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HYDROXYNITRILES AS FLOTATION MODIFIERS

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This invention relates to improved flotation processes for mixed ores which contain several metallic values and require selective separations of their mineral components.

Mixed ores, such as lead-zinc ores, iron-bearing lead-zinc ores, copper-zinc ores, copper-iron ores, complex copper-lead-zinc ores and the like, present problems of selective separations. Differential flotation processes have been developed in which one or more of the minerals, usually zinc and/or iron, are depressed so that a concentrate of the remaining metal or metals can be obtained, whereupon the zinc can be reactivated with reagents such as copper sulfate and the like and then floated as a concentrate. The standard depressant is sodium cyanide, and with many ores excellent results can be obtained, provided a sufficient and controlled amount of sodium cyanide is used.

Commercially useful as the selective flotation processes using sodium or other soluble cyanides have proven to be, they are by no means perfect. For one thing the cost of cyanide adds to the processing cost and further, with some ores, the completeness of the selective depression is not as perfect as could be desired. This latter factor is of considerable importance especially when the mineral to be depressed is present in fairly large concentration or at least in concentration comparable to that of the desired mineral. Also in the latter case with lean ores, it is difficult to obtain high-grade concentrates. Contamination of each concentrate with other minerals is, therefore, still a problem which varies in seriousness from ore to ore.

According to the present invention, certain organic nitriles, namely alpha-hydroxynitriles, have been found to give results as depressants which are as good as sodium cyanide; in many cases better; and which, in the depression of certain minerals, such as iron minerals, can be used in smaller quantities than is practical with sodium cyanide. While the invention is not limited to any particular alpha-hydroxynitrile, we have found that lactonitrile, and particularly crude lactonitrile, is extremely effective. The latter, which is obtainable as a brownish black liquid by-product in the manufacture of acrylonitrile, can be obtained at a very low price. It is an advantage of the present invention that there is no significant difference between a pure alpha-hydroxynitrile and crude material such as the very dirty, crude lactonitrile referred to above. Why the extensive impurities, amounting to 15% and more in the case of the crude lactonitrile, do not interfere with its depressant action is not known, but the possibility of using very crude and dirty material is a distinct advantage of the present invention and such crude by-product material constitutes the preferred reagents to be used.

The alpha-hydroxynitriles are organic liquids and thus can be fed readily either directly or in water solutions to conditioning or flotation operations. With the solid depressants formerly used, solution is an unavoidable prerequisite for uniformity of feeding. This added flexibility is an advantage of the present invention.

The exact mechanism of the depressing action of the alpha-hydroxynitriles is not fully known. It is not merely a question of the presence of a CN group because other nitriles, even other hydroxynitriles, either have no depressing action whatever or depress so slightly as to be of no commercial significance. We are therefore not dealing purely with a question of using any compound which has a CN group.

In the well-known selective flotation processes using various soluble cyanides of inorganic nature, it is customary to rate consumption on the basis of sodium cyanide equivalent; that is, the weight of a particular cyanide used which has the same weight of cyanide as a given standard weight of sodium cyanide. Throughout the present specification this conventional nomenclature will be used. It is an advantage of the present invention that the froth flotation processes are in no way changed by using the alpha-hydroxynitriles of the present invention. The same techniques can be employed as have been used in the past with sodium cyanide as a depressant. It is therefore unnecessary for the practical operating man to learn any new techniques. These flotation conditions will vary, of course, from ore to ore, each ore having optimum requirements for the type and amount of flotation promoter used, frother, flotation time, pH, etc., and in the following illustrative examples in each case the flotation conditions will be used which have been found to be optimum for the operation when sodium cyanide is used. All examples are carried out in laboratory-type Fagergren flotation machine using 600 g. charges at standard flotation pulp density of about 25% solids. The standard laboratory procedure used in the examples is highly reliable and is applicable to plant practice.

Example 1

The tests in this example were carried out with pyrite only to show relative depressing powers with different amounts of reagent.

