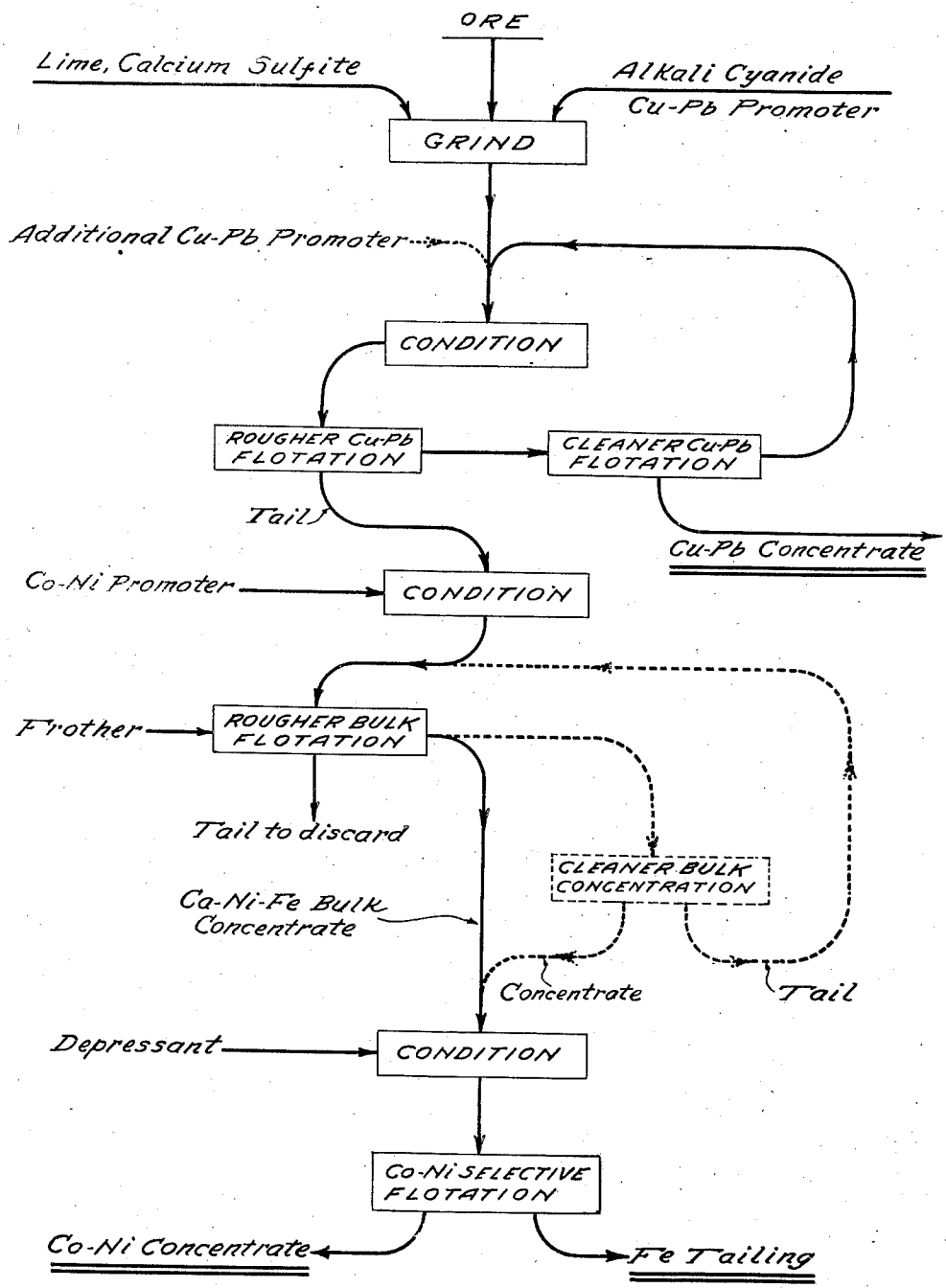
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TREATMENT OF ORES CONTAINING COBALT AND NICKEL

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TREATMENT OF ORES CONTAINING COBALT AND NICKEL

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The present invention relates to the beneficiation of cobalt-nickel ores. More particularly, the invention relates to an improved method of beneficiating cobalt and nickel sulfide ores by froth flotation using selective depressants for the pyrite and/or marcasite gangue which is frequently found in intimate association therewith.

Low-grade sulfide ores of cobalt and nickel, particularly those containing linnaeite and the complex cobalt-nickel sulfide, siegenite, are frequently found to contain other sulfide minerals such as chalcopyrite and galena in a gangue of pyrite, marcasite, calcite and quartz. Commonly, the nickel-cobalt content of these ores is low, often being as little as 0.5 to 2% or less, of the nickel and cobalt sulfides. To be commercially useful as a source of the metals, a concentrate containing at least 5% of cobalt in the combined cobalt-nickel product is desirable. The problem, therefore, involves two factors, the removal of gangue and the reduction of the iron content.

