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CONCENTRATION OF SYLVINITE ORES

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This invention relates to the concentration or separation of the values from soluble ores. More particularly, it relates to the separation of sylvite (potassium chloride, KCl) from sylvinite ores such as, for example, those found in the Carlsbad district of New Mexico.

The invention resides in improved methods of effecting the separation of the desired sylvite from such ores by froth flotation, skin flotation, agglomeration tabling and other methods involving wet stratification with the use of appropriate agents which effect the separation of the sylvite from the other ore constituents.

It is already known that sylvite can be recovered from a saturated solution of the soluble constituents of sylvinite ore in accordance with well-established concentration operations by using as a collector an aliphatic amine containing a straight chain hydrocarbon group of at least 7 carbon atoms, or the salts of such amines resulting from their combination with water-soluble acids.

The general objects of the present invention are to produce concentrates of the desired sylvite which are of high commercial grade, with high percentages of recovery, with economy in the use of reagents and with reliable and easily controlled operation of the plant. These objects are attained by the processes embodying the present invention which are hereinafter described.

The methods of the present invention are the result of the discovery that greatly improved results, as to grade and recovery of the desired sylvite and as to control of operations, can be obtained by the use as auxiliary agents in conjunction with the aforesaid straight chain alkyl amines used as collectors, of certain cellulosic materials as hereinafter defined, which are dispersible in aqueous media.

The straight chain alkyl amines useful as collectors for sylvite, the action of which is improved by the concurrent use of said dispersible cellulosic materials as auxiliary agents, include the following aliphatic primary amines: n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, n-undecylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-heptadecylamine, n-octadecylamine, and n-octadecenylamine. The lower members of this series may be added to the ore pulp in the form of the free base or as the salts formed by their combination with acids which are themselves relatively devoid of surface active properties, such for example, as hydrochloric acid, nitric acid, acetic acid, etc. The higher members of the series, being much less soluble, are generally used in the form of their more soluble salts.

These amine collectors may be used individually or as mixtures. The mixtures need not necessarily consist only of aliphatic primary amines

or their salts but may also contain varying proportions of aliphatic secondary and tertiary amines or their salts, such as are commonly found in commercial products. For example, the product of Armour and Company sold under the designation "Am. Ac. 1180-C" is very suitable and is understood to consist of approximately 73% mono-octadecylamine acetate, about 24% mono-hexadecylamine acetate, together with small quantities of secondary and tertiary amine acetates. Another suitable commercial product is that sold by E. I. du Pont De Nemours & Company, Inc., as "D. P. 243" which is a 50% aqueous paste of technical laurylamine hydrochloride understood to contain approximately 18% octylamine hydrochloride, 10% decylamine hydrochloride, 55% laurylamine hydrochloride, 17% myristylamine hydrochloride, and traces of secondary and tertiary amines.

Cellulose, as is well known, is a carbohydrate which occurs abundantly in plants. Those cellulosic materials which have been found useful are those materials in which the inherent cellulose structure is largely retained as in unmodified cellulose and in substituted cellulosic compounds, such as, for example, cellulose esters, cellulose ethers, cellulose xanthates, cellulose carbamates, etc. The term "cellulosic material" as used herein and in the claims is to be taken as including materials of the types just mentioned but as excluding such advanced degradation products, as, for example, glucose, which we have found to be non-effective in the process. The aqueous dispersions of the cellulosic materials of our invention may be true molecular dispersions (solutions) or colloidal dispersions of large molecular aggregates. The cellulosic materials may be added to the flotation brine as aqueous dispersions in water or brine, or they may be added as solutions or dispersions in organic solvents to form an aqueous dispersion in the flotation brine.

Among the cellulose materials which may be sufficiently dispersed in aqueous media to function effectively when added to the ore pulp are the esters known as cellulose xanthates, and the ethers known as methyl cellulose and ethyl cellulose. Methyl cellulose, which is commercially available as "Methocel," manufactured by the Dow Chemical Company, is a very effective auxiliary agent in the concentration of sylvite from its ores.