A 90–10 silica-pyrite mixture was ground to −65 mesh with 1 lb./ton of lime and successive portions after dilution to flotation pulp density were floated in a Fagergren flotation machine at a pH of 9 with 0.1 lb./ton sodium ethyl xanthate as the promoter and 0.03 lb./ton polypropylene glycol as the frother. The flotation was effected for five minutes and the percentage of pyrite depressed determined. Varying amounts of sodium cyanide and lactonitrile were used in the different tests and one was run as a blank with the addition of no depressant. The results appear in the following table.

Lb./ton NaCN equiv.	Percent pyrite depressed	
	NaCN	Lactonitrile
None	4.4	4.4
0.01	None	45.0
0.015	8.5	80.0
0.03	83.0	82.7

It will be noted that the lactonitrile is a very much more active depressant for pyrite than is sodium cyanide. At 0.01 lb./ton NaCN equivalent there was no depression with sodium cyanide and quite substantial depression with lactonitrile which reached 80% at an amount (0.015 lb./ton) in which the NaCN gave no significantly useful results. More than twice as much NaCN had to be added before comparable depressions were obtained.

Example 2

This example gives tests on the depression of pyrrhotite. The precedure of Example 1 was followed except that a 90–10 silica-pyrrhotite mixture was used. The amount of lime was 1.3 lb./ton, and the pH was 9.4. Otherwise, the conditions were the same. The lactonitrile used was crude lactonitrile and the sodium cyanide, standard commercial white sodium cyanide of good purity. The results appear in the following table.

Lb./ton NaCN equiv.	Percent pyrrhotite depressed	
	NaCN	Lactonitrile
None	49.0	49.0
0.010	-------	72.0
0.015	65.0	73.0
0.05	74.8	80.7

It will be noticed that lactonitrile showed very substantial depression in concentrations where sodium cyanide had no effectiveness at all and even at fairly high concentrations, the results were significantly better with the crude lactonitrile.

Example 3

This example used a test ore which is the same as in Example 1, the flotation being effected at 22% solids. On successive portions different nitriles were used and the results appear in the following table.

Compound tested as depressant:	Percentage of pyrite depressed
Lactonitrile (pure)-$CH_3CH(OH)CN$	79.4
By-product lactonitrile (85%)-$CH_3CH(OH)CN$	79.6
Glycolonitrile-$H_2C(OH)CN$	68.4
Acetone cyanohydrin-$(CH_3)_2C(OH)CN$	79.5
Benzaldehyde cyanohydrin-$C_6H_5CH(OH)CN$	67.5
Ethylene cyanohydrin-$CH_2OH—CH_2CN$	5.0
Acrylonitrile-$CH_2{=}CHCN$	5.0
Acetonitrile-CH_3CN	None
Succinonitrile-$NCCH_2CH_2CN$	None
None added	None

It will be noted that most nitriles showed either no depression at all or a negligible amount, whereas the alpha-hydroxynitriles gave excellent depression. A particularly significant comparison is between ethylene cyanohydrin and lactonitrile, the latter being almost sixteen times as effective.

Example 4

A Missouri lead-zinc ore containing a small amount of pyrite and carbonate gangue minerals was ground to 65 mesh, diluted to about 20% solids, conditioned for two minutes with 0.12 lb./ton sodium silicate and for three minutes longer with 0.09 lb./ton of sodium cyanide, followed by another two minutes with 0.03 lb./ton sodium ethyl xanthate and for one minute longer with a 0.12 lb./ton pine oil. The mixture was then floated for four minutes to obtain a lead concentrate.

The resulting tailing was conditioned for two minutes with 0.43 lb./ton soda ash and for a further four minutes with 1.0 lb./ton copper sulfate pentahydrate, followed by two minutes longer with 0.2 lb./ton technical sodium diethyldithiophosphate and for one minute longer with 0.07 lb./ton pine oil. The flotation was then carried on for four minutes to produce a zinc concentrate.

The procedure above was repeated, replacing the sodium cyanide with an equivalent amount of lactonitrile, and a third test was run again under the same conditions but with no depressant at all. The metallurgical results appear in the following table.

