United States Patent

[11] **3,623,605**

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[33]		**Italy**
[31]		**11310A/69**

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[54] **PROCESS FOR THE FLOTATION OF FLUORITE**
7 Claims, No Drawings

[52] **U.S. Cl.** **209/166**
[51] **Int. Cl.** **B03d 1/02**
[50] **Field of Search** 209/166, 167; 252/61

[56] **References Cited**

UNITED STATES PATENTS

2,300,827	11/1942	Christmann	209/166
2,757,797	8/1956	Eckert	209/166 X
2,803,345	8/1957	Jacobs	209/166
3,179,250	4/1965	Bunge	209/166
3,430,765	3/1969	Allen	209/166 X

FOREIGN PATENTS

142,232	3/1961	U.S.S.R.	252/61
782,107	9/1957	Great Britain	252/61

OTHER REFERENCES

A P C Application of Goette Ser. No. 274,858, Published July 13, 1943.

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ABSTRACT: Improvement in flotation of calcium fluoride from clay-containing ores which comprises conditioning the flotation slurry with an alkyl phenol ethoxide and a fatty acid ethoxide prior to adding the usual flotation reactants. Flotation slurry may be prepared from common calcium fluoride crude ore or from clay slime discarded from prior flotation processes.

PROCESS FOR THE FLOTATION OF FLUORITE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for the flotation of CaF_2, more particularly, to an improved process for separating, by flotation, the calcium fluoride from the crude ore, wherein it is in admixture with gangues and clays.

2. Description of the Prior Art

It is known that the beneficiation of the ores by flotation is often influenced by the clay-containing substances present in the crude ore. Especially in the flotation of nonmetallic minerals, the sludges of the flotation slurry, that is, the clays contained in such sludges, adversely affect the recovery efficiency and amount of the reactants consumed.

In order to overcome this drawback, in general, resort has been had to the preliminary desliming of the slurry, or, when possible, to the neutralization of the effects of the clays by means of suitable reactants.

The desliming operation, however accurately conducted, involves losses in the useful component that one wishes to beneficiate. These losses increase with intensified grinding and with decreased hardness of the valuable component.

The neutralization of the sludges by means of specific reactants, while having found widespread application in recent years, does not provide an entirely satisfactory solution to the problem since the reactants used not only depress the flotability of the sludge but also of the other, desirable components of the flotation slurry, thereby increasing the loss of the mineral sought to be recovered.

In the particular case of the fluorite minerals, i.e., CaF_2, the sludge presented a particularly difficult problem because no specific reactant was known that would neutralize the sludges without appreciably reducing the flotability of the CaF_2. The lack of specific reactants compelled one to resort to physical desliming of the slurry, also with considerable losses of fluorite. In fact, since the fluorite is a rather soft mineral and since it is necessary to employ rather intensive grinding in order to free the granules, there occurs an accumulation of CaF_2 in the finest fractions which are removed with the sludges. The losses of CaF_2 due to the desliming sometimes amount to 20 percent by weight of the CaF_2 contained in the raw material.

The mining industry over the years has accumulated this muddy material or slime in suitable basins, generally located near the processing installations, in the hope of eventually being able to recover the CaF_2 contained in the slime. In these basins the fine fractions of the flotation wastes that contain appreciable quantities of CaF_2 are also collected.

SUMMARY OF THE INVENTION

This invention provides means for recovering the fluorite contained in the muddy material or slime in the collection basins as well as for obtaining from such slime or from normal crude ore a CaF_2 product of an "acid" degree (that is, with a CaF_2 titre higher than 95 percent and with a useful CaF_2 titre higher than 91 percent; the useful CaF_2 being defined as the total CaF_2 less 4 times the weight percent of SiO_2). More particularly, we have found new reactants which, used together with those previously employed for the flotation of fluorite, provide a simple and inexpensive solution to the problem.

