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BENEFICIATION OF BERYLLIUM ORES BY FROTH FLOTATION

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8 Claims. (Cl. 241—20)

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The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to me of any royalty thereon in accordance with the provisions of the Act of April 30, 1928 (Ch. 460, 45 Stat. L. 467).

This invention relates generally to the beneficiation of beryllium-containing material, and more particularly to the concentration of beryl from berylliferous pegmatitic ores.

Beryllium occurs in nature principally in the form of the mineral beryl. This mineral is found chiefly in granite formations known as pegmatites. Most berylliferous pegmatites are composed essentially of quartz, feldspar, and muscovite, with the beryl being present in minor quantities along with a host of other minerals. Because of the low quantity of beryl in these materials, it is not economical to recover the beryllium by direct treatment of the ore by beryllium extraction methods. Methods that have been used for concentration of beryl are inefficient and wasteful and generally do not result in a high recovery of beryl of a concentration desired for use in extractive processes for beryllium.

Accordingly, an object of this invention is to provide a method for the recovery of beryl from berylliferous material of a suitable grade for further processing to recover the beryllium contained therein.

Another object of this invention is to provide a method for the recovery of larger quantities of beryl from berylliferous ores than may be recovered by presently known processes.

A further object of this invention is to provide a froth flotation method for the separation, concentration, and recovery of beryl from its natural ores or other beryl-bearing materials with production of a product of sufficient beryllium content to be utilized by extractive metallurgical processes.

A still further object of this invention is to provide a method for recovery of beryl from berylliferous ores in which associated minerals such as muscovite and feldspar are also separately recovered.

Other objects and advantages of the invention will be apparent as the description proceeds.

The invention, in general, comprises a flotation process for the separation of beryl from associated minerals in which the beryl is activated for flotation by treatment of the material with a hypochlorite solution and the beryl is then selectively floated with a reagent combination of sulfuric acid and water-soluble petroleum sulfonate.

The activation and flotation of beryl from other material may be employed directly upon any

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berylliferous material in which the mineral muscovite is absent, either having been removed by known separation methods or not present in the original material. However, when the mineral feldspar is present in the berylliferous material, it is advantageous to first isolate a beryl-feldspar concentrate from the other material by flotation, as an up-grading of the material is realized with respect to beryl prior to the final selective beryl flotation operation.

The process of this invention when carried out on berylliferous pegmatitic ores containing muscovite, quartz and feldspar, comprises grinding the berylliferous material to free the beryl and other minerals one from the other, desliming the ground material, removing muscovite from the deslimed material, isolating feldspar and beryl together from the remaining material which is mainly quartz and selectively floating the beryl from the feldspar. Muscovite, quartz, feldspar and beryl are separately recovered as marketable products.

The berylliferous pegmatitic material may be crushed to minus 20 mesh (Standard Tyler Screen) or finer. Care should be taken to avoid the production of a large amount of fines. If desired, the minus 20-mesh material may be wet-ground in a ball mill or other suitable apparatus with about an equal amount of water to minus 35-mesh particle size. The degree of fineness to which the material must be ground is dependent upon the size at which the bulk of the mineral particles are freed one from the other, and thus varies with the particular ore treated.

The ground ore is deslimed by washing or by other methods known to the art for removing the so-called slime or finest particles. For example, the ore may be agitated with water and the suspended slimes decanted.

The deslimed material is then treated by flotation or by other convenient methods for selective removal of muscovite. For example, in removing muscovite by flotation, the deslimed sands may be agitated with about an equal weight of water, and from 1 to 5 pounds of sulfuric acid, about 0.05 to 0.15 pound of a long-chain alkyl amine salt collector, preferably coco amine acetate (technical grade), and a small amount of a frother, such as, methyl amyl alcohol, in an amount not in excess of 0.01 pounds per ton of feed. The agitation is continued for about two to three minutes and the pulp is diluted to about 25 per cent solids. Air is admitted and the muscovite present is floated off in the froth formed. If a high-grade muscovite product is desired, the froth is retreated as many times as necessary to yield the grade required. It is to be understood, however, that the present invention is not dependent on any particular method of flotation of

muscovite and that the suggested method is merely illustrative of a procedure that may be used.

The muscovite-free material is then conditioned and floated for removal of beryl and feldspar together, thus producing a bulk beryl-feldspar concentrate. Flotation processes for selectively floating feldspar from mineral aggregates are known to the art, but these processes have never taken cognizance of the flotation of beryl along with the feldspar. A suitable flotation procedure consists of conditioning the muscovite-free material with an acidic fluorine compound or compounds and flotation with a collector of the cationic type, such as an amine reagent, and a suitable frother.