Other cellulosic materials within the scope of the invention may be more difficult to disperse in aqueous solutions, for example, cellulose acetate, cellulose nitrate (nitrocellulose) and cellulose acetate hydrogen phthalate. In many cases such materials can be used effectively for the purposes of the invention if they are first dissolved or dispersed in a suitable organic liq-

uid, and the organic liquid solution of the cellulosic material, then agitated with the ore pulp. As one example, dioxane has been found to be very effective as an organic liquid dispersant. In some cases it may be advantageous to add small amounts of emulsifying agents to the organic liquid solution of the cellulosic material to aid in the subsequent dispersion of the material in the aqueous brine. In the case of any particular cellulosic material which is difficult to disperse, a few simple tests with various solvents or mixtures of solvents may be necessary to determine the best means of obtaining a suitable dispersion in the brine.

We have found that cellulose dissolved in concentrated zinc chloride solution acts as an auxiliary reagent in the flotation of sylvite with amine acetate. While this process is not commercially important due to the inhibiting effect of the large amount of zinc chloride present, it is an interesting illustration of the use of an unmodified cellulosic material according to the teachings of our invention.

The following specific examples of embodiments of the invention show, by comparison with the comparative tests in which no cellulosic material was used, the advantages to be obtained from the use of these materials as auxiliary agents.

In practicing the methods of the present invention, desliming of the sylvinitic ore is desirable; and it is also sometimes desirable to add a frothing agent, such as pine oil, in addition to the collector and the auxiliary agent, when the desired mineral is to be concentrated by froth flotation, or a petroleum oil such as fuel oil when concentration is to be effected by tabling.

Comparative test A.—Sylvinitic ore from Carlsbad, New Mexico, was crushed so that it would pass through a 10-mesh screen, and was then deslimed and ground so that it would pass through a 35-mesh screen, after which it was made into a pulp of about 20% solids with a saturated solution of ore constituents. Reagents, as hereinafter specified, were added to this pulp, the pulp was agitated about 10 seconds to distribute the reagent and flotation was then effected. The first or rougher froth concentrate was returned to the flotation machine, diluted and refloatated. This was repeated on the second froth concentrate. The reject of the first flotation operation was final tailings. Rejects of the second and third flotation operations were middlings to be returned to the flotation circuit and further values recovered therefrom. The reagents used were "Am. Ac. 1180-C" 1.00 lb. and pine oil 0.2 lb., both per ton of ore treated. The results were as follows:

Product	Per cent weight	Per cent KCl	KCl recovery
Feed.....	100.0	31.2	100.0
Concentrate.....	15.6	90.9	45.4
Middling-2.....	6.0	86.1	18.6
Middling-1.....	8.9	62.6	17.8
Tailing.....	64.4	7.2	14.8
Slime.....	5.1	33.2	5.4

Example 1.—This operation was identical with Comparative test A except that methyl cellulose was employed as an auxiliary agent. 0.8 lb. per ton of ore of this material (Dow Chemical Company's "Methocel") was added to the pulp in the form of a 5% aqueous solution in addition to

the reagents used in Comparative test A. The results were as follows:

Product	Per cent weight	Per cent KCl	KCl recovery
Feed.....	100.0	30.4	100.0
Concentrate.....	25.3	91.1	75.8
Middling-2.....	3.5	67.3	7.7
Middling-1.....	6.1	27.5	4.6
Tailing.....	59.0	1.4	2.7
Slime.....	6.1	45.8	9.2

It will be noted that the use of the methyl cellulose in conjunction with the other reagents, as is shown by comparison of Example 1 with Comparative test A, improved the recovery by 30.4% (75.8% KCl when methyl cellulose was used as against 45.4% KCl recovery without it) and grade remained about the same (91.1% as against 90.9%).