In accordance with the present invention, an ethoxylated alkyl phenol and an ethoxylated fatty acid are employed to condition the ore prior to flotation. Thus, we have surprisingly found that the ethoxylated alkyl phenols depress the sludges without interfering with the flotability of the fluorite whereas, on the contrary, the previously known common depressors of the sludges also decrease the flotability of the fluorite. Moreover, we have surprisingly found that the ethoxylated fatty acids act as strong activators of the fluorite flotability, particularly the fine fluorite which is accompanied by very fine gangue.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The ethoxylated alkyl phenols, also called alkyl phenylpolyethylene glycols, are generally obtained by reaction of an alkyl phenol with ethylene oxide. They have, as a substituent on the phenyl radical, an alkyl having from nine to 15 carbon atoms, and contain from 10 to 16 glycolic groups, —CH_2—CH_2—O—.

These compounds are described as surfactants, for example, in J. P. SISLEY—Index des détergents-Editions Teintex, Paris (wherein they are classified in class III/C and are called polyethoxy ethers of alkyl phenols); A. M. SCHWARTZ, J. W. PERRY—Surface Active Agents and Detergents—Interscience Publishers, New York (1966)—Vol. II, page 125; McCUTCHEON's—Detergents and Emulsifiers—DAE 1966 Annual—Morristown, N.J.

These nonionic surfactants are produced industrially in great quantities and are easily found on the market. These commercially available products include, for instance the Tergitols of Union Carbide Corp., such as: Tergitol 12–P–9, Tergitol 12–P–10, Tergitol 12–P–12 dodecylphenyl-polyethylene glycol ethers); the Igepal CA and Igepal CO of General Aniline & Film Corp.; the Sapogens A of Anorgana Gendorf; the Hostapals C of Farbwerke Hoechst; the Carboxanes of Testilana Corp.; and the Tritons X of Rohm & Haas.

The ethoxylated fatty acids, also called polyoxyethylated fatty acids or, better still, polyethyleneoxy esters of the fatty acids, are obtained by reacting the fatty acid with ethylene oxide or with a polyethylene glycol. The polyethyleneoxy esters used in the process of the present invention are formed from a fatty acid having from 12 to 20 carbon atoms and from 10 to 20 —CH_2—CH_2—O—(oxy ethylene) groups. They are, for instance, described in Sisley (loc. cit.) wherein they are classified in class III/B and are called polyethoxy esters of fatty acids; in Schwartz (loc. cit. on page 130); and in McCutcheon's (loc. cit.).

These anionic surfactants are also produced on an industrial scale in large quantities and are easily found on the market.

Commercial products of this kind include, for instance, the Emulphors of Sinnova Sadic Company, of BASF and of General Aniline & Film Corp. (obtained from oleic acid, castor oil, talloil and ethylene oxide; the Emulsenes of Sapchim-Fournier-Cimig; the Ethofats of the Armour Industrial Chem. Co.; and the Lipals E and S of Drew Chemical Corp.

The preparation or conditioning of the mineral may be carried out in accordance with the present invention in the following way:

The muddy material is pulped in water to form a slurry having a solids content of 15 to 30 percent by weight. The slurry thus obtained is conditioned for 1–10 minutes, preferably from 2 to 4 minutes, with polyethyleneoxy alkyl phenol (100–200 g./t. [grams per metric ton] of dry solid) and then for an additional 1 to 10 minutes, preferably from 3 to 5 minutes, with the polyethyleneoxy ester (200–300 g./t. of dry solid). The slurry thus prepared is ready for being conveyed to flotation, which latter operation is carried out with the known reactants and with the usual technique.

Thus, for the flotation, the following reactants are then added to the already conditioned slurry. (The quantities depend on the composition of the mineral treated.) An unsaturated fatty acid, such as oleic acid, as collector for the CaF_2 (it forms a water-repellent coating on the fluorite granules); from 250 to 500 g./t. of solids are used, according to the fluorite contents of the slurry.

