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3,014,585

FLOTATION PROCESS FOR CONCENTRATING NIOBIUM-BEARING MINERALS

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No Drawing. Filed June 18, 1959, Ser. No. 821,112
3 Claims. (Cl. 209—167)

This invention relates to processes of concentrating valuable minerals by froth flotation from ores containing such minerals, and is particularly applicable to those ores whose valuable minerals may be successfully floated after treatment with a combination of an amine or a diamine and a wetting agent or several amines or diamines and wetting agents.

Minerals included in this category comprise pyrochlore, betafite, perovskite, magnetite, sulphides, niocalite, biotite and other micas, diopside, monticellite, melilite, sphene, garnet, potash feldspar, and nephelite. All or most of these minerals are usually found in association with alkaline rocks in which niobium minerals are present. Minerals not so included comprise calcite, dolomite and apatite.

In copending application, Serial No. 759,768, filed September 8, 1958, Herbert G. Burks, now Patent 2,951,585, there is described a flotation process in which a combination of an amine and a wetting agent, one or more diamines and a wetting agent or a combination of amine, diamine or diamines and a wetting agent is used to effect the separation of several minerals including pyrochlore from calcite and apatite. The flotation reagent is defined in Patent 2,951,585 as selected from the group consisting of monoamines and diamines containing 14 to 22 carbon atoms in the molecule. This process is quite satisfactory in the treating of ores of carbonatite nature where there is a minimum of ferromagnesian minerals such as pyroxenes and amphiboles. When applied to ores from certain North American occurrences results are not so satisfactory since the reagent combination tends to float the ferromagnesian minerals along with pyrochlore thereby reducing the amount and grade of the desired product.

It is an object of this invention to provide an improved process for the flotation of niobium-bearing minerals from alkaline ores wherein the flotation of said minerals is enhanced and the amount of waste floated is decreased.

It has now been found that, in the flotation of niobium-bearing minerals from alkaline ores utilizing as a collector one or more amines or diamines, when a modifying agent comprising a water-soluble bicarbonate is present in the flotation solution, a surprisingly and significantly higher recovery and better grade of product is obtained.

Both the anionic and cationic portions of the bicarbonates in accordance with the invention have a direct effect. The bicarbonate ion, when present in the concentrations used in primary flotation, has a buffering effect. During the treatment of some 80 tons of rock, as will presently appear, the pH is steady at 8.0 to 8.1. Maintenance of such a pH would therefore not be capable of making a separation between pyrochlore, perovskite, mica, and the like on the one hand and calcite, dolomite and apatite on the other. In other words, it is not to be supposed that if a pH of 8.0 to 8.1 were maintained with any other reagent the same separation would result. The reagent combination has a cationic effect, i.e., the active collector-coating-forming ions are positive. This means that they attach to negative bonds on the minerals surfaces, not to positive charges. Hence, there can be no attachment of a cationic reagent to calcium or magnesium since they are mutually repellent. The bicarbonate ion, however, is negative and can compete for surface positions by attachment to calcium and magnesium. Minerals having a bicarbonate coating are not floatable. Attachment of bicarbonate to calcium is due, of course,

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to the low solubility of calcium carbonate. If, for instance, a sulphate were used instead of a bicarbonate it appears that due to the lower solubility of calcium sulphate all calcium minerals would be covered with a sulphate coating and would not float. This would depress pyrochlore and perovskite and thus defeat the purpose of the treatment. A full carbonate behaves as if it were between the bicarbonate and the sulphate in effect because carbonate is in equilibrium with the bicarbonate.

The following table gives particulars of solubilities of typical bicarbonates:

TABLE I

Bicarbonate	Solubility in Water (lbs. per ton)	Atmosphere (at 20° C.)
1. (a) Hydrogen (Carbonic Acid) -----	4.76	CO ₂ .
(b) Hydrogen -----	0.0022	Air.
2. Calcium -----	3.32	Air.
3. Sodium -----	96	Air.
4. Ammonium -----	210	Air.
5. Potassium -----	249	Air.

