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REMOVAL OF SILICA FROM NONMETALLIC
ORES BY FROTH FLOTATION

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This invention relates to an improved method of froth flotation of silica using certain classes of cationic reagents.

The flotation of silica by means of various cationic reagents has become of considerable importance, particularly in the beneficiation of phosphate ore from the Florida Pebble Phosphate field because of the fact that it is possible to obtain improved grade.

A number of cationic flotation reagents have been proposed, among which the condensation product of polyalkylene polyamines with fatty acids have proven to be extraordinarily useful, both by reason of their activity and the simpler and less critical flotation procedure which may be employed. The use of reagents of this type are described and claimed in the patent to Christmann, Jayne and Erickson, No. 2,278,060 of March 31, 1942. The present invention relates to an improvement in the process of floating silica using the abovementioned class of reagents.

In the flotation of silica, particularly in phosphate ores, the problem of slime is a critical one and in many cases it is not sufficient for best results to completely deslime a flotation feed because the flotation operation itself tends to produce secondary slime from the soft coated surfaces of the phosphate particles. This has led to a process in which the deslimed feed is subjected to polishing followed by a secondary slime as described and claimed in the patent to Mead and Maust, No. 2,216,040 of September 24, 1940. Improved results are thereby obtained, but at the expense of further processing steps. It has been found that polishing may be eliminated or reduced if the flotation is carried out very rapidly before any time has elapsed in the flotation cell which would permit the formation of secondary slime. This procedure is described and claimed in the copending patent of Mead and Maust, No. 2,293,470, issued August 18, 1942. High speed in flotation is therefore of great utility in the removal of silica.

The present invention is based on a temporary improvement in the speed of flocculation effected by reagents of the polyalkylene polyamine fatty acid condensation type. It was found that reagents of this type when formed into a solution and added to the flotation process colloidal material appears to be present and gives a kind of silky appearance. Speed of flocculation, while higher than with many other cationic reagents, is still not as great as might be desired, and it has been found that if a water solution of the polyalkylene polyamine fatty acid condensation products are

heated to approximately 100° C. or the boiling point, they become clear. The silky appearance disappears entirely and the solution remains clear for a considerable period of time even after cooling down to room temperature. In fact, it takes about 30 minutes or more before the silky appearance again sets in and clarification by heating can be repeated indefinitely. It is not known just what takes place when the colloidal material goes into solution. It may be pure solution phenomenon, or there may be some reversible chemical changes. The invention is not intended to be limited to any theory of what happens when the heating takes place. The importance of the invention, however, lies in the fact that when froth flotation is effected with the clarified solution an enormously increased flocculation speed results, and not only is it possible to obtain good grade with a very rapid flotation but even if the ordinary flotation time is used, an improvement in grade is noted. Maximum improvement results when the heating is carried out to about 100° C. but improvement starts when the heating exceeds 30° C. and is quite marked about 65° C. Therefore while it is preferred to heat to about 100° C., the invention is not broadly limited to the use of this particular temperature.

It is probable that speed of flocculation is not the only phenomena because when a small amount of reagent in water is subjected to aeration in a flotation cell, the froth characteristics are quite different. The cold reagent containing colloidal material produces a brittle froth which is brittle but will not overflow or perforate the lip of the machine. When, however, the reagents have been heated and clarified, the froth is composed of much smaller bubbles which readily overflow the lip of the flotation cell so that it is possible to remove a third of the water from the cell in the form of froth. As froth characteristics are important in most flotation operations, it seems reasonable to assume that the improvement in froth obtained by clarifying the reagent solution by heat is a factor in the improved result in addition to the increased speed flocculation which can be demonstrated in a more nearly quantitative manner. However, it is not intended to limit the invention to any particular theory.

The improved results are shown in the following tests which were performed in a laboratory Fagergren flotation cell and which can be checked in larger scale operation.

A standard deslimed phosphate flotation feed of -35 mesh obtained from phosphate deposits in the Florida Pebble Phosphate field is condi-

tioned at high solids in a 2% water solution of the acetate of a condensation product of coconut oil fatty acids with a mixture of polyethylene polyamines containing predominantly diethylenetriamine, triethylenetetramine and tetraethylene-pentamine. A portion was conditioned with the ordinary cold solution of the reagent and the other portions conditioned with the reagent after heating to 20°, 35°, 50°, 65°, 80° and 100° respectively. In each case after 10 seconds, the silica froth is skimmed as in standard test procedure, the skimming being continued for approximately 2 minutes which is normally referred to as a regular test. After 10 seconds, however, a small portion of the pulp in the flotation cell is removed from the bottom and analyzed to determine the amount of beneficiation which is effected in it for the period of 10 seconds. This is a common test used to determine speed of flocculation.

As the greatest importance of the present invention is in improved grade, the results of the tests are shown in percent of insoluble in the phosphate tailing which is directly relatable to grade. The results are shown in the following table:

Table I

Solution temperature	Per cent insoluble in phosphate	Seconds floated
20° C.....	2.80	Regular test.
	10.40	10 seconds.
35° C.....	2.30	Regular test.
	9.20	10 seconds.
50° C.....	2.20	Regular test.
	8.80	10 seconds.
65° C.....	1.90	Regular test.
	6.00	10 seconds.
80° C.....	1.65	Regular test.
	4.60	10 seconds.
100° C.....	1.50	Regular test.
	2.65	10 seconds.

