

Patented Sept. 29, 1942

2,297,664

UNITED STATES PATENT OFFICE

2,297,664

CONCENTRATING LANGBEINITE

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No Drawing. Application November 28, 1941,
Serial No. 420,818

21 Claims. (Cl. 209—167)

This invention relates to the concentration of potash minerals from ores containing langbeinite and more particularly to the concentration of potash minerals from ores containing langbeinite and halite or langbeinite, sylvite and halite as their principal constituents. This is a continuation-in-part of our application Serial No. 323,228, filed March 9, 1940. In the process of the invention as herein described the potash minerals, langbeinite and sylvite may be recovered separately or in the form of a mixed concentrate from ores which contain both minerals.

The invention further relates to the concentration of potash minerals by means of certain sulphonates, particularly alkali sulphonates, of derivatives of fatty acids of high molecular weight such as oleic, for example, or other saturated or unsaturated acids having eleven or more carbon atoms.

We have found that when ores of the class described are made into a pulp with water saturated with the soluble constituents of these ores, to which has been added a relatively small amount of such sulphonate, the potash minerals may be quickly and easily separated from the other minerals by such well-known processes as froth flotation or agglomeration and tabling. As a general rule we prefer to use the froth-flotation process.

The sulphonates that we have discovered to be effective for this purpose have the general formula: $\text{RCOXR}'\text{SO}_3\text{M}$, in which R is a straight chain hydrocarbon group having at least 11 carbon atoms such as $\text{C}_{17}\text{H}_{33}$, for example, X is oxygen or a NH group, R' is a divalent short chain hydrocarbon group of the general formula C_nH_{2n} such as C_2H_4 , and M is a metal, usually an alkali metal.

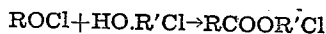
Compounds of this general formula that we have found to be particularly effective in the process of this invention are:

$\text{C}_{17}\text{H}_{33}\text{COOC}_2\text{H}_4\text{SO}_3\text{Na}$ (Igepon AP—Extra)
and

$\text{C}_{17}\text{H}_{33}\text{CONHC}_2\text{H}_4\text{SO}_3\text{Na}$ (Igepon T)

both of which are available under the trade name of "Igepon."

Three other compounds of this general formula $\text{RCOXR}'\text{SO}_3\text{M}$ were prepared by the action of acid chlorides on chlorohydrins as follows:



and subsequent reaction with sodium sulphite:



and were found to operate successfully in the process as shown below.

These compounds may be employed in conjunction with any other flotation reagents known to the art, as for example pine oil or other froth-

ing agent, or fatty acids which have the effect of reducing the amount of sulphonate required although not capable of effecting the separation by themselves, or soluble salts of amines of high molecular weight which are effective in bringing about the separation of sylvite from the other constituents of the ores. When fatty acids are used in conjunction with sulphonates as described above we have found that greatly improved recovery of langbeinite is obtained if a part of the sulphonate is used to emulsify the fatty acid before it is added to the pulp, as illustrated in Example VI, or smaller amounts of the sulphonated reagents may be employed when the fatty acids are emulsified than when they are not emulsified, to obtain equal recoveries.

It is known that these amines are effective in the separation of sylvite from halite by froth flotation and we make no claim to this separation, but by this invention we use amines in conjunction with the sulphonates herein described to effect the separation of langbeinite and sylvite from the other constituents of the ores in the form of a mixed concentrate, or, alternatively, we use the sulphonates and amines successively and separately to produce separate and successive concentrates of langbeinite and of sylvite from potash ores containing them.

In carrying out the process of the invention we have found it advisable to crush the potash minerals to such a size that they will pass through a 35-mesh screen. In certain cases better results are obtained when the ore is deslimed before flotation, particularly when sylvite is to be floated first, but in other cases the desliming step is unnecessary.

It is to be understood that other known flotation reagents such as frothing agents, dispersing agents, agents controlling the pH value of the pulp, etc., may be used in addition to the sulphonates herein described.

Further advantages of the process of the present invention will be apparent from the following examples, which are merely illustrative and are not to be construed as limiting the scope or spirit of the invention.

