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CONCENTRATING MANGANESE ORES

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My invention relates to improvements in the concentration of ores, minerals and the like by the flotation process, and particularly to improvements in the flotation of manganese ores.

The object of my invention, among other things, is to provide improved methods in froth flotation in which suitable substances, when added with other reagents which produce flotation of manganese ores, will render the operation more selective by depressing, retarding, or preventing the flotation of such impurities as are objectionable contaminants in the desired manganese concentrate.

I have discovered that tannin or tannic acid, or substances which contain tannin or tannic acid, or substances which are derived from tannic acid, when added to the flotation operation for the treatment of manganese ores produce a more selective flotation wherein the manganese minerals are more perfectly concentrated into richer and purer concentrate. The action of the tannin, or tannic acid, or products containing them, or products derived therefrom is to depress, retard, or prevent the flotation of impurities or objectionable matter into the froth concentrate wherein the manganese minerals concenetrate and are recovered therefrom.

As an illustration of the application of this process in which the flotation manganese concentrate was produced by actual milling of an oxide manganese ore with fish oil soap, crude oil, and kerosene as the only reagents used, the best concentrate obtainable, even after several recleaning operations, gave an average analysis of:

Example A

	Per cent
Manganese	43.0
Insoluble substances	12.7
Silica (SiO_2)	8.0
Ferric oxide (Fe_2O_3)	3.4
Alumina (Al_2O_3)	3.8
Sulfur	0.07
Phosphorus	0.09
Carbon dioxide (CO_2)	0.60
Manganese after sintering	50.7

Upon the introduction into the same mill flotation circuit of one-quarter pound of tannic acid per ton of head ore and with no other change in mill conditions or reagents added, there was promptly obtained a concentrate which gave an average analysis of:

Example B

	Per cent
Manganese	46.9
Insoluble substances	7.5
Silica	4.8
Ferric oxide	2.9
Alumina	2.7
Sulfur	0.06
Phosphorus	0.08
Carbon dioxide	0.05
Manganese after sintering	54.7

Furthermore, by taking mill concentrate as made in Example A and subjecting the same to a separate recleaning flotation operation wherein tannic acid, or a substance containing tannic acid was added, there was obtained a cleaned concentrate as shown in analysis of Example B and a reject or waste product which gave the following average analysis:

Example C

	Percent
Manganese	4.4
Insoluble substances	64.9
Silica	35.5
Ferric oxide	8.4
Alumina	14.7
Sulfur	0.16
Phosphorus	0.19
Carbon dioxide	6.10
Manganese after sintering	9.2

These illustrative examples are typical of the many forms of my invention, for upon examination it will be found that the introduction of tannin as herein described has increased the manganese content in the final concentrate and also in those substances rejected as a waste or valueless product containing the following objectionable chemical matter or impurities, such as insoluble substances or that portion of an ore which remains insoluble after treatment with nitro-hydrochloric acid and dehydration, silica,

iron oxides, alumina, total sulfur, phosphorus, carbon dioxide.

It is also evident that the results of my improved methods show small losses in manganese, and that a much less desirable grade of manganese concentrate, as shown in Example A, has been greatly improved into a very desirable grade of manganese concentrate as shown in Example B.

These differences are sufficient to have an exceptionally important and beneficial effect in the metallurgical and sales value of the final product.

Petrographical examination made of the waste product shown in analysis of Example C discloses that the undesired minerals which have been retarded or prevented from floating by the application of the reagents of this invention are: Quartz, pyroxene, feldspar, barite, pyrite, dolomite, apatite, kaolin, hematite and limonite.

This illustration is also very typical of the results obtained with the use of the following substances or reagents containing tannin, tannic acid, or are derivatives of tannic acid, such as, tannin, tannic acid, gallic acid, pyrogallic acid, metagallic acid, tannin extracts, both liquid and solid, infusions of plant barks, leaves, berries, galls, seeds and nuts, molasses, waste residues from sugar refineries, hide tanning compounds, animal dungs, such as rat, horse, cow, sheep and goat manures.

As an example as to the ways my invention may be practiced, the ore is first ground to such a degree of fineness as to detach from each other the intergrown minerals. The grinding is conducted in water and the finely ground mixture of ore and water, which is called a pulp, is delivered to a flotation machine where the pulp is agitated with finely divided air. Here frothing and collecting reagents are added, such as fish oil soap, crude oil, and kerosene.

Fish oil soap is used in amounts ranging from five to fifty pounds per ton of ore treated and hydrocarbons, such as crude oil and kerosene, in amounts ranging from one to thirty pounds per ton of ore. The respective amounts of these reagents depend on the character of the ore; both types of reagents are instrumental in causing the manganese minerals to attach themselves to air bubbles constantly rising to the surface of the pulp.

This procedure results in the production of a froth on the surface of the pulp and into this froth is found to collect, among other things, the desired manganese minerals of the ore where the same may be recovered by the removal of the froth.

When this procedure is followed, however, it is found that the manganese concentrate is contaminated or rendered impure with many impurities or objectionable minerals which have been mentioned. Any one or more of the tannin products which I have heretofore listed may now be added, either with the other frothing and collecting reagents, or separately in a cleaner operation wherein the froth concentrate is retreated.

