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*EFFECT OF XANTHATE
IN CYANIDATION*

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EXTRACTION METALLURGY DIVISION

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Effect of xanthate in cyanidation

By H. H. McCREEDY and W. R. HONEYWELL*

FLOTATION IS OFTEN USED IN A GOLD MILL as a means of preconcentrating the gold bearing minerals prior to extracting the gold by cyanidation. Most of the mills that use this method, use xanthate as one of the flotation reagents. Some of the xanthate is carried over into the cyanidation circuit as mineral coating and as flotation concentrate moisture. It is known that xanthate causes trouble in the subsequent cyanidation step but most information is very vague about the extent or nature of the problem. In view of this, a program was initiated two years ago to determine whether the exclusive use of xanthate in a flotation operation could have a significant effect on the efficiency of the subsequent cyanidation step.

The results of the work covered in the first progress report [1] given at the 1965 meeting of the Canadian Gold Metallurgists showed that the rate of extraction of gold in an alkaline-cyanide solution was appreciably reduced when a xanthate compound was added. Using a piece of pure gold leaf in a solution containing 1 pound of sodium cyanide per ton of solution at pH 12, the rate of dissolution of the gold was reduced by a factor of four when 0.01 pounds of secondary butyl xanthate per ton of solution was added while 0.2 pounds of xanthate per ton of solution appeared to stop the gold dissolution entirely. With an ore from which 93 per cent extraction of the gold took place in 72 hours by a solution containing 1 pound of sodium cyanide per ton of solution at pH 12, the addition of 0.4 pounds of xanthate per ton of solids retarded the gold dissolution rate so that it required an extra 24 hours to obtain the same extraction and as a result it produced a higher reagent consumption. The work also showed that the adverse effect of the xanthate on the gold dissolution rate could be counteracted by increasing the cyanide concentration of the leaching solution. With 0.4 pounds of xanthate per ton of solids added to a gold ore, the cyanide concentration had to be increased by a factor of three to maintain the same extraction rate as when the xanthate was not present. In turn, the increased cyanide concentration produced a higher cyanide consumption. Various procedures such as pre-aeration of the pulp prior to the cyanide addition or the addition of lead salts or hydrogen peroxide to the leach failed to reduce the adverse effects of the xanthate.

In view of these results, it appeared that the best solution to the problem of xanthate in cyanidation was to control the xanthate so that no more was added than the amount required for efficient flotation. A program was planned to determine if xanthate analysis of the flotation

water could be used as an indication of the xanthate required for efficient flotation of a gold ore.

A review of some of the literature on flotation showed that the two most important factors that governed the density of adsorption of xanthate onto the solid were the xanthate concentration in solution and the conditioning time [2]. It is also known that the bigger the alkyl group of the collector, the greater the tendency for it to be adsorbed by the mineral [3]. Because of this difference in the tenacity of the collector film on the mineral, there was a possibility that one type of xanthate or a different collector might be less detrimental to gold dissolution than another type. This problem was also investigated during the past year.

Procedure

The first problem was to find a relatively simple procedure for determining residual xanthate in solution and which would be suitable in an operating plant. The method finally adopted involved the determination of the total reducing capacity of the solution and a similar determination on another sample of the same solution with the xanthate removed. The difference in these two determinations was due to the xanthate. (*See appendix for details*).

Once the method was thoroughly tested, a series of tests was done to determine if the residual xanthate concentration in solution was related to the amount of xanthate originally added to a flotation operation.

The major metallic mineral in the particular ore used was pyrite but there were minor amounts of pyrrhotite, chalcopyrite and free grains of gold. The ore contained 0.9 per cent sulphur, 3 per cent iron, 0.01 per cent copper and 0.19 ounces of gold per ton.

In order to produce more uniform flotation concentrates as feed for the cyanidation tests, the ore after grinding was passed over a blanket to remove the free gold. The blanket tailing which was used as the flotation feed assayed 0.065 ounces of gold per ton of solids.

