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MINES BRANCH
DEPARTMENT OF MINES, OTTAWA, CANADA.

Memorandum Series: March 1924 No. 11.

SELECTIVE FLOTATION

AS APPLIED TO CANADIAN ORES

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INTRODUCTORY

It is the intention in this article to review in a general way the results of investigations conducted in the Ore Dressing and Metallurgical Laboratories of the Department of Mines at Ottawa, that have particular reference to selective flotation as applied to Canadian ores.

The Department has, at Ottawa, one of the most fully equipped flotation laboratories in existence. Flotation work has been carried on since 1912 and over 8000 flotation tests have been made on more than 250 different ores. Connections are maintained with large flotation laboratories in the United States and with the leading private investigators. The laboratories at Ottawa are fitted with both small scale and tonnage scale equipment and it is the practice, where possible, to check all small scale tests by tonnage tests on the larger machines. The members of the staff have had practical experience in the design, construction, and operation of flotation plants.

SELECTIVE FLOTATION PROBLEMS

For the purpose of this article selective flotation is taken to mean the separation by flotation of one mineral from another, where two or more flotative minerals are present in an ore. The separations generally required are on complex ores, consisting of combinations of lead, zinc and iron sulphides; copper, zinc and iron sulphides; molybdenum and iron sulphides; antimony and arsenical iron sulphides; graphite and iron sulphides, and other like combinations.

The logical way to separate these minerals by flotation is to float first the mineral which has the highest floating properties. A list of the more common minerals met with in selective flotation,

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in order of the ease with which they are floated, from the writer's own experience is, graphite, molybdenite, stibnite, galena, chalcopyrite, sphalerite, pentlandite, pyrite, arsenides and antimonides, etc., pyrrhotite, arsenical pyrite. For instance, as a general rule, in the selective flotation of a lead-zinc sulphide ore, the lead should be floated first, as it is the more easily floated mineral of the two; in a copper-zinc ore, the copper should be floated first, and so on.

OILS USED FOR SELECTIVE FLOTATION*

During the early stages in the development of the flotation process the search for new flotation oils was very keen, and much more weight was then given to the function of the oil than is given at present, as it was supposed that every ore required special oils. Dozens of different oils and oil mixtures were tested on each ore. Some mills were operated in which oil mixtures containing four or five different oils were used, whereas in all probability only one or two were essential. At the present time, with few exceptions, commercial plants operate on combinations made up from a few varieties of oils. The Department has over 300 samples of oils, but of this number 90 per cent are never used in the regular test work. It has been found that satisfactory results can be obtained on the majority of ores from a group containing a few varieties. A list of the oils in this group is given, together with the selective properties of each as found by actual experience.

Reagents used for the flotation of lead sulphides in the presence of zinc and iron sulphides:

- Mixture of coal tar and coal tar creosote
- Cresylic acid
- Z cake or thio carbanilide
- Steam distilled pine oil
- Light hardwood creosote oil

Reagents used for the flotation of zinc sulphides from iron sulphides after lead or copper sulphides have been removed:

- KK oil No.2 - Southwestern Engineering Co.
- #634 creosote oil - Barrett Co.
- Sodium creosote from hardwood.
- YZ mixture, or xylidine and thiocarbanilide
- #34 gravity fuel oil - G. J. Oil Co.
- TT mixture
- Water gas tar - Barretts

* Oil in flotation - terminology is a generic term used to designate the organic substance that is used to produce a froth or effect selection of metalliferous minerals (Taggart)

Reagents used for the flotation of copper sulphides from zinc and iron sulphides

Mixture of coal tar and coal tar creosote
XY mixture or xylydine and alpha-naphthylamine
Neutral fractions of hardwood oils

Reagents used for the flotation of copper sulphides from iron sulphides:

Barretts #634
XY mixture)
TT mixture)
Thio fizzaan } Reagents of the General Engineering Company
ZY mixture }
Sodium resinate - use very limited
Fuel oils (paraffin base)

Reagents used for the flotation of copper nickel sulphides from iron sulphides:

Thio fizzaan
TT mixture
XY mixture
Fuel oil (paraffin base)
Coal tar and coal tar creosote mixtures

Reagents used for the flotation of molybdenite and graphite from iron sulphides:

Kerosene oil

Frothing reagents used with the above.

Steam distilled pine oil
Fumol - manufactured by Canadian Electro Products Co.
Ketone oil - manufactured by the Standard Chemical Co.

