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FROTH FLOTATION OF COMPLEX ZINC-TIN ORE

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ABSTRACT OF THE DISCLOSURE

A complex zinc-tin sulfide ore containing finely disseminated metal values is ground to minus 325 mesh. A bulk zinc-tin sulfide float is made with a fatty acid collector. The bulk float is dewatered partially and an alkaline deflocculating agent is added. The mixture is aged and diluted to form a pulp which is aerated and floated. The zinc mineral concentrates in the froth and tin concentrates in the flotation tailings.

BACKGROUND OF THE INVENTION

The benefication of complex ores containing finely disseminated metal values is invariably a difficult problem. To liberate the metal values from the matrix requires very fine grinding. The ultrafine particles are not as amenable to differential flotation as coarser ores. In the case of finely dessiminated complex sulfide ores containing zinc and tin sulfide minerals, it is especially difficult to obtain good separation of metal values because tin sulfide and zinc sulfide minerals have quite similar flotation characteristics.

It has been suggested to separate the zinc and tin values from complex sulfide ores by a conventional sulfide flotation using sodium cyanide and pH control to depress zinc sulfide (sphalerite). The tin sulfide (stannite) concentrates along with any galena that is present in the float product. The sphalerite is reactivated with copper sulfate and floated to produce the zinc concentrate. Excellent concentration of zinc sulfide minerals is obtatined by such a flotation procedure. However, the tin mineral does not respond well to the type of flotation and the recovery of the tin is quite poor.

THE INVENTION

An object of the invention is to provide a novel method for separately recovering tin and zinc sulfide minerals in finely disseminated complex ores.

A specific object is to improve the tin recovery from a complex zinc-tin sulfide ore.

Another object is to provide a method for recovering zinc and tin sulfide minerals from slimed flotation tailings.

I have discovered a novel method for separating zinc and tin minerals in a finely divided complex sulfide ore pulp by a series of flotation steps.

Stated briefly, in accordance with this invention, zinc and tin minerals in a finely divided complex sulfide ore pulp are separated from each other and from gangue by producing a bulk float with a fatty acid collector, partially dewatering the bulk float, incorporating a strong alkaline dispersing agent into the partially dewatered bulk float, aging the concentrated pulp, diluting the aged pulp and subjecting it to froth flotation without addition of collector reagents. Zinc mineral values report in the froth and tin values are recovered in the flotation tailings.

When the finely disseminated zinc-tin ore also contains liberated lead values, e.g., galena, it is preferable to remove the lead minerals by flotation with a xanthate reagent using a depressor for zinc and tin before making the bulk float with a fatty acid collector.

In accordance with an embodiment of this invention, finely divided calcium carbonate mineral particles are incorporated into the pulp before or after the bulk float is obtained with the fatty acid collector. The presence of calcium carbonate during the subsequent differential tin-zinc flotation step depresses the tin and thereby aids in tin recovery.

DETAILED DESCRIPTION

In practicing this invention, the ore material that is employed may be whole, run-of-mine ore containing tin sulfide and zinc sulfide minerals and oxidized gangue. The sulfide minerals may be partially oxidized. The process is also useful in recovering tin and zinc sulfide minerals from ores which have undergone preliminary refinement, such as tabling or flotation of minerals such as galena. Excellent results have been realized with activated tailings from a process in which tin sulfide was floated from sodium cyanide depressed zinc sulfide. Irrespective of the preliminary treatment, it is essential that the ore be ground to a size sufficient to liberate the zinc and tin sulfide minerals. This frequently requires grinding to 200 mesh (Tyler) or finer. In many cases, the ore should be ground to minus 325 mesh.

As mentioned, it is preferable to float galena from the zinc or tin before producing a bulk zinc-tin float. This may be done by conditioning a pulp with a starvation quantity of xanthate collector using sodium cyanide and pH control to depress zinc and tin sulfide minerals such as sphalerite and stannite. The tailings are reactivated with copper sulfate before a bulk float is taken with a fatty acid collector.