Example I

In this example, the langbeinite is floated first, using "Igepon AP—Extra" as the collector. The tailings of this float are returned to the flotation machine and the sylvite is then concentrated. More specifically a synthetic mixture of equal weights of minus 10-mesh sylvinitic ore and minus 10-mesh langbeinitic ore was prepared, containing 6.5% K_2O as sylvite and 6.5% K_2O as langbeinite. This is equivalent to 10.3% sylvite and 28.7% langbeinite. A charge of this mixture was ground through a 65-mesh standard Tyler sieve in a laboratory rod mill. The ground material was added to a Fagergren laboratory

flotation machine and Igepon AP—Extra was added to the pulp which was diluted to about 20% solids. The diluent was a saturated aqueous solution of ore constituents. The Igepon AP—Extra was added in stages of 2.50, 4.00, and 2.00 pounds per ton respectively, a froth being collected after each addition. There was no conditioning of reagent with the pulp. The froth products were joined and refloats twice. The tailing of the langbeinite float was returned to the flotation machine, diluted, the aliphatic amine was added, and a sylvite float was made. This froth was also cleaned twice. Results were as follows:

Product	Weight	K ₂ O	SO ₄	Cl	KCl	Lang.	NaCl	K ₂ O Rec.
Total.....	100.0	13.17	20.99	39.17	10.03	80.21	56.67	100.0
Lang. Conc.....	24.9	25.58	58.07	5.34	10.50	83.60	0.56	48.3
Lang. Midd-2.....	6.6	17.66	36.78	25.40	-----	-----	-----	8.9
Lang. Midd-1.....	21.1	12.89	16.81	42.40	-----	-----	-----	20.7
Sylvite Conc.....	3.7	57.09	0.69	46.00	90.49	0.99	4.68	16.0
Sylvite Midd-2.....	0.8	21.95	1.96	49.00	-----	-----	-----	1.4
Sylvite Midd-1.....	4.2	2.95	1.94	55.00	-----	-----	-----	0.9
Tailing.....	38.7	1.30	1.08	57.20	-----	-----	-----	3.8

The middlings may be recirculated, thus enabling much of the values contained therein to be recovered.

EXAMPLE II

Same as Example I, except "Igepon T" was used

Reagent	Lbs. per ton of original feed	
	Sylvite float	Langbeinite float
Octadecylamine acetate.....	1.00	-----
Pine oil.....	0.12	-----
Chatham fatty acid.....	-----	4.29
Pine oil.....	-----	0.24
Igepon AP—Extra.....	-----	3.00

Product	Weight	K ₂ O	SO ₄	Cl	KCl	Lang.	NaCl	K ₂ O Rec.
Total.....	100.0	11.60	12.98	46.74	11.68	18.68	67.85	100.0
Sylvite Conc.....	8.2	58.94	1.19	47.00	92.80	1.71	4.50	41.6
Sylvite Midd-2.....	1.9	55.33	1.48	47.20	87.10	2.13	9.31	9.1
Sylvite Midd-1.....	4.7	13.61	7.21	50.00	-----	-----	-----	5.5
Lang. Conc.....	17.7	21.68	62.56	3.60	2.01	90.05	4.35	33.1
Lang. Midd-3.....	0.8	8.41	19.30	41.90	-----	-----	-----	0.6
Lang. Midd-2.....	1.9	2.59	6.05	54.40	-----	-----	-----	0.4
Lang. Midd-1.....	7.4	1.76	2.05	58.40	-----	-----	-----	1.1
Tails.....	52.9	1.25	1.03	59.60	-----	-----	-----	5.7
Slime.....	4.5	7.35	10.96	39.60	-----	-----	-----	2.9
Sylvite Conc.+Midd-2.....	10.1	58.22	1.29	47.03	91.61	1.86	5.49	50.7

as the collector. The feed was deslimed prior to grinding. No sylvite float was made. "Igepon T" was added in stages of 3.00, 2.00, and 2.00 pounds per ton respectively, the froths being joined and retreated together. The results were:

Product	Weight	K ₂ O	SO ₄	Cl	KCl	Lang.	NaCl	K ₂ O Rec.
Total.....	100.0	11.31	20.01	39.38	7.58	28.81	58.94	100.0
Lang. Conc.....	15.4	24.25	53.50	7.20	10.76	77.01	3.41	33.0
Lang. Midd-2.....	6.2	14.67	39.09	24.60	-----	-----	-----	8.0
Lang. Midd-1.....	21.8	12.61	32.62	30.60	-----	-----	-----	24.3
Tailing.....	51.8	6.19	1.51	56.00	-----	-----	-----	28.4
Slime.....	4.8	14.79	30.51	22.00	-----	-----	-----	6.3

EXAMPLE III

In this example the fatty acid-Igepon combination is used to float langbeinite and amine to float sylvite.

