2-4-6 TRIHYDROXYPHENYL ALKYL KETONES AS FLOTATION REAGENTS FOR MANGANESE DIOXIDE

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This is to certify that the

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AS FLOTATION REAGENTS FOR
MANGANESE DIOXIDE

By

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TABLE OF CONTENTS

INTRODUCTION

Froth flotation is one of the most important ore dressing processes for the economic treatment of relatively low grade ores. It is to be expected that the importance of flotation processes will increase with the decrease in availability of rich ores. The froth flotation is well adapted to the recovery of insoluble metal sulfides. It has also been extended to the separation and recovery of many other minerals. There is a constant search for new flotation reagents which may be used for the recovery of non-sulfide ores.

Purpose and Scope

The purpose of this investigation is to show that 2-4-6 trihydroxyphenyl alkyl ketones act as collectors in the flotation of pyrolusite, the natural manganese dioxide. The use of these ketones is not recorded in metallurgical literature. An outline of the procedure used for the preparation of these compounds is given in the Appendix. Three trihydroxy-ketones were used in this investigation. These compounds are 2-4-6 trihydroxyphenyl heptyl ketone, 2-4-6 trihydroxyphenyl nonyl ketone and 2-4-6 trihydroxyphenyl undecyl ketone.

Froth flotation has its beginning in 1906. Many publications, including those of Taggert,[18] Gaudin,[9] Wark,[20] Peterson,[15] and DeWitt,[6] clearly set forth both principles and practice of froth flotation. It is carried out in an aqueous suspension of finely ground minerals into which suitable reagents and air bubbles are introduced. Certain minerals have a greater attraction for the air bubbles than for the water and becomes attached to the bubbles. The mineral clad bubbles then rise to the surface and are skimmed off as froth. An addition agent must be added to the cell to form a more permanent froth. Other reagents are usually added to aid in a better separation of ores and gangue. These reagents have the specific purpose of rendering the ore more, and the gangue less flotable.

Frothers

The purpose of a frother is to form a more or less stable froth on the surface of the pulp. Ore particles attached to the bubbles are thus drained from the cell with the froth.

The frothers function by decreasing the surface tension. DeWitt[6] states that the frothing agent with the most negative slope of surface tension-molal concentration curve, in general, shows the greatest frothing power.

Some of the frothers commonly used are pine oil, eucalyptus oil, terpineol, amyl alcohol, and soaps. The frother should not act as a collector, also it should not be used in excess. It has a tendency to coat the ore particles to the exclusion of the collectors and thus decrease flotation. The amount used as mentioned by Taggert lies between 0.05 and 0.20 pounds per ton.

Collectors

The function of a collector[6] is to attach itself to the mineral and present an outward oily film to the air bubble. One end of the collector molecule contains an active polar group, and the other end contains a hydrocarbon chain. The length of hydrocarbon group on a collector which permits flotation depends upon both the mineral to be recovered and upon the active polar group in the collector molecule.

There are a great number of compounds that would serve as collectors but relatively few are used commercially. The two general types of collectors used are negative or anionic reagents and positive or cationic reagents. The anionic reagents ionize into negative organic ions and positive metal or hydrogen ions. The organic anions can be considered to combine with the metal atom of the mineral and form an insoluble salt which is susceptible to flotation. The cationic reagents form positive organic ions. This positive ion is formed eighter by loss of negative ions as a bromide or by the addition of hydrogen ions as in the case of amines.

Activators

An activator[6] for any mineral is a substance generally inorganic the addition of which induces flotation in the presence of some collector that otherwise is without effect on the mineral. Heavy metal sulfides are quite readily caused to float by the use of xanthate collector. The oxidized minerals do not have this property.

Peterson[15] outlined the procedure for sulfidising oxidized ores with alkali sulfides. When a suitable sulfide coating is formed, the mineral may be recovered by the use of a xanthate flotation collector and pine oil as the frothing agent.

Depressant

When two minerals of a mixture are normally concentrated together in the froth, depressants can sometimes be used to restrict the flotation of one of them. A depressant[6] for any mineral is a substance, generally inorganic, the addition of which prevents a collector from functioning as such for that mineral. Their action should be specific and their concentration in the pulp must be closely governed, because an excess may cause complete depression of the minerals.

