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DIGESTION IN SULPHURIC ACID OF TITANIFEROUS ORE CONCENTRATES CONTAINING ORGANIC FLOTATION AGENT

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This invention relates to the attack of ores. More specifically, it relates to the attack of titaniferous ores such as ilmenite with concentrated sulfuric acid. This invention also relates to the dissolution in strong sulfuric acid of ores containing small amounts of flotation agents.

In the preparation of ores and minerals for metallurgical treatment it is common practice to remove gangue and foreign material, and concentrate the desired fraction of the ore by any of numerous known procedures. Among the procedures that have been used may be mentioned magnetic separation, wet and dry classification, and flotation concentration. It is with ores that have been concentrated by flotation methods that the present invention is particularly concerned.

The flotation agents used in the flotation concentration of ores and minerals are generally surface-active organic compounds capable of preferentially wetting a desired fraction of the ore, which may be, for example, fatty acids such as stearic or oleic acid, soaps and similar types of compounds, usually in conjunction with petroleum agents, such as fuel oil and the like. These compounds, when used in the flotation process, are strongly adsorbed on or absorbed by the ore or possibly react with it to some extent so that it is exceedingly difficult or impossible to remove the last traces of organic flotation agents from the "float" fraction of the ore by normal washing methods and the like.

When ore concentrates containing residual amounts of such flotation agents are further treated by attacking them with strong sulfuric acid, difficulties in operation are frequently encountered by reason of changes in the character of the reaction resulting from the presence of these flotation agents. Such ores foam violently and sometimes uncontrollably and the difficulties which arise from the excessive foaming and frothing are caused by the flotation agents. In the dissolution of titaniferous ores such as ilmenite to produce titanium solutions useful in the preparation of titanium pigment for example, the "digestion" or attack of the ilmenite with concentrated sulfuric acid is ordinarily a vigorous, rapid reaction which may, however, be controlled by using suitable digestion equipment and appropriate techniques, both of which are well known to the art. When the ilmenite contains flotation agents the vigorous and copious foaming reaction frequently readers it uncontrollable and dangerous.

When excessive foaming takes place during the digestion reaction an appreciable economic loss is sustained because the foaming carries part of the reaction mixture out of the tank altogether, while an additional portion is removed from the heat of the reaction zone and does not react properly, much of the ore remaining entrapped in the foam and unattacked by the acid.

A severely foaming ore, moreover, will actually be extruded from the tank, and the large quantities of steam and gas evolved during the reaction carry entrained ore, acid and reaction products out through the tank stack. The hot, strongly corrosive froth endangers personnel

and may cause extensive damage to equipment and structural work in the area. Moreover, the violence of the foaming is unpredictable since the precise quantity of residual flotation agent present, and the consequent effects thereof, will vary from batch to batch.

This element of unpredictability renders it difficult or impossible to so vary the digestion conditions as to offset the effect of the flotation agent present. The digestion reaction must be sufficiently strong and vigorous to supply its own heat requirements, and therefore the reaction conditions cannot be excessively mild; on the other hand, reaction condition (acid concentration, acid/ore ratio, initial temperature of reactants, etc.) if so adjusted as to promote a normal vigorous reaction, may easily render the reaction altogether uncontrollable when flotation agents are present.

While this invention is here described with particular reference to the dissolution of ilmenite ore in concentrated sulfuric acid, it will be obviously that the invention is equally applicable to other reactive titaniferous ores as well as to any other flotation-concentrated ore which reacts exothermically with sulfuric acid.

Although foam-producing agents are most commonly introduced during the ore-dressing operations, by flotation processes, they may also occur in the ore for other reasons. For example, it has been suggested to spray outdoor ore piles with fuel oil or asphalt in order to cut down wind losses. These agents, which are similar to or identical with the fuel oils used as oily collectors in flotation processes, produce the same troublesome foaming at reaction as do the flotation agents used as such, and the process of the present invention is equally applicable to the prevention of foaming from this cause. Moreover, other but less common sources of contamination from fuel supplies or the like will produce the same troublesome foaming and may be effectively treated in the same way. The term "flotation agents" as used herein should therefore be construed to include materials such as asphalt and fuel oil, even when not actually used for flotation purposes.

An object of this invention, therefore, is to provide a method for rendering amenable to digestion in concentrated sulfuric acid an ore concentrate containing organic flotation agents. Another object is to provide a method for treating an ore concentrate which will overcome the tendency of residual flotation agents to render foaming at the digestion reaction violent and uncontrollable. A still further object is to provide an economical method for treatment of an ore concentrate containing organic flotation agents which will make possible a normal digestion procedure with good digestion efficiencies. An additional object is to provide such a method which produces from a titaniferous ore a reaction product suitable for the manufacture of high-grade titanium pigments and the like. These and other objects will become apparent from the following more complete description of the present invention.

