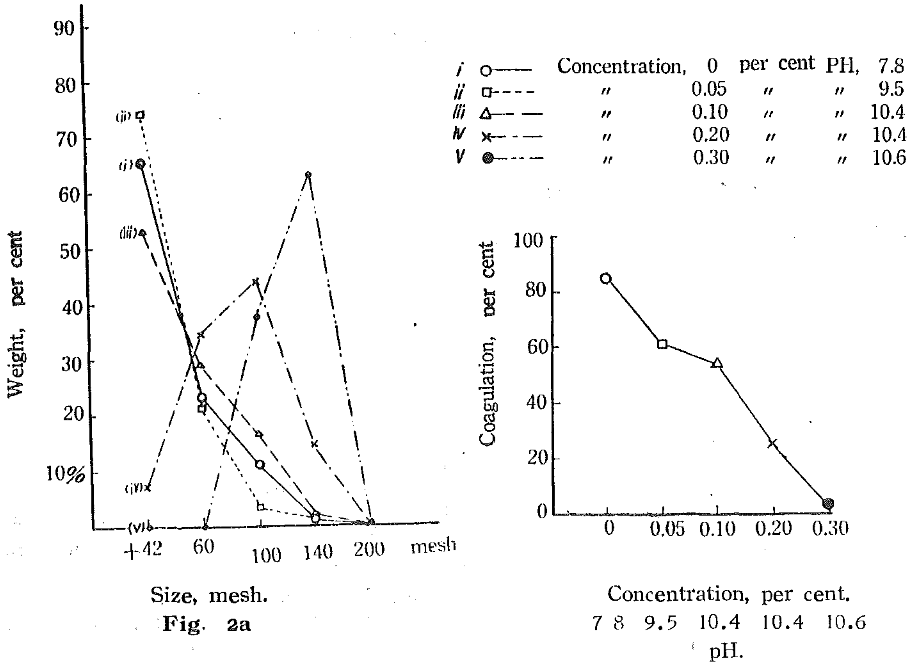
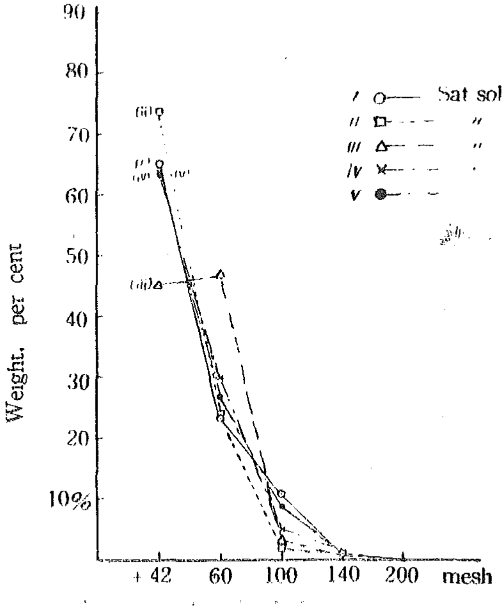


Fig. 2a **Fig. 2b**

Fig. 3. The Effect of Soluble part of Lime.

i	○——	Sat sol. 0 cc	Water 200 cc	PH.	7.8
ii	□- - -	〃 50 〃	〃 150 〃	〃	8.0
iii	△— —	〃 100 〃	〃 100	〃	8.0
iv	×-·-·	〃 150 〃	〃 50 〃	〃	9.8
v	●-·-	〃 200 〃	〃 0	〃	10.4



