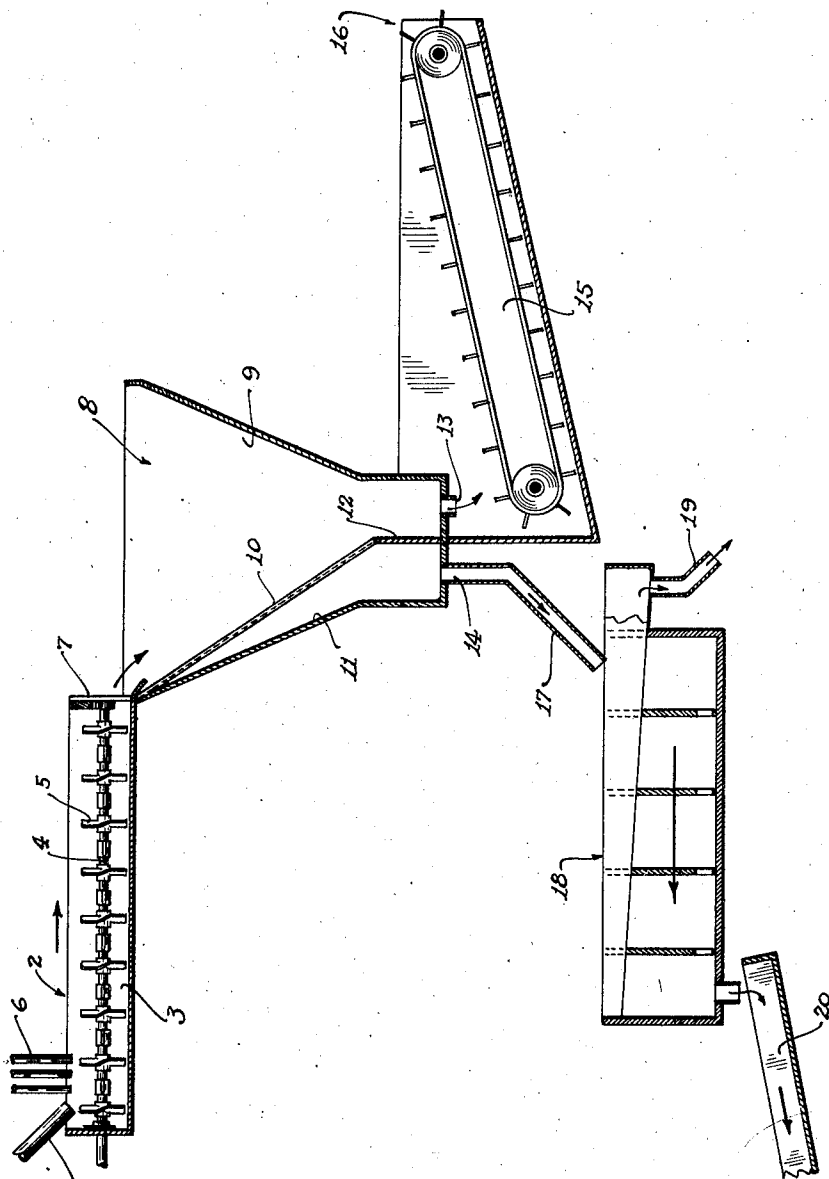


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J. P. HALL ET AL
PHOSPHATE ROCK RECOVERY

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Jesse Parkey Hall and
William Arthur Hodges

INVENTOR

BY *Stan W. Johns*

ATTORNEY

WITNESS -
Wm C. Meiser

UNITED STATES PATENT OFFICE

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PHOSPHATE ROCK RECOVERY

Jesse Pankey Hall, Bartow, and William Arthur
Hodges, Plant City, Fla., assignors, by mesne
assignments, to Swift and Company, a corpo-
ration of Illinois

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This invention relates to an improved process for recovering phosphate values.

Phosphate rock, or calcium phosphate is produced in large quantities in the Florida phosphate fields. In this section, phosphate mineral is found in a stratum which may vary in thickness as from three to sixteen feet under an overburden of earth and sand varying in depth as from five to twenty-five feet. It is customary practice to remove the overburden by draglines, that is, by huge power operated scoops. The matrix or phosphate ore is mined hydraulically by playing streams of water under high pressure against a bank of matrix which is disintegrated and carried away in the water which is pumped to a washer where the silica and clay is disassociated from the phosphate particles as efficiently as is possible by the action of disintegrating machinery such as log washers and a series of screens.