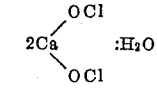
For example, in floating feldspar and beryl from the muscovite flotation operation described above, the tailing or reject from this operation, without removal of any water, is conditioned for a period of 2 to 4 minutes by admixing 1 to 4 pounds of hydrofluoric acid to the ton of material treated, 0.1 to 0.3 pound of an amine collector, generally of the same type used in the muscovite flotation step, and 0.01 to 0.05 pound of frother, also of the same type used in the muscovite flotation step. Air is again introduced and a bulk beryl-feldspar is removed in the froth formed. Depending upon the mineral composition of the material being treated, the reject or tailing from this operation is usually a high grade quartz product, which may be cleaned if required by repeating the feldspar flotation step.

The bulk beryl-feldspar product is then conditioned with a given amount of either calcium or sodium hypochlorite or other material containing HClO or capable of releasing HClO upon acidification, hereafter called hypochlorite, depending upon the beryl content. The amount generally ranges from 0.5 to 2.0 pounds per ton of ore treated, and the time of conditioning is limited to not more than 5 minutes. The product is then washed for the removal of the hypochlorite and thickened to obtain a pulp of approximately 50 per cent solids. The thickened pulp is conditioned with a sufficient amount of sulfuric acid to maintain an acid pulp in the pH range of 2.0 to 3.0, a suitable amount of petroleum sulfonate of the water soluble or so-called green acid type, depending upon the amount of beryl present, and a small amount of frother of the mixed higher alcohol type. The quantities of these reagents usually employed in the flotation of the beryl from the feldspar are, in pounds per ton of material treated: sulfuric acid, 0.5 to 3.0 pounds; petroleum sulfonate, 0.5 to 2.5 pounds; and frother, 0.01 to 0.05 pound. The time of the conditioning period ranges between 2 and 3 minutes. After dilution with water to 20 to 25 per cent solids, the beryl is floated from the feldspar in the froth formed by these reagents. This froth is collected and may be retreated by the same procedure with additional small amounts of all the reagents, except for the hypochlorite, until the beryl content of the floated product has reached the desired grade. The cleaner tailings or residues from the retreatment may be returned to any point in the operation for further treatment to recover the beryl present therein.

As aforementioned, the beryl flotation operation may be employed directly upon any beryl-liferous material in which muscovite is absent, and the invention, therefore, resides in this operation alone on such materials, and also in combination with the operations for separation of muscovite, quartz, and feldspar from beryl-liferous pegmatitic ores and similar beryl-liferous material.

The invention employs water solutions of hypochlorites, preferably either calcium or sodium hypochlorite, for the preparation and activation of the beryl mineral particles so that they can be selectively filmed with the reagent combination of sulfuric acid and water soluble petroleum sulfonate. Either soft or hard water may be used in this flotation procedure without adversely affecting the flotation of the beryl.

The flotation of the beryl mineral particles, while not limited to any particular theory of operation, is believed to be successful because of the following facts. Calcium hypochlorite has the chemical formula



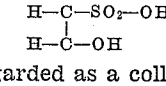
and when weakly acidified it liberates HClO, which is a powerful oxidizing agent hydrolyzing as follows:

$$HClO=HCl+O$$

Sodium hypochlorite reacts in a similar manner. This oxidizing agent apparently selectively reacts or modifies the surfaces of the beryl mineral particles to make them become selectively filmed when subjected to the conditions produced by the sulfuric acid, water soluble petroleum sulfonate, and a frother. The acid required for acidifying the hypochlorite is supplied, as the case might be, from the muscovite float or from the bulk beryl-feldspar float, or in the case of a muscovite-free material, it must be added if the bulk beryl-feldspar float is not employed.

The hypochlorite solution appears to perform a dual function when used in the conditioning of the bulk beryl-feldspar product in that it breaks down the heavy amine froth formed in this flotation step, thereby facilitating the washing of this product with a minimum mineral loss, as well as the above described apparent activation of the beryl.

The petroleum sulfonates are chemically complex mixtures derived from sulfuric acid treatment of various petroleum stocks. They may be classified into two broad types, those which are water soluble or green acids, and those which are hydrocarbon soluble or the mahogany acids. The water soluble type, or the so-called green acid, is the only type found suitable for the flotation of beryl. This compound has the following general chemical formula:



and may be regarded as a collector which selectively films the beryl mineral particles which have been pre-treated by the hypochlorite so that they will become attached to air bubbles and float.