In its broadest aspects this invention contemplates a method for treating an ore containing organic flotation agents which comprises adding to said ore a small amount of the monoglyceride of a saturated fatty acid, said acid containing from about 12 to about 20 carbon atoms. It has been found that when such a compound is added to the ore in appropriate amount, which is generally between 0.01% and 0.5%, preferably between 0.05% and 0.2% on an ore-weight basis, the flotation agents present are apparently rendered ineffective or their effect is offset so that the reaction proceeds in a normal vigorous but controllable manner entirely similar to the type of reaction to be expected from a similar ore not containing residual flotation agents.

Diglycerides and triglycerides, wherein 2 or 3 respectively of the hydroxyl groups of the glycerin molecule are esterified with fatty acids, while in some cases manifesting a degree of controlling action upon the digestion reaction, are in general not effective, especially when added in economically feasible amounts.

It is essential that the treating agents of this invention contain substantially only saturated alkyl groups since unsaturated groups, when present in substantial amounts greatly diminish or destroy entirely the ability of the treating agents to modify and control the course of the reaction, and moreover, actually aggravate the troublesome frothing and foaming encountered in ores which contain flotation agents.

The manner of addition of the agent to the ore appears to be unimportant providing it is distributed in the reaction mixture prior to the actual reaction. The degree of distribution also is not critical and the ordinary mixing employed during such digestion reactions appears to be sufficient to distribute the agent adequately through the reaction mass. The treating agent may, for example be added to the ore at any convenient stage prior to its introduction into the digestion vessel itself, or may be added to or dissolved in the sulfuric acid used for the attack of the ore.

The quantity of monoglyceride treating agent employed should ordinarily be from 0.1% to 0.2% of the weight of ore treated. The use of larger amounts of treating agent than those above specified is contemplated, but is ordinarily not economically justified. Smaller amounts than those given above will also in some cases be effective in controlling the foaming at reaction depending upon the amount of residual flotation agent present. The amounts of flotation agents present in the ore concentrate are generally extremely small. Normally, from 1 to 5 pounds of the flotation agents are employed per ton of ore in flotation methods. The amount present in the ore concentrate is ordinarily somewhat lower than the amount initially employed owing to partial elimination of the flotation agents during subsequent washing, drying, etc., but the major portion of the organic agents usually remains associated with the ore concentrate. Owing to the difficulty of analyzing the ore concentrate for minute amounts of residual flotation agents, and the utter impracticality of evaluating the agents in commercial-scale digestion equipment, which ordinarily employs from 10 to 20 tons of ore and from 15 to 30 tons of concentrated sulfuric acid for a single digestion batch, it has been found more practical and desirable to evaluate the reactive characteristics of the ore and the quantity of monoglyceride treatment agent required by means of an empirical test which is carried out as follows:

A 6" I. D. cylindrical tank 14" high and having ¼" steel walls and 5/16" steel plate bottom is provided with an iron sweep agitator having 5 sweeps, each 5½" x 9/16", and adjusted to operate at 200 R. P. M. 1500 grams of the ore to be tested are digested in this tank using the same relative concentration of acid, the same relative acid-to-ore ratio (based on 100% H_2SO_4) and the same relative quantity of set-off water as are to be employed in the full scale operation. Approximately half of the acid is first introduced into the tank, the ore is next added and washed down with the remainder of the acid to be used. The monoglyceride treating agent is then added, and finally the set-off water, which has the dual function of diluting the acid to proper strength for reaction and heating up the reaction mixture. The strongly exothermic reaction is initiated and maintained by allowing a Meker burner to play directly on the bottom of the tank throughout the reaction cycle. The course of the reaction is followed by visual observation and may be recognized as complete when copious evolution of steam has taken place and subsided, followed by the setting-up of the reaction mixture to a rigid, porous cake ordinarily from 15 to 20 minutes after the start of heating.

When subjected to this test, an ore which does not contain flotation agents will undergo a vigorous but controlled reaction, and the reaction mass will ordinarily stay at least 4" below the top of the tank. An ore which contains flotation agents but is treated with the monoglyceride treating agents of this invention will behave in a substantially identical manner. An ore which contains flotation agents and is not so treated will be seen to foam violently and in many cases will overflow and project itself out of the reaction tank. The effectiveness of the quantity of monoglyceride treating agent used is gauged by the height to which the reaction mass rises in the tank and the treatment is considered completely effective if the highest point reached by the reaction mass is 4 or more inches below the top of the tank. When such is the case, the quantity of treating agent employed is sufficient for the purpose and the same relative amount of treating agent, calculated on an ore weight basis, may be employed safely in large-scale operations.