A starch (e.g. corn starch), as depressor of the silica, in quantities of from 500 to 1500 g./t. of solids.

Sodium fluoride as activator of the fluorite, in quantities of from 300 to 800 g./t. of solids (the sodium fluorite may be totally or partially replaced by the polyethyleneoxy ester).

A tannin, such as quebrache, for depressing the calcite in the successive flotation runs of the concentrate, in quantities of from 100 to 200 g./t. of solids.

The reactants are added under stirring, in short time intervals from each other in accordance with common prior art flotation procedures. The polyethyleneoxy ester, an activator for the fluorite, may be added together with the flotation reactants. Once the addition of the reactants has been completed, the slurry is conditioned for some minutes (usually 2–20 minutes), then air is blown into the slurry and the mass is floated up to exhaustion of the mineralization of the foam (5 to 10 minutes). The concentrate of the first flotation (rough or primary concentrate) is floated again (reflotation or rerun) for three or four times until obtaining an definitive concentrate of an "acid degree" as hereinabove defined.

The conditioning of the slime, carried out with the foregoing polyethyleneoxy reactants in accordance with the process of the present invention, provides for the first time a method for obtaining by known flotation methods a concentrate of fluorite of an "acid degree" and with high yields (greater than 80 percent).

As previously mentioned, the conditioning with the particular reactants in accordance with this invention may also be carried out on the raw mineral (tout-venant), in particular on the clay-containing raw materials; in the case of tout-venant ore, the pulp can contain up to 50 percent solids. With this treatment the need for any desliming operation is eliminated with the advantage of the thereby eliminating a processing phase and, moreover, of obtaining a greater yield of fluorite. (The conditioning is, naturally, followed by flotation by known methods.)

The following examples are given to further illustrate the present invention and are not intended to limit the scope thereof.

EXAMPLE 1

A test was carried out on a slime, containing, on a dry basis, 37.50 percent by weight of CaF_2, 39.83 percent by weight of SiO_2, 8.55 percent by weight of carbonates, with the remainder (14.12 percent) being made up of clay and various oxides. The granulometric analysis indicated that 87 percent by weight of the sample had a particle size below 400 mesh U.S. Tyler (0.034 mm.), and that 70 percent by weight of the sample comprised very fine substances, below 20 microns in diameter. The test was carried out by the known technique (described in "Revue de l'Industrie Minérale" [1967], 1–9) according to the procedures summarized in table 1. The slurry had a mineral/water weight ratio of 1:2.5. The consumption of reactants is expressed in grams/ton (metric) of dry solid.

The results of the test are recorded in table 1A. As can be seen from this table, the concentrate thus obtained displayed a fair CaF_2 titre, but was not of "acid degree." Moreover, the recovery is quite low (61.25 percent).

Another test was carried out on the same slimy material employed in the preceding test, using, however, the polyethyleneoxy reactants in accordance with this invention. The operational procedures have been indicated in table 2. The slurry had a solid/water weight ratio of 1:2.5 The consumption of reactants is expressed in grams per ton of dry solid. The results obtained are recorded in table 2A. The final concentrate showed a titre in carbonates of 1.10 percent and in silica of 0.9 percent; thus, it is of an "acid degree." The recovery was good, about 85 percent.

EXAMPLE 2

A test was carried out on a tout-venant mineral, without physical desliming, according to the known technique.

The raw substance was ground to below 65 mesh, U.S. Tyler The granulometric analysis was the following:

Mesh	By weight
65+100	13.2%
100+150	22.0%
150+200	12.0%
200+400	16.2%
<400	36.0%

The conditions of the test are indicated in table 3, while the results are recorded in table 3A.

Another test was carried out on the same mineral of the preceding test, using the known technique, but effecting a desliming of the slurry before the flotation. The operational conditions are indicated in table 4, while the results are recorded in table 4A.

A third test was carried out on the same mineral as used for the two preceding tests, without desliming the slurry, using, however, the particular surfactant agents in accordance with this invention.

