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[54] **FLOTATION OF OXIDE MINERALS IN HOT PULP**

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[58] **Field of Search** 209/11, 4, 3, 166

[56] **References Cited**

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[57] **ABSTRACT**

A flotation method for concentrating iron-bearing oxide ores wherein the ore is both activated by a cation of a heavy metal and conditioned with a collector at a temperature within the range of 80°–100°C and floated at a temperature within the range of 50°–80°C.

4 Claims, No Drawings

FLOTATION OF OXIDE MINERALS IN HOT PULP

Improvement in a method of concentrating oxide ore minerals of heavy metals by flotation, where the activating agent used is an ion of a heavy metal, the collector a fatty acid and the gangue depressant a known depressing agent. The invention is characterized in that the method comprises an activation-conditioning step in a hot pulp, preferably within the temperature range of 80° – 100°C, and a succeeding flotation step preferably within the temperature range of 50° – 80°C. The method is particularly suitable for processing of such Fe^{++}-bearing oxide minerals as ilmenite, chromite, hematite and magnetite. By this method it is also possible to treat non-deslimed pulps so that both the selectivity of the process and the recovery of values are high.

It is already known that the flotation of iron bearing oxide minerals with fatty acids can be improved by activating them with an ion of a heavy metal (e.g. U.S. Pat. No. 2,861,687). Because the activation-conditioning step has been carried out by the conventional way in cold pulp, the results are, with reference to the explanatory part of the said patent, in many ways unsatisfactory:

- the amount of activator needed is high, sometimes even up to 8 kg/t of solids;
- the amount of collector needed is great, even up to 14 kg/t of solids;
- to improve the effect of the collector it is often necessary to emulsify the collector in water with the help of an emulgator, or the collector used is a water soluble soap of the said fatty acid;
- it has also been found useful to improve the effect of the collector by the addition of a non-polar oil e.g., fuel oil; the amounts of fuel oil used are again high, even up to 25 kg/t of solids;
- the activation-conditioning time is long and therefore the energy consumption in the said activation-conditioning step is high;
- the selectivity of the process and the recovery of the values has turned out to be poor particularly when floating non-deslimed pulps; desliming before the activation-conditioning step is therefore often necessary;
- because the amounts of reagents used are high the concentrate, and even the tailing contain substantial quantities of fatty acids and fuel oil, which may cause trouble during the further treatment of the products.

As a summary it can be stated that by carrying out the activationconditioning step in cold pulp, the application of the method as described in U.S. Pat. No. 2,861,687 is difficult, uneconomic, even impossible in practice.

It is also already known that flotation as a technical process can be carried out in hot pulp. The hot flotation process has been applied e.g. to the cleaning of sulphide concentrates, to the flotation of rare earth minerals and to the cleaning of hematite concentrates. These applications of hot flotation, however, have usually been concentrated to the cleaner flotation step of various primary concentrates and to the hot flotation step itself. The method described in this application, which comprises both the activation-conditioning step and the succeeding flotation step carried out in hot pulp, represents a different method for flotation of oxide ore minerals of heavy metals.

In my investigations of the flotation of oxide ore minerals of heavy metals I have found out that by carrying out the first phase of the process or the activation-conditioning step in hot pulp, preferably within the temperature range of 80° – 100 °C and at the same time in high pulp density, 60 – 75 % solids by weight, and the second phase of the process or the flotation step proper within the temperature range of 50° – 80 °C and by using hydrofluoric acid as the gangue depressant, it is possible to make concentrates of extremely high quality while the recovery of the values at the same time is high. In addition the following advantages can be gained:

- the amount of activator needed is small, usually less than 500 g/t of solids;
- the amount of collector needed is also small, usually less than 1 kg/t of solids;
- no fuel oil and no emulgator are needed;
- the activation-conditioning time is short;
- no desliming is needed;
- the tailing especially contains only minute amounts of fatty acids and no fuel oil at all so that the wastewaters from the process are exceptionally pure.

The following examples are presented to illustrate the method described. In some examples the test material used was a concentrate from magnetic separation or a synthetic ore, both of a narrow size fraction. In this way it was possible to minimize the disturbing factors and to make the experiments well analogous. Recoveries are based on the assays and weights of the products. Thus it was possible to avoid the errors due to variations in feed and due to material losses during flotation.

Copper sulphate used was a water solution of 100 mg $CuSO_4$ in 1 ml and hydrofluoric acid a water solution with one part of strong HF to 4 parts of water. The amounts of hydrofluoric acid used are expressed as strong acid.

EXAMPLE 1

The test material used was magnetite concentrate of size fraction 65/**200** mesh. A sample of 500 g of this material was mixed with water to form pulp containing 60 % solids by weight. The temperature of the pulp was raised up to 100 °C and 140 g/t of solids of linolenic acid was added as a collecting agent. The conditioning time was 5 minutes.