The flotation tests were carried out in a conventional laboratory flotation cell using a constant amount of Dowfroth and Aerofloat 25 but varying the xanthate. Since only the leaching rate was of interest, the effect of the presence of xanthate was based on the gold remaining in the residue after 24 hours of leaching. This value was not intended to represent the maximum gold extraction possible.

On completion of the flotation step, the remaining xanthate concentration was determined on a sample of solution filtered from the flotation pulp.

The flotation concentrate was reground prior to cyanidation. The regrinding time was varied according to the weight of the concentrate produced. Cyanidation conditions were chosen which were similar to those used in plant practice on this type of concentrate.

In the previous work [1] it was shown that reliable results of the relative effects of various compounds on gold extraction could be obtained by their addition to a gold ore at the start of cyanidation rather than it being

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TABLE I—Summary of Flotation Tests.

Test No.	Xanthate 301 lb/ton solids added	Residual Xanthate In Tailing Sol'n g/l	% of Xanthate Remaining in Sol'n	Ratio of Conc.	Wt. of Solids in Conc. %	Recovery of Gold by Flotation %	Calc Head for Cyanidation Au oz/ton	Cyanide Residue at 24 hr Au oz/ton	Extraction of Gold by Cyanidation %	Overall Gold Recovery %	Reagent Consumption			
											lb/ton conc		lb/ton ore	
											NaCN	CaO	NaCN	CaO
1	0.05	0.0033	30	13.6	7.36	82.7	0.66	0.17	74.2	61.4	28.1	13.9	2.1	1.0
2	0.10	0.0049	22	11.8	8.46	85.1	0.62	0.19	69.5	59.1	24.8	11.9	2.1	1.0
3	0.15	0.0064	19	12.4	8.11	86.7	0.69	0.27	60.8	52.1	23.8	13.3	1.9	1.1
4	0.20	0.0089	20	12.7	7.87	87.7	0.63	0.26	58.7	51.4	23.0	13.6	1.8	1.1
5	0.25	0.0111	20	11.9	8.44	87.1	0.81	0.36	55.6	48.4	21.6	18.1	1.8	1.1

necessary to first float the sulphides and gold before proceeding with the cyanidation step. Consequently, this was the procedure used in this present work to determine the effects of the different commercial xanthate compounds and dithiophosphoric acid-type flotation reagents.

Results

In the work on the residual xanthate after a flotation operation, the xanthate was added with an initial concentration ranging from 0.011 to 0.055 grams of xanthate per litre which under the test conditions used was equivalent to 0.05 to 0.25 pounds of xanthate per ton of solids. The results in Table I and Figs. 1, 2 and 3 show that as the xanthate concentration was increased by up to a factor of 5, the residual xanthate increased over this range in a linear relationship by a factor of up to only 3, i.e. from 0.033 to 0.11 grams of xanthate per litre. Also, as the xanthate was increased, the gold recovery by flotation only, increased from 82.7 to 87.1 per cent. About 65 per cent of the gold was removed by the blankets prior to flotation and therefore with the added recovery by flotation, this represented a total gold recovery of from 94.2 to 95.6 per cent.

After cyanidation of only the flotation concentrates for 24 hours, it was found that the gold extraction decreased when the xanthate concentration was increased. This extraction ranged from 74.2 per cent with 0.05 pounds of xanthate per ton of solids to 55.6 per cent extraction when 0.25 pounds of xanthate per ton of solids was added to the flotation step. The overall extraction from the flotation and cyanidation steps decreased from 61.4 per cent to 48.4 per cent over the range of xanthate added. The cyanide consumption in these tests dropped slightly from 2.1 down to 1.8 pounds of sodium cyanide per ton of ore. The lime consumption stayed essentially the same at about 1 pound of CaO per ton of ore.