The invention is further illustrated but is not limited by the following examples of practice:

EXAMPLE 1

Beryl-liferous pegmatitic material from the Peerless mine near Keystone, South Dakota, which contained 0.5 per cent beryl in a gangue composed essentially of feldspar, quartz, and muscovite, with lesser amounts of tourmaline, apatite, and purpurite, was treated in accordance with the process of the invention. The

operational data and results are tabulated as follows:

Operational data

Reagents	Circuit									
	Muscovite		Beryl-feldspar		Beryl					
					Conditioner			Cleaner		
	Conditioner	Rougher	Conditioner	Rougher	1	2	Rougher	1	2	3
Sulfuric acid lbs./ton	4.0					3.0		0.25	0.25	0.25
Coco amine acetate (technical grade)	0.1		0.25							
Methyl amyl alcohol	0.01		0.02			0.02				
Petroleum sulfonate						1.5		0.1	0.1	0.1
Hydrofluoric acid			2.5							
Calcium hypochlorite					2.0					
Time, minutes	3	2½	3	2½	5	2	3	2	2	2
pH		2.4		2.5			2.5	2.5	2.6	2.7

Results of flotation

Product	Weight, percent	Analysis percent beryl	Percent of total beryl
Muscovite	2.5	Trace	Nil
Beryl	0.5	73.2	73.1
Beryl cleaner No. 3	0.3	10.9	6.6
Beryl cleaner No. 2	0.9	1.0	1.8
Beryl cleaner No. 1	2.0	0.6	2.3
Feldspar	53.8	0.1	10.8
Quartz	26.8	0.1	5.4
Slime	13.2	Trace	Nil
Composite heads	100.0	0.5	100.0

EXAMPLE 2

Berylliferous pegmatitic material from the same mine as Example 1 but which contained 1.9 per cent beryl was similarly treated in accordance with the process of this invention. The

gangue minerals were the same as indicated in the description of the ore in Example 1. Operational data and the results of this test are given in the following tables:

Operational data

	Circuit								
	Muscovite		Beryl-feldspar		Beryl				
					Conditioner			Cleaner	
	Conditioner	Rougher	Conditioner	Rougher	1	2	Rougher	1	2
Sulfuric acid lbs./ton	4.0					3.0		0.25	0.2
Coco amine acetate (technical grade)	0.15		0.25						
Methyl amyl alcohol	0.01		0.02			0.02			
Calcium hypochlorite					2.5				
Petroleum sulfonate						2.5		0.1	0.1
Hydrofluoric acid			2.5						
Time, minutes	3	2½	3	2½	5	2	2	2	2
pH		2.4		2.4			2.5	2.3	2.3

Results of flotation

Product	Weight, percent	Analysis percent beryl	Percent of total beryl
Muscovite	5.0	trace	nil
Beryl	2.5	65.0	87.2
Beryl cleaner No. 2	1.1	2.0	1.2
Beryl cleaner No. 1	5.2	trace	nil
Feldspar	46.2	0.3	7.5
Quartz	27.4	0.1	1.4
Slime	12.6	0.4	2.7
Composite heads	100.0	1.9	100.0

EXAMPLE 3

Berylliferous pegmatitic material from the same deposit as Examples 1 and 2 and containing similar gangue minerals but which had a beryl content of 2.7 per cent was treated by the process of this invention. The operational data and results are tabulated as follows:

Operational data

Reagents	Circuit									
	Muscovite		Beryl-feldspar		Beryl					
					Conditioner			Cleaner		
	Conditioner	Rougher	Conditioner	Rougher	1	2	Rougher	1	2	3
Sulfuric acid lbs./ton	4.0					4.0		0.25	0.25	0.25
Coco amine acetate (technical grade)	0.1		0.25							
Methyl amyl alcohol	0.01		0.02			0.02				
Calcium hypochlorite					2.0					
Petroleum sulfonate						2.0		0.25	0.25	0.25
Hydrofluoric acid			3.0							
Time, minutes	3	2	3	2½	5	2	2½	2	2½	3
pH		2.6		2.6			2.5	2.2	2.5	2.6

Results of flotation

Product	Weight, percent	Analysis percent beryl	Percent of total beryl
Muscovite	7.1	Trace	Nil
Beryl	2.9	78.0	84.6
Beryl cleaner No. 3	0.9	17.1	5.6
Beryl cleaner No. 2	2.6	3.0	3.0
Beryl cleaner No. 1	9.0	Trace	Nil
Feldspar	44.7	0.4	6.8
Quartz	17.6	Trace	Nil
Slime	15.2	Trace	Nil
Composite heads	100.0	2.7	100.0

EXAMPLE 4

A fourth sample of berylliferous material from the Peerless mine, containing similar gangue minerals as the three foregoing samples but which contained 10.7 per cent beryl, was treated by the process of the invention. The operational data and results of the treatment are as follows:

Operational data

Reagents	Circuit							
	Muscovite		Beryl-feldspar		Beryl			
	Conditioner	Rougher	Conditioner	Rougher	Conditioner 1	Conditioner 2	Rougher	Cleaner
Sulfuric acid lbs./ton	4.0					3.0		1.0
Coco amine acetate (technical grade)	0.15		0.25					
Methyl amyl alcohol	0.01		0.02			0.02		
Calcium hypochlorite					2.5			
Petroleum sulfonate						2.0		0.5
Hydrofluoric acid			2.5					
Time, minutes	3	2½	3	2½	5	2	2½	3
pH		2.5		2.6			2.6	3.3

Results of flotation

Product	Weight, percent	Analysis percent beryl	Percent of total beryl
Muscovite	6.3	0.1	0.1
Beryl	10.8	80.0	80.3
Beryl cleaner	4.5	3.0	1.2
Feldspar	47.6	2.9	12.7
Quartz	19.0	4.2	5.7
Slime	11.8	trace	nil
Composite heads	100.0	10.7	100.0

The results of the foregoing examples show that products high in concentration of beryl can be produced at high recovery rates from berylliferous materials containing various quantities of beryl. Thus, in Example 1 a product was obtained which analyzed 73.2 per cent of beryl from a berylliferous pegmatitic material that contained only 0.5 per cent beryl, and 73.1 per cent of the beryl of the original material was recovered in this product. In Example 4, wherein a berylliferous pegmatitic material containing 10.7 per cent beryl was treated, a product was obtained which analyzed 80.0 per cent beryl and contained 80.3 per cent of the beryl of the original material. In Examples 2 and 3, a recovery of 87.2 and 84.6 per cent of the original beryl was realized and the products analyzed 65.0 and 78.0 per cent beryl, respectively. All of these products are suitable for use in direct extractive processes for recovery of beryllium.

It is apparent from the foregoing descriptions and examples that a desirable treatment has been provided whereby beryl can be concentrated from

berylliferous pegmatitic materials. Although the procedure has been described in connection with concentration of beryl from pegmatitic gangue materials and is especially useful with this material, it is applicable to other beryl-bearing ores as well.

It will be appreciated from a reading of the foregoing specification that the invention herein described is susceptible of various changes and modifications without departing from the spirit and scope thereof.

What is claimed is:

1. A process for the flotation of beryl from berylliferous material comprising treating a pulp of the berylliferous material with a hypochlorite solution to activate the beryl particles for flotation, and then froth floating the beryl particle from the residual gangue in the presence of a water-soluble sulfonate.

2. A process for the flotation of beryl from berylliferous material comprising treating a pulp of the berylliferous material with a hypochlorite solution to activate the beryl particles for flotation, acidifying the solution, and then floating the beryl particles from the residual gangue with a water-soluble petroleum sulfonate and a frothing agent.

3. The process of claim 2 in which a calcium hypochlorite solution is employed to activate the beryl particles.

4. The process of claim 2 in which a sodium hypochlorite solution is employed to activate the beryl particles.

5. A process for the flotation of beryl from berylliferous material comprising treating a pulp of the berylliferous material with a hypochlorite solution to activate the beryl particles for flotation, adjusting the pH of the resulting pulp to about pH 2.0 to 3.0, agitating the pulp with a water-soluble petroleum sulfonate and a frothing agent, and floating the beryl particles from the residual gangue.

6. A process for the flotation of beryl from berylliferous material comprising treating a pulp of the berylliferous material with about 0.5 to 2.0 pounds of a hypochlorite per ton of material, washing the treated pulp, conditioning the treated pulp with about 0.5 to 3.0 pounds of sulfuric acid, about 0.5 to 2.5 pounds of water soluble petroleum sulfonate, and about 0.01 to 0.05 pound of methyl amyl alcohol per ton of material, and selectively floating the beryl from the residual gangue.

7. A process for concentrating beryl from berylliferous material containing feldspar and other gangue minerals comprising subjecting the beryl-

liferous material to a cationic flotation operation to isolate a feldspar-beryl concentrate, activating the beryl particles of the feldspar-beryl concentrate by treatment with a hypochlorite solution, and then froth floating the beryl from the feldspar in the presence of a water soluble sulfonate.

8. A process for concentrating beryl from berylliferous pegmatitic ores containing muscovite, feldspar, beryl, quartz, and other gangue materials, comprising grinding and desliming the ore, agitating the deslimed material with sulfuric acid, an amine collecting agent and a frothing agent, selectively floating off the muscovite, conditioning the remaining material with hydrofluoric acid, an amine collecting agent and a frothing agent, selectively floating off a beryl-feldspar concentrate activating the beryl particles of the beryl-feldspar concentrate by treatment with a

hypochlorite solution, conditioning the treated material with sulfuric acid, a water soluble sulfonate and a frothing agent, and selectively floating the beryl particles from the feldspar.

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