	Depressant used		
	NaCN	Lacto-nitrile	None
Lead concentrate:			
Assay, percent Pb	50.8	57.3	44.4
Assay, percent ZN	3.2	2.2	3.8
Recovery, percent Pb	88.0	88.2	89.5
Recovery, percent Zn	1.0	0.6	1.3
Zinc concentrate:			
Assay, percent Zn	53.3	55.1	53.1
Assay, percent Pb	0.2	0.3	0.2
Recovery, percent Zn	97.3	98.1	95.2
Recovery, percent Pb	3.5	1.8	1.1

It will be apparent that while substantial depression was effected with sodium cyanide, the results with lactonitrile were definitely better; and in the lead concentrate, the lead was recovered with only 0.6 as much overall zinc contaminant. Similarly, the lactonitrile permitted a slightly better recovery of zinc in the zinc concentrate with only about half as much lead.

Example 5

A pyrite-bearing lead-zinc ore from northern New York analyzing 0.35% Pb, 9.1% Zn and 9.3% Fe was ground to −65 mesh at 65% solids, diluted to about 22% solids, conditioned with 0.06 lb./ton sodium cyanide for three minutes and for two minutes longer with 0.06 lb./ton technical dicresyldithiophosphoric acid containing about 6% diphenyl thiourea. The pulp was then floated for four minutes to produce a lead concentrate, the pH being 7.4.

The tailings were then conditioned for two minutes with 4.0 lb./ton of lime to produce a pH of 10.9, then for three minutes longer with 1.3 lb./ton copper sulfate pentahydrate, followed by two minutes with 0.13 lb./ton sodium ethyl xanthate and one minute with 0.16 lb./ton pine oil as a frother. Flotation as in the preceding examples was for four minutes to produce a zinc concentrate.

The procedure was repeated twice with equivalent amounts of lactonitrile and of acetone cyanohydrin in place of the sodium cyanide. The lactonitrile was a by-product from the manufacture of acrylonitrile and contained about 85% of lactonitrile, the product being dirty and brownish black in color. Finally a control float was made under the same conditions with no depressant. The results of the tests appear in the following table.

	Depressant used			
	None	NaCN	Lacto-nitrile	Acetone cyano-hydrin
Lead concentrate:				
Assay, Percent Pb	3.77	3.31	4.02	4.09
Assay, Percent Zn	3.04	2.18	2.00	1.98
Recovery, Percent Pb	94.5	93.5	95.4	95.6
Recovery, Percent Zn	2.9	2.3	1.8	1.8
Zinc concentrate:				
Assay, Percent Pb	0.06	0.09	0.06	0.07
Assay, Percent Zn	43.3	52.3	53.7	53.8
Assay, Percent Fe	12.1	6.8	6.2	6.1
Recovery, Percent Pb	3.4	4.3	4.6	4.4
Recovery, Percent Zn	96.4	94.4	94.4	94.5

It will be noted that a substantially better grade lead concentrate was obtained with the nitriles than with sodium cyanide and it was contaminated with less zinc. Recoveries were also somewhat better. In the case of the zinc concentrate again the grade was a little better for the nitriles and the contamination with iron somewhat less.

Example 6

A complex lead-zinc ore containing 5% lead and 5.6% zinc from Mexico also contained 6.3% iron and some silver and copper. It was ground at 60% solids to −65 mesh with 1.0 lb./ton of sodium cyanide, 1.0 lb./ton zinc hydrosulfite, 1.0 lb./ton lime and 0.04 lb./ton of a 1:1 mixture of sodium mercaptobenzothiazole and sodium di(secondary butyl)dithiophosphate. After conditioning, the mixture was diluted to 20% solids and conditioned with 0.02 lb./ton of ammonium dicresyldithiophosphate and 0.02 lb./ton pine oil. Flotation was for three minutes to remove a lead concentrate which was cleaned by refloating with a 0.25 lb./ton zinc hydrosulfite and 0.25 lb./ton sodium cyanide.

The tailings from the lead rougher flotation operation were conditioned for five minutes with 2.0 lb./ton lime, 1.5 lb./ton copper sulfate penthahydrate and 0.1 lb./ton of a 1:1 mixture of sodium mercaptobenzothiazole and sodium di(secondary butyl)dithiophosphate. Thereupon the mixture was floated to remove a zinc concentrate which was cleaned by refloating with 0.5 lb./ton lime and 0.05 lb./ton of the mercaptobenzothiazole-dithiophosphate mixture together with 0.04 lb./ton of pine oil as a frother.