Previous Work on Pyrolusite Flotation

Pyrolusite is the one of the more common manganese ores. Its chemical formula is MnO_2, and its chemical name is manganese dioxide. In 1932 the concentration by flotation of manganese dioxide[9] was first reported. It was found that pyrolusite being macrocrystalline should offer little difficulty to contration by froth flotation, particularly if the gangue is siliceous. If the gangue is calcareous flotation of these minerals with the usual collecting agent precedes or occurs simultaneously with the flotation of the manganese dioxide.

The reagents used in the above investigation by the U. S. Bureau of Mines were substantially the same as are required for the flotation of other nonmetallic minerals, namely soap or oleic acid for collection, pine oil for frothing, water glass to inhibit silica flotation and an alkali for pH REGULATION. Earlier experiments performed in the Gaudin laboratory[9] indicated no separation of manganese dioxide from associated minerals. These experiments were made using the same reagents as the Bureau of Mines experiments; failure was said to be caused by the sliminess of the ores tested and by the unsatisfactory liberation of minerals that resulted in spite of the fineness of grinding.

Frank J. Cahn[1] describes a method for the preparation of suitable manganese dioxide flotation reagents, An aliphatic carboxylic acid acyl halide of high molecular weight is treated with an hydroxy alkyl nontertiory amine salt in presence of catalyst such as sulfoacetic acid at temperature below 100c. Use of 2.1 to 6.7 pounds per ton of these reagents lead to the recovery of 70-80 percent pyrolusite from charge. Silicon dioxide is floated and manganese dioxide remains in the flotation cell.

In the present report 2-4-6 trihydroxyphenyl alkyl ketones are used for the flotation of the pyrolusite.

Procedure

Flotation Reagent: Collector

The 2-4-6 trihydroxyphenyl alkyl ketones which were used in this investigation may be classified as cationic collectors. They react with the negative ions of the mineral with the formation of a hydrophobic film on the mineral surface.

Particle Size

The ore must be ground to such a fineness that the particles of valuable mineral are separated from the gangue. The particles must be of sufficient fineness so that the bubbles can raise them through the suspension. The usual particle size in this investigation is minus -80- to plus -200- mesh.

Addition of Reagents

Reagents are usually added to the pulp in the order: conditioning agent, collector, and frother.

For cationic collectors the time and rate of addition of the reagent has an important influence on flotation results. An excess concentration of cationic collector in the pulp at any time must be avoided.[3] Dean and Ambrose showed that the reagent is more effective immediately after addition than any time later; thus a 90 percent yield may be decreased to 10 percent by an eight minute conditioning period before flotation.

Small changes in pH may have a profound influence on the flotability of many minerals. Charts by Dean and Ambrose[4] show that silicate minerals and silica are generally recovered with cationic agent within pH range 6 to 8.

Synthetic ore mixtures of pyrolusite and gangue were subjected to flotation tests. The collector action is found by the determination of the manganese dioxide content of the concentrate as compared to that of the head mixture.

Preparation of Ore

A relatively pure pyrolusite sample which passes through a -20- mesh screen was ground wet in a pebble mill, deslimed, dried, screened and the fraction minus -200- and minus -80- to plus -200- mesh are used in this investigation.

Manganese dioxide analysis of pyrolusite sample gives an average of 30.8 percent of manganese dioxide.

Clean white sand, available in laboratory, is similarly ground wet in the pebble mill, deslimed, dried, screened and the sample fraction as of pyrolusite are used. The synthetic ore mixture for flotation were compounded from the above, taking 2 gms of pyrolusite and 98 gms of sand. Hence the standard ore mixture contains .616 percent of manganese dioxide.

Dean and Ambrose[5] suggested that the method of preparing the sample has an effect on flotation results. The surface of sample from wet pebble mill grinding should be cleaner than the surface of dry ground material. Being cleaner it has a tendency to combine with the reagents and thus a greater tendency to be collected. In this investigation samples from dry grinding have been used for tests.

Flotation Cell

The flotation cell is similar to that used by DeWitt and Ludt; DeWitt and Thakkar. The flotation cell is a 100gm batch cell provided with an air inlet at the bottom and immediately above with a variable speed agitator. The agitator and shaft are made up of stainless steel, and the cell itself of Lucite. (See figure 1.)

