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PROCESS OF CONCENTRATING NON-METALLIFEROUS ORES

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This invention relates to processes of concentrating non-metalliferous ores, and it comprises processes wherein a mixture of such an ore and silicious gangue associated therewith is washed with an alkaline solution to condition the ore mixture for the froth separation of silicious gangue, and the ore mixture is thereafter subjected to froth separation in the presence of one or more primary aliphatic amines containing at least twelve carbon atoms, and at pH values higher than 7.

In the co-pending Ralston and Pool application, Serial No. 260,222, processes for the concentration by froth flotation of phosphate minerals are described. These processes consist in subjecting phosphate ores to froth flotation in the presence of primary aliphatic amines under alkaline conditions whereby the silicious gangue associated with the phosphate ore is preferentially concentrated in the concentrate, and the phosphate values collect in the tailings. The primary amines of relatively high molecular weight, that is to say, those compounds having twelve or more carbon atoms, are unusual flotation agents for non-metalliferous ores associated with silicious gangue because they "float" the silicious gangue in preference to the ore values. This is the reverse of most flotation procedures. The rule is not a general one, however, since, in some instances, ore values may be floated away from the silicious material by the use of primary amines, and what is or is not floated frequently depends upon the particular minerals in the ore mixture. With phosphate ores these primary amines preferentially float the silicious gangue, and this is particularly true in the case of phosphate ores in which the phosphate is present as calcium phosphate or bone phosphate of lime. Some few phosphate ores, such as apatite, may tend to concentrate more of the phosphate values in the float, but it is the general rule that silicious gangue is preferentially floated away from non-metalliferous values when the primary amines are used as flotation agents.

In the co-pending application above referred to, it is brought out that the better results, with particular respect to economy of flotation agent, are obtained when the flotation of the silicious material is conducted on the alkaline side, that is to say at pH values above 7 and generally within the range of about 8.5 to 10 or 11. Flotation on the alkaline side obviously precludes the presence of any primary aliphatic amine salts during the flotation step, although, of course, the primary amine can be added to the slurry of ore as a water-soluble salt and the salt thereafter decomposed to liberate the free amine upon alkalinizing the slurry. One curious thing about flotation in the presence of primary amines is that the flotation is occurring in the presence of flotation agents which are quite insoluble in water.

These primary aliphatic amines are unusually selective, and they are readily obtainable from the higher fatty acids by processes involving conversion of the latter to nitriles and the hydrogenation of the nitriles. But at the present time the primary aliphatic amines of twelve or more carbon atoms are expensive in comparison with many other flotation agents on a per-ton-of-ore-treated basis. Hitherto fatty acids have been used for the flotation of phosphate rock with some minor degree of success so if the primary aliphatic amines, which are necessarily derived from the fatty acids, are to be used commercially and thus obtain the markedly improved selectivity of the separation, ways must be found for decreasing the quantity of primary amine necessary for commercial separation of the ore. With this object in mind we have made many experiments, and as a result of our experimental work we have discovered that the non-metalliferous ore mixture can be "conditioned" before the froth separation and the separation thus markedly improved with respect to sharpness of concentration, and with respect to reduction in the quantity of flotation agent necessary. We have discovered that when the ore mixture is conditioned by giving it an alkaline wash that these desirable objects can be achieved.

Therefore, the present invention is concerned with ways of conditioning non-metalliferous ore and gangue mixtures prior to subjecting them to froth separation in the presence of primary aliphatic amines used under alkaline conditions.

The conditioning process of the present invention consists in treating the ore mixture, while suspended in water, with an alkali, such as sodium hydroxide. The ground ore is simply formed into a pulp or slurry, caustic soda added thereto, and the mixture stirred for a shirt time. A few minutes is enough. Then the aqueous alkali solution is drained from the ore, and the ore reformed into a slurry for the amine flotation step. Or the drained ore can be washed with water to remove adhering alkali, formed into a slurry and the pH adjusted on the alkaline side. In the first instance the alkali solution adhering to the ore is used for imparting alkalinity to the slurry during the froth separation. In the sec-

ond instance the alkali solution is substantially washed from the ore and then the conditioned ore made into a slurry and the pH adjusted, as stated.

In the practice of our invention we can use any primary aliphatic amine having twelve or more carbon atoms. These are, for example, dodecylamine, hexadecylamine and octadecylamine, having twelve, sixteen and eighteen carbon atoms respectively. The intermediate amines between twelve and eighteen carbon atoms not specifically mentioned can also be used, but those stated by name are the ones most readily available. The hydrogen ion concentration of the ore slurry or pulp during the flotation should be above 7 and is advantageously kept at about 9 to 10 for best results.