Size, mesh.
Fig. 3a

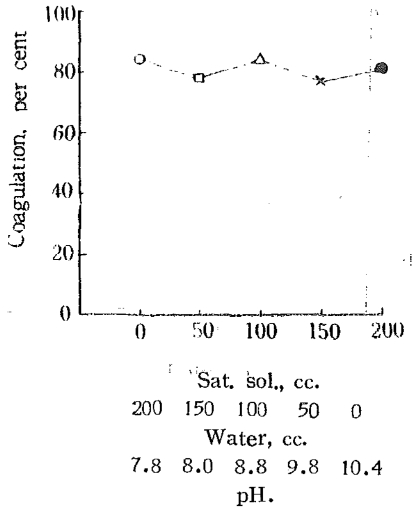
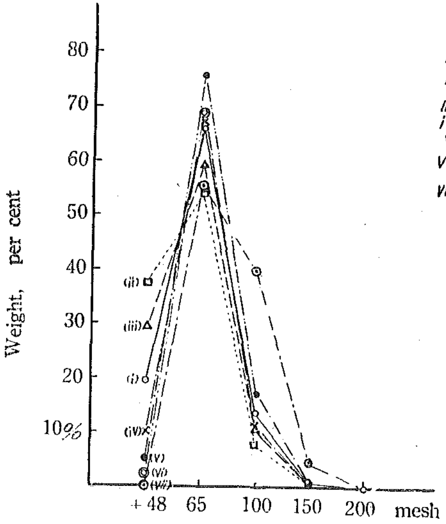


Fig. 3b

Fig. 4. The Effect of Caustic Soda.

i	○——	Weight of Caustic Soda,	0 gr	per ton of Ore.	PH,	8.2
ii	□- - - -	〃	200 〃	〃	〃	8.7
iii	△— —	〃	1000 〃	〃	〃	10.1
iv	×-·-	〃	2000 〃	〃	〃	10.3
v	●-·-	〃	3000 〃	〃	〃	10.4
vi	◎-···-	〃	4000 〃	〃	〃	10.4
vii	◉-·-	〃	5000 〃	〃	〃	10.5



Size, mesh.
Fig. 4a

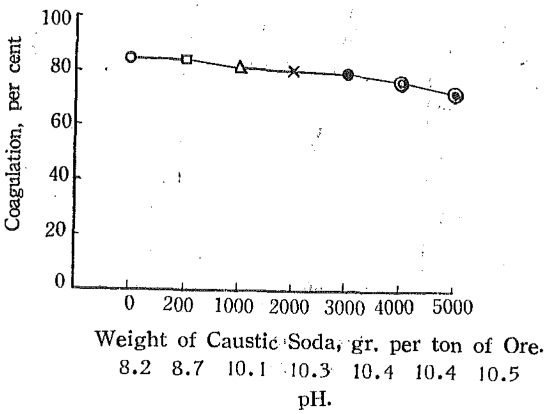


Fig. 4b

Fig. 5. The Effect of Ethyl-Xanthte.

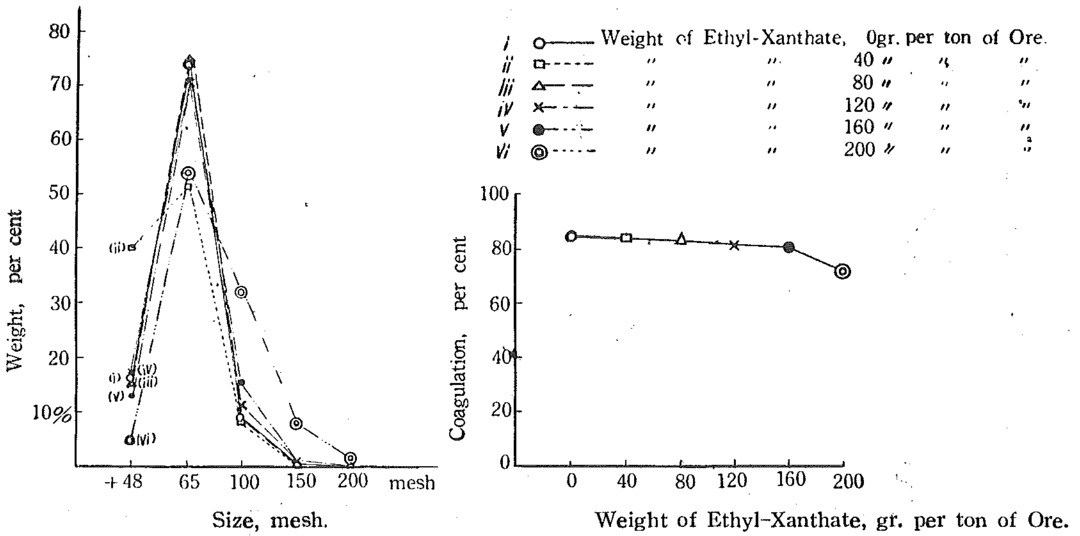


Fig. 5a

Fig. 5b

Fig. 6. The Effect of Butyl-Xanthate.