A second test was run substituting an equivalent amount of crude lactonitrile for the sodium cyanide. The results appear in the following table.

	Depressant used	
	NaCN	Lacto-nitrile
Lead concentrate:		
Assay, Percent Pb	56.6	57.0
Assay, Percent Zn	7.0	6.6
Assay, Percent Fe	7.2	7.2
Recovery, Percent Pb	83.1	86.1
Recovery, Percent Zn	9.3	8.4
Zinc concentrate:		
Assay, Percent Zn	42.7	46.3
Assay, Percent Pb	4.3	2.5
Assay, Percent Fe	8.0	8.0
Recovery, Percent Zn	76.0	79.0
Recovery, Percent Pb	12.5	4.5

It will be noted that the lead concentrate was of slightly higher grade with the lactonitrile, showing less zinc contaminant and the recovery of lead was also somewhat higher. The grade of the zinc concentrate showed substantial improvement with the lactonitrile. The recovery of zinc was substantially better. Overall contamination of lead was almost 2½ times as great with the sodium cyanide as with the lactonitrile.

Example 7

An iron-bearing copper ore from Utah containing 0.9% Cu and 2.3% iron was ground to 60% solids 65 mesh with 2.6 lb./ton lime and 0.3 lb./ton sodium cyanide. The mixture was then diluted to 22% solids, conditioned for a minute with 0.03 lb./ton technical dicresyldithiophosphoric acid as promoter and then for one minute with 0.2 lb./ton of a 1:1 cresylic acid-fuel oil mixture as a frothing agent. Flotation was for five minutes to remove a copper concentrate.

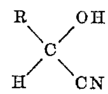
The test was repeated, substituting by-product lactonitrile in equivalent amount for the sodium cyanide. The results of the tests appear in the following table.

	Depressant used	
	NaCN	Lacto-nitrile
Copper concentrate:		
Assay, Percent Cu	23.9	24.2
Assay, Percent Fe	15.6	15.6
Recovery, Percent Cu	91.3	92.3
Tailings: Assay, Percent Cu	0.11	0.06

It will be noted that the lactonitrile gave slightly higher assay of copper with a somewhat increased recovery. This test illustrates that the nitriles are fully as good depressants as sodium cyanide, even on an ore which is specially suited for sodium cyanide repressant. As has been pointed out above, the improvements obtained with the nitriles will vary from ore to ore.

We claim:

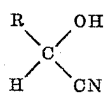
1. A method of selective froth flotation of ores containing depressable minerals selected from the group of zinc and iron minerals which comprises effecting flotation in the presence of an effective amount of an alpha-hydroxynitrile selected from the group consisting of acetone cyanohydrin and those represented by the formula



wherein R is selected from the group consisting of hydrogen, methyl and phenyl whereby a concentrate is obtained relatively poor in the depressed minerals.

2. A flotation process according to claim 1 in which the alpha-hydroxynitrile is lactonitrile.

3. A process of selective froth flotation of an ore containing zinc minerals and a mineral selected from the group consisting of lead minerals and copper minerals which comprises effecting froth flotation in the presence of an amount of an alpha-hydroxynitrile selected from the group consisting of acetone cyanohydrin and those represented by the formula



wherein R is selected from the group consisting of hydrogen, methyl and phenyl to produce a concentrate of the lead or copper relatively poor in zinc minerals, subjecting the tailings of the flotation operation to activation of the zinc minerals, refloating to produce a zinc concentrate relatively high in zinc and relatively low in lead or copper.

4. A flotation process according to claim 3 in which the ore is a lead-zinc ore.

5. A process according to claim 4 in which the alpha-hydroxynitrile is lactonitrile.

6. A process according to claim 3 in which the alpha-hydroxynitrile is lactonitrile.

7. A process according to claim 3 in which the ore is a copper-iron ore.

8. A process according to claim 7 in which the alpha-hydroxynitrile is lactonitrile.

9. A process according to claim 4 in which the nitrile is acetone cyanohydrin.

10. A process according to claim 1 in which the nitrile is acetone cyanohydrin.

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