The synthetic ore mixture was the same as in Example I. It was deslimed at 10-mesh, then ground until all the grains were fine enough to pass through a 35-mesh Tyler standard sieve. Pulp was then added to Fagergren laboratory flotation machine and diluted to 20% solids. The amine was added to this pulp and a sylvite float was made. The froth obtained was retreated twice. Tailing of the sylvite float was returned

to the flotation machine, diluted, and fatty acid was added, then Igepon. A float was then made and the froth retreated three times. The same saturated solution of original ore constituents was used for both the sylvite float and the langbeinite float. The results were:

EXAMPLE IV

This example deals with a "bulk float" in which both langbeinite and sylvite are floated together. The feed was prepared as in Example III. To

the pulp at 20% solids in Fagergren flotation machine, all the reagents were added and a float was then made. The froth obtained was re-treated twice. The results were:

Reagents, lbs./ton of original feed

Octadecylamine acetate-----	1.00
Chatham fatty acid-----	4.29
Pine oil-----	0.24
Igepon AP—Extra-----	3.00

Product	Weight	K ₂ O	SO ₄	Cl	KCl	Lang.	NaCl	K ₂ O Rec.
	<i>Percent</i>							
Total.....	100.0	12.36	11.58	47.37	13.60	16.67	67.37	100.0
Conc.....	23.3	30.60	44.94	15.37	25.24	64.69	5.49	57.6
Midd-2.....	3.5	44.91	1.50	49.60	-----	-----	-----	12.7
Midd-1.....	7.3	18.58	1.70	55.30	-----	-----	-----	11.0
Tail.....	60.8	2.79	0.88	59.10	-----	-----	-----	13.8
Slime.....	5.1	11.71	7.89	40.70	-----	-----	-----	4.9

EXAMPLE V

This example shows the effectiveness of the fatty acid-Igepon combination on a langbeinite ore containing a slight quantity of sylvite.

The charge of ore was ground so that all grains passed through 35-mesh Tyler standard screen.

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Product	Weight	K ₂ O	SO ₄	Cl	KCl	Lang.	NaCl	K ₂ O Rec.
	<i>Percent</i>							
Total.....	100.0	13.56	38.90	24.14	1.36	56.00	38.71	100.0
Conc.....	38.1	21.78	61.55	4.07	1.46	88.60	5.55	61.2
Midd-2.....	5.4	15.23	45.78	12.00	2.68	-----	4.60	6.0
Midd-1.....	11.1	12.56	37.37	24.20	-----	-----	-----	10.3
Tails.....	45.4	6.72	19.44	42.40	-----	-----	-----	22.5

EXAMPLE VI

A charge of minus 10-mesh natural mixed ore of langbeinite, sylvite and halite from 850-foot level of the mine of the Union Potash & Chemical Co. of Carlsbad, N. M., was deslimed, then the oversize on a 35-mesh screen was ground through. The screened ore was added to a Fagergren flotation machine and diluted to 20% solids.

Reagents, lbs./ton of original feed

Emulsion:

Chatham fatty acid-----	4.44
Igepon AP—Extra-----	0.90
Pine oil-----	0.24
Octadecylamine acetate-----	1.70
Igepon AP—Extra-----	2.10

Product	Weight	K ₂ O	SO ₄	Cl	KCl	Lang.	NaCl	K ₂ O Rec.
	<i>Per cent</i>							
Total.....	100.0	19.58	28.85	29.59	-----	-----	-----	100.0
Conc.....	50.1	32.02	43.83	16.70	22.09	63.09	5.44	81.9
Midd-3.....	1.6	20.76	45.30	18.80	-----	-----	-----	1.7
Midd-2.....	2.0	15.77	37.61	23.00	-----	-----	-----	1.6
Midd-1.....	5.2	8.63	20.55	40.90	-----	-----	-----	2.3
Tails.....	28.6	2.35	4.63	55.20	-----	-----	-----	3.4
Slime.....	12.5	14.25	24.25	19.80	-----	-----	-----	9.1

The pulp was then placed in a Fagergren laboratory flotation machine, diluted to 20% solids with saturated solution of ore constituents, the reagents were added and a float was made. The froth was re-treated twice. The results were:

Reagents, lbs./ton of original feed

Chatham fatty acid-----	4.29
Igepon AP—Extra-----	3.00
Pine oil-----	0.24

The flotation K₂O recovery, excluding slime loss, was 90.1%.

EXAMPLE VII

The same procedure was followed as in Example VI, except that the reagents for the langbeinite were added first and the langbeinite was floated, and then the reagents for the sylvite were added and the sylvite was then floated.