Fig. 1.

The froth discharges into a Buchner funnel where the concentrate is collected on a filter paper. The liquid is drawn through the funnel and into the glass bottle, and fed continuously back to cell at a rate of a little over one drop a second. This regulates the rate at which the froth leaves the cell.

The total pulp charge to the cell consists of 100 gm of ore mixture and 300 gm of water. A variable amount of this water, depending upon froth depth in cell, is in the bottle outside the cell.

Collector Addition. The 2-4-6 trihydroxyphenyl alkyl ketones were used for collectors. They were dissolved in a water alcohol mixture of concentration of 1 gm per 100 ml. In some other cases they were dissolved in pure water where the pH was to be changed.

Operation of the Cell. The agitator and the air pump are started. About 150 gm of water, then the gangue and pyrolusite are put in the cell. About 50 gm of water are drawn into the water supply bottle; the rest of 300 gm of water is run into the cell. Modifying agent if any are added and the pulp is allowed to mix for fifteen minutes. Pine oil as needed is added on the end of fine wire. The excess of pine oil must be avoided. The collector is then added by stage addition over the period of run. The collector solution is added slowly from the pipette which is inserted well down into the pulp. When added to the top of the pulp, the froth picks up the collector and carries it over immediately.

At the end of the run the pulp is run from the cell and the pH is measured. The filter paper holding the concentrate is dried and weighed to get weight of the concentrate.

The percentage of manganese dioxide is then determined in the concentrate.

Determination of Mn.[11]

This is an indirect method. The sample is dissolved by treating with sulfuric acid and a suitable reducing agent, such as ferrous sulfate, or oxalic acid; the excess of reducing agent is finely determined by titrating with standard Potassium permanganate (0.102 N.).

$$MnO_2 + C_2O_4^{--} + 4H^{+} \longrightarrow Mn^{++} + 2CO_2 + 2H_2O$$

$$MnO_2 + 2Fe^{++} + 4H \longrightarrow Mn^{++} + 2Fe^{+++} + 2H_2O$$

For each analysis weigh out portions of finely ground ore, which has been dried to constant weight at 120, into 300 ml. flasks using samples that do not vary more than .05 gm from .45 gm. Add to each portion of ore a carefully weighed amount of pure sodium oxalate, using at least one-half times as much oxalate as pyrolusite, but not more than .8 gm in any case. Add 50 ml.

of water and 50 ml. of 6n. sulfuric acid, and heat without boiling hard, until no more pyrolusite remains undissolved. Keep the flask covered with watch glass and do not allow the solution to evaporate to below 85 ml., adding hot water from time to time if necessary. When all the black ore has dissolved dilute to 200 ml. and titrate with .Io2N potassium permanganate keeping the solution above 60°c.

If s is the weight of pyrolusite used, r the weight of sodium oxalate, and n the millilitres of N normal potassium permanganate required for the excess oxalate, the percentage of Manganese dioxide in the sample is determined according to the formula:

$$\left(\frac{r}{0.067 \times N} - n\right)\left(\frac{N \times 0.0435 \times 100}{s}\right) = \begin{array}{l}\text{percentage of} \\ \text{manganese dioxide}\end{array}$$

In the equation .067 is the equivalent weight of sodium oxalate and .0435 the eq. wt. of manganese dioxide.

DATA

TABLE 1

Synthetic ore 98 gms of sand and 2 gms of pyrolusite.
Manganese dioxide in synthetic ore is .616 percent.
Collector used: 2-4-6 trihydroxyphenyl undecyl ketone.
Depressing agent used: sodium silicate.
Time in all experiments: 6 minutes.

Exp. No.	Mesh	pH	Depressing Agent	Collector	Concentrate	
			#/Ton	#/Ton	gms.	ml. of $KMnO_4$
1	-200	6.5-6.8	---	.2	6.72	8.65
2.	-200	"	---	.4	7.32	10.15
3	-200	"	---	1.0	9.74	9.94
4	-80-200	"	---	2.0	5.6	17.80
5	"	"	---	4.0	6.8	14.90
6	"	8	---	1.0	9.1	10.30
7	"	8.7-9.2	---	.2	4.2	16.40
8	"	"	---	.5	4.65	16.90
9	"	"	---	1.0	5.35	16.80
10	"	11	---	1.0	6.15	14.30
11	"	4	---	1.0	5.5	16.70
12	"	6.5-6.8	2.0	2.0	8.8	7.70

TABLE 2

Synthetic ore 98 gms of sand and 2 gms of pyrolusite.
Manganese dioxide in synthetic ore is .616 percent.
Collector used: 2-4-6 trihydroxyphenyl nonyl ketone.
Depressing agent used: Sodium silicate.
Time of run in all experiments: 6 minutes.