ADDITION REAGENTS

The use of addition reagents is as important, if not more so, than the use of oils for selective flotation. If the conditions in the pulp are correct there is generally found to be considerable latitude with regard to the kind of oil used. In the writer's experience, the chief functions of the more common addition reagents used in practice for selective flotation are:

Lime: The use of lime for the selective flotation of certain minerals was first brought to our attention in 1917, when the Department was operating a customs plant for the concentration of molybdenite ores from all points in the Dominion. A few carloads of very badly oxidized ore were received and trouble was encountered in floating the molybdenite. On investigation it was found that large quantities of soluble salts were contaminating the pulp. Lime was added to the ball mill with the object of preventing these salts from going into solution and it was surprising to find that the lime, besides eliminating the trouble with soluble salts, also had the effect of preventing the iron sulphides from floating, resulting in a much higher grade concentrate being obtained. In this connection

a very interesting phenomenon was observed. When the pulp was contaminated with soluble sulphates as much as 100 pounds per ton of kerosene oil could be added without causing any raw oil effect on the cells, a voluminous but absolutely barren froth being obtained. On ordinary clean ores the addition of one pound of kerosene oil would produce a raw oil effect on the cells and kill the froth. The only explanation that could be advanced was that the presence of soluble sulphates in the pulp caused the oil to form a stable emulsion. It was found that if the soluble salts were subsequently washed from the pulp, the emulsion was broken down and the oil appeared on the surface of the cells.

When lime is used it should always be added ahead of the ball mill as long contact with the pulp is essential owing to the time required for the lime to go into solution. Lime is used in the selective flotation of copper sulphide ores to prevent the iron sulphides, also the zinc sulphide, if present, from floating. In the selective flotation of lead-zinc sulphide ores it prevents the zinc sulphide as well as the iron sulphides from floating. In the flotation of antimony ores it has been found to absolutely prevent stibnite from floating. It is used in the flotation of molybdenite and graphite, where iron sulphides are present, for the same purpose. The quantity added varies from one to twenty pounds per ton of ore.

Soda Ash: The addition of soda ash to the flotation pulp will enhance the flotation of zinc sulphides, copper, and nickel sulphides and stibnite, and has a tendency to prevent iron sulphides from floating. The quantity used varies from one to ten pounds per ton of ore.

Sodium Sulphite: This reagent is used in the selective flotation of lead-zinc sulphide ores. It prevents zinc sulphide from floating but has a slight tendency to float iron sulphides, so that if these are present in any quantities, lime must be used also.

Copper Sulphate: The addition of one to two pounds of copper sulphate per ton of ore, when an alkaline pulp is used, will generally assist the flotation of zinc sulphide.

CONTROL OF FLOTATION PULP

The control of the pulp in a flotation plant is very important and should be given as careful attention as in a cyanide plant. Commencing at the discharge of the primary, wet-grinding mills, control samples should be taken at various intervals of time, of each succeeding step in the operations. The correct condition of the pulp for flotation must be obtained before it enters the flotation cells. Characteristics displayed by the pulp in the ball mill discharge and in the classifier circuits will in most cases indicate to the operator how the cells are working and whether the pulp is in the right condition for flotation.

Density control: Careful control must be maintained of the density of flotation pulps. The densities should be kept as uniform as possible and only vary between very narrow limits. The reason for this is obvious as any variation in the dilution of the pulp will change the concentration of the modifying reagents used to enhance the selective flotation. It is often found necessary to sacrifice efficiency in the grinding circuits to obtain efficiency in the flotation circuit. For instance, in order to obtain a low tailing in the selective flotation of a copper-iron sulphide ore, it has been necessary to maintain a pulp density in the flotation cells of 1 : 2.5. Dewatering of the flotation feed could not be practiced because a definite protective alkalinity with lime must be maintained in the cells to prevent the iron sulphides from floating.

Temperature control: The control of temperature in the grinding mills is very important in the case of easily oxidized ores, such as the copper-nickel ores of the Sudbury district and copper ores where the chalcopyrite is associated with large quantities of iron sulphides. Trouble in this connection is seldom met with in conducting the small scale tests. The temperature can be controlled by pulp dilution, but to do so generally means sacrificing the grinding efficiency.

The control of temperatures in the flotation circuits for selective flotation is practiced in certain plants where large tonnages are being concentrated, to raise the grade of the concentrate being produced. It introduces an extra item of cost and should only be done where absolutely essential, and where a profit can be shown as against flotation at ordinary temperatures.

Control of Soluble Salts: In conducting selective flotation tests the greatest care should be taken to obtain samples which will truly represent the ore to be concentrated. The samples should be of freshly mined ore. In an ore consisting of a large percentage of sulphides, soluble salts form very rapidly. The writer has found that the lead and nickel sulphides in samples of lead and copper-nickel ores crushed to 10 mesh will oxidize so rapidly that in as short a time as ten days the flotation properties of the minerals will be seriously affected. All ores contain soluble salts which are generally sulphates of iron, aluminium, calcium, and magnesium. These salts play a very important part in selective flotation and no definite rules can be given as to how they will act. Large amounts of them will interfere with and even prevent flotation. Small amounts sometimes interfere and sometimes improve the selective flotation of one mineral from another. In conducting selective flotation tests, the amount and nature of the salts should be determined for every ore. The subject of overcoming or taking advantage of their effect is too large a one to consider in detail in this article. Further reference is made to them in dealing with the type of testing apparatus.