The operational conditions are indicated in table 5, while the results are recorded in table 5A.

From the titre in the final concentrate and from the yield, the advantage of the process of the present invention is evident.

TABLE 1

Operations	Consumption of reactants in g./t. (mixture)					Time in min.
	Sodium silicate	Chromium III sulphate	Starch	Sodium fluoride	Acintol FA1	
Conditioning	350	140	2,000	800	----------	5
Conditioning					400	5
Roughing flotation					100	10
1st re-run	70	28	200	170	----------	7
2nd re-run	70	28	200	170	----------	5
3rd re-run	70	28	200	170	100	5
4th re-run	70	28	200	170	----------	5

NOTE,—The Acintol FA1 of Arizona Chemical Co, is an emulsified mixture of unsaturated fatty acids obtained from talloil,

TABLE 1A

Products	Weight percent	Composition, percent			Distribution, percent		
		CaF_2	MCO_3	SiO_2	CaF_2	MCO_3	SiO_2
Feeding	100.00	37.50	8.55	39.83	100.00	100.00	100.00
Roughing flotation:							
Tailing	54.50	8.98	7.42	63.25	13.07	47.40	86.59
Concentrate a	45.50	68.56	8.87	14.61	86.93	52.60	13.41
1st run of concentrate a:							
Tails	8.00	28.30	14.50	37.90	6.03	13.56	7.60
Concentrate b	37.50	80.88	8.90	6.16	80.90	39.04	5.87
2nd run of concentrate b:							
Tails	6.50	43.70	25.40	20.80	7.57	19.29	3.39
Concentrate c	31.00	88.70	5.45	3.09	73.33	19.75	2.42
3rd run of concentrate c:							
Tails	4.50	56.30	20.60	8.50	6.75	10.75	0.97
Concentrate d	26.50	94.21	2.90	2.18	66.58	9.00	1.45
4th run of concentrate d: Tails	2.50	80.2	10.70	4.35	5.33	3.16	0.27
Final concentrate	24.00	95.7	2.10	1.95	61.25	5.84	1.18

NOTE.—MCO_3 denotes carbonates and hydroxides, usually of Ca and Mg, soluble in acetic acid.

TABLE 2

Operation	Consumption of reactants in g./t.					
	Aionico F. 560	Aionico T. 510	Dextrine	Emulsified olein	Quebrache	Time in min.
Conditioning	300					2
Do		400				2
Do			1,000	500		3
Roughing flotation						5
1st re-run					150	4
2nd re-run					100	4
3rd re-run					50	4
4th re-run						4

NOTE.—The surfactant "Aionico D, 560" is a Montecatini Edison S.p.A. product; it is a dodecylphenol having 12 groups of ethylene oxide. The surfactant "Aionico T. 510" is a Montecatini Edison S.p.A. product; it is a condensation product of Tall oil with 17 molecules of ethylene oxide.

TABLE 2A

Products	Weight percent	Composition, percent			Distribution, percent		
		CaF_2	MCO_3	SiO_2	CaF_2	MCO_3	SiO_2
Feeding	100.00	37.50	8.55	39.83	100.00	100.00	100.00
Roughing flotation:							
Tailing	53.00	2.56	8.41	64.54	3.63	52.13	85.89
Concentrate a	47.00	76.89	8.70	11.95	96.37	47.87	14.11
1st re-run of concentrate a:							
Tails	6.00	8.50	30.20	50.30	1.36	21.22	7.55
Concentrate b	41.00	86.90	5.56	6.36	95.01	26.65	6.56
2nd re-run of concentrate b:							
Tails	4.50	28.60	28.40	35.50	3.41	14.97	3.99
Concentrate c	36.50	94.10	2.73	2.79	91.60	11.68	2.57
3rd re-run of concentrate c:							
Tails	2.50	50.00	22.5	26.30	3.34	6.54	1.65
Concentrate d	34.00	97.34	1.26	1.05	88.26	5.14	0.92
4th re-run of concentrate d:							
Tails	1.40	89.00	5.70	4.80	3.33	1.04	0.19
Final concentrate	32.60	97.70	1.10	0.90	84.93	4.10	0.73

