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METHODS FOR SEPARATING CHLORIDE, SULFATE AND CARBONATE SALTS AND THE LIKE

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ABSTRACT OF THE DISCLOSURE

A froth flotation method for the separation of chloride, carbonate, and sulfate salt mixtures using cresylic acid as a flotation reagent to selectively float carbonate salts from other salts of the mixture and selectively separating other salt components of the mixture by using naphthenic acid or one of its salts, an amine or amine acetate or a hydrocarbon sulfate or sulfonate as a flotation reagent.

This application is a continuation-in-part of our application S.N. 491,013 filed Sept. 28, 1965, now abandoned.

The present invention relates to methods for separating mixtures of chloride, carbonate, and sulfate salts and the like, such as may occur in natural deposits, evaporated salt brines, or other residues from synthetic or natural sources, by the use of a flotation process employing selected reagents to produce such separation.

Heretofore, the separation of mixtures of salts such as sodium chloride, soda ash, salt soda, trona, Glauber's salt, and burkeite, into the various individual salts has involved serious disadvantages and limitations. Among these are the great difficulty and expense which have been encountered, primarily because the phase relationships controlling their respective solubilities are unfavorable for simple fractional crystallization processes, thereby requiring multi-step processes which involve high energy consumption and high capital expenditures. Further, existing flotation processes include the addition of activators such as calcium, barium, strontium, and ferric ions, with acids such as oleic acid as the collector. Other processes involve the floating of sodium chloride from other salts of similar characteristics by the use of lead, bismuth and similar metal activators with straight chain primary amine collectors, or, in certain instances, with fatty acids and their salts alone. The presence of such metallic activators results in prohibitive contamination problems where the salt products are to be sold. The utilization of fatty acids alone requires a very demanding composition for the flotation liquor and is usually expensive to maintain, for the reagent consumption by the process is high. No flotation processes heretofore known, have successfully separated soda ash from sulfates, such as burkeite, a combination of salts frequently encountered.

An object of the present invention is to provide a froth flotation method for selectively separating soda ash, burkeite, salt cake, sodium chloride and the like from salt mixtures.

Another object is to provide a froth flotation process for the separation of soda ash from burkeite.

Another object of the invention is to provide froth flotation methods for the separation of chlorides, carbonates, and sulfates and similar materials by use of reagents which avoid contamination of the final product.

Another object of the invention is the provision of froth flotation methods for separation of salt mixtures by use of relatively inexpensive reagents.

Another object of the invention is to provide froth flotation methods for separating salts in high yields and high purities from salt mixtures.

Another object of the invention is the provision of froth flotation methods for separating salt mixtures which do not require high energy and high capital costs.

Another object of the invention is the provision of methods according to the foregoing objects which utilize relatively standard or conventional flotation equipment.

Other objects, features and advantages of the present invention will become apparent to those versed in the art from a consideration of the following description and the appended claims.

The present invention may utilize conventional froth flotation equipment and techniques, along with the selected reagents of the invention to produce selective separation of chloride, carbonate, and sulfate salt mixtures. It will be understood that the salt residues or ores will be reduce prior to flotation to pulping size range, if necessary, as known in the art. The selected salt or salts are floated from an aqueous solution saturated with respect to the salt mixture and containing the particular flotation reagent of the invention.

Where the term "soda ash" is used herein it is intended to include both the anhydrous and hydrated forms of sodium carbonate as well as sodium bicarbonate and trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, that is all carbonates that can be converted by heat to anhydrous Na_2CO_3. It does not include co-crystallized carbonate and sulfate salts such as burkeite, $Na_2CO_3 \cdot 2Na_2SO_4$.

We have found that cresylic acid and related phenols derived from coal tar, including lower alkyl substituted phenolis such as ortho-, meta- and para-cresol and mixtures thereof, all generally referred to herein as "cresylic acid," are excellent flotation reagents for the selective forth flotation of soda ash from mixtures of soda ash with other salts including sodium sulfate, sodium chloride, burkeite, and the like. Many different reagents will float soda ash but at the same time they activate and float other salts such as the sulfates so that selective separation cannot be accomplished. Thus, such reagents as sodium naphthenate, straight chain amines, and hydrocarbon sulfates and sulfonates will float soda ash but can be used advantageously only when the only other salt of the mixture is sodium chloride. Cresylic acid and the related phenols, on the other hand will selectively float soda ash from the sulfates as well as the chlorides and other salt residues.

Once the problem of removing soda ash from the salt mixtures has been solved the other salts may be readily separated by other flotation reagents.

We have found that sodium sulfate (commonly known as salt cake) and burkeite may be separated from sodium chloride by a flotation process using any of three classes of chemical compounds, (1) naphthenic acid or its salts such as sodium naphthenate, (2) straight chain amines or their acetates such as octadecylamine and its acetate, and (3) hydrocarbon sulfates or sulfonates such as the sulfate or sulfonic acid of octadecane and the alkyl-aryl sulfonates.

Conversely, these same chemical compounds will permit flotation of sodium chloride from Glauber's salt, $Na_2SO_4.10H_2O$, or from a mixture of Glauber's salt and salt cake.