In the examination of the effects of the various xanthate products, 0.4 pounds per ton of solids of either isopropyl, secondary butyl or amyl xanthate was added to the gold ore. The results are shown in Table II and Fig. 4. In the control test where xanthate was not added, about 93 per cent of the gold was extracted in 24 hours. In the presence of xanthate, the extractions were reduced to 84, 80 and 78 per cent with the isopropyl, butyl and amyl xanthate respectively. In a similar series of tests in which three dithiophosphoric acid-type collectors were used instead of xanthate, it was observed that these Aerofloat collectors also reduced the gold extraction but to a lesser degree than the xanthates. The gold extraction rates in 24 hours were 89, 87 and 81 per cent with 0.4 pounds of Aerofloat 15, Aerofloat 25 and Aerofloat 242 respectively.

Discussion

Some of the other methods for determining xanthate in solution that were tried involved ion exchange techniques [4], precipitation with copper procedures [5] and color comparison methods [6]. The method using a spectrophotometer [7] for measuring the adsorption of light of a

TABLE II—Effect of Various Collectors on Gold Recovery in Cyanidation.

Collector used		lb/ton solids	Residue Au oz/ton	Extraction Au, %	Common
Type					
nil	—	—	0.011	93.1	Au in feed
Sodium isopropyl xanthate	4	0.025	0.025	84.4	0.16 oz/ton Sol'n 1 lb
Secondary butyl xanthate	"	0.032	0.032	80.0	NaCN 1 ton, 30% solids
Amly xanthate	"	0.035	0.035	78.1	pH 12
Aerofloat 15	"	0.017	0.017	89.4	24 hours
Aerofloat 25	"	0.021	0.021	86.9	
Aerofloat 242	"	0.031	0.031	80.6	

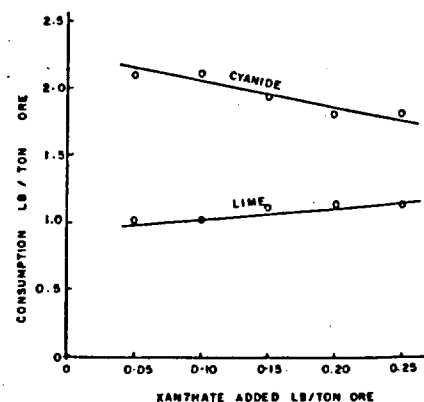
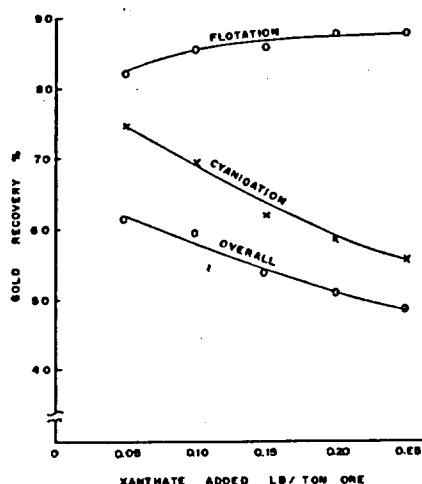
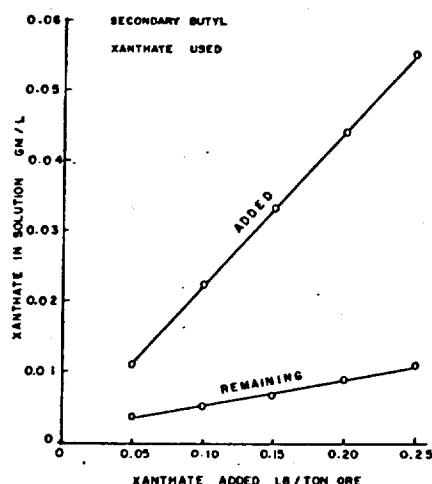


Fig. 1. (Left) Residual xanthate compared to various amounts added. Fig. 2. (Centre) Effects of various amounts of xanthate on gold recovery. Fig. 3. (Right) Effects of various amounts of xanthate added to flotation on reagent consumption in cyanidation.