Hereafter the pulp was transferred into a Denver laboratory flotation unit and water was added to form a pulp containing 30 – 40 % solids by weight. The temperature of the pulp was 50° – 70 °C.

The concentrate was dried and weighed, whereafter the weight recovery of magnetite could be determined. The weight recovery was 90.4 %.

The same procedure was repeated except that the temperature during the conditioning and flotation step was 18 °C. The weight recovery was now 67.0 %.

The different between weight recoveries of flotations in hot and cold pulp was 23.4 % units.

EXAMPLE 2

The procedure of Example 1 was repeated except that the collector used was oleic acid 140 g/t of solids added to the conditioning step. The weight recovery in hot flotation was 90.6 % and that in a respective cold pulp 31.2 %. The difference between weight recoveries was now 59.4 % units.

EXAMPLE 3

The procedure of Example 1 was repeated except that the collector used was tall oil fatty acid, acid number 194, 140 g/t of solids. The weight recovery from a hot pulp was 91.0 % and 46.0 from a cold pulp.

The difference between weight recoveries was 45 % units.

EXAMPLE 4

The procedure of Example 1 was repeated except that the collector used was distilled tall oil 140 g/t of solids. The weight recovery from a hot pulp was 76.0 % and that from a cold pulp 11.4 %.

The difference between weight recoveries was 64.6 % units.

As the preceding examples show, pulp temperature has a great influence on the recovery values. It is also notable that the differences in results between various fatty acids become smaller if the flotation is carried out in hot pulp. As a result less refined products can be used without increasing the amount of collector unreasonably.

In the following examples is analysed the activation-conditioning step in hot pulp.

EXAMPLE 5

The test material used was a magnetite concentrate of size fraction 65/**200** mesh. A sample of 500 g of this material was mixed with water to form a pulp containing 60 % of solids by weight. The temperature of the pulp was raised up to 100 °C and 400 g/t of solids of copper sulphate was added as an activating agent. The activation period was 10 minutes. Hereafter 360 g/t of solids of a mixture containing 1 part of tall oil fatty acid (acid number 194) and 2 parts of fuel oil No. 2 was added as a collecting agent. The conditioning time was 10 minutes.

Hereafter the pulp was transferred into a Denver laboratory flotation unit and water was added to form a pulp containing 30 – 40 % solids by weight. The temperature of the pulp was 50 °– 70 °C.

The concentrate was dried and weighed whereafter the weight recovery of magnetite could be determined. The weight recovery was 99.4 %.

The same procedure was repeated without the activation step. The weight recovery was now 66.5 %.

The difference between weight recoveries with and without the activation step was 32.9 % units.

EXAMPLE 6

The procedure of example 5 was repeated except that the testmaterial used was a chromite concentrate of size fraction 65/**200** mesh. The amount of collector added was 180 g/t of solids.

The weight recovery with an activation step was 94.4 % and without 59.6 %.

The difference between weight recoveries was 34.8 % units.

EXAMPLE 7

The test material used was ilmenite flotation feed from the Otanmaki concentrator, Finland. It was a deslimed product having fineness of 25.6 % -200 mesh. It contained following minerals: ilmenite, hornblende, chlorite, micas, plagioclase and some magnetite, apatite and pyrite.

A sample of 500 g of this material was mixed with water to form a pulp containing 60 % solids by weight. The temperature of the pulp was raised up to 100 °C and 400 g/t of solids of copper sulphate was added as an activating agent. The activation period was 2 minutes. Hereafter 1300 g/t of solids of a mixture containing 1 part of tall oil fatty acid (acid number 194) and 2 parts of fuel oil No. 2 was added as a collecting agent. The conditioning time was 10 minutes.

Hereafter the pulp was transferred into the Denver laboratory flotation unit and water was added to form a pulp containing 30 – 40 % solids by weight. The temperature of the pulp was 50°– 70 °C. 400 g/t of solids of hydrofluoric acid was added as a depressant for gangue minerals.

The concentrate and the tailing were dried, weighed and analysed for TiO_2. The weight distribution between the concentrate and the tailing was 59.4 % and 40.6 %, resp.. The TiO_2 contents were 42.9 % and 5.9 %, resp., and the TiO_2 recoveries 91.4 % and 8.6 %, resp..

The procedure was repeated without the activation step. The weight distribution between the concentrate and the tailing was now 48.0 % and 52.0 %, resp.. The TiO_2 contents were 44.9 % and 14.0 %, resp., and the TiO_2 recoveries 74.7 % and 25.3 %, resp..

The difference between recoveries with and without an activation step was now 16.7 % units.