Example 2.—The ore, procedure and reagents were the same as in Example 1 except that instead of methyl cellulose the auxiliary agent was cellulose acetate, 0.8 lb. per ton of ore added to the pulp in the form of a 3% solution in dioxane. The results were as follows:

Product	Per cent weight	Per cent KCl	KCl recovery
Feed.....	100.0	30.1	100.0
Concentrate.....	21.8	87.8	63.6
Middling-2.....	5.2	68.8	11.9
Middling-1.....	10.2	36.9	12.5
Tailing.....	58.5	4.4	8.6
Slime.....	4.3	24.0	3.4

By comparison of Example 2 with Comparative test A, it will be seen that the addition of the cellulose acetate increased recovery by 18.2% with a slight loss in grade amounting to but 3.1%.

Example 3.—The ore, procedure and reagents were the same as in Example 1 except that the auxiliary agent was cellulose acetate hydrogen phthalate, in the amount of 1.6 lbs. per ton of ore, added to the pulp as a 5% solution in dioxane. The results were as follows:

Product	Per cent weight	Per cent KCl	KCl recovery
Feed.....	100.0	26.9	100.0
Concentrate.....	25.0	92.0	85.4
Middling-2.....	2.0	43.3	3.2
Middling-1.....	7.3	10.1	2.7
Tailing.....	60.1	2.2	8.0
Slime.....	5.6	17.6	3.7

By comparison of Example 3 with Comparative test A, it will be seen that the addition of the cellulose compound increased recovery by 40% while grade was better by 1.1%.

Example 4.—The ore, procedure and reagents were the same as in Example 1 except that the auxiliary agent was cellulose xanthate, in the amount of 1.6 lbs. per ton of ore, added to the pulp as a 3% aqueous colloidal solution. The results were as follows:

Product	Per cent weight	Per cent KCl	KCl recovery
Feed.....	100.0	30.8	100.0
Concentrate.....	18.8	92.2	58.4
Middling-2.....	3.7	74.8	9.0
Middling-1.....	8.0	48.0	12.4
Tailing.....	63.2	8.1	18.7
Slime.....	6.3	27.0	5.5

By comparison of Example 4 with Comparative

test A, it will be seen that the addition of cellulose xanthate increased recovery by 11% while grade was better by 1.3%.

Comparative test B.—This test will serve as a basis of comparison for Example 5 and together therewith illustrates use of the invention with table concentration. The ore was the same as used in Comparative test A. It was crushed to pass a 6-mesh screen and then the plus 35-mesh fraction was screened out and deslimed in saturated brine. It was then made into a pulp in which the ratio of brine to ore was 1:1.88 by weight and conditioned with the reagent for one minute. The sole reagent was "Am. Ac. 1180-C", 0.5 lb. per ton of dry ore. The conditioned pulp was fed to a shaking table with a saturated aqueous solution of soluble ore constituents. The sylvite concentrate was recovered at the side of the table and rejected constituents went off at the end of the table. The results were as follows:

Product	Per cent weight	Per cent KCl	KCl recovery
Feed.....	100.0	28.6	100.0
Concentrate.....	14.3	97.2	48.6
Middling-2.....	7.8	72.4	19.6
Middling-1.....	9.3	21.4	7.0
Tailing.....	67.4	10.4	24.5
Slime.....	1.2	12.0	0.3

Example 5.—The ore, procedure and reagent were the same as in Comparative test B except that 0.4 lb. per ton of ore of methyl cellulose was added to the pulp as an auxiliary agent in the form of a 5% aqueous solution. The results were as follows:

Product	Per cent weight	Per cent KCl	KCl recovery
Feed.....	100.0	30.6	100.0
Concentrate.....	27.2	94.6	84.0
Middling-2.....	2.2	61.6	4.4
Middling-1.....	4.7	12.0	1.8
Tailing.....	65.2	4.3	9.1
Slime.....	0.7	31.7	0.7

By comparison of Example 5 with Comparative Test B, it will be seen that the addition of methyl cellulose increased recovery by 35.4% while there was a slight decrease in grade of but 2.6%.