TABLE 3

Operations	Consumption of reactants in g./t. (mixtures)							Time in mins.
	Sodium silicate	Chromium III sulphate	Diapon T	Dextrine	Sodium fluoride	Emulsified olein	Quebracho	
Conditioning	350	140						3
Do			300	800	200			15
Roughing flotation						200		7
1st re-run	70	28						5
2nd re-run	70	28						4
3rd re-run	70	28					100	4

NOTE.—The surfactant "Diapon T" is produced by Montecatini Edison S.p.A.; it is the sodium salt of N-methyl-N-oleyl-taurine.

TABLE 3A

Products	Weight percent	Composition, percent			Distribution, percent		
		CaF_2	MCO_3	SiO_2	CaF_2	MCO_3	SiO_2
Feeding	100	55.00	6.80	31.20	100	100	100
Roughing flotation:							
Tailing	50.20	25.83	8.69	53.00	23.59	64.20	85.29
Concentrate a	49.80	84.39	4.88	3.21	76.41	35.80	14.71
1st re-run of concentrate a:							
Tails	8.70	42.30	16.50	36.10	6.69	21.10	10.06
Concentrate b	41.10	93.30	2.43	3.52	69.72	14.70	4.65
2nd re-run of concentrate b:							
Tails	4.50	65.30	12.50	19.50	5.35	8.27	2.81
Concentrate c	36.60	96.73	1.19	1.56	64.37	6.43	1.84
3rd re-run of concentrate c:							
Tails	1.80	84.10	6.80	8.50	2.57	1.83	0.51
Final concentrate	34.80	97.70	0.90	1.20	61.80	4.60	1.33

TABLE 4

[The slurry shows a solid/liquid ratio equal to 1:1.5]

Operations	Consumption of reactants in g./t. (mixture)						Time in mins.
	Sodium silicate	Chromium III sulphate	Diapon T	Dextrine	Emulsified olein	Quebrache	
Conditioning	175	70					3
Do			200	200			15
Roughing flotation					100		7
1st re-run						150	5
2nd re-run						100	4
3rd re-run						50	4

TABLE 4A

Products	Weight percent	Composition, percent			Distribution, percent		
		CaF_2	MCO_3	SiO_2	CaF_2	MCO_3	SiO_2
Feeding	100	55.00	6.80	31.20	100	100	100
De-sliming sludge	9.70	68.20	7.30	18.50	12.04	10.42	5.76
Deslimed toutvenant	90.30	53.56	6.74	32.55	87.96	89.58	94.24
Roughing flotation:							
Tailing	39.10	10.43	8.95	65.35	7.42	51.47	81.91
Concentrate a	51.20	86.52	5.06	7.51	80.54	38.11	12.33
1st re-run of concentrate a:							
Tails	6.70	28.48	26.35	40.35	3.47	25.96	8.66
Concentrate b	44.50	95.25	1.85	2.57	77.07	12.15	3.67
2nd re-run of concentrate b:							
Tails	2.80	62.53	13.64	21.75	3.18	5.61	1.95
Concentrate c	41.70	97.46	1.06	1.28	73.89	6.54	1.72
3rd re-run of concentrate c:							
Tails	1.20	83.80	8.30	7.40	1.83	1.48	0.30
Final concentrate	40.50	97.85	0.85	1.10	72.06	5.06	1.42

TABLE 5

[The slurry shows a solid/liquid ratio equal to 1:1.5]

Operations	Consumption of reactants in g./t.						Time in mins.
	Aionico D. 560	Aionico T. 510	Diapon T	Dextrine	Emulsified olein	Quebracho	
Conditioning	200						2
Do		300					2
Do			300	400			15
Roughing flotation					250		7
1st re-run	50					150	5
2nd re-run						100	4
3rd re-run						50	4