The results of the laboratory test can be obtained on a larger scale but it is not as readily possible to determine flocculation in 10 seconds on a large machine.

The effect of the falling temperature after clarification was tested by conditioning the same feed as in Table I with samples of the solution heated to 100° C. and then cooled down, samples being used at various temperatures on the way down. The result is shown in the following table:

Table II

Solution temperature	Per cent insoluble in phosphate	Seconds floated
100° C.....	1.20	Regular test.
	2.80	10 seconds.
80° C.....	.80	Regular test.
	2.00	10 seconds.
65° C.....	.80	Regular test.
	1.60	10 seconds.
60° C.....	.80	Regular test.
	1.60	10 seconds.
35° C.....	1.60	Regular test.
	1.20	10 seconds.
22° C.....	1.20	Regular test.
	1.60	10 seconds.

It will be apparent that the grade on the regular test remained substantially constant within experimental error, it being impossible to get quantitative results when the percentage of insoluble is down as low as 1%.

After the solution of reagent had cooled down to room temperature, a portion was allowed to stand for 30 minutes and began to take on a

slightly milky appearance. When used in this state for conditioning the phosphate feed, the results were as follows:

Table III

Per cent insoluble in phosphate	Seconds floated
1.60	Regular test.
4.40	10 seconds.

It will be apparent that while on the regular test there is as yet no diminution of efficiency, the speed of flocculation is beginning to drop rapidly. After longer standing the results are the same as a cold solution which has not been clarified.

Another test was made to determine how short a time of flocculation would give useful results and also to further determine the effect of cooling and standing. The feed was the same as described above and the test procedure was as follows:

Batches of feed were agitated in a laboratory Fagergren machine for 3 seconds, then silica was floated for various periods of time, after which a small amount of phosphate was discharged from the bottom of the cell while the machine was still running. This sample of phosphate was used to determine the B. P. L. and insoluble.

The metallurgical results are shown in the following table:

Table IV

Seconds silica floated before taking sample of phosphate	Solution heated to 100° C. to make up, then used while hot		Solution heated to 100° C. to make up, then allowed to cool and stand for several hours. Used cold.		Solution made up cold and used cold	
	B. P. L.	Insol.	B. P. L.	Insol.	B. P. L.	Insol.
Regular test.	78.95	1.70	78.73	2.30	78.66	2.55
5.....	76.10	6.05				
10.....	78.51	2.80	62.42	22.85	74.60	7.95
15.....	78.82	1.95				

The results at 10 seconds with cold reagent when compared with reagent that has never been heated up is not particularly significant. When a reagent does not flocculate rapidly in an extremely short test, very wide fluctuations are to be expected. The significant factor is that the cold material in 10 seconds will give no useful grade.

When a slightly different polyalkylene polyamine condensation product was used, namely the condensation product of palm oil with a mixed polyethylene polyamine, the improvements noted were similar to reagents showing slightly different activities.

The invention has been described in more detail in conjunction with the flotation of silica from phosphate rock as this is the most important commercial process at the present time. However, the action of the reagent is primarily on the silica and the presence of the phosphate except insofar as it tends toward slime formation is secondary. Comparable improved results are obtained in floating silica away from other non-metallic ores.

Throughout the specification and claims the term "higher fatty acids" is used in its customary practical sense as meaning fatty acids having twelve or more carbon atoms.

We claim:

1. A method of floating silica from a non-metallic ore which comprises conditioning an ore pulp with a solution of a condensation product of higher fatty acids with polyalkylene polyamines, at temperatures below those at which substantial quantities of imidazolines are formed by ring closure, which has been heated until clarified and subjecting the conditioned pulp to froth flotation before the clarified reagent has stood in the pulp for a sufficient time to reprecipitate colloidal matter.

2. A method of floating silica from a phosphate ore which comprises conditioning an ore pulp with a solution of a condensation product of higher fatty acids with polyalkylene polyamines, at temperatures below those at which substantial quantities of imidazolines are formed by ring closure, which has been heated until clarified and subjecting the conditioned pulp to froth flotation before the clarified reagent has stood in the pulp for a sufficient time to reprecipitate colloidal matter.

3. A method of floating silica from a non-me-

tallic ore which comprises conditioning an ore pulp with a solution of a condensation product of higher fatty acids with a mixture of polyethylene polyamines, at temperatures below those at which substantial quantities of imidazolines are formed by ring closure, which has been heated until clarified and subjecting the conditioned pulp to froth flotation before the clarified reagent has stood in the pulp for a sufficient time to reprecipitate colloidal matter.

4. A method of floating silica from a phosphate ore which comprises conditioning an ore pulp with a solution of a condensation product of higher fatty acids with a mixture of polyethylene polyamines, at temperatures below those at which substantial quantities of imidazolines are formed by ring closure, which has been heated until clarified and subjecting the conditioned pulp to froth flotation before the clarified reagent has stood in the pulp for a sufficient time to reprecipitate colloidal matter.

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