About fifty per cent of the phosphate values present in the matrix is removed in the form of coarse phosphate particles known as "pebbles", by the screening operation. The remaining fifty per cent of the phosphate values pass through the screens, together with the major portion of the silica, clay and other impurities, by reason of the fact that the smaller particles of phosphate material are too small to be retained on screens without also retaining an excessive amount of silica or sand.

In recent years, various methods of recovering this finer material from the washer tailings have been employed. Perhaps the most widely used method of recovering the finer phosphate particles from the washer tailings, has been the method of flotation in which the washer tailings are ground and treated with suitable reagents to selectively oil the phosphate values by aeration in suitable flotation cells. By this method the major portion of the phosphate values in the washer tailings may be floated as froth and recovered in the form of what is known as "flotation concentrates."

The phosphate particles are composed primarily of calcium phosphate with minor quantities of other elements which can not be separated from the calcium phosphate by flotation concentrates. In concentrates made from the ores of the Florida deposits, there remains a small proportion of silica and other material which it is not economical to separate, and consequently, the best Florida phosphate concentrates contain from 70% to 80% calcium phosphate, or bone phosphate of lime, commonly known by the abbreviation, B. P. L. It is common practice in the

operation of washers in the Florida field to establish a washer cutoff of between fourteen mesh and twenty mesh. By this is meant that if the washer cutoff is fourteen mesh, any material finer than fourteen mesh passes through the finest mesh screen used with the tailings. A fourteen mesh screen is a screen having fourteen rows of openings per linear inch in either direction. It will be understood, of course, that by reason of the variation of the size of the wires of which the screen is constructed, that the size of the openings will vary within rather narrow limits. It is the more usual practice in the Florida field to employ a washer cutoff of about fourteen to twenty mesh. For the purpose of describing the size of the particles involved, the screen mesh is based on screens having square openings, although many screens are employed with openings of various shapes, which may be more or less elongated.

It has been found in practice that concentration of the phosphate values in washer tailings may not be successfully carried out by flotation with fractions coarser than approximately twenty-eight mesh, and with fractions between twenty-eight mesh and thirty-five mesh, flotation is not satisfactory. To secure the best results with flotation concentration of phosphate values, the phosphate material should be finer than thirty-five mesh. Since the washer cutoff may vary from fourteen to twenty it will be readily appreciated that a considerable portion of the phosphate values rejected by the washer can not be successfully recovered by flotation, due to the spread between the washer cutoff and the fineness of particle size required for successful flotation.

It is one of the objects of the present invention to provide a concentration method which will permit a substantial recovery of all sizes of phosphate particles not recovered in ordinary washer operations. It will be seen, therefore, that the method of the present invention permits the recovery of those phosphate particles which are not contained in the slimes and which are smaller than typical pebbles. By reason of the inefficiency of the flotation method on what is commonly known as the coarser fractions, that is, the fractions between fourteen mesh and thirty-five mesh, it is necessary to provide means for grinding or sub-dividing these coarser fractions if the phosphate values contained therein are to be recovered by flotation. To perform this function, a conventional rod mill is ordinarily employed. It has been found, however, that the action of

the rod mill is to grind some of the material so fine that it may not be successfully recovered by flotation since the material finer than one hundred fifty to two hundred mesh is lost in slimes and not recovered by flotation. Bearing in mind that the effective limits of flotation are between thirty-five mesh and one hundred fifty to two hundred mesh, attention is called to the following tables in which are set out analyses of the screen fractions of the feed sent through the rod mill and the discharge from the rod mill, compiled by testing composite samples of discharge accumulated by taking smaller samples at approximately hourly intervals during one shift of eight hours during each day of a week's operation of the Waldo flotation plant of Swift & Company Fertilizer Works near Agricola, Florida, during July 1935. During this period of time, approximately five thousand tons of feed was passed through the rod mill.

