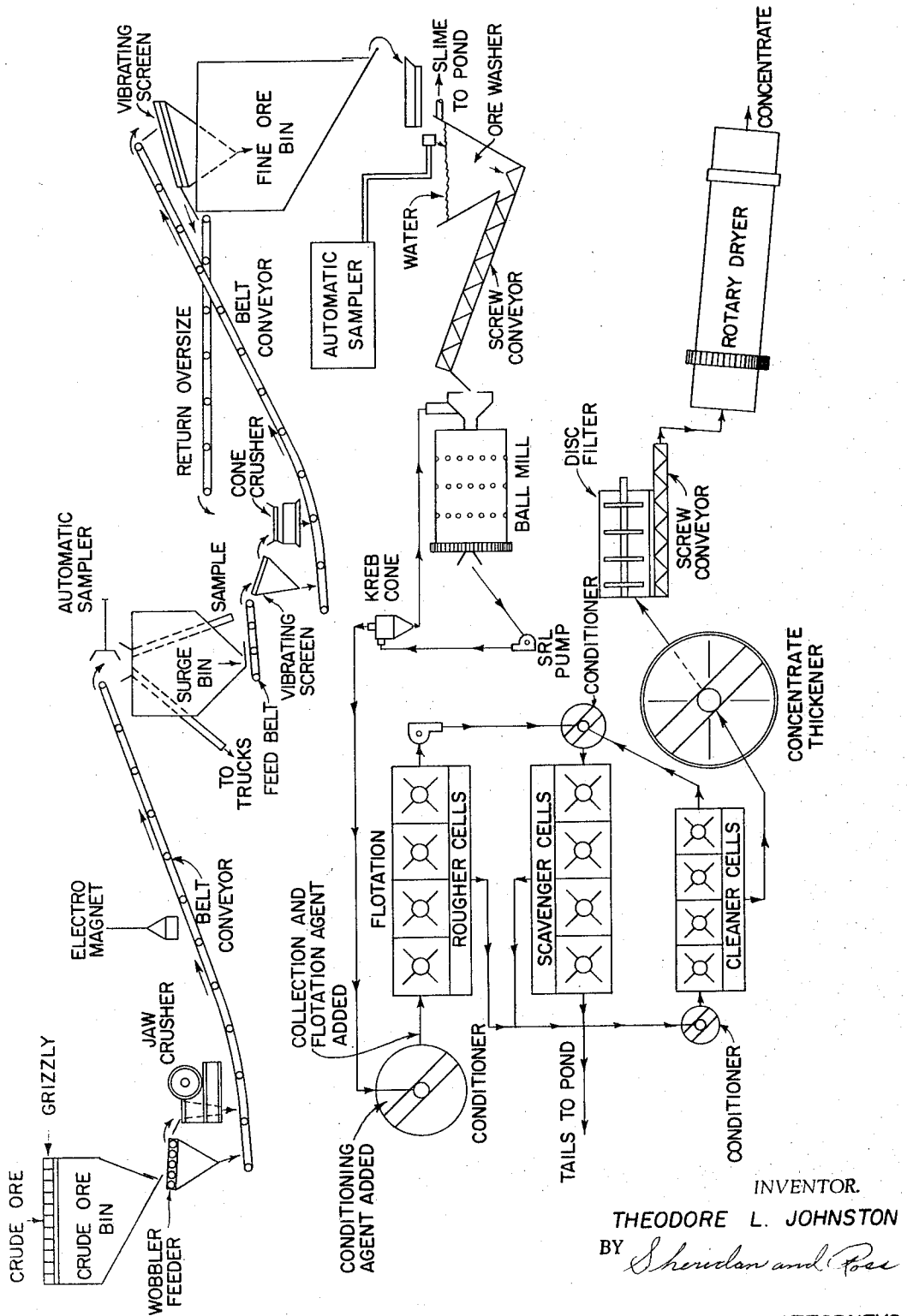
Jan. 24, 1967 T. L. JOHNSTON 3,300,147

CONCENTRATION OF BERYLLIUM ORES

Filed Nov. 8, 1963



INVENTOR.
THEODORE L. JOHNSTON
BY Sheridan and Ross
ATTORNEYS

United States Patent Office 3,300,147 Patented Jan. 24, 1967

3,300,147

CONCENTRATION OF BERYLLIUM ORES

Theodore L. Johnston, Manitou Springs, Colo., assignor to Mineral Concentrates and Chemical Company, Inc., Denver, Colo., a corporation of Colorado

Filed Nov. 8, 1963, Ser. No. 322,333
14 Claims. (Cl. 241—20)

This invention relates to a process for the concentration of beryllium ores, more particularly, it relates to a flotation process for the production of high grade concentrates representing a high percentage recovery of beryllium from the ores.