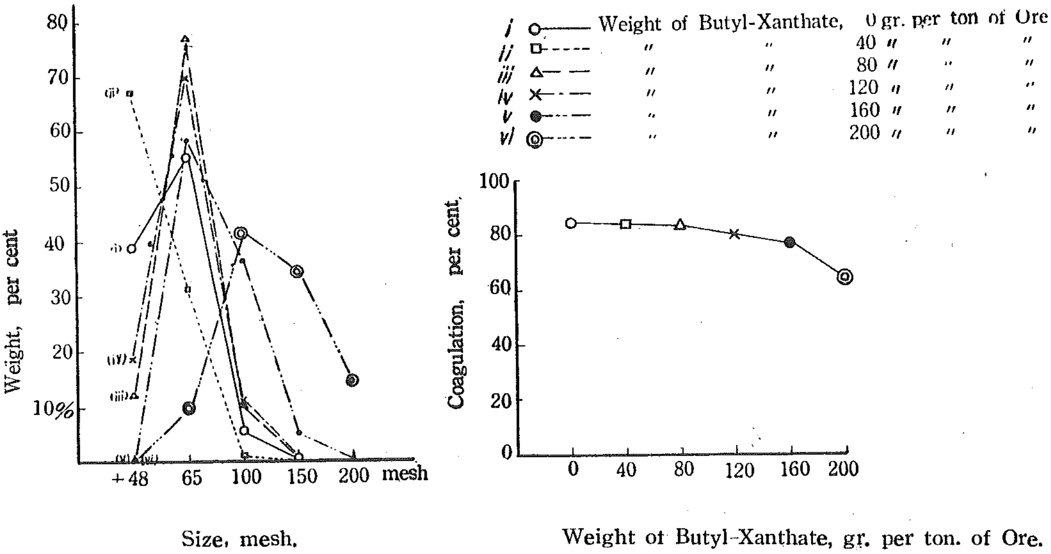


Fig. 6a.

Fig. 6b

Fig. 7. The Effect of Amyl-Xanthate.

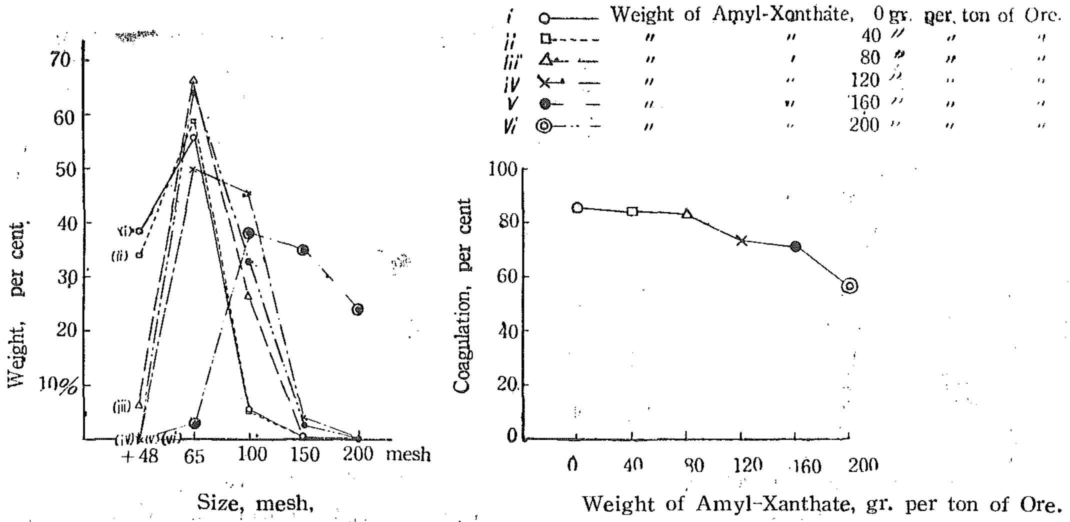


Fig. 7a

Fig. 7b

Fig. 8. The Effect of "New-Float"