EXAMPLE "A"

Feed to rod mill

Mesh	Percent weight	B. P. L.	Percent of B. P. L. content
Plus 20	5.2	74.42	9.75
-20 plus 28	11.3	61.39	17.48
-28 plus 35	15.6	38.81	15.24
-35 plus 48	32.5	28.59	23.39
-48 plus 65	24.2	35.83	21.83
-65 plus 100	9.2	46.19	10.70
All plus 100	98.0	39.87	98.39
-100 plus 150	1.5	32.49	1.23
-150	0.5	29.14	0.38
All -100	2.0	31.15	1.61
Total	100.0	39.71	100.00

EXAMPLE "B"

Discharge rod mill

Mesh	Percent weight	B. P. L.	Percent of B. P. L. content
Plus 20	1.01	72.11	2.04
-20 plus 28	5.18	58.92	8.54
-28 plus 35	10.93	37.64	11.56
-35 plus 48	30.81	21.93	18.92
-48 plus 65	29.42	35.98	29.67
-65 plus 100	13.38	41.98	15.73
All plus 100	90.78	34.01	86.46
-100 plus 150	3.79	41.75	4.42
-150	5.43	60.17	9.12
All -100	9.22	52.60	13.54
Total	100.00	35.72	100.00

It is clear from the foregoing examples that although it is necessary to grind the washer tailings before passing them through a flotation plant if satisfactory results are to be secured, since approximately seventeen per cent of the phosphate values in the feed are found in fractions not amenable to flotation, a decided loss in B. P. L. content is noted in the coarser fractions of the material passing through the rod mill.

In view of the fact that the coarser fractions may not be recovered by flotation, various efforts have been made to develop a process by which the coarser fractions could be economically concentrated, an example of which method is exemplified in United States Patent No. 1,968,008 to Chapman and Littleford, which discloses a method of concentration by tabling, causing the sand to stratify on the deck of a modified Wilfley table and carrying the phosphate values in the form of floccules suspended in the water, or as a skin float in a current of water transversely of the riffles.

Another method which has been found satisfactory in practice for concentrating the coarser fractions, is described and claimed in United States Patent No. 2,017,468 to McCoy, Wright, and Hall. By the method of this patent, the feed is treated with reagents to agglomerate the phosphatic material and form particles of larger size which are separated from the smaller particles of sand in an underwater screening operation. It has been found in practice that although this underwater screening process is effective both with the coarser fractions and with the finer fractions, which alone are amenable to flotation, in order to form the most efficient agglomerates for use in such a process, relatively large quantities of reagents are necessary. We have discovered, however, that a substantial recovery may be secured in such an agglomeration process by using relatively smaller quantities of reagents of the order, for example, used in typical flotation.

The present invention involves employing certain features of a non-flotation concentration method, and certain features of flotation in a novel process which results in efficient recovery of both the coarse and fine fractions, eliminates the necessity of grinding, and employs the relatively low quantities of reagents which are required for ordinary flotation. We have further found that the present novel process may be carried out without grinding the coarser fractions and with reagents less expensive than are required for flotation.

The quantity and proportions of reagents employed in carrying out the present process have been found to be inefficient for non-flotation concentration procedure alone, and inefficient for flotation alone, but give surprising results in the method of the present invention.

The method of the present invention may be carried out with apparatus such as is disclosed in the accompanying drawing. After the washer tailings have been deslimed as in a Dorr bowl classifier, they are fed through pipe 1 to mixer 2 comprising a trough 3, in which two rotary shafts 4 are mounted one beside the other. Blades 5 are mounted at an incline on shafts 4 and are of a construction suitable for conveying the material through the mixer from left to right as shown in the drawing. As the material is conveyed through the mixer, it is caused to be agitated and intimately mixed with reagents which may be introduced through one or more pipes such as 6. After the mixture is so treated, the material is discharged from the end 7 of the mixing apparatus and passes into the separator 8. The separator 8 comprises a tank 9 provided with an inclined stationary screen 10 above the floor 11. The screen extends downwardly at about the same angle as the floor. At the lower end of the screen, a vertical partition 12 and outlet valves 13 and 14 are provided. Material too large in size to go through the screen passes thereover and through outlet valve 13 and may be removed by a pump or any other conveying means such as is represented in the drawing by drag conveyor 15. Elevator 15 is of ordinary construction and will not be described in detail, it being merely understood that the conveyor permits the water to flow away from the concentrates which are discharged at upper end 16 into bins, railroad cars, or the like. The material which has dropped through the screen passes out through outlet 14 and through pipe 17 to flotation cells 18, passing through the cells in the direction of the arrows. The concentrates removed from the flotation cells

by froth flotation are pumped to suitable bins through line 19 and the tailings from the flotation cells, which are relatively free of the phosphate values, are carried away by a launder 20 to the debris dumps.