Reagents		Lbs./ton of original feed	
		Lang. float	Sylvite float
Emulsion:			
Chatham fatty acid.....		4.44	
Igepon AP—Extra.....		0.90	
Pine oil.....		0.24	
Igepon AP—Extra.....		2.10	
Octadecylamine acetate.....			1.70

Product	Weight	K ₂ O	SO ₄	Cl	KCl	Lang.	NaCl	K ₂ O Rec.
	<i>Per cent</i>							
Total.....	100.0	18.66	29.83	29.35				100.00
Lang. Con.....	36.4	21.79	63.50	3.60	1.70	91.41	4.60	42.50
Lang. Midd-3.....	1.7	20.50	53.12	11.80				1.88
Lang. Midd-2.....	2.2	20.00	37.32	24.20				2.36
Lang. Midd-1.....	4.8	16.70	13.70	43.60				4.29
Sylv. Con.....	11.2	60.05	0.71	46.80	94.81	1.02	2.60	36.07
Sylv. Midd-3.....	0.5	9.16	4.26	52.90				0.27
Sylv. Midd-2.....	1.7	3.56	2.90	56.40				0.32
Sylv. Midd-1.....	4.9	1.74	2.58	56.80				0.48
Tail.....	24.1	1.78	3.16	56.40				2.30
Slime.....	12.5	14.26	26.41	20.60				9.53
Lang. Con. + Midd-3.....	38.1				1.85	90.71	5.08	44.38

The total overall K_2O recovery was 80.45%. The total flotation recovery, excluding slimes, was 88.90%.

Where fatty acids are mentioned it is to be understood that these fatty acids may be used in emulsified form and that part of the sulphonated reagents may be used in preparing the emulsions.

EXAMPLE VIII

A compound prepared from lauric acid chloride, ethylene chlorohydrin and sodium sulphite and having the formula $C_{11}H_{23}COOCH_2CH_2SO_3Na$ was employed in this example in which the procedure was the same as in Example V. This compound was used in the amount of 3.0 lbs. together with 7.0 lbs. of Chatham's fatty acid and 0.3 lb. of pine oil, all per ton of feed.

The concentrate was retreated twice giving a final product containing 89.5% of langbeinite, 1.9 KCl and 4.3% NaCl. This represented a 74.7% recovery of K_2O and a ratio of concentration of 2.91.

EXAMPLE IX

A compound prepared from oleic acid chloride and propylene chlorohydrin having the formula $C_{17}H_{33}COOCH_2CH_2CH_2SO_3Na$ was used in this example, the procedure again being the same as in Example V. This compound was used in the amount of 6.0 lbs. together with fatty acid 7.0 lbs. and pine oil 0.3 lb., all per ton of feed.

The concentrate was retreated twice giving a final product containing 86.3% langbeinite.

The langbeinite recovery was 64.1% and ratio of concentration 2.75.

EXAMPLE X

In this example a compound prepared from lauric acid chloride and propylene chlorohydrin having the formula $C_{11}H_{23}COOCH_2CH_2CH_2SO_3Na$ was used. The recovery was not as high as in previous examples but a fairly good langbeinite concentrate was produced.

Where the term "alkali metal" is used in the claims, it is intended to include ammonia.

What is claimed is:

1. In the wet concentration of potash ores containing langbeinite, the step of mixing with a pulp of the ore, prepared by adding the ore to a saturated aqueous solution of its soluble constituents, a metallic sulphonate of the general formula $RCOXR'SO_3M$, where:

R is a straight chain aliphatic hydrocarbon group containing at least eleven carbon atoms;

X is oxygen or a NH group;

R' is a divalent straight short chain hydrocarbon group containing not more than five carbon atoms; and

M is an alkali metal,

and separating the langbeinite from the pulp in the form of a concentrate.

2. The process according to claim 1, in which R is an unsaturated straight chain hydrocarbon of at least eleven carbon atoms.

3. The process according to claim 1, in which R' is the ethylene group C_2H_4 .

4. In the flotation concentration of potash ores containing langbeinite, the step of mixing with a pulp of the ore prepared by adding the ore to a saturated solution of its soluble constituents an alkali sulphonate of the general formula $RCOXR'SO_3M$, where:

R is a straight chain aliphatic hydrocarbon group containing at least eleven carbon atoms;

X is oxygen or a NH group;

R' is a divalent straight short chain hydrocarbon group containing not more than five carbon atoms; and

M is an alkali metal,

5. and separating the langbeinite in the form of a floating froth.

5. In the concentration by flotation of potash ores containing langbeinite, the step of agitating the ores in a saturated solution of their soluble constituents with an alkali sulphonate of the formula $C_{17}H_{33}COOC_2H_4SO_3M$ where $C_{17}H_{33}$ is the hydrocarbon radical of oleic acid and M is an alkali metal, and separating the langbeinite in the form of a floating froth.