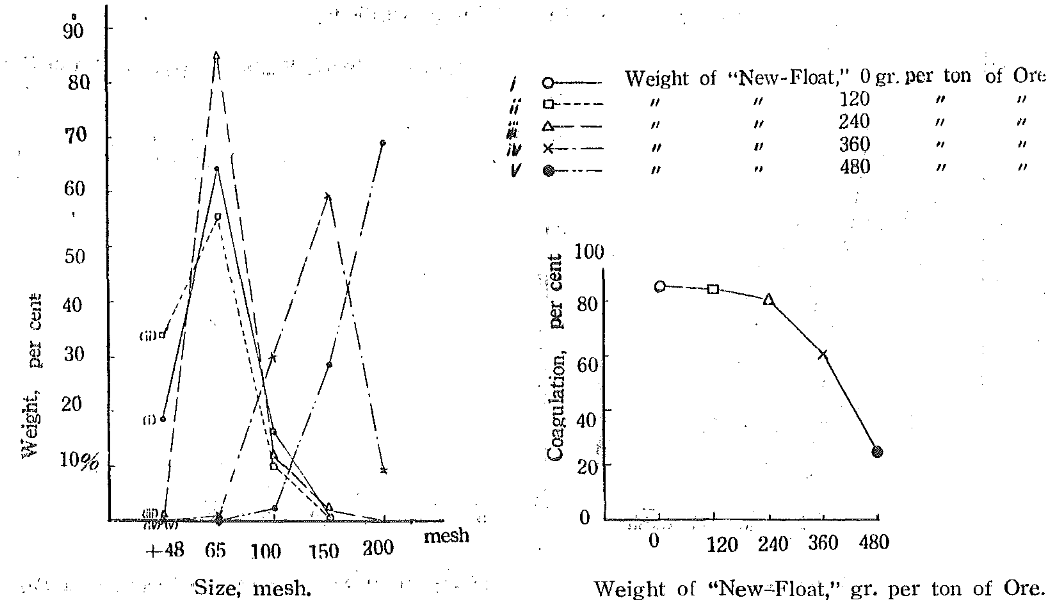


Fig. 8a

Fig. 8b

Fig. 9. The Effect of Pine-Oil.

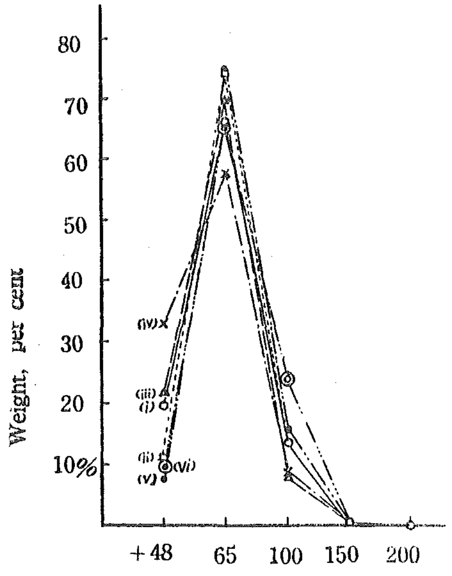


Fig. 9a.

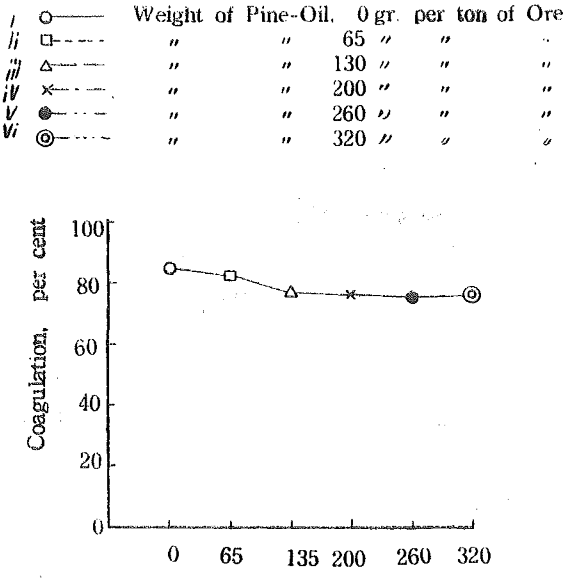


Fig. 9b

Fig. 10. The Effect of Shaking Time.