We have compared the results of the method of the present invention with results secured on the same type of feed by froth flotation. In the following examples, washer tailings from the same day's run at the Waldo mine of Swift & Company Fertilizer Works were treated both by flotation and by the combination of flotation and agglomeration of the present invention. The flotation data given in the four examples were secured in laboratory tests. The concentration ratio given in the following examples was secured by subtracting the B. P. L. of the tailings from the B. P. L. of the concentrates and dividing this result by the figure obtained by subtracting the B. P. L. of the tailings from the B. P. L. of the feed. It will be seen, therefore, that in each instance the method of the present invention was more efficient since in each case the concentration ratio was lower, indicating less rock loss by the method of the present invention than was the case with flotation of the same feed. It should be further noted that in each instance, less of the relatively expensive fish acid and more of the relatively inexpensive fuel oil was used in carrying out the method of the present invention than was the case in practicing flotation with the same feed. The less expensive reagents used with the present method have been found to be inefficient in practicing either flotation or the agglomeration method such as is taught in the patent of McCoy, et al., No. 2,017,468.

The caustic used in each of the examples was commercial sodium hydroxide. The rosin residue was a commercial rosin residue dissolved in kerosene. The fish acid in each instance was the commercial product commonly known as fish oil fatty acid and contained about 85% free fatty acid. The fuel oil used in each instance was a mixture of distillate of twenty-eight degrees Baumé and Bunker C fuel oil in about equal proportions.

EXAMPLE 1

Reagents per ton feed

	Flotation	Present method
Caustic.....lbs.....	0.46	0.50
Rosin residue.....lbs.....	.07	.14
Fish acid.....lbs.....	1.19	.80
Fuel oil.....lbs.....	2.32	3.36

Flotation

Product	Percent weight	B. P. L.	B. P. L. recovered	Concentration ratio
Feed.....	100	34.73		
Concentrates.....	41.0	72.18	85.2	2.440
Tails.....	59.0	8.73		

Present method

Feed.....	100.00	35.42		
Agglomeration concentrates.....	15.48	72.80	31.8	
Flotation concentrates.....	29.28	72.93	60.3	
Total concentrates.....	44.76	72.88	92.1	2.234
Tails.....	55.24	5.06		

EXAMPLE 2

Reagents per ton feed

	Flotation	Present method
Caustic.....lbs.....	0.46	0.60
Rosin residue.....lbs.....	.08	.14
Fish acid.....lbs.....	1.36	.85
Fuel oil.....lbs.....	2.20	3.09

Flotation

Product	Percent weight	B. P. L.	B. P. L. recovered	Concentration ratio
Feed.....	100.0	37.18		
Concentrates.....	44.1	71.62	84.9	2.270
Tails.....	55.9	10.06	15.1	

Present method

Feed.....	100.0	38.28		
Agglomeration concentrates.....	36.1	74.37	70.1	
Flotation concentrates.....	11.3	72.24	21.3	
Total concentrates.....	47.4	73.86	91.4	2.109
Tails.....	52.6	6.19	8.6	

EXAMPLE 3

Reagents per ton feed

	Flotation	Present method
Caustic.....pounds.....	0.47	0.50
Rosin residue.....do.....	.08	.14
Fish acid.....do.....	1.32	.90
Fuel oil.....do.....	2.17	3.14

Flotation

Product	Percent weight	B. P. L.	B. P. L. recovered	Concentration ratio
Feed.....	100.0	40.33		
Concentrates.....	46.8	74.99	87.0	2.137
Tails.....	53.2	9.84	13.0	

Present method

Feed.....	100.0	41.94		
Agglomeration concentrates.....	27.9	75.62	50.3	
Flotation concentrates.....	25.4	73.42	44.5	1.875
Total concentrates.....	53.3	74.87	94.8	
Tails.....	46.7	4.62	5.2	