The amounts of such tannin products so introduced are widely varied from 0.1 lb. to 1.0 lb. per ton of ore treated with a preferred range of from 0.25 lb. to 0.50 lb. The exact amount used will depend upon a number of variable factors such as the per cent of tannin contained in the reagent employed, the quantity of undesirable contaminants to be dropped, and the general conditions accompanying the particular flotation.

The reactions that occur with the introduction of these tannin products are somewhat involved and are not thoroughly understood. However, without limiting myself to any exact theory, I believe that fish oil soap, crude oil and kerosene produce a flocculation of the manganese minerals causing them to cling together as clots. While in this agglomerated state the manganese minerals are carried to the surface of the pulp on the froth or bubbles. Such flocculation of the manganese minerals is quite pronounced and so strong as to include mechanically considerable gangue in such clots. The tannin shows a reverse reaction in that upon addition of this substance a considerable weakening of the clots of manganese minerals is noted with a general dispersion of the pulp; the disentanglement of the gangue in such clots allows the gangue particles to drop out as the manganese clots rise to the surface of the froth. It would appear therefore that tannin acts as a dispersive agent causing the mineral clots to scatter or disperse in the ore pulp.

The resulting product is a superior grade of concentrate with metallurgical advantages hitherto not attained in producing manganese ore concentrations.

The specific process above described is given only by way of example and many modifications may be made therein without departing from my invention. For instance, the proportions of the frothing agents may be widely varied depending upon the character of the ore treated and the degree of frothing required. Furthermore different frothing agents may be employed in conjunction with the introduction of tannin products as given in the preceding description, but I prefer those flotation reagents which I have prescribed.

In the appended claims the terms "manganese ores" are intended to cover oxidized manganese ores as well as oxide manganese ores used in the example, and furthermore the term "tannin" as used in the claims is intended to cover tannic acid or substances containing tannin or tannic acid or derivatives thereof as I have hereinbefore described and

all tannin products so related thereto as to function in substantially the same manner. Likewise the term "gangue" as embodied in the claims is intended to cover the various objectionable chemical impurities and mineral insolubles I have mentioned which are retarded or prevented from floating by the use of the improved methods and reagents set forth in this disclosure.

Likewise the term "crude oil" as embodied in the claims is intended to cover various crude mineral or hydrocarbon oils, for example, crude petroleum.

I claim as my invention:—

1. The froth flotation of manganese ores while in the presence of tannin combined with a reagent combination of fish oil soap and hydrocarbon compounds.

2. The froth flotation of manganese ores while in the presence of tannin combined with a reagent combination of fish oil soap, crude hydrocarbon oil and kerosene.

3. A process of concentrating manganese ores which comprises adding to the ore pulp a reagent combination comprising fish oil soap and hydrocarbon compounds, and subjecting the resulting mixture in the presence of a dispersive reagent to a froth flotation operation.

4. A process of concentrating manganese ores which comprises adding to the ore pulp a reagent combination comprising fish oil soap, crude hydrocarbon oil and kerosene, and subjecting the resulting mixture in the presence of a dispersive reagent to a froth flotation operation.

5. A process of concentrating manganese ores which comprises adding to the ore pulp a reagent combination comprising fish oil soap and hydrocarbon compounds, and subjecting the resulting mixture in the presence of tannin to a froth flotation operation.

6. A process of concentrating manganese ores which comprises adding to the ore pulp a reagent combination comprising fish oil soap, crude hydrocarbon oil and kerosene, and subjecting the resulting mixture in the presence of tannin to a froth flotation operation.

7. A new flotation reagent for use in concentrating manganese ores comprising fish oil soap and hydrocarbon compounds combined with tannin.

8. A new flotation reagent for use in concentrating manganese ores comprising fish oil soap, crude hydrocarbon oil and kerosene combined with tannin.

9. In a process for concentrating manganese ores by froth flotation, the step which consists in subjecting the ore pulp to froth flotation with water soluble fatty acid compounds and hydrocarbon compounds while adding tannin to the ore pulp during said froth flotation.

10. In a process for concentrating manganese ores by froth flotation, the step which consists in subjecting the ore pulp to froth flotation with water soluble fatty acid compounds and hydrocarbon compounds while adding tannin to the ore pulp during said froth flotation and prior to concentration.

11. In a process for concentrating oxide manganese ores by froth flotation, the steps which comprise subjecting the ore pulp to a flotation operation with a frothing reagent including water soluble fatty acid compounds and hydrocarbon compounds and adding thereto tannin during said froth flotation.

12. In a process for concentrating oxide manganese ores by flotation, the steps which comprise subjecting the ore pulp to a flotation operation with a reagent combination consisting of fish oil soap, crude hydrocarbon oil and kerosene and adding thereto tannin during flotation.

13. A process for concentrating oxide manganese ores which comprises subjecting the ore in the form of pulp to a floating operation with a reagent combination of fish oil soap and hydrocarbon compounds, and adding tannin to the resulting mixture during flotation to retard the flotation of gangue in the concentrate.

14. A process for concentrating oxide manganese ores which comprises subjecting the ore in the form of pulp to a floating operation with a reagent combination of fish oil soap, crude hydrocarbon oil and kerosene, and adding tannin to the resulting mixture during flotation to retard the flotation of gangue in the concentrate.

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