The invention is illustrated by its application to the production of concentrate from beryl and from ores containing both beryl and bertrandite; however, its application is not limited to these materials as it is equally applicable to bertrandite, phenacite and other beryllium ores alone or existing together in beryllium ores.

Phenacite has the formula $2BeO \cdot SiO_2$, bertrandite has the formula $4BeO \cdot 2SiO \cdot H_2O$ and beryl has the formula $3BeO \cdot Al_2O_3 \cdot 6SiO_2$. These ores are silicates and beryllium is recovered from them in the form of beryllium oxide in concentrates. The beryllium oxide content of bertrandite is approximately 42%, of phenacite 46% while beryl contains a maximum of only 14% beryllium oxide. Beryl is by far the most common of the three minerals and exists in widely scattered areas throughout the country in pegmatite dikes and veins, and also in micaceous greisens and quartz. Beryl occurs in ores with gangue materials or minerals which are principally quartz, feldspar and mica but other minerals may occur with the ores in smaller amounts including fluorite, tourmaline, garnet, topaz, hornblende and sometimes iron compounds. The percentage of BeO in minerals containing beryl is relatively small so that a highly effective recovery process is required to make processing of low grade ores economically feasible for beryllium recovery.

The chief difficulty attendant to the separation of beryl from the principal gangue materials, quartz, feldspar and mica, existing with it in its ore, is the similarity of physical properties of beryl with those of these gangue materials. Because of this similarity in physical properties, gravitation, electrostatic and other conventional separation methods are not particularly effective. Accordingly, any practicable method for separation of beryl from gangue materials must be highly selective for the recovery of beryl in the presence of the three principal gangue materials. In view of the low percentage of beryllium oxide in beryl minerals a process is dictated which provides a high percentage recovery of beryllium as well as a high grade concentrate in the initial separation without the requirement of several partial separations including middlings and tailings, or repeated processing steps.

Accordingly, it is an object of this invention to provide a method for producing high grade concentrates from beryllium ore which represents a high percentage recovery of beryllium from the ore.

It is another object of this invention to provide a process for producing high grade concentrates from beryllium ore with high percentage recoveries of beryllium in a single pass without the necessity of repetitive processing.

It is a further object of this invention to provide a continuous flotation process for the recovery of beryllium from its ores which is economically feasible when applied to low grade beryllium ores, such as, beryl.

In accordance with this invention, the above and other objects are accomplished by a continuous flotation process consisting of steps performed in a required sequence in which the beryllium containing ore is comminuted to a particle size between about —50 and —100 mesh, formed

into a water base pulp having a solids content between about 15 and 50 percent, the pulp subjected to a conditioning treatment with an alkaline conditioning agent at a temperature between about 55–90° C. at a pH above about 9.5, a fatty acid collecting and flotation agent added to the conditioned pulp after the conditioning step, and the pulp subjected to a froth flotation treatment followed by removal of the beryllium component of the ore in the froth. The preferred conditioning agent is sodium sulfide and the preferred fatty acid collecting and flotation agent is oleic acid, used, respectively, in amounts corresponding to ratios of about 4 to 6 pounds per ton of ore and not more than about 25 grams per ton of ore. Preferred limitations within the above ranges are a particle size in which at least 90 percent of the particles are —100 mesh, a 25 percent solids content for the pulp, a conditioning time for the pulp of about 2–5 minutes, and a temperature and pH for the conditioning and flotation steps of 75–80° C. and 10, respectively.

The use, in a flotation process for the recovery of beryl from its ores, of sodium sulfide as a conditioning agent and oleic acid as a frothing and collecting agent is well known and is disclosed in an article entitled, "Floatability of Beryl," in the "Proceedings of the Second United Nations Conference on the Peaceful Uses of Atomic Energy," volume 3, 1958, pages 162–166, written by M. A. Eigeles and I. T. Leviush. The method disclosed in this article has not gained acceptance as indicated by a report given by Moir, Collins, Curwen and Manser at the International Mineral Processing Congress at Cannes, France, May 26–June 2, 1963 which is abstracted at page 46 of the publication, "Mining Engineering" for August 1963 in an abstract entitled "Flotation Process." It is stated in this abstract that "the Eigeles method, the Lamb method, the Runke method and 'Rapid City Method' were investigated as means of floating beryl. The first three methods gave concentrates of 2% to 6% BeO, while the fourth method yielded concentrates of 13% BeO."