As the preceding examples show, activation carried out in a hot pulp remarkably improves the recovery of oxide ore minerals of heavy metals. Test were also made by carrying out the activation-conditioning step in a cold pulp but they did not succeed with any reasonable amounts of collector.

The following example shows the effect of hydrofluoric acid as a gangue depressant.

EXAMPLE 8

The test material used was a synthetic ore of size fraction 65/**200** mesh containing 50 % magnetite and 50 % qartzite by weight. A sample of 500 g of this material was mixed with water to form a pulp containing 60 % solids by weight. The temperature of the pulp was raised up to 100 °C. 200 g/t of solids of hydrofluoric acid was added as a depressant and the pulp was conditioned for 1 minute. Hereafter 360 g/t of solids of a mixture containing 1 part of tall oil fatty acid (acid number 194) and 2 parts of fuel oil No. 2 was added as a collecting agent. The condition time was 5 minutes.

Hereafter the pulp was transferred into a Denver laboratory flotation unit and water was added to form a pulp containing 30 – 40 % solids by weight. The temperature of the pulp was 50° – 70 °C.

The concentrate and the tailing were dried, weighed and analysed for Fe_3O_4 (with a Satmagan instrument). The weight distribution between the concentrate and the tailing was 49.6 % and 50.4 %, resp.. The Fe_3O_4 contents were 88.0 % and 11.3 %, resp., and the Fe_3O_4 recoveries 88.5 % and 11.5 %, resp..

The sme procedure was repeated without hydrofluoric acid as the gangue depressant. The weight distribution between the concentrate and the tailing was 77.9 % and 22.1 %, resp.. The Fe_3O_4 contents were 54.7 % and 22.1 %, resp., and the Fe_3O_4 recoveries 85.6 % and 14.4 %, resp..

As it is seen from the preceding results, the function of the collector has been fully unselective without the use of hydrofluoric acid as gangue depressant; the

Fe_3O_4 content of the concentrate has decreased 33.3 % units.

The following examples illustrate the applicability of the method described in this application to practical ores and also that the process can be carried out with a fatty acid alone as a collector. Furthermore it is shown that flotation of non-deslimed pulps is also possible.

EXAMPLE 9

The test material used was the same as in Example 7. A sample of 500 g of this material was mixed with water to form a pulp containing 60 – 75 % solids by weight. The temperature of the pulp was raised up to 100 °C and 440 g/t of solids of copper sulphate was added as an activating agent. The activation period was 10 minutes. Hereafter 400 g/t of solids of tall oil fatty acid (acid number 194) was added as a collecting agent. The conditioning time was 20 minutes. 220 g/t of solids of hydrofluoric acid was added as a depressant for gangue minerals and the conditioning period was continued for 10 minutes.

Hereafter the pulp was transferred into a Denver laboratory flotation unit and water was added to form a pulp containing 30 – 40 % solids by weight. The temperature of the pulp was 50 ° – 70 °C.

The rougher concentrate was refloated at a pulp temperature of 50 ° – 60 °C. 220 g/t of original solids of hydrofluoric acid was added as a depressant. The cleaner concentrate, the cleaner and rougher tailings were dried, weighed and analysed for TiO_2.

The weight distribution between the cleaner concentrate, cleaner tailing and rougher tailing was 59.6 %, 21.3 % and 19,1 %, resp.. The TiO_2 contents were 47.6 %, 6.3 % and 1.7 %, resp., and the TiO_2 recoveries 94.4 %, 4.4 % and 1.1 %, resp..

EXAMPLE 10

The test material used was the same as in Example 7, but not deslimed. The fineness of the material was 33.1 % -200 mesh.

The procedure of Example 9 was repeated except that the amount of the collector used was 990 g/t of solids. 480 g/t of solids of hydrofluoric acid was added to the conditioning step and 700 g/t of solids to the cleaner flotation step.

The weight distribution between the cleaner concentrate, cleaner tailing and rougher tailing was 35.6 %, 12.2 % and 52.1 %, resp.. The TiO_2 contents were 45.1 %, 3.5 % and 2.2 %, resp., and the TiO_2 recoveries 91.0 %, 2.4 % and 6.5, resp..

EXAMPLE 11

The test material used was the same as in Example 10; its fineness was now 42.1 % -200 mesh.

The procedure used in Example 10 was repeated except that the amount of hydrofluoric acid added to the cleaner flotation was 750 g/t of solids.

The weight distribution between the cleaner concentrate, cleaner tailing and rougher tailing was 35.3 %, 22.7 % and 42.0 %, resp.. The TiO_2 contents were 44.8 %, 2.7 % and 2.3 %, resp., and the TiO_2 recoveries 90.9 %, 3.5 % and 5.6 %, resp..

EXAMPLE 12

The test material used was the same as in Example 7, but not deslimed. The fineness of the material was 44.0 % -200 mesh.