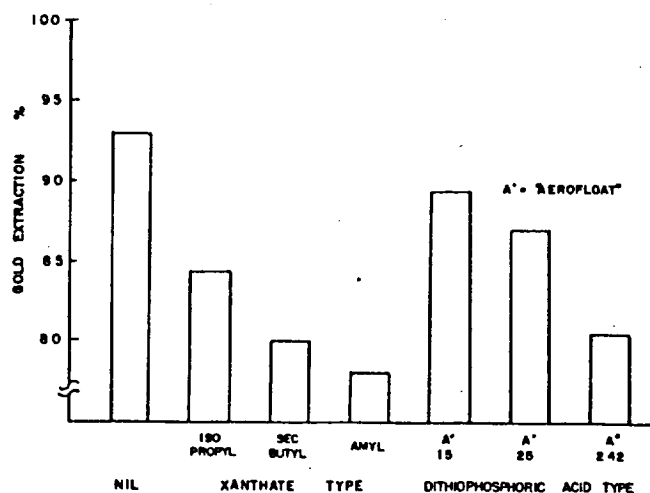


Fig. 4. Effect of various types of collectors on gold extraction from ore.

specific wavelength was not included since it was the aim of the project to find a relatively simple but also inexpensive method. The method chosen appears to be reliable and will give reproducible results under conditions found in most flotation systems and does not involve any costly equipment.

Because adequate contact time was not given to obtain the maximum extraction by cyanidation, an examination of the economics of the overall results would be of little value.

At the lowest xanthate concentration used, namely 0.05 pounds of xanthate per ton of solids, there was 30 per cent of the xanthate in solution at the end of the flotation period while there was only 20 per cent of the xanthate remaining when the highest concentration was used. This shows that there was a greater adsorption on the mineral surfaces at the higher concentrations which would constitute a greater waste and be a cause for more adverse effects in the cyanidation step.

Some operators of flotation-cyanidation circuits have reported an increase in cyanide consumption with an increase in the addition of flotation reagents but many of these mills use copper sulphate as an activator. With copper being adsorbed on the metallic minerals in the form of cuprous xanthate, it is quite possible that the increased cyanide consumption is caused by the copper ions and not directly due to the xanthate ions. Since copper was not used in these tests, the effect of copper was not established under these conditions.

In the experiments on the effect of various types of collectors on the gold extraction from an ore, the high concentration of xanthate or dithiophosphoric acid, namely 0.4 pounds per ton of solids, was used to increase the probability of detecting small effects on the gold dissolution rate. The results indicated that the detrimental effects of xanthate in the extraction of gold were related to the carbon chain attached to the xanthate radical; the longer the chain, the greater was the adverse effect on the extraction rate. However, because of the uncertainty as to all of the constituents of the dithiophosphoric acid-type collectors which were tried, one could not conclude that it was the length of the carbon chain in this type of reagent that controlled the detrimental effects in cyanidation.

It is generally accepted that Aerofloat 25 is a stronger collector than Aerofloat 15 and that Aerofloat 242 is a stronger collector than Aerofloat 25 [8]. It can be suggested then, that in both the xanthate and the dithiophos-

phoric acid-type collectors, the stronger collector is more strongly adsorbed and therefore is more difficult to remove from the mineral surface to expose the gold to the cyanide solution. The stronger collectors therefore have the greatest effect on the rate of gold extraction in the subsequent cyanidation step.

Conclusions

The results of the work have shown that the presence of xanthate in a cyanide circuit retards the dissolution rate of gold and therefore it would be to the operator's advantage to keep the xanthate added to a minimum required for successful flotation.

It has also been shown that the residual xanthate in the flotation water can be used as an indication of the amount added.

A suitable analytical technique has been tested for the determination of residual xanthate and therefore the means are available which would allow an operator to control the xanthate addition to a predetermined level.