Attempts to obtain high grade concentrates from large scale amounts of beryl ores using the method disclosed in the Eigeles et al. article have met with failure by the present inventor. The minimum amount of oleic acid to be used for a ton of ore is disclosed in Table V of the above article as 100 grams. It has been found in accordance with the present invention that if oleic acid is used on large scale amounts of ore at a ratio of more than about 25 grams per ton of ore, irrespective of pH and temperature conditions, gangue material is floated in increasing amounts as added amounts of oleic acid are increased. Accordingly, oleic acid added in amounts in excess of about 25 grams per ton of ore ratio results in a low grade concentrate. Tests on laboratory samples of 750 grams of ore using amounts of oleic acid proportionate to the amounts disclosed in the article for one ton lots of ore give results closer to those disclosed in the article, indicating that the amount of oleic acid used with laboratory techniques and under laboratory conditions on small samples may not be quite as crictical as it is for production lots of ore. This illustrates what is frequently found to be the case, that laboratory parameters, such as reagent amounts, somewhat satisfactory in a laboratory process cannot be extrapolated linearly to obtain acceptable parameters for a production process.

FIG. 1, a schematic flow diagram illustrating the process of the invention, will be referred to hereinafter in describing the invention.

The grinding, classification and sampling procedures as illustrated in the flow diagram, are, of course, conventional. Unless otherwise stated all percentages given are based on weight.

In the practice of the invention, the ore is preferably

ground to produce a comminuted product in which at least 90 percent of the particles will pass through a 100 mesh screen, that is, 90 percent of the particles are —100 mesh. However, the invention is operative if the particle size varies between —55 and —100 mesh, it being an advantage of this process that de-sliming is not necessary and relatively smaller particles can be used than is possibe with prior art processes. Water is added as shown in the flow diagram prior to entry of the ore into the ball mill and the ore is wet ground. The ore particles must be carefully washed at some step prior to entry into the conditioning tank in order to remove oil, wood chips, grease and other objectionable foreign material. The water used to pulp the ground ore is softened before use. Sufficient water is added before entry of the pulp into the conditioning tank to produce a pulp having about 25 percent solids content by weight. While this is the preferable content, a solid-liquid ratio up to 1:1 can be used. A pulp density of 1150, in accordance with the Deco Pulp Density Tables, is the preferred pulp density, this being provided by a pulp having about a 25 percent solids content.

The conditioning apparatus used is of the standard type and produces circulation of the pulp to provide effective mixing. The conditioning tank is provided with steam coils to heat the pulp to the desired temperature. Other means of heating may be used, such as, the introduction of live steam into the pulped ore. The preferred conditioning agent is sodium sulfide and it is used in amounts varying from about two to about eight pounds per ton of ore although the amount may vary from these limits depending upon the type of ore. Other alkaline conditioning agents may be used, such as, sodium hydroxide, sodium carbonate, and other alkali metal sulphides. Sufficient conditioning agent is added to raise the pH to between about 9.5 and about 11, a preferable pH being 10. The conditioning temperature of the pulp is maintained between about 55° C. and 85° C. with a preferable temperature being between about 75° C. and about 80° C. The pulp is preferably conditioned for a period of about two to five minutes.

After the conditioning step, the hot pulp at a pH not below about 9.5 is introduced into a standard flotation cell preferably at the bottom of the cell accompanied by aeration with air introduced at the bottom of the cell. As the pulped ore at a pH of about 10 and at a temperature between about 75°–80° C. flows from the conditioning tank to the flotation cell, oleic acid is introduced dropwise into it at the rate of about 1 drop every 6–10 seconds or about 10 drops a minute maximum. It is preferable that the oleic acid is added after and not during the conditioning step, and is added just prior to or during the flotation step. Regardless of the rate of introduction of the conditioned pulp into the flotation cell, the maximum amount of oleic acid used must not exceed about 25 grams per ton of ore or a proportionate amount for different amounts of ore, and it is preferably added dropwise to provide for an even distribution.