The present process, while primarily adopted for the concentration of phosphate minerals, can also be used successfully for the removal of silicious gangue from any non-metalliferous commercial ore. Fluorite ores, namely, those containing calcium fluoride, are especially adaptable in the process of the present invention.

We shall now give examples illustrating how our invention can be practiced.

Example 1

Fifty grams of a phosphate ore designated as Tennessee mud pond sand was placed in a Denver type flotation cell and deslimed twice with water. The original ore analyzed 40.20% CaO, 29.22% P_2O_5 and 14.07% SiO_2. After desliming, the ore was treated with a sodium hydroxide solution containing the equivalent of one-half pound of sodium hydroxide per ton of phosphate ore. The sodium hydroxide solution was then removed and the ore washed with water. The cell was then filled with water and the pH of the slurry adjusted to 10.2 by the addition of sodium hydroxide solution. The equivalent of 0.5 lb. per ton of octadecylamine was then added and the ore subjected to a froth flotation separation. This resulted in a concentrate which weighed 5.22 grams and a tailing which weighed 34.5 grams. The slimes weighed 10.28 grams. The composition of the various fractions were as follows: slimes: CaO, 22.14%; P_2O_5, 17.93%; SiO_2, 32.26%; concentrate: CaO, 30.30%; P_2O_5, 18.94%; SiO_2, 39.29%; tailing: CaO, 49.98%; P_2O_5, 35.95% and SiO_2, 3.73%. This corresponds to a recovery of 81.42% of the available phosphate in the original as a product containing 78.60% B. P. L. The selectivity index for the flotation based on these results is 4.34.

We shall now show the comparison between the flotation concentration of such a conditioned ore and one which has not been conditioned.

Fifty grams of the same ore was deslimed in a similar manner, but the pretreatment with sodium hydroxide solution was omitted. The pH of the slurry was then adjusted to 10.2 by the addition of sodium hydroxide solution. One and six-tenths pounds per ton of octadecylamine per ton of ore was then added and the ore subjected to a froth flotation. This resulted in a concentrate which weighed 7.80 grams and a tailing which weighed 30.96 grams. The slimes weighed 11.24 grams. The composition of the various fractions was as follows: slimes: CaO, 23.16%; P_2O_5, 18.46%; SiO_2, 36.10%; concentrate, CaO, 41.40%; P_2O_5, 29.52%; SiO_2, 16.92%; tailings: CaO, 44.79%; P_2O_5, 31.74% and SiO_2, 11.23%. This corresponds to a recovery of 69.24% of phosphate originally present in the ore as a 69.46% B. P. L. product. Based on these results the selectivity index was calculated to be 2.09.

It can be seen from a comparison of the above results that the pretreatment with sodium hydroxide markedly increases the efficiency of the separation. When the ore was previously treated with sodium hydroxide solution an 81.42% recovery of 78.60% B. P. L. product was obtained whereas in the absence of this treatment a 69.24% recovery of a 69.46% B. P. L. product was obtained. The former would be considered as a commercially satisfactory flotation, while the latter is unsatisfactory both as regards recovery and quality of product obtained. This is shown by a comparison of the selectivity indices which were 4.34 in the case of the pretreated ore and 2.09 for the untreated ore. It will also be noted that the more satisfactory separation required approximately one-third the amount of octadecylamine which was required in the absence of the pretreatment.

Example 2

Fifty grams of the ore described under Example 1 were placed in the flotation cell and deslimed twice with water. The ore was then treated with a sodium hydroxide solution containing the equivalent of one-half pound of sodium hydroxide per ton of ore. The sodium hydroxide solution was then decanted and fresh water added. The pH was then adjusted to 10.5 by the addition of dilute sodium hydroxide solution. The equivalent of 0.75 pound per ton of octadecylamine was then added and the ore subjected to a froth flotation. This resulted in a concentrate which weighed 3.81 grams and a tailing which weighed 36.69 grams. The slime weighed 9.50 grams. The composition of the various fractions was as follows: slimes: CaO, 19.95%; P_2O_5, 16.49%, SiO_2, 31.25%; concentrate: CaO, 22.17%; P_2O_5, 13.50%; SiO_2, 53.06%; tailing: CaO, 48.57%; P_2O_5, 34.42% and SiO_2, 4.06%. This corresponds to a recovery of 85.76% of the phosphate values originally present in the ore. The B. P. L. content of the product is 75.23%. Based on these results the selectivity index is 4.79.