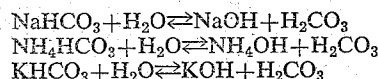
It will be observed that the concentration of bicarbonate from carbon dioxide dissolved in water exposed to air is too small to be effective.

Calcium bicarbonate has a low solubility and, moreover, while it can have a decided effect on anionic collectors, it has very little effect on cationic collectors such as are employed in the flotation process of the present invention. Normally, surface waters are not saturated with calcium bicarbonate. For instance, raw Ottawa River water contains about 0.17 pound per ton bicarbonate calculated as sodium bicarbonate. Thus, the maximum to be expected as calcium bicarbonate would be of the same order and this is too small to have any beneficial action.

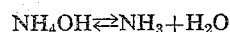
The useful bicarbonates for the purpose of the present invention may be defined as those having a solubility in water of at least 50 pounds per ton and use of the expression "water-soluble bicarbonates" in this specification and claims means those bicarbonates having such a solubility factor.

It will be observed that the bicarbonates of sodium, ammonium and potassium come within this definition of useful bicarbonates. The bicarbonates of cesium, lithium and rubidium are also water-soluble bicarbonates within the meaning of the present invention. However, since the latter group of bicarbonates are of a costly nature, the preferred bicarbonates are those of sodium, ammonium and potassium.

Of the three preferred bicarbonates, two are relatively stable in a flotation pulp solution. However, all three combine with water to some extent as follows:



Since NaOH and KOH are stable in solution the reactions to the right in the first and third equations soon cease. However, with ammonium hydroxide there is a further decomposition:



Ammonia, being a gas, eventually bubbles through the flotation pulp solution to the surface and thence to the air. There is, therefore, a slow but steady loss of bicarbonate from the solution when ammonium bicarbonate is used and at all times there is an odor of ammonia about the flotation cells.

It has been observed that potassium bicarbonate results in flotation of more of the pyrochlore than sodium bicarbonate but it has a lower depressing effect on iron

minerals. In other words, sodium bicarbonate with most ores floats a little less pyrochlore than the potassium salt but rejects more gangue material.

The invention is best carried out by selecting the particular bicarbonate on the basis of availability, cost and suitability to the specific ore under treatment and by dissolving it in the water that is being supplied to the grinding and flotation circuits. The amount of bicarbonate employed is in the range of 0.5 pound to 10 pounds per ton of solution, the preferred range being 2 pounds to 8 pounds per ton of solution. Bicarbonate may be recovered from the end products by filtration and the filtrate containing the bicarbonate reused.

The following examples are illustrative of the process of the present invention:

Example I

15 identical flotation tests were carried out on three pyrochlore-containing ores. The results of each test are given in Table II. In each test, 500 g. of the ore, crushed to pass a screen having 10 mesh to the inch, were ground with approximately 330 ml. of distilled water, to which the modifying agent in the form of a water-soluble bicarbonate was added, as well as 2.8 pounds per ton of feed of a combination of 1 part Duomeen T, 1 part Ultrawet DS and 2 parts Amine 220 dissolved therein.

Duomeen T is the trade name of a commercial flotation reagent and is a diamine made from tallow. Ultrawet DS is the trade name of a commercial wetting agent and is an aryl alkyl sulfonate. Amine 220 is the trade name of a commercial flotation reagent and is believed to be 1-hydroxyethyl-2-heptadecenyl glyoxalidine.

Grinding was continued for 7 to 8 minutes after which all +35 mesh particles were removed. The pulp was charged to a Fagergren flotation machine and froth was removed until no further dark minerals appeared in the froth. The froth was diluted with water modified by the addition of a water-soluble bicarbonate and refloat-
ed once in the same machine. All three products, rougher tailing, cleaner tailing and cleaned concentrate, were filtered, dried, weighed, sampled and analysed for niobium pentoxide (Nb_2O_5).