TABLE 5A

Products	Weight percent	Composition, percent			Distribution, percent		
		CaF_2	MCO_3	SiO_2	CaF_2	MCO_3	SiO_2
Feeding	100	55.00	6.80	31.20	100	100	100
Tailing	40.40	8.25	9.03	66.38	6.06	53.63	85.96
Concentrate a	59.60	86.69	5.29	7.35	93.94	46.37	14.04
1st re-run of concentrate a:							
Tails	7.50	29.42	27.44	39.26	4.01	30.26	9.44
Concentrate b	52.10	94.93	2.10	2.75	89.93	16.11	4.60
2nd re-run of concentrate b:							
Tails	2.60	61.48	13.85	22.76	2.91	5.29	1.89
Concentrate c	49.50	96.69	1.48	1.71	87.02	10.82	2.71
3rd re-run of concentrate c:							
Tails	1.80	63.07	16.70	18.35	2.07	4.42	1.06
Final concentrate	47.70	97.96	0.91	1.08	84.95	6.40	1.65

Variations can, of course, be made without departing from the spirit and scope of the invention.

Having thus described our invention, what we desire to secure by Letters patent and hereby claim is:

1. In a flotation process for the recovery of fluorite from clay-containing ores, the improvement which comprises, prior to carrying out conventional flotation, conditioning a flotation slurry by treating said slurry for a period of from about 1 to 10 minutes with from about 100 to 200 grams per metric ton of slurry solids of a polyethyleneoxy alkylphenol, and thereafter treating said slurry for a period of from about 1 to 10 minutes with from about 200 to 300 grams per metric ton of slurry solids of a polyethyleneoxy ester of a fatty acid, said polyethyleneoxy alkylphenol being made up of (1) an alkylphenol radical in which the alkyl has from about 9 to 15 carbon atoms and (2) from about 10 to 16 ethyleneoxy units, and said polyethyleneoxy ester being made up of (1) a fatty acid having from about 12 to 20 carbon atoms, and (2) from about 10 to 20 ethyleneoxy units and floating a fluorite product of high acid degree.

2. The process of claim 1 wherein said treatment with said polyethyleneoxy alkylphenol is carried out for from about 2 to 4 minutes.

3. The process of claim 1 wherein said treatment with said polyethyleneoxy ester of a fatty acid is carried out for from about 3 to 5 minutes.

4. The process of claim 1 wherein said polyethyleneoxy alkylphenol is made up of a dodecylphenol and 12 ethyleneoxy units.

5. The process of claim 1 wherein the fatty acid for said polyethyleneoxy ester is tall oil, and said ester contains 17 ethyleneoxy units.

6. The process of claim 1 wherein said flotation slurry comprises an aqueous suspension of a raw material ore.

7. The process of claim 1 wherein said flotation slurry comprises fluorite-containing slime and flotation wastes discarded from prior flotation processes.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,623,605 Dated November 30, 1971

Inventor(s) Giovanni Perri, Gianfranco Aquili

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 19, "for instance" should read -- for instance, --; line 44 "Cimig;" should read -- Cimag; --.

Column 4, Table 1A, under the heading "Distribution, percent" third column headed "SiO_2", line 5, "5.87" should read -- 5.81 --.

Column 5 and 6, Table 3, the heading of the eighth column, "Quebracho" should read -- Quebrache --; Table 3A, under the heading "Composition, percent" third column headed "SiO_2", line 3, "3.21" should read -- 9.21 --.

Column 7, line 49, "Leters patent" should read -- Letters Patent --.

Column 8, line 60 (claim 6, line 2) "raw material ore." should read -- raw mineral ore. --.

Signed and sealed this 10th day of October 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.	ROBERT GOTTSCHALK
Attesting Officer	Commissioner of Patents