During the addition of the oleic acid it is important that the pH be maintained at 9.5 or higher with a maximum upper limit of about 11. It was found that if the pH drops below 9.5 the oleic acid immediately begins to pick up gangue materials. This will also occur if the temperature is not maintained within the stated range. It is apparent, therefore that there is a critical relationship between temperature, pH range and optimum amounts of oleic acid. This is in contrast to prior art processes, such as that disclosed in the Eigeles et al. article, in which the amounts of oleic acid disclosed as being used are prohibitively excessive for obtaining a high grade concentrate, and this no doubt explains why the process disclosed in the article has not gained wide acceptance.

Other fatty acid collection and flotation agents may be used in place of oleic acid, these materials being referred to herein broadly as fatty acid collection and flotation agents. These include, for example; caprylic acid, lauric acid, stearic acid, fish oil acids, tall oil, linoleic acid, etc.

Aeration of the pulp in combination with the collection and frothing agent results in a froth containing the beryl which is removed from the pulp as it reaches the top.

Examples 1–5 below tabulate results obtained using the process of the invention on large scale lots of ore in a production operation. The examples are illustrative of the invention and not limiting thereof.

The ore used in all of the examples came from the Boomer mine of U.S. Beryllium Co. near Colorado Springs, Colorado, and contained beryl, mica, quartz and feldspar, with minor amounts of tourmaline, hornblende, hematite, topaz, and fluoride. A typical analysis of the ore used in Examples 1–3 showed 2.0 percent BeO, 69.0% SiO_2, 12.5% Al_2O_3, 3.8% Fe, 1.2% $CaCO_3$, and 1.0% CaF. This ore contained small amounts of bertrandite and euclase.

Example 1

The large scale tests of the following Examples 1–5 were carried out in a flotation mill as schematically illustrated in the drawing wherein a continuous feed of about one ton per hour of ore was fed to a ball mill with enough water to make a pulp of 50% solids. The pulp was pumped to a conditioning tank where it was diluted to 25% solids and heated to 75° C. Sodium sulfide was added at the rate of about 6 pounds per ton of ore, or enough to obtain a pH 10 alkalinity. After 5 minutes' conditioning the pulp was transferred from the conditioning tank to the first cell of a bank of four flotation cells. Oleic acid was added dropwise at the rate of 30 grams per ton of ore to the pulp between the conditioning tank and the flotation cells.

RESULTS

[Example 1]

Product	Weight, Tons	Weight percent	Weight percent, BeO	Dist., weight percent
Beryl concentrate	2.5	26.3	7.2	85.7
Beryl middlings	0.5	5.2	3.4	8.1
Tails	6.5	68.5	0.2	6.2
Composite	9.5	100.0	2.2	100.0

The batch of 9.5 tons of ore yielded an excessive amount of froth and the concentrates assayed only 7.2 BeO while the combined middlings from the other three cells assayed 3.4% BeO; both contained excessive amounts of gangue minerals. The large amount of froth produced with consequent flotation of excessive gangue minerals and production of a low grade concentrate illustrates the results of use of oleic acid above the critical maximum amount.

Example 2

This example was carried out using the same procedure as Example 1 except that only 16 grams of oleic acid were used per ton of ore.

RESULTS

Product	Weight, Tons	Weight percent	Weight percent, BeO	Dist., weight percent
Beryl concentrate	3.0	12.4	12.2	79.3
Beryl middlings	0.5	2.1	6.6	7.2
Tails	20.7	85.5	0.3	13.5
Composite	24.2	100.0	1.9	100.0

The froth which formed in the first flotation was light colored, contained smaller bubbles and was heavily mineralized. The quantity produced was considerably less than that produced in Example 1. The concentrate assayed 12.2% BeO and contained 79.3% of the total beryl. The combined froth from the other three cells was collected as middlings which assayed 6.6% BeO. The results show that the bulk of the beryllium minerals float in clean

concentrate when the amount of oleic acid used is within the critical range.

Example 3

Example 3 using 11.5 tons of ore was carried out with the same procedure as Example 1 except that the froth (or middlings) from reprocessing cells was pumped back to the conditioner and mixed with the pulp from the ball mill and only 12 grams of oleic acid per ton of ore were used.