Exp. No.	Mesh	pH	Depressing Agent #/Ton	Collector #/Ton	Concentrate gms.	Concentrate ml. of $KMnO_4$
1	-200	6.5-6.8	---	.2	6.5	8.6
2	"	"	---	.4	6.0	11.3
3	"	"	---	1.0	8.0	11.6
4	-80-200	"	---	2.0	8.5	11.8
5	"	"	---	4.0	13.1	7.80
6	"	8	---	1.0	12.2	7.6
7	"	8.7-9.2	---	.2	7.25	7.3
8	"	"	---	.5	5.75	10.2
9	"	"	---	1.0	5.0	14.2
10	"	11	---	1.0	8.50	5.80
11	"	4	---	1.0	6.8	12.0
12	"	6.5-6.8	2.0	2.0	10.0	8.80

TABLE 3

Synthetic ore 98 gms of sand and 2 gms of pyrolusite.
Manganese dioxide in synthetic ore is .616 percent.
Collector used: 2-4-6 trihydroxyphenyl heptyl ketone.
Depressing agent used: Sodium silicate.
Time of run in all experiments: 6 minutes.

Exp. No.	Mesh	pH	Depressing Agent #/Ton	Collector #/Ton	Concentrate	
					gms.	ml. of $KMnO_4$
1	-200	6.5-6.8	---	.2	4.74	6.2
2	"	"	---	.4	6.5	7.5
3	"	"	---	1.0	6.85	13.2
4	-80-200	"	---	2.0	9.0	10.8
5	"	"	---	4.0	8.5	11.8
6	"	8	---	1.0	10.0	7.8
7	"	8.7-9.2	---	.2	3.5	5.7
8	"	"	---	.5	6.0	7.7
9	"	"	---	1.0	6.55	11.2
10	"	11	---	1.0	6.25	7.1
11	"	4	---	1.0	6.25	12.3
12	"	6.5-6.8	2.0	2.0	10.2	7.5

TABLE 4

Synthetic ore 43.7 gms of pyrolusite and 56.3 gms sand.
Manganese dioxide in synthetic ore: 14.42 percent.
Particle size: -80 to plus 200.
pH: 6.5 to 6.8

Exp. No.	Collector Used #/Ton	Time Minutes	Concentrate Gms	ml. of $KMnO_4$
1	2-4-6 trihydroxyphenyl undecyl ketone 1 #/Ton	6	24.2	114.0
2	2-4-6 trihydroxyphenyl undecyl ketone 2.5 #/Ton	24	29.0	107.0
3	2-4-6 trihydroxyphenyl nonyl ketone 1 #/Ton	6	31.0	90.0
4	2-4-6 trihydroxyphenyl heptyl ketone 1 #/Ton	6	34.0	81.0

Results

TABLE 5

Synthetic ore 98 gms of sand and 2 gms of pyrolusite.
Manganese dioxide in ore: .616 percent.
Collector used: 2-4-6 trihydroxyphenyl undecyl ketone.
Depressing agent used: sodium silicate.
Time of run in all experiments: 6 minutes.