Beneficiation by ordinary concentrating methods dependent upon surface conditions, such as froth flotation, is extremely difficult. Not only is there an intimate association of the minerals, but the commonly-found pyrite and marcasite gangue, and the cobalt and nickel minerals are similarly affected by surface-conditioning reagents. In general, they exhibit similar reactions toward standard promoters, depressants, dispersants and the like. Consequently, an effective concentration of the nickel and cobalt minerals has been difficult, if not impractical, to obtain. Nevertheless, because these ores represent a principal proportion of the available domestic source of both nickel and cobalt, the importance of a practicable method of concentrating the cobalt-nickel content is quite apparent.

It is, therefore, the principal object of the present invention to develop a selective process of concentration by froth flotation whereby the cobalt and nickel values may be effectively separated from the pyrite and marcasite gangue. It is also an object of this invention to develop a process which enables the production of a concentrate which when sintered, will be sufficiently high in cobalt-nickel and sufficiently low in iron to be commercially acceptable.

In general, the first step in accomplishing the principal objects of the present invention is to remove a copper-lead concentrate as these minerals are present in appreciable amounts. The residue, or alternatively a bulk cobalt-nickel-iron concentrate obtained therefrom by flotation, is conditioned with the novel depressants of the present invention and subjected to a selective flotation of the cobalt-nickel sulfides to produce a concentrate richer in cobalt and nickel, and having the iron content minimized.

Surprisingly, it has been found that the alkali ferricyanides and/or ferrocyanides in combination with a suitable oxidizing agent act as selective depressants for pyrite and marcasite under operating conditions. The selective action of this reagent combination is most striking when it is considered that the principal gangue constituents are iron sulfide minerals which ordinarily exhibit substantially the same flotation characteristics as do the cobalt and nickel minerals, and that the materials being used as depressants include alkali-iron complexes. Further, alkali cyanides which have been commonly used as reagents in lead-copper flotation do not produce any noticeable benefit when used in the cobalt-nickel concentration.

The practice of the present invention may be readily understood by reference to the accompanying drawing which diagrammatically illustrates the steps in one preferred method of carrying out the process.

In general, the process of the present invention has the distinct advantage of being easily carried out. However, in the first stage of the process, namely the lead-copper float, several considerations have been found to be important in connection with the desired object of keeping the cobalt-nickel minerals out of the copper-lead concentrate. Preferably, the circuit should be alkaline. According to the present invention, a pH of about 9 to 10 has been found to be practically suitable, although this may be varied somewhat in either direction as other conditions may require. The alkaline materials used may be quite widely varied. Use of caustic soda is not required. Both soda ash and such alkaline-earth metal hydroxides as hydrated lime or magnesia have been found to be perfectly acceptable. Lime, being more economical and, when used in optimum amount, apparently having some specific beneficial effect on the minerals, is perhaps preferable. Otherwise, the lead-copper flotation is not particularly unusual.

Excellent results have been obtained in this part of the process using as flotation reagents either the commercially available xanthate-type promoters or those of the dithiophosphate type such, for example, as the ammonium salt of dicresyl dithiophosphoric acid and the sodium salt of di-sec. butyl dithiophosphoric acid in conjunction with a suitable alkali or alkaline-earth metal.

Commercial black calcium cyanide is quite satisfactory so the more expensive alkali cyanides are not necessary. Also, the addition of a small amount of calcium sulfite has also been found to be helpful as an aid to selectivity in some cases.

It has been found most practical to add these reagents during the grinding which is necessary to unlock the intimately associated variety of minerals in the ore. If, however, it is so desired, the grinding can be carried out and the reagents subsequently added in a separate conditioning step. If this is done, it is preferable that the conditioning be done at high solids but the operation may be carried out either in the flotation machine or in a separate mixer. Preferably, a part of the promoter is added during grinding and the remainder conditioned with the pulp after transfer to the flotation machine. A frother is usually required during the lead-copper flotation. The commercially available mixed cresylic acids frothers have been found to work well. Other types such as certain of the mixed higher aliphatic alcohols, averaging about 7–8 carbon atoms, or pine oil may be used if so desired. They may be added as required in accordance with standard practice.

The procedure up to this point may be considered more or less as preparatory to the practice of the present invention which is found to be highly critical in many respects. The flotation is not particularly critical as to the promoter used or as to the frother used. Commercial xanthate promoters and higher aliphatic alcohol frothers were used in the development work but these may be replaced by equivalent reagents of similar properties when so desired.