RESULTS

Product	Weight, Tons	Weight percent	Weight percent, BeO	Dist., weight percent
Beryl Concentrate	1.75	15.2	11.2	83.5
Tailings	9.75	84.8	0.4	16.5
Composite	11.50	100.0	2.06	100.0

The beryl concentrate from the first flotation assayed 11.2% BeO and contained 83.5% of the total beryl. The high grade concentrate in Examples 2 and 3 as compared to the low grade concentrate of Example 1, taking into consideration the respective amounts of oleic acid used, illustrate the criticalness of the operative range of the amount of oleic acid.

Example 4

The ore used in this example included a small amount of bertrandite with the beryl and had a combined beryllium oxide content of 4.4%. The same procedure as used in the above examples was followed in this example with the exception that oleic acid was added in an amount of approximately 4.54 grams per ton of ore. A concentrate was obtained which assayed 18.4% beryllium oxide, indicating that the bertrandite content was upgrading the beryl content. The tailings assayed 0.42% beryllium oxide indicating a 90.5% recovery of the beryllium content of the ore.

Example 5

The ore used in this example also contained a small amount of bertrandite with the beryl and assayed 6.09 beryllium oxide. The same procedure and amounts of reagents as was used in Example 4 was used in this example. A concentrate was obtained containing 30.8% beryllium oxide while the tailing assayed 0.4% beryllium oxide indicating an approximate recovery of 94% of the beryllium content of the ore.

The above comparative examples illustrate that the upper range of oleic acid required to float only the beryllium minerals corresponds to a ratio of about 25 grams per ton of ore. It is seen from the examples that if the amount of oleic acid used in the process of this invention is maintained within the critical range, concentrates are produced assaying at least 10% BeO and generally in the neighborhood of 12% BeO with a high percentage recovery of beryllium from the ore.

The explanation of the above discovery is not known and is certainly not obvious from prior art teachings, such as, the Eigeles et al. article. It appears, however, that oleic acid exhibits priority in selectivity for beryl over the gangue materials with which it is associated and that it will float the conditioned beryl particles first before it floats the gangue materials. Accordingly, it is necessary to use only the maximum critical amount required for flotation of all of the beryl minerals within the critical temperature and pH ranges. The dropwise addition of this agent added in the proper sequence of process steps is also of importance.

The invention provides an improved flotation process for the selective flotation of beryllium minerals from the gangue minerals with which they are associated in their ores. The process of the invention produces a high grade marketable concentrate ordinarily having at least a 10% beryllium oxide content and insures a high percentage yield of beryllium from the ore. The process can be carried out as a continuous operation with a minimum degree of surveillance. Its application does not require de-sliming of the ore as it is effective for selective floating of small particles or beryl. The invention results in an economical use of oleic acid but its chief economical feature is the fact that by its use a high grade concentrate with a high percentage yield of beryllium is obtained in the first pass without the necessity of further processing.

Although the invention has been illustrated and described with reference to the preferred embodiments thereof, it is to be understood that it is in no way limited to the details of such embodiments, but is capable of numerous modifications within the scope of the appended claims.

What is claimed is:

1. A process for the concentration of beryllium minerals from an ore containing them along with gangue materials which comprises: comminuting the ore to a relatively finely divided state; forming an aqueous pulp of the ore; treating the pulp with from about 2 to 8 pounds per ton of an alkaline conditioning agent selected from the group consisting of alkali metal hydroxides, alkali metal carbonates and alkali metal sulfides at a pH above about 9.5 and at a temperature between about 55° C. to 90° C.; adding a higher fatty acid collection and flotation agent to the conditioned pulp in an amount not in excess of about 25 grams per ton of ore; and froth floating the beryllium minerals from the gangue materials.

2. A process for the concentration of beryllium minerals from an ore containing them along with gangue materials which comprises: comminuting the ore to a particle size between about minus 50 and minus 100 mesh; forming an aqueous pulp of the ore having a solids content from about 15 to about 60 percent; thoroughly mixing the pulp with from about 4 to about 6 pounds per ton of ore of an alkaline conditioning agent selected from the group consisting of alkali metal hydroxides, alkali metal carbonates and alkali metal sulfides at a pH between about 9.5 and 11 at a temperature between about 55° C. to 90° C.; adding a higher fatty acid collection and flotation agent to the conditioned pulp in an amount not in excess of about 25 grams per ton of ore; and froth floating the beryllium minerals from the gangue materials.