Exp. No.	Mesh	Depressing Agent #/Ton	pH	Collector #/Ton	Concentrate gms.	Concentrate % MnO_2	Concentrate % recovery
1	-200	---	6.5-6.8	.2	6.72	3.84	41.8
2	"	---	"	.4	7.32	4.51	53.6
3	"	---	"	1.0	9.74	4.42	69.8
4	-80- 200	---	"	2.0	5.6	7.98	72.6
5	"	---	"	4.0	6.8	6.62	73.1
6	"	---	8	1.0	9.1	4.57	67.3
7	"	---	8.7-9.2	.2	4.2	7.28	49.7
8	"	---	"	.5	4.65	7.50	56.6
9	"	---	"	1.0	5.35	7.46	64.8
10	"	---	11	1.0	6.15	6.35	63.8
11	"	---	4	1.0	5.5	7.4	66.1
12	"	2.0	6.5-6.8	2.0	8.8	3.42	42.9

TABLE 6

Synthetic ore 98 gms of sand and 2 gms of pyrolusite.
Manganese dioxide in synthetic ore: .616 percent.
Collector used: 2-4-6 trihydroxyphenyl nonyl ketone.
Depressing agent used: sodium silicate.
Time of run in all experiments: 6 minutes.

Exp. No.	Mesh	Depressing Agent #/Ton	pH	Collector #/Ton	Concentrate		
					gms.	% MnO_2	% recovery
1	-200	---	6.5-6.8	.2	6.5	3.81	40.3
2	"	---	"	.4	6.0	5.01	48.8
3	"	---	"	1.0	8.0	5.14	66.6
4	-80 200	---	"	2.0	8.5	5.23	72.2
5	"	---	"	4.0	13.1	3.43	73.7
6	"	---	8	1.0	12.2	3.37	66.7
7	"	---	8.7-9.2	.2	7.25	3.24	38.0
8	"	---	"	.5	5.75	4.52	42.2
9	"	---	"	1.0	5.0	6.29	51.0
10	"	---	11	1.0	8.5	2.57	35.6
11	"	---	4	1.0	6.8	5.32	58.6
12	"	2.0	6.5-6.8	2.0	10.0	3.9	63.4

TABLE 7

Synthetic ore 98 gms of sand and 2 gms of pyrolusite.
Manganese dioxide in synthetic ore: .616 percent.
Collector used: 2-4-6 trihydroxyphenyl heptyl ketone.
Depressing agent used: sodium silicate.
Time of run in all experiments: 6 minutes.