EXAMPLE 4

Reagents per ton feed

	Flotation	Present method
Caustic.....pounds.....	0.50	0.50
Rosin residue.....do.....	.14	.14
Fish acid.....do.....	1.05	.85
Fuel oil.....do.....	2.97	3.09

Flotation

Product	Percent weight	B. P. L.	B. P. L. recovered	Concentration ratio
Feed.....	100	34.51	100.0	
Concentrates.....	41.6	74.53	89.8	2.4065
Tails.....	58.4	6.02	10.2	

Present method

Product	Percent weight	B. P. L.	B. P. L. recovered	Concentration ratio
Feed.....	100.0	36.25	-----	-----
Agglomeration concentrates.....	26.5	75.75	55.4	-----
Flotation concentrates.....	17.0	71.05	33.3	-----
Total concentrates.....	43.5	73.91	88.7	2.299
Tails.....	56.5	7.26	11.3	-----

In carrying out the process of the present invention, it is found that the washer cutoff may be relatively coarse. If the phosphate particles fed to the agglomeration mixer are in part too large for successful agglomeration, they will be sufficiently large not to pass through the screen, but will pass over the screen with the agglomerated material. In carrying out the tabling process described in the Chapman and Littleford patent, No. 1,968,008, more reagents are required than is necessary for flotation as will be apparent from the specification of that patent. Furthermore, a greater quantity of reagents is specified in that patent than is required for carrying out the present method. It will be noted that in the single example given in the Chapman and Littleford patent, 0.4 pound of caustic, 1.2 pound of red oil, and 4 pounds of fuel oil were used per ton of solids. In carrying out the process of the McCoy, et al. patent, it has been found by tests that satisfactory results on washer tailings finer than fourteen mesh require about 2.5 pounds of soap, and about 10 pounds of fuel oil per ton of solids.

It is evident by comparing this data with the Examples 1 to 4 which have been given in this specification, that the quantity of reagents employed in carrying out the present method is less costly than the reagents required for tabling or under-water screening. Due to the fact that the relatively coarse fraction, that is, the fraction between 14 mesh and 35 mesh, is included in the feed, the reagents necessary for the present method are less costly than the usual flotation reagents. Furthermore, it is found that with the lower quantity of fish acid employed with the present method, less sand is carried away with the concentrates during the flotation step than would be the case were the usual flotation proportions and quantities of reagents employed. The present invention provides a simple, economical method for concentrating phosphate values from washer tailings with less reagents than would be necessary for tabling or under-water screening, and with greater efficiency than can be secured by flotation.

The process of the present invention may be carried out successfully by substituting tabling apparatus of the type described in the Chapman and Littleford patent, No. 1,968,008, for under-water screening apparatus of the type disclosed in the McCoy et al. patent, No. 2,017,468. The present invention involves a complete process in which the coarser fractions are first removed with the aid of a selective flocculating agent or agglomerating agent, and substantially all of the balance of the recoverable phosphate fines are recovered by flotation. For the purposes of the present invention, it is unimportant whether the coarser fractions are removed by agitative wet stratifying classification according to the relative settling values such as is involved in tabling or by agglomeration and under-water screening on the

basis of the difference in size between the agglomerates and the gangue particles.

The phosphate bearing material may be preliminarily treated with caustic soda or the caustic soda may be simultaneously added with the other reagents. Soap and an unsaponifiable oil may be used effectively, the preferred soap being sodium oleate.

As has been described, the best results occur from the use of caustic soda and oleic acid, but other alkaline substances and other saponifiable oils may be used with varying degrees of success. Although the process has been found particularly adapted to phosphate rock concentration in the Florida field, the process may also be used for the concentration of other nonsulphide minerals, particularly where the values to be concentrated contain an element of the alkaline earth group.

The reagents described in this specification are described by way of illustration and not by way of limitation.

Examples of minerals which may be concentrated by the process of the present invention in addition to calcium phosphate ores include apatite and Cassiterite, copper carbonate, beauxite, manganese oxide, iron oxide, barytes, lead carbonate, zinc carbonate, and zinc silicate.

We claim:

1. The method of concentrating phosphatic fines which comprises adding a selective agglomeration and flotation agent to phosphate bearing material, agitating the material in the form of an aqueous pulp to form agglomerates of phosphatic fines, separating the agglomerates from the pulp, subjecting the pulp freed of agglomerates to agitation and aeration to produce a phosphate bearing froth, and recovering the phosphate values from the froth.