Example 3

Fifty grams of a Florida phosphate ore were weighed into the Denver type flotation cell and deslimed once with water. The ore used has the following composition: SiO_2, 61.21%; CaO, 19.82% and P_2O_5, 11.94%. The ore was then treated with a sodium hydroxide solution which contained the equivalent of one pound of sodium hydroxide per ton of ore. The sodium hydroxide solution was then decanted, fresh water added and the pH of the slurry adjusted to 9.9. An amount of octadecylamine equivalent to 1.25 pound per ton of ore was then added and the mixture subjected to a froth flotation. This resulted in a concentrate which weighed 30.8 grams and analyzed as follows: CaO, 5.96%; P_2O_5, 4.11% and SiO_2, 88.92%. The tailings weighed 19.2 grams and had the following composition: CaO, 41.70%; P_2O_5, 23.90% and SiO_2, 20.18%. This corresponds to a recovery of 78.3% of the phosphate values. The B. P. L of the product is 52.3%.

A fifty gram sample of the same ore was deslimed and handled in a similar manner with the exception that the pretreatment with sodium hydroxide solution was omitted. One and twenty-five hundredths pounds of octadecylamine per ton of ore was added and the ore subjected to a

froth flotation separation. This resulted in a concentrate which weighed 32.34 grams and a tailing which weighed 17.66 grams. The composition of the concentrate was as follows: CaO, 8.97%; P_2O_5, 5.64% and SiO_2, 83.25%. The composition of the tailing was: CaO, 42.00%; P_2O_5, 21.90% and SiO_2, 19.48%. This corresponds to a recovery of 68.0% of the phosphate present. The B. P. L of the product is 47.9%.

It is readily seen that the pretreatment of the sample with sodium hydroxide solution markedly improved the flotation.

Example 4

A phosphate ore which analyzed 60.25% silica, 20.90% calcium oxide and 15.25% phosphoric oxide was pretreated with a sodium hydroxide solution containing one-half pound of sodium hydroxide per ton of ore. One-half pound per ton of dodecylamine gave an 85.30% recovery of the phosphate values as a 78.03% B. P. L product. A similar flotation omitting the pretreatment with sodium hydroxide required 1.25 pounds of dodecylamine per ton of ore. The recovery in this case dropped to 69.85% and the B. P. L. of the tailings to 71.31%. It is evident that the pretreatment with sodium hydroxide solution improved the quality of the product obtained and greatly reduced the amount of reagent required.

While we have specifically drawn the above examples to the flotation of silica from phosphate, we have found that pretreatment with alkali hydroxides markedly improves the efficiency of other froth flotation separations when primary amines are used as the flotation agents. The separation of barites, fluorite and various carbonates from silicious gangues is markedly improved by this process.

It should be pointed out that this process enables many ores to be effectively separated by the use of high molecular weight primary amines which cannot be satisfactorily separated with amines in the absence of this treatment. The improvements brought about by this process are, therefore, much greater than simply that a reduced amount of amine is necessary to bring about the flotation. We, of course, consider that other alkali metal hydroxides may be used as a substitute for the sodium hydroxide, disclosed in this invention. Potassium hydroxide is effective. The quantity of alkali based on the weight of the ore is not critical. Amounts as high as five pounds per ton of ore can be used.

Having thus described our invention, what we claim is:

1. In the froth separation of silicious gangue from phosphate ores, the steps which comprise treating the ore with an alkali metal hydroxide solution draining the solution from the treated ore, and then subjecting an aqueous slurry of the treated ore to a froth separation in the presence of a primary aliphatic amine having at least twelve carbon atoms, the slurry having a pH in excess of 7.

2. The process as in claim 1 wherein the pH is 9 to 10.

3. In the froth separation of silicious gangue from phosphate ores, the steps which comprise treating the ore with a caustic alkali solution, draining the alkali solution therefrom, washing the ore with water, forming the ore into an aqueous slurry and subjecting the slurry to a froth separation in the presence of a primary aliphatic amine having at least twelve carbon atoms, the slurry having a pH in excess of 7.

4. The process as in claim 3 wherein the pH is 9 to 10.

5. In the separation of siliceous gangue from non-metalliferous ores the steps which comprise treating the ore with an alkali metal hydroxide solution, draining the solution from the treated ore, and then subjecting an aqueous slurry of the treated ore to a separation step for the removal of siliceous gangue in the presence of a primary aliphatic amine having at least twelve carbon atoms, the slurry having a pH in excess of 7.

6. In the separation of siliceous gangue from non-metalliferous ores the steps which comprise treating the ore with a caustic alkali solution, draining the alkali solution therefrom, washing the ore with water, forming the ore into an aqueous slurry and separating siliceous gangue therefrom in the presence of a primary aliphatic amine having at least twelve carbon atoms, the slurry having a pH in excess of 7.

7. The process as in claim 5 wherein the pH is 9 to 10.

8. The process as in claim 6 wherein the pH is 9 to 10.

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