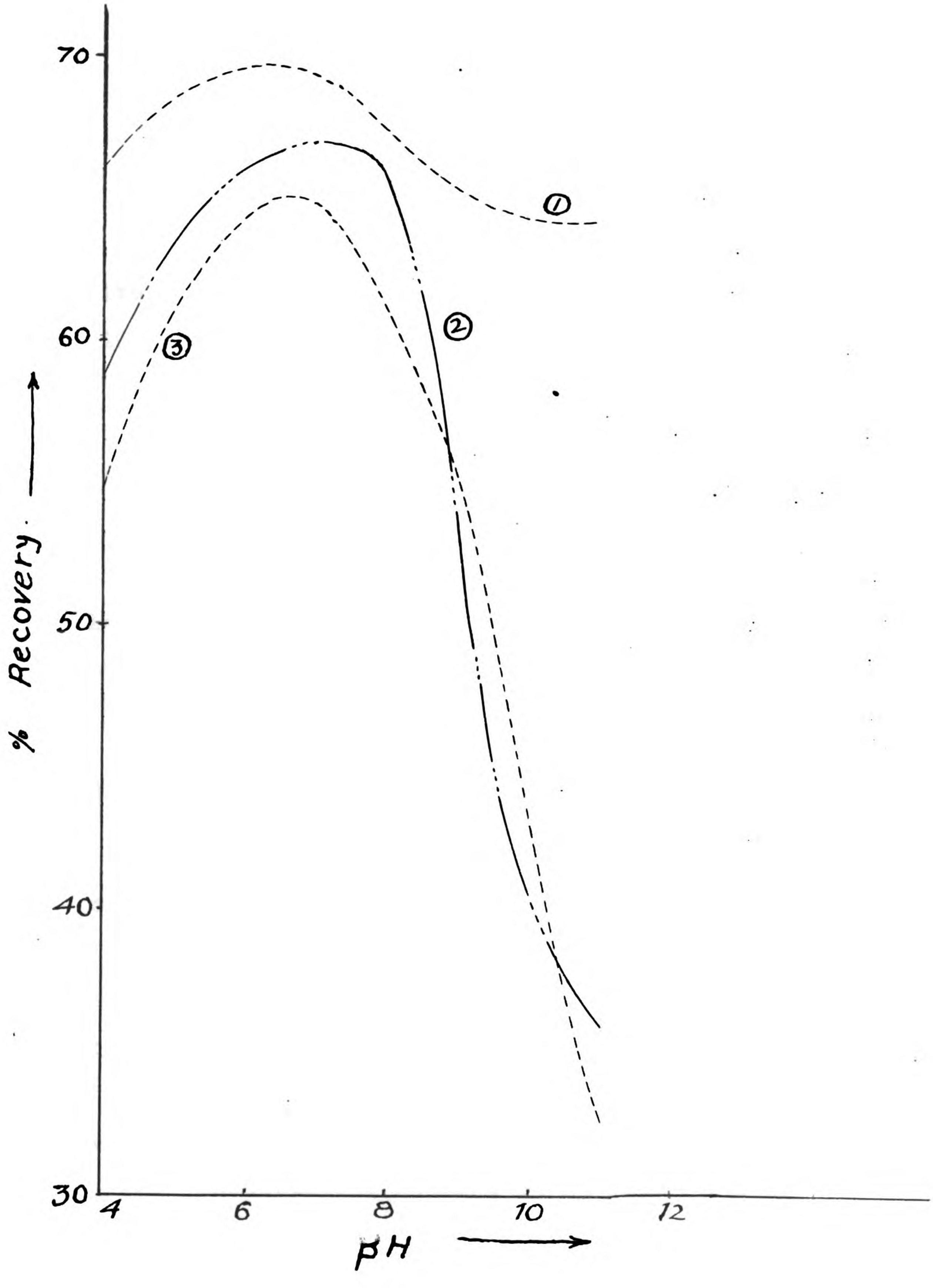
Exp. No.	Mesh	pH	Depressing Agent #/Ton	Collector #/Ton	Concentrate		
					gms.	% MnO_2	% recovery
1	-200	6.5-6.8	---	.2	4.74	2.75	21.1
2	"	"	---	.4	6.5	3.32	35.5
3	"	"	---	1.0	6.85	5.85	65.4
4	-80 200	"	---	2.0	9.0	4.79	70.0
5	"	"	---	4.0	8.5	5.24	72.1
6	"	8	---	1.0	10.0	3.46	56.1
7	"	8.9-9.2	---	.2	3.5	2.54	14.4
8	"	"	---	.5	6.0	3.42	33.3
9	"	"	---	1.0	6.55	4.96	52.7
10	"	11	---	1.0	6.25	3.15	31.9
11	"	4	---	1.0	6.25	5.45	55.2
12	"	6.5-6.8	2.0	2.0	10.2	3.46	57.2

TABLE 8

Synthetic ore 43.7 gms of pyrolusite and 56.3 gms sand.
Manganese dioxide in synthetic ore: 14.42 percent.
Particle size: minus 80 to plus 200.
pH: 6.5 to 6.8.

Exp. No.	Collector	Time	Concentrate		
		Minutes	Gms.	% MnO_2	% Recovery
1	2-4-6 trihydroxyphenyl undecyl ketone 1 #/Ton	6	24.2	5.06	85.1
2	2-4-6 trihydroxyphenyl undecyl ketone 2.5 #/Ton	24	29	4.74	95.8
3	2-4-6 trihydroxyphenyl nonyl ketone 1 #/Ton	6	31.0	3.91	84.2
4	2-4-6 trihydroxyphenyl heptyl ketone 1 #/Ton	6	34	3.6	85.0

The graph of pH against recovery, using constant amount of collector (1 pound per ton), is shown on the next page. Graph 1 corresponds to 2-4-6 trihydroxyphenyl undecyl ketone, 2 corresponds to 2-4-6 trihydroxyphenyl nonyl ketone and 3 corresponds to 2-4-6 trihydroxyphenyl heptyl ketone.


70
60
50
40
30
% Recovery
①
②
③
4
6
8
10
12
pH

Discussion of Data

Addition Agents

Sodium silicate as an addition agent does not give encouraging results. However, it is seen that sodium silicate exerts some depressing effect. In some of the above experiments more than 1200 percent enrichment of manganese dioxide in concentrate, based on manganese dioxide in head mixture, is obtained. In some of the experiments only 400 percent enrichment, based on head mixture, is obtained. It is noted that addition of collector throughout the period of run gives better results than adding the same amount of collector at the beginning of the run.