To produce the bulk zinc-tin float, the ore pulp is conditioned with a fatty acid collector such as tall oil or oleic acid. An emulsified fatty acid collector is preferred. The bulk flotation is carried out in an alkaline pulp containing sodium silicate to depress silica and silicate minerals when they are present. It is recommended that flotation be carried out with pulps having low solids (e.g., 10 to 20%). In most cases it is advantageous to clean the bulk float one or more times to improve the grade.

The bulk float typically contains about 10 to 20% solids. Water is removed from the bulk float to increase the solids content to about 65 to 85%. This may be done by filtering the pulp and recovering the filtered solids. To ease the loads on the filters, some of the water in the pulp may be removed by flocculating the pulp with acid and decanting supernatant liquid. With some pulps, the bulk concentrate may be adequately thickened by flocculation without subsequent filtration. Alternatively, the concentrate may be dewatered by drying.

An alkaline deflocculating agent (dispersant) such as sodium silicate, sodium carbonate, or a sodium condensed phosphate such as tetrasodium pyrophosphate, is thoroughly mixed with the thickened fatty acid reagentized bulk float concentrate. Mixtures of deflocculating agents may be employed. Relatively large quantities of deflocculating agent are used. Since the dewatered bulk float

concentrate is at high solids and a large quantity of deflocculating agent is employed, the deflocculating agent is present as a concentrated aqueous solution. A representative quantity of deflocculating agent is from 10 to 30 lb. per ton of solids in the dewatered bulk float.

The mixture is allowed to age for at least about 2 hours, preferably 12 hours or more (e.g., a week). During the aging, the ingredients may be agitated or mixed. However, this is not necessary. The aging may be carried out at elevated temperature or at ambient temperature. For economic reasons, aging at ambient temperature is preferred.

The aged, dispersant-treated bulk float concentrate is diluted with water to a level suitable for flotation, e.g., 5 to 30% solids. The diluted pulp is aerated in a suitable flotation cell. The resulting alkaline pulp already contains the fatty acid collector employed in the bulk float step and the differential zinc-tin flotation step does not require the addition of collector reagents. However, auxiliary depressors or activators may be added. As a result of this flotation step, the zinc concentrates in the froth. The tin, which is depressed, concentrates in the tailings. The froth concentrate is usually cleaned one or more times and the tailings are combined. When galena is present with the zinc, the froth may be floated with selective reagents to separate the lead from the tin. The tailings may be further refined by chemico-physical methods. Middlings may be recirculated.

Examples

The following examples illustrate the flotation separation of zinc and tin from a complex zinc-tin Bolivian sulfide ore containing sphalerite, stannite (present as inclusions in the sphalerite), teallite (a solid solution of the composition $PbS.SnS_2$), and tuffahlite (a zinc sulfide-tin sulfide mineral). Small amounts of cassiterite were also present. Gangue minerals included galena, pyrite, quartz and aluminosilicates.

A petrographic inspection of a representative sample of the ore indicated that the zinc and tin sulfide minerals were present in a state of extremely fine dissemination.

Chemical assays of a representative sample showed the ore analyzed 14.37% by weight Zn, 2.03% Sn, 2.01% Pb, 14.54% Fe_2O_3, 7.62% Al_2O_3, 41.25% total SiO_2 and 20.06% free SiO_2. In the examples, all reagent quantities are reported as lbs. per ton of dry mineral solids.