Control of Modifying Reagents: Samples of the water from the flotation cell tailing should be taken at regular intervals and analyzed for protective amounts of modifying reagents.

EXAMPLES OF SELECTIVE FLOTATION PROBLEMS

A Copper-Zinc-Iron sulphide ore: This particular ore was a complex association of copper, zinc, and iron sulphides on which grinding to 200 mesh was necessary to free the minerals. It contained chalcopyrite 7 per cent; zinc blende 7 per cent; iron sulphides 73 per cent; and gangue minerals 13 per cent.

It was found that a high grade copper concentrate could be obtained by using lime to prevent the pyrite and zinc blende from floating. The pulp after flotation of the chalcopyrite was dewatered to eliminate the lime. Fresh water and soda ash were added for the flotation of the zinc blende. The governing condition for the separation was in the control of the lime added for the selective flotation of the chalcopyrite. It was found that lime in excess of the requirements to produce a high grade copper concentrate was necessary to prevent the pyrite from floating with the zinc blende. The addition of lime to the zinc heads did not produce the same effect, nor did running the pulp direct from the copper cell without dewatering. In both cases so much lime was present that the zinc blende could not be floated. The lime had to be added to the grinding circuit before flotation of the chalcopyrite. The reason for this was investigated and it was found that, apparently, a skin formed around the grains of pyrite resulting in a greater concentration of lime around the pyrite than in the remainder of the pulp. The concentration of the lime in the skin-film around the pyrite grains would vary according to the amount of lime in the pulp so that it was necessary to add an amount of lime in the first place sufficient to obtain a concentration in the film which would maintain the wetting effect on the pyrite after dewatering for the selective flotation of the zinc blende.

A Copper-Iron sulphide ore: This was a heavy sulphide ore of copper containing 3 per cent copper as chalcopyrite, 59 per cent ^{iron} as pyrite, and 8 per cent insoluble. Grinding to 100 mesh was necessary to free the minerals. An alkaline pulp was maintained by the addition of 10 pounds of lime to the ball mill. The most important point was found to be the control of the pulp density in the flotation cells. A low tailing could only be obtained when a density of 1 : 2.5 to 1 : 3 was maintained in the cells. Under these conditions a concentrate containing 22 per cent copper with a recovery of 95 per cent of the copper values was obtained from this ore without the least difficulty.

Lead-Zinc-Iron sulphide ores: The following method has been proved to have the most general application. Lime and sodium sulphite are added and ground in contact with the ore in the ball mills. The lime is added to keep the iron down, and the sodium sulphite to keep the zinc from floating. After the flotation of the lead, the tailing pulp from the lead cells is dewatered, eliminating the bulk of the lime and sodium sulphite. The pulp is then made up to the required density with fresh water, and soda ash and copper sulphate added for the flotation of the zinc. This method was used to obtain the

separations given in examples Nos. 1 and 2 in the accompanying tables. The method used by the Consolidated Mining & Smelting Co., at Trail, to concentrate the ore from the Sullivan mine has also been used with success. An ore containing 1.96 per cent lead, 5.52 per cent zinc, and 7.42 per cent iron, all as sulphides was treated by this method. Example No. 3 in the accompanying tables gives the results of a tonnage test on the ore. In this particular case the ore was ground to 65 mesh to free the minerals. The oils used in the Sullivan ore were found to be unsatisfactory, but no change in the addition reagents was found to be necessary. Soda ash at the rate of 5 pounds per ton was fed to the ball mill together with a mixture of coal tar and coal tar creosote. A little cresylic acid was added to the lead cells together with 0.1 lb. per ton of sodium cyanide. The tailing from the lead cell went to a mixer where the Barretts #634 oil, TT mixture, and 1 lb. copper sulphate per ton were added for the flotation of the zinc in the zinc cells.

A Zinc-Iron sulphide ore: The selective flotation of the zinc can generally be obtained by the use of an alkaline soda ash pulp, but in some cases the soda ash will not hold down the iron and it is necessary to use lime. When lime is used it should be added in the ball mills and the pulp dewatered before the soda ash is added. Copper sulphate will often increase the recovery of zinc.

The oils used in the above methods of separation have been purposely omitted. The reason for this is that while the chemical reagents have been found to give more or less consistent results on a variety of ores, the oils have not.