Accuracy of Results

The conclusion drawn from these tests should be considered as trends and not as a specific numerical relationship because the tests were run only once a time and the analysis was also done only once in most of the cases.

The 2-4-6 trihydroxyphenyl alkyl ketones promote the flotation of the mineral pyrolusite.

The flotation of manganese dioxide from silica gangue is accomplished with an enrichment of the concentrate of 1200 percent as compared to manganese dioxide in feed sample. It was also observed that if the percentage of manganese dioxide in feed was .616 gms, the recovery in concentrate was obtained as 70 percent. When the percentage of manganese dioxide in the feed mixture was increased to 14.42, the recovery in the concentrate was obtained as 95-96 percent. It was also observed that running the particular test for a longer time than 6 minutes, also helped in the recovery.

It can be seen from the graphs that 2-4-6 trihydroxyphenyl undecyl ketone works better than the other lower alkyl ketones. It can also be seen from the graphs that as the number of carbon atoms of the hydrocarbon chain increases, there is less effect of change in pH value on collector.

Discussion of the Results

The main object of this investigation is to show that the 2-4-6 trihydroxyphenyl alkyl ketones cause the flotation of pyrolusite. The final results are summarized in tables 5, 6, 7, 8, and graphs show that these ketones can be used effectively as flotation agents.

The detailed investigation as well as the optimum condition for operation were carried out to study the effect of different amounts of collector. Then, keeping the best amount of collector constant, the effect of change in pH value was experimentally determined to be between 6 and 8 pH.

Particle Size

The particle size used for this investigation was minus 200 mesh, and minus -80- to plus -200- mesh. Both particle sizes work equally well.

Amount of Collector

An excess of collector does not seem to help the collector action. The optimum amount of collector that should be used is one pound per ton if the percentage of manganese dioxide in feed mixture is less than 1. If the percentage of manganese dioxide in head mixture is increased, the pounds per ton of collector should also be increased.

APPENDIX

Organic Preparations

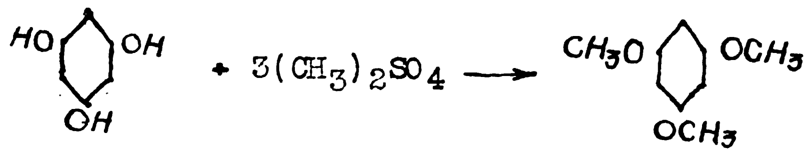
General Discussion

There are several methods suggested for preparing 2-4-6 trihydroxyphenyl alkyl ketones. Some of them are discussed below. The 2-4-6 trihydroxyphenyl alkyl ketones are prepared for the using as flotation reagents. For the purpose of this work the chemical structure of the product is secondary to the flotation properties of the final product; although the structure of the product is important in other fields.

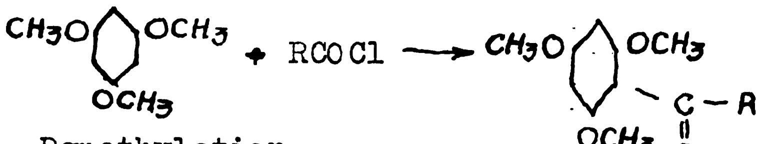
PROCEDURE I.

Starting with phloroglucinol the following series of reactions can be used to synthesis the 2-4-6 trihydroxyphenyl alkyl ketones.

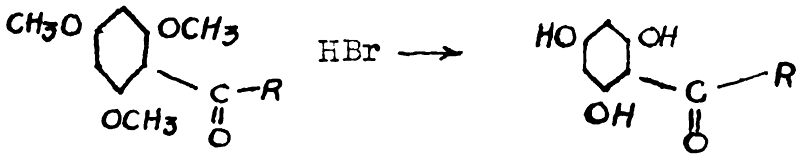
1. Phloroglucinol trimethyl ether.



2. Ether of trimethyl phenol.



3. Demethylation.



The steps in above method and the method discussed below leading to synthesis 2-4-6 trihydroxyphenyl alkyl ketones involve standard procedures. Variations from these procedures must be made in some cases because of high mol. wt. of the compound.