Comparative test C.—Sylvinitic ore from the same locality as that used in Comparative test A was prepared and subjected to flotation as described in that test except that it was initially ground to pass a 28-mesh instead of a 10-mesh screen. The sole reagent used in this test, however, was Du Pont's "DP-243" in the amount of 0.9 lb. per ton of dry ore, introduced as a 5% aqueous solution. The results were as follows:

Product	Per cent weight	Per cent KCl	KCl recovery
Feed.....	100.0	29.2	100.0
Concentrate.....	17.4	85.8	51.2
Middling-2.....	5.2	59.9	10.7
Middling-1.....	12.8	44.2	19.4
Tailing.....	62.1	7.7	16.4
Slime.....	2.5	27.6	2.3

Example 6.—The ore, procedure and reagent were the same as in Comparative test C except that 0.9 lb. per ton of ore of methyl cellulose was

added as an auxiliary agent in the form of a 2.5% aqueous solution. The results were as follows:

Product	Per cent weight	Per cent KCl	KCl recovery
Feed.....	100.0	29.0	100.0
Concentrate.....	21.2	85.1	62.2
Middling-2.....	4.4	58.5	8.6
Middling-1.....	10.8	31.7	11.8
Tailing.....	60.8	7.1	14.8
Slime.....	2.8	27.6	2.6

By comparison of Example 6 with Comparative test C it will be seen that the use of methyl cellulose in conjunction with "DP-243" increased recovery 11% while grade remained practically the same.

It is to be understood that the foregoing examples are merely illustrative of the present invention and that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

What is claimed is:

1. The improvement in the method of separating sylvite from a pulp containing it which comprises subjecting said pulp to a concentrating process employing a collector selected from the group consisting of aliphatic amines containing a straight chain hydrocarbon group of at least 7 carbon atoms and their soluble salts formed by their combination with acids which are relatively devoid of surface active properties, which resides in distributing in said pulp a useful amount of an auxiliary agent consisting of a molecular or colloidal dispersion of a cellulosic material in aqueous media, and thereafter subjecting the pulp to a separation treatment to remove the desired sylvite.
2. A method as set forth in claim 1, wherein the pulp is formed from sylvinitic ore and a substantially saturated aqueous solution of the soluble ore constituents.
3. A method as set forth in claim 1, wherein the sylvinitic ore is substantially deslimed before the collector and the auxiliary agent are added.
4. A method as set forth in claim 1, wherein the separation treatment is a froth-flotation treatment in a froth-flotation machine.
5. A method as set forth in claim 1, wherein the separation treatment is by means of a shaking table.
6. A method as set forth in claim 1, wherein a frothing agent is used in conjunction with the collector and auxiliary agent and the separation of the sylvite is effected by froth flotation.
7. A method as set forth in claim 1, wherein a petroleum oil is used in conjunction with the collector and auxiliary agent, the sylvite agglomerated and the agglomerates separated.
8. A method as set forth in claim 1, wherein the cellulosic material is a cellulose ester.
9. A method as set forth in claim 1, wherein the cellulosic material is cellulose acetate.
10. A method as set forth in claim 1, wherein the cellulosic material is cellulose xanthate.
11. A method as set forth in claim 1, wherein the cellulosic material is a cellulose ether.
12. A method as set forth in claim 1, wherein the cellulosic material is a water-soluble substituted cellulose compound.
13. A method as set forth in claim 1, wherein the cellulosic material is methyl cellulose.
14. A method as set forth in claim 1, wherein

octadecylamine acetate is used as the collector.

15. A method as set forth in claim 1, wherein laurylamine hydrochloride is used as the collector.

16. A method as set forth in claim 1, wherein octadecylamine acetate is used as the collector in conjunction with a frothing agent and separation is effected by froth-flotation to remove the sylvite.

17. A method as set forth in claim 1, wherein octadecylamine acetate is used as the collector in conjunction with a petroleum oil and separation is effected by tabling treatment to remove the sylvite.

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