The critical procedure is in the use of the selective depressant mixture which enables the production of good cobalt-nickel concentrates which are sufficiently low in iron to be commercially acceptable. As shown in the drawing, the tailings from the copper-lead rougher flotation circuit are conditioned with the chosen cobalt-nickel promoter and then subjected to flotation in the presence of a frother added during the flotation step in the flotation cell for the production of a bulk cobalt-nickel-iron sulfide concentrate. A gangue tailing is obtained which may be discarded. The bulk rougher concentrate, or a cleaned concentrate if a cleaner stage is used, is then conditioned with the depressants and subjected to a selective cobalt-nickel flotation which yields the desired concentrate. Either the bulk rougher or the selective cobalt-nickel flotation may be carried out in stages or in single operations in accordance with standard practice.

So far as the depressant mixture is concerned, it is found that two constituents are required, the first being a suitable alkali ferro- or ferricyanide and the second a suitable oxidizing agent. A number of available alkali ferro- and ferricyanides are available such as sodium or potassium ferricyanide, sodium potassium ferricyanide and sodium or potassium ferrocyanide. The ferrocyanides are usually cheaper and if necessary considerably more of them can be used without raising the total reagent cost. They are also usually much more readily available. Therefore, the ferrocyanides are perhaps preferable.

A number of oxidizing agents are available for the purpose. Of those tried, the best results were obtained using alkali dichromates and/or permanganates. Either may be used if so desired. The optimum results, however, are obtained using a mixture of dichromate and permanganate with the ferro- or ferricyanide. The effectiveness of this depressant mixture is particularly surprising when it is considered that none of the materials when used individually produce concentrations of cobalt and nickel which are either as high in cobalt or nickel or as low in iron as can be obtained using the mixture.

The invention will be more fully illustrated in conjunction with the following example which is meant to be illustrative only and not by way of limitation. All parts are in pounds per ton of ore treated unless otherwise noted. In the following examples various reagents are represented by the following symbols:

A=Sodium, potassium ferricyanide
B=Sodium ferrocyanide
C=$K_2Cr_2O_7$
D=$KMnO_4$

Example 1

A sample of low grade cobalt-nickel ore, assaying about 0.6% Co and 0.8% Ni, was ground for fifteen minutes at about 60% solids with a mixture of 1.0 part lime, 0.5 part calcium sulfite, 0.25 part commercial calcium cyanide and 0.04 part of a promoter comprising an ammonia neutralized mixture of thiocarbanilid and dicresyldithiophosphoric acid. After reduction to about 22% solids and conditioning for about one minute with 0.1 part of additional promoter, the pulp was floated for about four minutes to produce a rougher Cu-Pb concentrate. This concentrate was given a three minute float with 0.03 part of an alcoholic type frother to produce the cleaner Cu-Pb concentrate.

Example 2

A sample of tailings produced according to Example 1 was then broken up into a series of test samples which were successively treated to a two minute conditioning at flotation density with 0.1 part of a xanthate promoter and floated for five minutes with 0.03 part of an alcoholic frother. The resulting bulk concentrate from this treatment was then conditioned for about five minutes with the iron minerals depressant being tested and floated for about two minutes to produce the final Co-Ni-concentrate. Illustrative depressants used and their metallurgical results are shown in the following table:

Iron depressant				Assays—concentrate			Recovery (percent) in Co-Ni conc.		
A	B	C	D	Percent Co	Percent Ni	Percent Fe	Co	Ni	Fe
	None			4.92	6.50	30.30	59.34	58.34	30.54
0.5				5.54	7.94	30.12	58.30	59.27	29.27
1.0				5.36	7.54	31.25	58.99	59.23	30.78
	3.0			4.98	7.04	31.19	59.57	58.41	32.34
	0.25	0.75		5.16	7.22	31.01	68.99	62.37	36.05
0.5			0.1	8.20	11.50	26.11	56.33	56.41	14.53
	0.25	0.75	0.1	11.10	16.30	17.81	45.33	46.15	6.19

We claim:

1. In concentrating sulfide minerals of cobalt and nickel by froth flotation from an ore in which they are intimately associated with iron sulfide minerals, the improvement which comprises conditioning a pulp containing the cobalt-nickel sulfides with a selective collector for the cobalt and nickel minerals and with a selective depressant mixture for the iron sulfide minerals, said depressant mixture comprising at least one compound selected from the group consisting of the alkali ferricyanides and the alkali ferrocyanides and at least one oxidizing agent selected from the group consisting of the alkali permanganates and dichromates, subjecting the conditioned pulp to forth flotation and collecting the resultant froth concentrate.

2. A process according to claim 1 in which the selective depressant mixture comprises at least one compound selected from the group consisting of the alkali ferricyanides and the alkali ferrocyanides together with an alkali permanganate.

3. A process according to claim 1 in which the selective depressant mixture comprises at least one compound selected from the group consisting of the alkali ferricyanides and the alkali ferrocyanides together with an alkali dichromate.

4. A process according to claim 1 in which the selective depressant mixture comprises at least one compound selected from the group consisting of the alkali ferricyanides and the alkali ferrocyanides together with an alkali permanganate and an alkali dichromate.

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