2. The method of concentrating phosphatic fines which comprises adding a selective agglomeration and flotation agent to phosphate bearing material, agitating the material in the form of an aqueous pulp to form agglomerates of phosphatic fines, causing the pulp to pass down an inclined screen submerged in water of a size permitting the agglomerated phosphatic fines and coarser particles of phosphatic fines to pass thereover, and permitting sand and the finer particles of phosphatic material to pass therethrough, separating the agglomerates and coarser particles of phosphatic fines from the pulp, subjecting the pulp freed of agglomerates and coarser particles of phosphatic fines to agitation and aeration to produce a phosphate bearing froth, and recovering the phosphate values from the froth.

3. The method of concentrating phosphatic fines which comprises adding a selective agglomeration and flotation agent to phosphate bearing material, agitating the material in the form of an aqueous pulp to form agglomerates of phosphatic fines, subjecting the mixture to agitative wet stratifying classification, gathering the relatively large agglomerates and coarser particles of phosphatic fines in an overlying stratum and the sand and finer particles of phosphatic fines in an underlying stratum, separating the relatively large agglomerates and coarser particles of phosphatic fines from the pulp, subjecting the pulp freed of the relatively large agglomerates and coarser particles of phosphatic fines to agitation and aeration to produce a phosphate bearing froth, and recovering the phosphate values from the froth.

4. The method of concentrating phosphatic fines contained in finely divided phosphate bearing material containing both coarse and fine fractions which comprises treating the material with caustic, rosin residue, fatty acid, and fuel oil in the presence of water, subjecting the treated material to agitative wet classification according to the relative settling values of the phosphatic fines and the gangue, recovering the coarser fractions of phosphatic fines in an overlying stratum and the sand and finer fractions of phosphatic fines in an underlying stratum, subjecting the material of the underlying stratum to agitation and aeration to produce a phosphate bearing froth, and recovering the phosphate values from the froth.

5. The method of concentrating phosphatic fines which comprises adding a selective oiling agent to phosphate bearing material, moving the treated material under water to cause relative movement of the particles thereof, separating the coarser fractions of the phosphate values from the gangue, subjecting the gangue freed from the coarser fractions of the phosphate values to agitation and aeration to produce a phosphate bearing froth, and recovering the phosphate values from the froth.

6. The method of concentrating finely divided ores of non-sulphide minerals which comprises adding a selective agglomeration and flotation agent to the ore, agitating the ore in the form of an aqueous pulp to form agglomerates of the mineral values of the ore, separating the agglomerates from the pulp, subjecting the pulp freed of agglomerates to agitation and aeration to produce a mineral bearing froth, and recovering the mineral values from the froth.

7. The method of concentrating finely divided ores of non-sulphide minerals which comprises

adding a selective agglomeration and flotation agent to the ore, agitating the ore in the form of an aqueous pulp to form agglomerates of the mineral values, causing the pulp to pass down an inclined screen submerged in water of a size permitting the agglomerated non-sulphide minerals and coarser particles of the non-sulphide minerals to pass thereover, and permitting sand and the finer particles of non-sulphide minerals to pass therethrough, separating the agglomerates and coarser particles of non-sulphide mineral values from the pulp, subjecting the pulp freed of agglomerates and coarser particles of non-sulphide minerals to agitation and aeration to produce a non-sulphide mineral bearing froth, and recovering the non-sulphide mineral values from the froth.

8. The method of concentrating finely divided ores of non-sulphide minerals which comprises adding a selective agglomeration and flotation agent to the ore, agitating the ore in the form of an aqueous pulp to form agglomerates of the mineral values, subjecting the mixture to agitative wet stratifying classification, gathering the relatively large agglomerates and coarser particles of non-sulphide minerals in an overlying stratum, and the sand and finer particles of non-sulphide minerals in an underlying stratum, separating the relatively large agglomerates and coarser particles of non-sulphide mineral values from the pulp, subjecting the pulp freed of relatively large agglomerates and other particles of the non-sulphide minerals to agitation and aeration to produce a non-sulphide mineral bearing froth, and recovering the mineral values from the froth.

JESSE PANKEY HALL.
WILLIAM ARTHUR HODGES.