15 6. In the concentration by flotation of potash ores containing langbeinite, the step of agitating the ores in a saturated solution of their soluble constituents with an alkali sulphonate of the formula $C_{17}H_{33}CONHC_2H_4SO_3M$ where $C_{17}H_{33}$ is the hydrocarbon radical of oleic acid and M is an alkali metal, and separating the langbeinite in the form of a floating froth.

7. The process according to claim 4, in which a fatty acid of high molecular weight is added to the pulp together with the alkali sulphonate.

8. The process according to claim 5 in which a fatty acid of high molecular weight is added to the pulp together with the alkali sulphonate.

9. The process according to claim 6, in which a fatty acid of high molecular weight is added to the pulp together with the alkali sulphonate.

10. In the concentration of potash ores containing langbeinite and sylvite, the step comprising adding to a pulp of the ore prepared by mixing the ore with a saturated aqueous solution of its soluble constituents a sulphonate of the general formula $RCOXR'SO_3M$, where:

R is a straight chain aliphatic hydrocarbon group containing at least eleven carbon atoms;

X is oxygen or a NH group;

R' is a divalent straight short chain hydrocarbon group containing not more than five carbon atoms; and

M is an alkali metal,

and a cationic flotation agent which is an aliphatic amine having a straight chain hydrocarbon group containing at least seven carbon atoms, and separating the langbeinite and sylvite in the form of a concentrate.

11. The process according to claim 10, in which the cationic flotation agent is a member of the group consisting of straight chain aliphatic amines containing at least eleven carbon atoms and water-soluble salts of these amines formed from water-soluble acids.

12. The process according to claim 10, in which a high molecular weight fatty acid is added to the pulp in addition to the sulphonate and amine salt.

13. In the flotation concentration of potash ores containing langbeinite and sylvite, the step of adding to a pulp of the ore prepared by mixing the ore with a saturated aqueous solution of its soluble constituents a compound of the general formula $RCOXR'SO_3M$, where:

R is a straight chain aliphatic hydrocarbon group containing at least eleven carbon atoms;

X is oxygen or a NH group;

R' is a divalent straight short chain hydrocarbon group containing not more than five carbon atoms; and

M is an alkali metal,

75 and a salt of a straight chain aliphatic amine

containing at least seven carbon atoms, agitating the pulp, and separating the langbeinite and sylvite in the form of a floating froth.

14. The process according to claim 9, in which a high molecular weight fatty acid is added to the pulp in addition to the other reagents.

15. The process according to claim 5, in which a fatty acid of high molecular weight and a cationic flotation agent which is an aliphatic amine having a straight chain containing at least seven carbon atoms is employed in addition to the alkali sulphonate.

16. The process according to claim 6, in which a fatty acid of high molecular weight and a cationic flotation agent which is an aliphatic amine having a straight chain containing at least seven carbon atoms is employed in addition to the alkali sulphonate.

17. In the concentration of potash minerals from ores containing langbeinite and sylvite, the steps of mixing with a pulp of the ore a compound of the general formula $RCOXR'SO_3M$ as defined in claim 1 and removing a concentrate consisting principally of langbeinite and then adding a cationic flotation agent which is an aliphatic amine having a straight chain containing at least seven carbon atoms and removing a second concentrate consisting chiefly of sylvite.

18. In the concentration of potash minerals from ores containing langbeinite and sylvite, the steps of mixing with a pulp of the ore a cationic flotation reagent which is an aliphatic amine having a straight chain containing at least seven carbon atoms and separating a concentrate consisting chiefly of sylvite and then adding a compound of the general formula $RCOXR'SO_3M$, where:

R is a straight chain aliphatic hydrocarbon group containing at least eleven carbon atoms;

X is oxygen or a NH group;

R' is a divalent straight short chain hydrocarbon group containing not more than five carbon atoms; and

M is an alkali metal,

and removing a concentrate consisting chiefly of langbeinite.

19. The process according to claim 18, in which a high molecular weight fatty acid is used in conjunction with the compound of the general formula $RCOXR'SO_3M$ as defined in claim 18.

20. In the flotation concentration of potash ores containing langbeinite and sylvite, the step of adding to a pulp of the ore prepared by mixing the ore with a saturated aqueous solution of its soluble constituents a compound of the general formula $RCOXR'SO_3M$, where:

R is a straight chain aliphatic hydrocarbon group containing at least eleven carbon atoms;

X is oxygen or a NH group;

R' is a divalent straight short chain hydrocarbon group containing not more than five carbon atoms; and

M is an alkali metal,

and octadecylamine acetate, agitating the pulp, and separating the langbeinite and sylvite in the form of a floating froth.

21. The process according to claim 13, where the potash ores contain langbeinite, sylvite and halite.

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