TABLE II

Modifier	Lb. per ton of solution	Percent Recovery	Percent Nb_2O_5	Percent Weight Floated
ORE A				
1. Distilled H_2O		48.82	2.05	4.83
2. Sulphuric Acid.....	0.85	84.23	0.91	17.96
3. NH_4HCO_3	6	84.83	2.85	6.62
4. NaHCO_3	6	81.26	5.70	2.37
5. KHCO_3	7.5	85.89	2.45	6.32
ORE B				
6. Distilled H_2O		90.96	0.785	29.61
7. Sulphuric Acid.....	0.85	92.32	0.80	28.84
8. NH_4HCO_3	6	95.48	0.765	32.09
9. NaHCO_3	6	90.57	0.925	24.96
10. KHCO_3	7.5	87.16	0.705	33.19
ORE C				
11. Distilled H_2O		86.55	0.90	27.54
12. Sulphuric Acid.....	0.85	86.82	1.06	26.00
13. NH_4HCO_3	6	90.02	1.00	28.52
14. NaHCO_3	6	88.20	1.115	25.10
15. KHCO_3	7.5	81.43	1.08	24.81

Ore A was mostly dolomite with a very little mica and pyrite; it was deeply weathered and iron-stained. It contained approximately 0.18% Nb_2O_5 .

Ore B was a fresh ore consisting of very little mica but much calcite and pyroxene (aegirinaugite) and magnetite. It contained from 0.22 to 0.25% Nb_2O_5 .

Ore C consisted of 60% calcite, much biotite and di-

opside, about 6% apatite, and lesser amounts of monticellite, melilite, nephelite, garnet, sphene, perovskite and soda-amphibole. It contained about 0.31% Nb_2O_5 .

As was expected, the different ores responded in different ways in these tests. With ore A, the bicarbonates gave good recovery and good grade; the distilled water gave very poor recovery; and the acidified float gave good recovery but poor grade. With ore B, the grade was lower due to the flotation of green silicates; ammonium bicarbonate showed definite superiority in recovery. With ore C, ammonium bicarbonate also gave best results.

Example II

In order to provide a comparison with modifying agents other than a water-soluble bicarbonate, a further ten flotation tests were carried out in the manner described in Example I using ore C. The results are listed below:

TABLE III

Modifier	Lb. per ton of solution	Percent Recovery	Percent Nb_2O_5	Percent Weight Floated
1. Acid.....	0.85	85.18	1.02	27.18
2. Acid+quebracho.....	0.85	76.14	1.72	15.4
3. Na_2CO_3	1.3	81.22	1.47	17.16
4. Na_2CO_3	4.5	77.04	1.59	15.28
5. K_2CO_3	1.8	91.06	1.45	18.57
6. KOH.....	0.22	91.04	0.70	40.31
7. K_2CO_3 +fuel oil.....	1.8	63.20	2.33	9.19
8. K_2CO_3 - NaHCO_3	{ 1.8 4.45 }	{ 87.24 75.30 }	1.01	24.97
9. K_2CO_3 +river water.....	{ 1.1 1.8 }	{ 75.30 88.91 }	1.46	15.87
10. K_2CO_3 - NaHCO_3	{ 1.8 0.44 }	{ 88.91 88.91 }	0.95	27.98

Example III

Approximately 30 tons of ore C were treated by continuous flotation over 130 hours at approximately 450 pounds per hour. In the first thirteen hours 6.78 lb. per ton of KHCO_3 were used in solution with about 2.35 lb. per ton of ore of the combination of diamines and wetting agent described in Example I. This resulted in an average recovery of 87.7% at a grade of 4.2% with four cleaning steps. Rejection of waste was 93.2%.

In the next 64 hours, NH_4HCO_3 was used at a concentration of 5.66 lb. per ton of solution. The average collector addition was 2.67 lb. per ton of ore. The recovery averaged 90.5% at a grade of 3.65% with five cleaning steps. Rejection of waste was 92.12%.