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APPENDIX

Determination of xanthate in flotation solutions

This simple procedure [9] provides reliable and reproducible results under most conditions in flotation for the determination of xanthate in the flotation tailing water. It involves the determination of the total reducing capacity of the solution and a similar determination on another sample of the same solution from which the xanthate has been removed by a solvent extraction step using kerosene. The difference in these two determinations is due to the xanthate. Using this method a determination can be made in less than half an hour.

The steps are as follows:

- 1) To 100 cc of filtered flotation tailing water in an Erlenmeyer flask, add 5 cc of potassium sulphate solution.
- 2) Add 0.2 grams of iodine indicator.
- 3) Titrate with iodine to a blue-purple end point. This is the total reducing power of the solution.
- 4) Repeat steps 1 to 3 using 100 cc of water that is used in the plant. This is Blank No. 1.
- 5) To another 100 cc of filtered flotation tailing

water in a separatory funnel, add 50 cc of tartaric acid.

6) Add 25 cc of kerosene.

7) Shake the contents of the funnel for 3 minutes.

8) Let settle for 12 minutes.

9) Transfer the aqueous layer (lower layer) to an Erlenmeyer flask and add 5 cc of potassium sulphate solution.

10) Add 0.2 grams of iodine indicator.

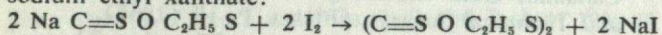
11) Titrate with iodine to a blue-purple end point. This is the reducing power of the solution with the xanthate removed.

12) Discard the kerosene left in the separatory funnel.

13) Repeat steps 5 to 12 using 100 cc of plant water. This is Blank No. 2.

14) The iodine equivalent of the xanthate concentration is: the total reducing power as determined in step 3 minus Blank No. 1 from step 4, minus the difference between the reducing power of the solution with the xanthate removed (step 11) and Blank No. 2 (step 13).

15) The number of cc's determined in step 14 times a factor equals the concentration of xanthate in solution. The factor is determined for the particular xanthate from an equation similar to the following one which is for sodium ethyl xanthate:



For a 0.002 N iodine solution, each cc of iodine used for the titration of 100 ccs of sample would be equivalent to 2.9 mgms of sodium ethyl xanthate per litre.

Concentration of reagents

Potassium sulphate or iodide	— 35 grams per litre
Tartaric acid	— 50 grams per litre
Iodine	— 0.002 N (So 1-86)
Iodine indicator	— Either Thyodene (T-138) or Starch Indicator solution (SoS-408) or 1 per cent potato starch solution (S-513)

Note: The numbers in brackets refer to catalogue numbers from the Fisher Chemical Index. Equivalent

products from other manufacturers can be used satisfactorily.

General comments

Other volumes of samples may be necessary because of low or high xanthate concentrations. The blanks should then be done on similar volumes.

If a flotation solution is much higher than pH 8 then it may be necessary to neutralize the solution to this value before using this method.

Other constituents of the flotation solution other than xanthate could be extracted by the kerosene. If this is the case then the results may be only relative.

Discussion

Question — Would a spectrophotometer be a satisfactory instrument to monitor the xanthate concentration entering the cyanide circuit and how much would it cost?

Reply — The spectrophotometer method is not fool proof as there are other interfering elements in solution that could prevent accurate reading of the xanthate strength. If the "Spectronic 20" would do the job the cost would be about \$800.00. If a more sensitive unit were required it could cost \$3000.00.

Question — Was this investigation confined to adsorbed xanthate only?

Reply — In addition to the adsorbed xanthate there was some residual moisture in the filter cake which was carried over to cyanidation.

Washing a concentrate in a filter is helpful but it is not possible to remove any more than 50 per cent of the adsorbed xanthate by washing alone. Steam treatment or heating will remove almost all of the xanthate but the cost of this treatment may be uneconomical and further more it would increase reactivity of the sulphides which would almost certainly increase the cyanide consumption. The ideal arrangement would be automatic control of the addition of xanthate so that just enough and no more was added to give maximum recovery by flotation. The cyanide consumption should then be at a minimum. ●