Example I

CONVENTIONAL FLOTATION OF BOLIVIAN ZINC-TIN SULFIDE ORE

A sample of the complex ore was crushed to minus 8 mesh (Tyler) and ground in a stainless steel rod mill at 50% solids in the presence of soda ash (15 lb./ton) to prevent activation of sphalerite and pyrite by iron from the mill. During the grinding, 0.6 lb./ton sodium cyanide and 2.0 lb./ton zinc sulfate were added to promote the deactivation of sphalerite. After grinding, the ore was diluted with water to 20% solids. The pulp was conditioned for flotation of stannite by adding sodium hydroxide to a pH of 9.5 and 0.025 lb./ton "Z–11" xanthate. A rougher tin-lead flotation was made. The rougher float was cleaned three times without addition of reagents, producing the final tin-lead concentrate and a combined cleaner tails. The rougher tailings were treated with 1.5 lb./ton copper sulfate pentahydrate to reactivate the sphalerite and 3.0 lb./ton lime for pH control. The pulp was then conditioned for sphalerite flotation with 0.075 lb./ton "Z–11" xanthate. A small amount of "Dowfrother 250" was added. A second float was taken after addition of 0.075 lb./ton "Z–11" xanthate. The float products were combined to make the zinc rougher concentrate. The pulp remaining in the float cell (tailings) was discarded. The zinc rougher concentrate was treated with 2.4 lb./ton of lime and was cleaned twice, producing a zinc cleaner concentrate and a zinc cleaner tails product.

Metallurgical results for the test are summarized in Table I.

TABLE I.—CONVENTIONAL SULFIDE FLOTATION OF COMPLEX BOLIVIAN ZINC-TIN ORE

		Chemical analysis		Percent distribution	
	Wt. percent	Sn percent	Zn percent	Sn	Zn
Zinc Conc..	20.23	0.85	54.22	9.2	75.1
Tin Conc...	2.80	3.65	16.38	5.5	3.2

The data in Table I showed that 75.1% of the Zn was recovered in the form of a concentrate of 54.22% Zn grade by the conventional sulfide process. However, only 5.5% of the Sn values were recovered in the form of a concentrate of 3.65% Sn grade. The results therefore indicate that the zinc mineral responded well to the conventional sulfide flotation but that tin did not.

Example II

PROCESS OF THE INVENTION

A minus 8 mesh sample of the Bolivian zinc-tin ore that had been used in Example I was ground at 50% solids in a pebble mill to 100% minus 325 mesh. The ground ore pulp was diluted with water to 10% solids and the diluted pulp was flocculated by adding sulfuric acid to a pH of 3.5. Supernatant liquid was decanted and the thickened pulp was fluidized and dispersed by adding 10 lb.% ton soda ash and 3 lb.% ton "O" brand sodium silicate (the registered trade mark of a sodium silicate solution containing 37% solids). The dispersed pulp was conditioned for flotation by adding 6.0 lb./ton ammonium sulfate as a 5% aqueous solution and an emulsion containing water, 1.0 lb./ton ammonium hydroxide, 6.2 lb./ton crude tall ore and 6.2 lb./ton "Calcium Petronate" (the registered trademark of a 50% solution of calcium petroleum sulfonate in mineral oil). The pulp was conditioned for 20 minutes and floated in a subaeration-type flotation cell.

The bulk cleaner froth concentrate was cleaned three times by reflotation.

The tailings were discarded and the cleaned bulk concentrate was filtered. The filter cake which contained about 70% solids was fluidized by incorporating 13 lb./ton soda ash and 26 lb./ton "O" brand sodium silicate. The fluidized cake was maintained in a closed container for 20 hours.

The aged, dispersed filter cake was then diluted to about 15% solids and aerated in the subaeration flotation machine. A froth product (the zinc concentrate) was withdrawn and recleaned twice by flotation without addition of reagents. The three tailings were combined, forming the tin concentrate.

A summary of the overall results appears in Table II.

TABLE II.—PROCESS OF THE INVENTION, FLOTATION OF BOLIVIAN ZINC-TIN ORE

		Differential Zn-Sn flotation			
		Chemical Analysis		Percent Distribution	
	Wt. percent	Sn	Zn	Sn	Zn
Zinc Conc..	20.2	1.23	45.68	12.7	65.9
Tin Conc...	26.5	5.03	12.44	68.5	23.5

Data in Table II shows that 68.5% of the tin in the ore was recovered in the final tin concentrate containing 5.3% Sn. The recovery of zinc in the zinc concentrate was about 65.9% and this concentrate contained 45.78% by weight.