For the next 12 hours, NaHCO_3 was added at a rate of 5.66 lb. per ton of solution. The reagent addition was at the rate of 3.33 lb. per ton of ore. The average recovery was 89.5% at a grade of 3.62% with five cleanings. Waste rejection was 91.35%.

For the remainder of the test NH_4HCO_3 was used at a concentration of 5.66 lb. per ton of solution. The average amount of collector added was 2.41 lb. per ton of ore. The average recovery was 90.7% at an average grade of 4.0% with seven cleaning steps. Rejection of waste was 93.9%.

The overall recovery was 90.0% at a grade of 3.89% with a waste rejection of 92.85% of the feed having an average grade of 0.031%. With ammonium bicarbonate, the pH of the flotation pulp varied from 8.0 to 8.1.

Example IV

Ore C was ground with 0.8 lb. per ton of a commercial flotation reagent known under the trade name Rosin Amine D Acetate (as the collector for pyrochlore) and distilled water. Rosin Amine D Acetate is the salt resulting from neutralization with acetic acid of amine made from rosin, properly known as abietylamine. The pulp was floated with three additions of 0.4 lb. of the amine per ton and the froth was collected and cleaned

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once with distilled water. The following results were obtained:

Product	Percent Weight	Percent Nb ₂ O ₅	Percent Distribution Nb ₂ O ₅
Rougher Tailing.....	50.32	0.048	7.68
Cleaner Tailing.....	36.82	0.60	70.24
Concentrate.....	12.86	0.54	22.08

Example V

An experiment was carried out as in Example IV except that only two additions of the amine were made to the float (1.6 lb. per ton in all) and all water was conditioned with 6 lb. per ton of ammonium bicarbonate. The following results were obtained:

Product	Percent Weight	Percent Nb ₂ O ₅	Percent Distribution Nb ₂ O ₅
Rougher Tailing.....	24.64	0.032	2.93
Cleaner Tailing.....	25.48	0.035	3.31
Concentrate.....	49.88	0.505	93.76

Rosin Amine D Acetate is not specific for pyrochlore and it tends to float almost all the minerals present except calcite and apatite. The results of Examples IV and V indicate the value of ammonium bicarbonate additions since the collector coating is much more stable when it is used as a water modifier. With the bicarbonate water there is no tendency for the pyrochlore to drop out on cleaning, while without it the cleaning step reduces the recovery of the pyrochlore to an uneconomic value.

It will be observed that a marked improvement in grade and recovery is obtained when the flotation solution is modified by the presence of a water-soluble bicarbonate.

The present invention is not specifically concerned with the particular amine or diamine or combinations thereof

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used as the flotation reagent or the particular wetting agent employed. As examples of amine or diamine flotation reagents there are given those known under the trade names Amine 1180, Duomeen T, Amine 220, and Rosin Amine D Acetate, some which have been previously mentioned. As examples of commercially available wetting agents there are given those known under the trade names Ultrawet 40A, Calsolene Oil H5, and Lissapol N.

Amine 1180 is a fully saturated (no double bonds) primary amine having the majority of its molecules with a carbon chain of 18 atoms. Calsolene Oil H5 is believed to be anionic reagent, a water solution of the sodium salt of a highly sulphated oil. Lissapol N is a nonionic reagent, believed to be a water solution of an alkylated phenol ethylene oxide condensate.

I claim:

1. In a flotation process for the flotation of niobium-bearing minerals from an alkaline ore containing said minerals, the step which comprises modifying the flotation solution containing said ore and as a collector at least one of the group consisting of monoamines and diamines containing 14 to 22 carbon atoms in the molecule, by adding to said solution at least one water-soluble bicarbonate.

2. A flotation process as defined in claim 1, said bicarbonate being added in the amount of 0.5 to 10 pounds per ton of solution.

3. A flotation process as defined in claim 1, said bicarbonate being selected from the group consisting of ammonium, potassium and sodium bicarbonates.

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