The procedure of Example 9 was repeated except that the collector used was distilled tall oil 400 g/t of solids added simultaneously with copper sulphate. The activation-conditioning time was 20 minutes.

The weight distribution between the cleaner concentrate, cleaner tailing and rougher tailing was 39.0 %, 9.9 % and 51.1 %, resp.. The TiO_2 contents were 47.3 %, 9.1 % and 2.1 %, resp., and the TiO_2 recoveries 90.3 %, 4.4 % and 5.3 %, resp..

The same procedure was repeated except that the activator used was $FeSO_4$ 440 g/t of solids.

The weight distribution between the cleaner concentrate, cleaner tailing and rougher tailing was now 41.9 %, 12.6 % and 45.5 %, resp.. The TiO_2 contents were 47.2 %, 9.8 % and 1.9 %, resp., and the TiO_2 recoveries 90.4 %, 5.6 % and 4.0 %, resp..

The same procedure was repeated again except that no activator was used.

The weight distribution between the cleaner concentrate, cleaner tailing and rougher tailing was 25.8 %, 14.9 % and 59.2 %, resp.. The TiO_2 contents were 47.5 %, 31.2 % and 5.0 %, resp., and the TiO_2 recoveries 61.7 %, 23.4 % and 14.9 %, resp..

As it is seen from the preceding example, activation carried out in a hot pulp has again markedly improved the recovery of ilmenite. It is also notable that also other activators than copper sulphate are possible.

The Examples 9, 10, 11 and 12 were also repeated so that the activation-conditioning step and the succeeding flotation step were carried out in cold pulp. Tests were, however, not satisfactory with any reasonable amounts of reagents.

As can be seen from the preceding examples it is possible, by applying the method described in this application to the flotation of oxide ore minerals of heavy metals e.g., to ilmenite, to produce concentrates of exceptionally high quality while the recovery of the values at the same time is high. Also the quality of concentrates obtained with non-deslimed pulps corresponds to those obtained in daily practice while the recovery of the values is much higher than the conventional figures.

When examining the TiO_2 contents of the ilmenite concentrates it should be borne in mind that the mineralogical TiO_2 content of the Otanmaki ilmenite is at its highest about 49.5 % TiO_2. Certain concentrates (over 48.0 % tiO_2) made with this ore represent indeed a very high ilmenite content.

Besides that the amounts of reagents needed are small and that the activation-conditioning time is short, the flotation time itself is also short. The number of cleaner steps is limited, as already one cleaner flotation step is enough to give a final concentrate of high quality.

The examples presented here are by no means restricting regarding amounts of reagents and other similar variables which must individually be fitted to each ore.

The activator used for Fe^{++} bearing oxide minerals was Cu^{++}, but other activators are equally possible.

The collector used was tall oil, but other fatty acids can also be applied. It is, however, more profitable to use less refined products, because the differences in re-

sults with these and with pure fatty acids have turned out to be small.

It is obvious that the collector used can be a fatty acid soap soluble in water.

It was found out that the best depressant for gangue minerals was hydrofluoric acid because it depresses well all knids of silicate minerals. Other known agents, which are used to depress gangue minerals during flotation of oxide minerals, are similarly applicable.

The oxide ore minerals of heavy metals which may be used in this method may contain any heavy metal of atomic weight over 40.

The heavy metals the ions of which are used as activators in the method of this invention may be any of the metals of atomic weight over 40.

The fatty acids used in this method may be any of those saturated and unsaturated acids suitable for mineral processing, preferably having at least 15 C-atoms, e.g. the following acids may be used: palmitic, stearic, oleic, linoleic, linolenic. Also the mixtures of the fatty acids may be used.

Depressant for gangue minerals may also vary widely and the following depressants may e.g., be used: fluoric compounds, inorganic acid (H_2SO_4), alkalic silicates (water glass), alkalic phosphates, alkalic carbonates, organic depressants (CMC, starch and so on).

I claim:

1. In a method of concentrating ironbearing oxide minerals such as ilmenite, chromite, hematite and magnetite by flotation which includes the steps of: (a) activation wherein an activating agent of cations of the metals of atomic weight over 40 is added to the pulp for improving the effectiveness of the collector, (b) conditioning wherein the collector is added to the pulp, (c) depressing wherein a gangue depressant is added for depressing the gangue minerals, and (d) flotation for separating the concentrate of minerals, the improvement which comprises: performing both the activation and conditioning steps within the temperature range of 80°–100°C, and the flotation step within the temperature range of 50°–80°C.

2. The method as described in claim **1,** wherein the activation-conditioning steps are carried out in a non-deslimed pulp.

3. The method as described in claim **1,** wherein Cu^{++} is the activator.

4. The method as described in claim **1,** wherein hydrofluoric acid is the gangue depressant.

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