A comparison of the data in Table II (process of the invention) with data in Table I (conventional sulfide flotation with depressant for sphalerite) shows that five times more tin was recovered in the tailings by the process of the invention than was obtained in the tin concentrate of the conventional tin flotation process. The data show also that the tin grade was higher when the separation was made in accordance with the process of the invention. Zinc recovery was slightly lower with the process of the invention, although the grades of the zinc concentrates

were comparable in the two processes. Thus, the process of the invention resulted in a marked improvement in tin recovery and grade without substantial sacrifice in zinc recovery or grade.

Example III

This example illustrates the application of the process of the invention to the separate recovery and lead and tin values in the flotation tailings of flotation tests carried out with conventional sulfide reagents, as described in Example I. As shown in the metallurgical results for that test, almost 50% of the tin values in the Bolivian ore had been lost in the attempt to selectively float stannite from depressed sphalerite with a xanthate reagent.

The tailings used in the test analyzed 1.91% Sn, 0.47% Pb and 0.78% Zn.

In one test (test A) the tailings pulp was flocced with sulfuric acid and the flocced pulp was thickened by settling and decantation. The thickened pulp was diluted to about 20% solids and dispersed by adding 3.2 lb./ton soda ash and 1.4 lb./ton "O" brand sodium silicate. One portion of this pulp was conditioned for flotation with 2.5 lb./ton ammonium sulfate as a 5% aqueous solution, an aqueous emulsion made from 0.4 lb./ton ammonium hydroxide, 4.5 lb./ton tall oil acids and 3.4 lb./ton "Calcium Petronate." After the emulsion was added the pulp was conditioned with 2.5 lb./ton "Eureka M" oil. A rougher flotation product was produced and it was cleaned three times. The final froth product was the bulk cleaner concentrate. The machine discharge products from the rougher and cleaner flotations were combined to form the tailings, identified as T–MD 1–4. The results are summarized in Table III.

In an attempt to improve further the metallurgical results, a similar flotation test (test B) was carried out with the exception that minus 325 mesh calcite was added to the pulp of dispersed tailings after addition of the dispersants and before adding the ammonium sulfate and emulsified tall oil. Most of the calcite reported in the bulk cleaner concentrate. The results of this test are also summarized in Table III.

The bulk cleaner concentrates from tests A and B were air dried and dried concentrates were dispersed (fluidized) by adding 13.0 lb. soda ash and 26.0 lb. of "O" brand sodium silicate per ton of solids in the concentrate and pugging the mixture to insure uniform mixing. The pugged material contained about 75% solids. The dispersed pugged materials were aged (allowed to stand in closed containers) for about 20 hours. After this, the material was repulped with water to about 10% solids and placed in a subaeration-type flotation cell. Without adding reagents, the pulps were subjected to froth flotation. With the pulp containing added calcite (test B), most of the calcite reported in the froth. A summary of the results appears in Table III.

The data in Table III for the bulk cleaner concentration step show that in test A the bulk concentrate contained 78.8% of the Sn and 80.6% of the Zn. In test B, 75.6% of the Sn and 94.5% of the Zn was recovered, indicating that the presence of calcite during the bulk float aided zinc recovery. In both cases, the grade of metal values in the bulk cleaner concentrate were very low. In test B, metal grades were lower than in test A because of the presence of calcite flotation reagent as a diluent in the bulk cleaner float.

Data in Table III for the differential zinc-tin flotation step show that in both tests over 80% of the tin was desirably depressed and recovered as a result of the dispersant treatment of the bulk cleaner concentrates at high solids. Thus, the zinc was selectively floated from the tin in the fatty acid reagentized bulk concentrate. The data indicate that the presence of calcium carbonate during the sodium silicate treatment of the reagentized bulk cleaner concentrate resulted in even better separation and recovery of tin.