The employment of the monoglyceride treating agents of this invention apparently has no other observable effect upon the course of the reaction than to offset the effect of the residual flotation agents; the reaction proceeds in substantially the same way as would be expected when using a similar ore not containing flotation agents, and efficiencies and recoveries are likewise unimpaired. Addition of the monoglyceride treating agents of this invention to ores which do not contain flotation agents has no noticeable effect.

In order to more clearly illustrate the process of this invention, the following examples are presented:

Example I

1500 grams of a titaniferous iron concentrate which had been prepared by treating a titaniferous iron ore in a flotation system with 1.5 pounds of fuel oil and 1.0 pound of oleic acid per ton of the unconcentrated feed ore, was tested according to the test method described above using 1370 milliliters of 93.2% sulfuric acid and 150 milliliters of water to give an acid strength at reaction of 88%. The reaction was vigorous accompanied by extremely violent foaming; and a considerable portion of the reaction mass flowed over the top of the tank. The test was repeated using 0.05% of glyceryl monostearate. The reaction in this case was accompanied by moderately violent foaming and the reaction mass rose to within about 2½" from the top of the tank. The test was again repeated using 0.10% of glyceryl monostearate and the reaction was observed to be normally vigorous but completely controlled; the reaction mass in this case never rising higher than about 5" from the top of the tank.

On the basis of these preliminary tests a large scale digestion was carried out using 10 tons of the same titaniferous iron ore concentrate, 16.8 tons of 93.2% sulfuric acid, 20 pounds of glyceryl monostearate and 1.1 tons of water. The reaction was rapid, complete and orderly, similar in all respects with reactions produced by ores not containing flotation agents. Over 95% of the titanium values in the treated ore concentrate were converted to soluble titanium sulfates.

Example II

Another ore concentrate was prepared by flotation concentration of a crude titaniferous ore using 1.0 pound of oleic acid and 1.5 pounds fuel oil for each ton of raw ore treated. Approximately half of the original ore feed (together with most of the flotation agents) was collected as the flotation concentrate. After subsequent washing and drying the flotation concentrate was tested as described in Example I using glyceryl monopalmitate as the treating agent.

On the basis of the preliminary tests another large scale digestion was made according to the procedure described in Example I, but using 0.10% of glyceryl mono-

palmitate as the treating agent. The character of the reaction obtained was substantially similar to that of Example I and resulted in the solubilization of over 95% of the titanium values.

Example III

An ore concentrate similar to that of Examples I and II was subjected to large scale digestion according to the procedure of Example I, using 0.20% of glyceryl monolaurate instead of the glyceryl monostearate as the monoglyceride treating agent. Again, a vigorous, orderly reaction took place resulting in solubilization of better than 95% of the titanium values.

Example IV

A sample of ore taken from an ore pile which had been sprayed with asphalt to reduce wind losses was tested in the laboratory and was found to have serious foaming characteristics. The amount of asphalt present in the ore was unknown, but laboratory tests as previously described indicated that foaming at digestion could be prevented by the addition of 0.025% of glyceryl monomyristate. This quantity was added to a plant-scale digestion batch, with results similar to those described in the previous examples.

As shown by the above examples, the present invention provides a method for treatment of ore concentrates containing organic flotation agents which treatment renders said concentrates amenable to dissolution in strong sulfuric acid according to the normal procedures used for such concentrates. The ordinary effect associated with the presence of organic flotation agents in the ore is to render the reaction with sulfuric acid uncontrollable; by means of the present invention this harmful and dangerous effect of organic flotation agents is prevented and the digestion proceeds as readily and conveniently as when using ore which does not contain flotation agents. The treatment process is simple and easy to employ.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto, and other modifications and variations may be employed within the scope of the following claims.

We claim:

1. A method for treatment of titaniferous ores containing organic flotation agents selected from the group consisting of anionic flotation agents, petroleum agents, and asphalt materials to render the same amenable to attack by concentrated sulfuric acid which comprises adding to said ore a small but effective amount of the monoglyceride of a saturated fatty acid containing from about 12 to about 20 carbon atoms.

2. In a method for dissolution in sulfuric acid of titaniferous ores containing organic flotation agents selected from the group consisting of anionic flotation agents, petroleum agents and asphalt materials, the improvement which comprises having present during said dissolution from 0.01 to 0.5%, based on the weight of said ore, of the monoglyceride of a saturated fatty acid containing from 12 to 20 carbon atoms.

3. Method according to claim 1 wherein said monoglyceride is glyceryl monostearate.

4. Method according to claim 1 wherein said monoglyceride is glyceryl monopalmitate.

5. Method according to claim 1 wherein said monoglyceride is glyceryl monomyristate.

6. Method according to claim 1 wherein said monoglyceride is glyceryl monolaurate.

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