3. The process of claim 2 in which the fatty acid collection and flotation agent is added along with the conditioning agent.

4. The process of claim 2 in which the alkaline conditioning agent is sodium sulfide.

5. The process of claim 4 in which the amount of added fatty acid collection and flotation agent varies from about 4 to about 25 grams per ton of ore.

6. A process for the concentration of beryllium minerals from an ore containing them along with gangue materials which comprises: comminuting the ore to a particle size in which 90 percent of the particles are minus 100 mesh; forming an aqueous pulp of the ore having a solids content of about 25 percent; thoroughly mixing the pulp with from about 4 to 6 pounds per ton of ore of an alkali metal sulfide conditioning agent at a pH between about 9.5 and 11 at a temperature between about 75° C. to 80° C.; adding oleic acid as a collection and flotation agent to the conditioned pulp in an amount not in excess of about 25 grams per ton of ore; and froth floating the beryllium minerals from the gangue materials.

7. A process for the concentration of a beryllium mineral selected from the class consisting of beryl, phenacite and bertrandite, and mixtures thereof, from an ore in which they are contained along with gangue materials, which comprises: comminuting the ore to a particle size in which 90 percent of the particles are minus 100 mesh; forming an aqueous pulp of the ore having a

solids content of about 25 percent; thoroughly mixing the pulp with from about 4 to about 6 pounds of sodium sulfide per ton of ore at a pH of about 10 at a temperature between about 75° C. and 80° C.; adding oleic acid to the conditioned pulp in an amount from about 4 to about 25 grams per ton of ore; and froth floating the beryllium minerals from the gangue materials.

8. The process of claim **7** in which the beryllium mineral is beryl.

9. In the process for the concentration of beryllium minerals from ores containing gangue materials in which process an alkali metal sulfide conditioning agent is used for conditioning the beryllium mineral particles for flotation and oleic acid is used as a froth flotation agent for the beryllium mineral particles, the improvement which comprises reducing said particles to a size not in excess of about minus 50 mesh; adding the oleic acid to the conditioned mineral particles and gangue materials at a pH between about 9.5 and 11 at a temperature between about 55° C. to 90° C. in an amount not in excess of about 25 grams per ton of ore.

10. The process of claim **9** in which the pH is about 10, the temperature is between about 75° C. and 80° C. and the amount of oleic acid added is between about 4 and about 25 grams per ton of ore.

11. A process for the concentration of beryllium minerals from ores containing gangue materials which comprises: comminuting the ore to a particle size in which 90 percent of the particles are minus 100 mesh; forming a water base pulp of the comminuted ore having about 25 percent solids content; conditioning the pulped ore at a temperature between about 75° C. to 80° C. by mixing it with about 4 to about 6 pounds of sodium sulfide per ton of ore as a conditioning agent at a pH between about 9.5 and 11; flowing the conditioned pulp into a flotation cell while introducing into the pulped and conditioned ore oleic acid at a rate not in excess of about 25 grams per ton of ore; and aerating and froth floating the beryllium minerals.

12. The process of claim **11** in which the oleic acid is added during the conditioning step.

13. The process of claim **11** in which the oleic acid is added during the froth flotation step.

14. A continuous process for the concentration of beryl from ores containing gangue materials which comprises: wet grinding the ore to a particle size in which 90 percent of the particles are minus 100 mesh; forming a water base pulp of the comminuted ore having about a 25 percent solids content; conditioning the pulped ore at a temperature between about 75° C. and 80° C. by mixing it with about 4 to about 6 pounds of sodium sulfide per ton of ore as a conditioning agent at a pH between about 9.5 and 11; flowing the conditioned pulp into a flotation cell while introducing into the pulped and conditioned ore oleic acid at a rate not in excess of about 25 grams per ton of ore; introducing the pulped and conditioned ore into the bottom of a flotation cell while simultaneously introducing air into it at the bottom of the cell to effect a froth flotation of the beryllium minerals.

References Cited by the Examiner

UNITED STATES PATENTS

3,078,997 2/1963 Havens ---------- 209—167 X

OTHER REFERENCES

Eigeles, M.A.: Second United Nations International Conference on Peaceful Uses of Atomic Energy, United Nations, 1958, volume 3, pages 162–166.

Plaksin: Chemical Abstracts, 1962.

HARRY B. THORNTON, *Primary Examiner.*

R. HALPER, *Assistant Examiner.*