TABLE III.—SEPARATION OF ZINC AND TIN FROM SULFIDE FLOTATION TAILINGS

Flotation Step I—Bulk Cleaner Concentration

	Chemical Analysis (Percent)				Percent Distribution		
	Wt.	Sn	Pb	Zn	Sn	Pb	Zn
Test A (w/o calcium carbonate)	35.6	4.22	0.69	1.76	78.8	32.5	80.6
Test B (with calcium carbonate)	32.4	3.75	0.78	1.80	75.6	60.9	94.5

Flotation Step II—Selective Flotation of Zn from Sn

	Froth product		Tailings (combined)	
	Zn percent	Percent Dist. Zn	Sn percent	Percent Dist. Sn
Test A	10.69	82.3	4.24	86.8
Test B	[1] 4.72	85.0	5.37	96.9

[1] Includes $CaCO_3$.

I claim:

1. A method for separately concentrating zinc and tin minerals from a finely divided pulp of a complex sulfide ore which comprises subjecting said ore pulp to froth flotation in the presence of an anionic collector, thereby producing as a bulk float product an aqueous concentrate of zinc and tin sulfide minerals, thickening said concentrate, incorporating an alkaline dispersing agent into the thickened concentrate and aging the concentrate thus treated, subjecting the aged concentrate to froth flotation in an alkaline pulp, thereby producing a froth product which is a concentrate of zinc minerals and a tailing which is a concentrate of tin minerals.

2. The method of claim 1 wherein said ore pulp also contains galena and said galena is selectively floated from said pulp in the presence of xanthate collector reagent before said bulk float is made.

3. The method of claim 1 wherein finely divided calcium carbonate mineral is incorporated into said pulp before said bulk float is obtained, whereby said calcium carbonate concentrates in said bulk float product and is subsequently floated with zinc minerals after said bulk float is treated with alkaline dispersant.

4. The method of claim 1 wherein said anionic reagent comprises an aqueous alkaline emulsion of tall oil.

5. The method of claim 1 wherein said bulk float is carried out in the presence of sodium silicate.

6. A method for separately recovering sphalerite and stannite from a complex Bolivian ore containing siliceous gangue and having finely divided metal values which comprises grinding said ore to minus 325 mesh, forming said ground ore into an aqueous pulp,

conditioning said pulp with sodium silicate and a fatty acid collector reagent, subjecting the conditioned pulp to froth floatation in an alkaline flotation circuit, thereby producing a bulk float which is a concentrate of sphalerite and stannite and a tailing,

removing sufficient water from said bulk float concentrate until the solids content thereof is within the range of about 60% to 85%,

incorporating an alkaline dispersant with said dewatered bulk float and aging the mixture for at least four hours, said dispersant being selected from the group consisting of sodium carbonate, sodium silicate, sodium condensed phosphate and mixtures thereof,

diluting the thus-treated bulk float and subjecting the diluted pulp to froth flotation without addition of

fatty acid collector, thereby producing a froth product which is a concentrate of sphalerite and a tailing which is a concentrate of stannite.

7. The method of claim 6 wherein said ore also contains galena which is floated from said pulp in the presence of a xanthate collector reagent and sodium cyanide before said bulk zinc-tin float is made.

8. The method of claim 6 wherein said dispersant is employed in amount of at least 10 lb./ton of solids in said bulk float.

9. The method of claim 8 wherein said dispersant is a mixture of sodium carbonate and sodium silicate.

10. The method of claim 9 where said tall oil is the source of said fatty acid.

References Cited

UNITED STATES PATENTS

1,337,548	4/1920	Edsel	209—167
2,395,639	2/1946	Monson	209—166
2,594,612	4/1952	Bates	209—167
2,990,958	7/1961	Greene	209—167 X
3,167,502	1/1965	Duke	209—167 X

OTHER REFERENCES

Concentration of the Novomonastyrsk Complex Ores, C.A. 60,895J, 1961.

HARRY B. THORNTON, *Primary Examiner.*

R. HALPER, *Assistant Examiner.*