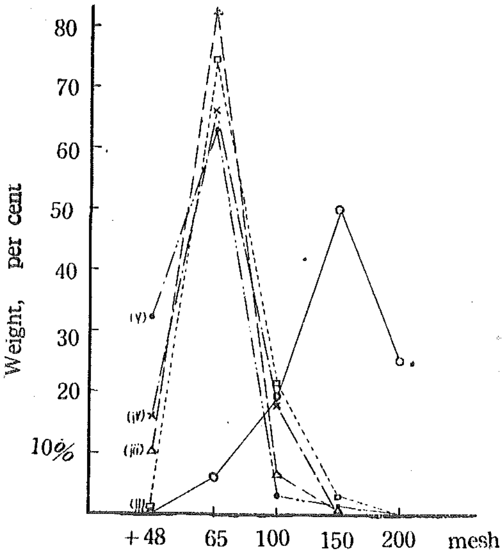


Fig. 10a

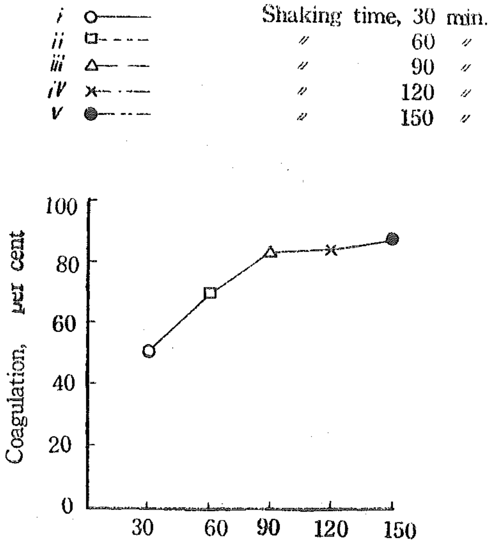


Fig. 10b

Part. II

Determination of the Merecury Content of the Ore.

The ore of the Itomuka Mercury Mine contains cinnabar and native mercury. To study any problem in the dressing work of this ore, the amount of mercury derived from cinnabar and from native mercury must be separately determined. For this obiect the ore is treated as follows.

(1) Dissolve perfectly the cinnabar with an excess of sodium sulphide without affecting the native mercury.

Cinnabar is soluble in the solution of sodium sulphide in excess; $HgS+Na_2S=Na_2HgS_2$. But native mercury is practically insoluble in this solution. It is recommended to add potassium hvdroxide to the solution of sodium sulphide to prevent hydrolysis.

The conditions adopted are as follows;

The solution of sodium sulfide;
concentration, 30 per cent (see "a"),
amount to be added, 30cc.
The temperature; 60°C. (see "a").
The duration of heating; 30 minutes (see "a").

The amount of sample; concentrates, 5 g.,
tailing, 10 g.,

(2) The dissolved mercury in this filtrate is changed to mercuric sulphide after seperating from the residue by adding ammonium nitrate or ammonium chloride.

$$Na_2HgS_2+2NH_4NO_3=HgS+2NaNO_3+(NH_4)_2S$$

(3) After washing the residue, the native mercury which remains in it is dissolved with nitric acid or aqua regia.

(4) After filtration, change the dissolved native mercury to mercuric sulphide by passing through hydrogen sulphide.

It is ascertained that in this case the falling of mercury is perfect (see "b").

(5) In both cases the mercuric sulphide obtained is changed to mercuric sulphate by adding sulphuric acid, and this mercuric sulphate is changed to mercuric nitrate by potassium nitrate under heating.

Sulphuric acid; 20cc..
The temperature; 300 to 350°C. (see "c").
The duration of heating; 20 to 25 minutes (see "c").
Potassium nitrate; 12 g..

(6) Titrate this solution of mercuric nitrate with the 1/100 normal solution

of potassium thiocyanate using ferric alum as the indicator.

Many tests were done to find the proper conditions for these treatments. Some of them are reported here.

(a) Dissolution of cinnabar.