EXAMPLES OF SELECTIVE FLOTATION

The following tables contain examples of separations obtained in the laboratory of the Department of Mines by selective flotation:

Separation of copper-zinc-iron sulphide ore:

Approximate analysis: Chalcopyrite 7%, zinc blende 7%,
Iron sulphides 73%, gangue minerals 13%.

Product	Analysis				Distribution of values		
	Cu %	Zn %	Fe %	Au oz	Cu	Zn	Au
Copper conc.	16.7	4.4	24.3	0.10	87.9	10.6	18.2
" midd.	1.8	8.7	28.3	0.10	1.89	4.17	3.6
Zinc conc.	0.45	40.7	17.9	0.11	1.27	52.52	10.8
" Midd.	0.5	8.9	33.7	0.07	1.34	10.90	6.6
Tailing	0.3	1.9	35.4	0.07	7.57	21.84	60.8

Separation of copper-iron sulphide ore:

Analysis: Copper 2.98% Fe 39.0% Insoluble 8.0%

Product	Analysis Cu %	Recovery of copper.
Copper concentrate	20.20	93.3 %
Tailing	0.12	-

Separation of lead-zinc-iron sulphide ores. Example No. 1.

Analysis: Lead 17.6% Zinc 28.88% Silver 13.45 oz/ton

Product	Analysis			Distribution of values		
	Pb %	Zn %	Ag oz.	Pb	Zn	Ag
Lead conc.	60.0	8.5	42.0	76.2	6.5	69.6
Zinc "	7.0	45.9	6.6	21.6	86.5	26.7
Tailing	1.6	8.5	2.1	2.1	6.8	3.6

Example No. 2

Analysis: 11.40% Lead 11.40% Zinc 32.25% Iron

Product	Analysis		Distribution of values	
	Pb %	Zn %	Pb	Zn
Lead concent.	52.60	6.10	63.0	7.5
Lead middling	21.9	10.0	9.4	4.3
Zinc concent.	8.3	37.4	17.1	77.3
Zinc middling	9.8	11.1	2.1	2.4
Tailing	1.67	1.7	8.4	8.5

Example No. 3

Analysis: Lead 1.95% Zinc 5.52% Iron 7.42%
Gold 0.32 ozs/Ton Silver 3.23 ozs/ton

Product	Analysis					Distribution of values		
	Pb %	Zn %	Cu %	Insol. %	Au. oz	Ag oz	Pb	Zn
Lead conc.	51.09	4.17	2.60	16.13	0.30	66.20	89.4	-
Zinc "	1.09	46.19						94.8
Tailing	0.15	0.32						

Separation of copper-nickel pyrrhotite ore.
 Analysis: Copper 1.56% Nickel 1.24%

Product	Analysis			Distribution of values	
	Cu %	Ni %	Cu + Ni %	Cu	Ni
Concentrate	12.5	9.6	22.10	97.2	85.6
Tailing	0.05	0.20	-	2.8	14.4

SMALL SCALE TESTING APPARATUS FOR SELECTIVE FLOTATION

The majority of testing laboratories are equipped with the small batch type of laboratory apparatus. The writer has found that the results obtained in this type of machine are, in many cases, unreliable and cannot be duplicated in practice. This particularly applies to selective flotation tests and to tests on ores which contain appreciable amounts of soluble salts. The batch machine is very satisfactory for preliminary work, but a continuous feed type of small testing unit with its own grinding circuit should be used to check the results. In this latter type of testing apparatus the reagents can be added continuously with the feed, as in practice, and not all at once which is generally the case in conducting batch tests. The batch method will usually give a better separation than can be obtained in practice. If a small scale flotation machine with a continuous grinding circuit is not available, the following procedure should be tried out to check the batch methods of adding reagents. During the grinding of the sample the ball mill should be stopped, opened up, and portions of the total amount of reagents to be used added from time to time instead of all at once, and in this way conditions more nearly approaching mill practice are obtained. In conducting flotation tests the ore should be prepared by wet grinding. Dry ground ore should never be fed to the flotation machine unless dry crushing is to be adopted in the milling practice.

CONCLUSIONS

The application of selective flotation for the separation of the minerals in complex ores has increased rapidly in recent years. The field of its usefulness is gradually being enlarged. It plays a very important part in the economic treatment of the complex ores, and brings within its scope the possibilities of the commercial use of many low grade ores of a complex character which it has hitherto been unprofitable to treat. It is a comparatively new field in ore dressing and one which will play an important part in the development of our mineral resources. The purpose of this paper is to introduce the subject of selective flotation in the hope that other investigators will publish the results of their work and the methods used in selective flotation both in the laboratory and in practice. Very little information has been published on the subject. It would be to the mutual advantage and benefit of all concerned if it were more openly and freely discussed.