For methylation the Ullman's[19] modification can be used which gives 86 percent yield. Aqueous sodium hydroxide solution (150 ml. containing 60 gms of sodium hydroxide) should be gradually added from the tap funnel during 3-4 hours to a mixture of phloroglucinol (42 gms), methyl sulphate (189 gms), and alcohol (100 ml) agitated vigorously by means of gas tight stirrer and contained in a flask (reflux condenser) from which air should be excluded by hydrogen. After the completion of reaction the vessel should be cooled in icebath and the addition of water (150 ml.) will cause the separation of ether in glistering, white prisms. The average yield in many experiments was very good.

The phloroglucinol ether should be reacted with heptyl chloride by Mannich and Hann[14] who used in a similar experiment 6.3 gms of ether 9.6 gms of heptyl chloride in 16 ml of carbon disulfide with 5.1 gms of aluminium chloride which will give heptyl phloroglucinol trimethyl ether.

The trimethyl ether should be demethylated by

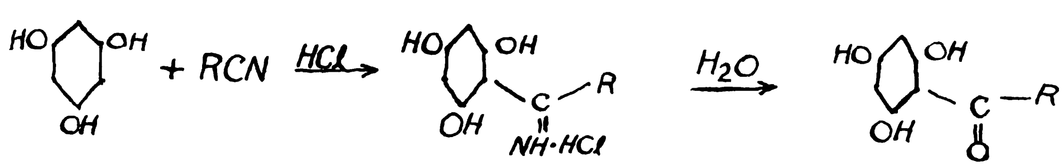
HBr and so we will get 2-4-6 trihydroxyphenyl heptyl ketone, and in the same way the other higher ketones.

The procedure I was not used, for in any of the three steps, there is the possibility of low overal yield. In the following method there is only one step. In the literature the reported yield is good, and in practice we have obtained 75% yield.

For preparing the 2-4-6 trihydroxyphenyl alkyl ketones the Hoesch synthesis[17] is the most satisfactory. Extensive investigations on condensation of nitriles with resorcinol, phloroglucinol and their ethers indicate that this reaction is very satisfactory for forming polyhydroxy ketones. The yields of ketones from phloroglucinol or its ether with aliphatic nitriles except those of very complex character are very good. Resorcinol or its ether usually gives lower yield. Aromatic nitriles do not react so readily as aliphatic nitriles.

PROCEDURE II.

Gulati, Sheth and Vankatraman[10] developed the following satisfactory method for the synthesis of 2-4-6 trihydroxyphenyl alkyl ketones.



In a 500 ml. filtering flask, fitted with $CaCl_2$ tube, and a rubber stopper carrying a wide mouthed glass tube are placed .16 mols of well dried phloroglucinol, .32 mols of anhydrous aliphatic nitrile, 125 ml. of anhydrous ether and 4 gms of finely powdered fused $ZnCl_2$. The wide mouthed glass tube for the entry of dry HCl gas is necessary to avoid clogging due to separation of solid. The phloroglucinol can be dried[2] by keeping overnight in a drier at 120°c. The nitriles should be used freshly distilled under vacuum.[16] Zinc chloride should be freshly fused each time. The reaction flask is then cooled in an ice-bath, and shaken occasionally. The rapid stream of dry HCl gas is passed through the reacting mixture for 25 hours until it is well saturated; keeping the flask in an ice-bath for all the time. After it is well saturated the flask with the contents is allowed to cool in an ice chest for three to four days.

The orange yellow precipitates are filtered and washed with dry ether. The precipitates should be well washed with dry ether so as to remove all the unreacted nitrile, otherwise this unreacted nitrile will form an insoluble acid on hydrolysis which is difficult to separate from the ketone.

After washing, the precipitates were transferred to a two-litre round bottom flask to which was added one litre of boiling water. The flask was provided with reflux condenser and the precipitates were boiled vigorously for two to three hours. It was allowed to stand overnight. The next day the precipitates were filtered and recrystallized from a water-alcohol mixture. Norite was used to remove colored material from the hot solutions.

The M. P. of the 2-4-6 trihydroxyphenyl heptyl ketone 106°c hydrous, and 124°c anhydrous checked with that found in literature.[13]

All these compounds are insoluble in cold water, and soluble in hot water provided the quantity of water is more than 35 times that of the compound. It is easily soluble in water-alcohol mixture.

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