To see the necessary and sufficient concentration of sodium sulphide to disslve cinnabar, a test was done with an ore from the Yamato Mercury Mine which contains cinnabar, quartz and no native mercury nor pyrite. Its content of mercury is 20.2 per cent. 1 g. of the sample which is ground to pass through 100 mesh is taken in a 300 cc. conical beaker and added 30 cc. of sodium sulpide solution with different concentration, 10, 20, 30. 40, and 50 per cent and some of 5 per cent solution of potassium hydroxide. It is heated for 30 minutes in a drying thermostat at 60°C.; metallic mercury being not evapolated under 60°C.. The amount of mercury which may be remained in the residue after filtration is determined by the normal method using sulphuric acid to dissolve cinnabar at 300°C.. There is no fear of escape of native mercury because the sample has no native mercury. Therefore the result is reliable. It was found that the solution weaker than 30 per cent could not dissolve the cinnabar perfectly. From this test the concentration of the sodium sulphide solution to dissolve cinnabar is fixed to 30 per cent. It was also found that 30 minutes of heating in the thermostat is sufficient.

(b) Precipitation of mercuric sulfide by hydrogen sulphide. 0.0426 g. of pure mercury is solved by 5 cc. of nitric acid, water is added to be 250cc., 100cc. of this solution, in which 17.04mg. of mercury is contained, is saturated with hydrogen sulphide, it is filtered through a filter glass. The filter glass with the residue in it weighed after being dried at 105°C. for I hour, the weight of the residue; this is mercuric sulphide; is calculated by subtracting the weight of the filter glass. The mercury in this mercuric sulphide is calculated from the symbol HgS. The results were. 16.89mg. and 16.73.mg. of mercury. From this test it is convinced that the dropping of mercury in the solution by hydrogen sulphide is practically perfect.

(c) The temperature of nitralization of mercuric sulphide. Mercuric sulphide obtained as above described is treated with sulphuric acid on a heating device and in presence of potassium nitrate which must be added step by step until the solution becomes transparent indicating that the filter paper which is used in the glass filter to cover its bottom plate and found in the solution is perfectly decomposed. In this case a slite fume of sulphuric acid is allowed. After cooling potassium permanganate solution is added. Here the mercury is perfectly changed to mercuric nitrate. To drive out the colour of potassium permangandte oxalic acid is added. This is the solution to be titrated.

In this treatment the temperature of heating is the most important, if it is too low the decomposition of the filter paper is difficult, on the other hand if it is too high the loss of mercury is serious. For example, the content of mercury of an ore is dertermined 0.80 per cent when heated on an electric heater covered with a wire-net-with-asbestos, 0.73 per cent on a gas flame covered with a wire-net-with-asbestos, 0.15 on a small flame of a gas burner. After many tests like these it is fixed that the best temperature is from 300°C. to 350°C. and the duration of heating is from 20 to 25 minutes. To verify this process it is tried on the determination of mercury in the pure mercuric sulphide and following results were obtained ;

No. of test	Weight of HgS, mg.	Weight of Hg calculated, mg.	Weight of Hg observed, mg.
1	23.5	20.26	20.25
2	33.0	28.45	28.35
3	46.0	39.66	40.05

Conditions ; Temperature, 300°C., Duration of heating, 25 minutes.

(d) Effect of pyrite in the ore on the degree of accuracy.

If the ore contains any pyrite, it is dissolved with native mercury and may diminish the accuracy of the determination. To see this effect, a known quantity of metallic mercury ; 22.2mg., 15.4mg., 1.56mg., and 0.78mg., and 2g. of pyrite ground through 100 mesh were taken in a 500cc. conical beaker, solved with 20cc. of aqua regia over night. Then the content of mercury in this solution is determined as follows ; the solution is filetred with a filter paper, water is added to this filtrate to be 80cc., about 5g. of potassium carbonate is added to weaken the acidity of the solution, hydrogen sulphide gas is passed through to be saturated, the precipitate is separated by filtering with a filter paper and washed with carbon bisulphide to solve and wash out the sulphur which is the product of the decomposition of hydrogen sulphide, after this the remaining carbon bisulphide is washed out with some alcohol. The content of mercury is the pure mercuric sulphide thus obtained is determined by the normal way described in this paper. The results are shown in following table ;

No. of test.	Original Hg,	Observed Hg.
1	22.2 mg.	20.52 mg.
2	15.4 mg.	14.74 mg.
3	1.564 mg.	1.590mg.
4	0.7832mg.	0.699mg.

From these results it is certain that procedure adopted here is reliable for the object to determine the mercury content of any product in the dressing work.

(10. Jan., 1950.)