Different ingredients are used to float sodium chloride from sodium sulfate alone. Thus, we have found that sodium chloride may be floated from salt cake using branched chain amine acetates such as 2-aminoundecane amine acetate which were experimentally known as L–7, L–9, L–11, or L–15 obtainable from Armour & Co. Diamine acetates N-(aminoethyl)methyl octylamine L–11

and L–15 may also be used with improved separation as a result.

A mixture of salts containing burkeite, trona, and sodium chloride may be separated by using cresylic acid to separate the trona from the burkeite and sodium chloride. The residue containing burkeite and sodium chloride may then be separated with alkali metal naphthenates, straight chain fatty amines, or hydrocarbon sulfates or sulfonates.

The same mixture may alternatively be treated initially with the said naphthenates, straight chain amines, or hydrocarbon sulfates or sulfonates to separate the burkeite and trona from the sodium chloride. The resulting floated mixture of burkeite and trona can then be separated with cresylic acid after suitable processing to remove the previous reagent employed.

For a mixture of salts containing burkeite, trona, salt cake, and sodium chloride, branched chain fatty amines may be used to separate the burkeite, trona, and sodium chloride from salt cake, and the resulting floated material of burkeite, trona, and sodium chloride could then be separated by either of the two methods described previously.

The following is a typical example employing our flotation methods for separation of these salts:

EXAMPLE 1

An African dry lake or playa contains salts making up an ore with the following composition:

Salt:	Parts by weight
Na_2CO_3	40
$NaHCO_3$	30
Na_2CO_4	15
NaCl	5
Insolubles	10

The ore is first ground by any suitable conventional means to —28 mesh and the solids are suitably de-slimed by conventional means. The ore is then floated in the presence of cresylic acid in the amount of 2 lb./ton or less, using a solution saturated with all solid phases present. This treatment with cresylic acid will produce a final flotation product containing 85% of the soda ash with .3% sodium chloride and 1.0% sodium sulfate. The non-floated residue may then be reground to —60 mesh and similarly treated with cresylic acid to produce a 95% flotation yield of purity equal to the first flotation product.

The remaining impurities can be reduced by 30 to 50% by finer grinding and a rougher cleaner operation. Alternatively, the impurities can be reduced readily to a total of less than .4% by a leach in carbonate liquor or water.

To float the sodium chloride from the salt cake in 92% yield and 90% purity, the residue resulting from the soda ash flotation process is treated with diamine acetate N-(aminoethyl)methyl octylamine L–11 or diamine acetate L–15 in the amount of 1 lb./ton or less. Both the floated sodium chloride and residual sodium sulfate may be leached to a purity greater than 99%. Alternatively, sodium naphthenate in the amount of less than 1 lb./ton may be used to flat the sodium sulfate from the sodium chloride.

Where the salt mixture contains burkeite the selective cresylic acid flotation of soda ash is illustrated in the following Example 2:

EXAMPLE 2

An Oregon lake contains a brine which may be solar evaporated to yield a mixture of salts forming solids of the following composition:

Salt:	Parts by weight
NaCl	40
$Na_3H(CO_3)_2.2H_2O$ (trona)	10
$Na_2CO_3.10H_2O$ (sal soda)	40
Burkeite	10

The trona and sal soda may be floated by grinding the solid mixture to —28 mesh and adding 2 lb./ton of

cresylic acid. A high yield and good product purity can be obtained because of the more controlled pond crystallization conditions, and correspondingly reduced liberation size. The residue of burkeite and sodium chloride can then be separated by floating the burkeite from the sodium chloride using the alkali metal naphthenates, straight chain fatty amines, or hydrocarbon sulfates or sulfonates. The first residue consists of fairly pure salt. Yields of from 85–95% and purities of about 95% are obtainable.

The residual burkeite can be redissolved during the following winter and the solution cooled to yield Glauber's salt and a carbonate rich solution for later solar evaporation.

The Glauber's salt may be dehydrated by "salting out" with the previously separated salt. The sal soda-trona mixture may be dried and recomposed directly, or dissolved and recrystallized for a high purity product.

The following Example 3 illustrates the use of our new method to separate sodium sulfate from sodium chloride in high yield and high purity:

EXAMPLE 3

A Nevada lake contains a brine which may be solar evaporated to yield a mixture of solids having the following composition:

Salt:	Parts by weight
NaCl	10
Na_2SO_4	85
Insolubles	5

The mixture of solids is first treated by thorough desliming and crushing to a —35 mesh particle size. 100 grams per ton of diamine acetate N-(aminoethyl)methyl octylamine L–11 is then added to float the sodium chloride from the sodium sulfate in 90% yield and 95% purity. The various fractions, sodium chloride, sodium sulfate, and residues, are leached to produce a 99.8% pure sodium sulfate product in 85% yield, a 99.8% pure sodium chloride in 90% yield, and leach liquors to be returned to the ponds for reevaporation which will make the overall yield close to 100% for both sodium chloride and sodium sulfate.

Those versed in the art will appreciate that the present invention achieves the objects and realizes the advantages hereinbefore mentioned.

Although specific embodiments of the present invention have been illustrated and described herein, it will be understood that the same are merely exemplary of presently preferred embodiments capable of attaining the objects and advantages hereinbefore mentioned, and that the invention is not limited thereto; variations will be readily apparent to those versed in the art, and the invention is entitled to the broadest interpretation within the terms of the appended claims.

What is claimed is:

1. A method for the froth flotation separation of soda ash from a salt mixture containing soda ash and at least a sulfate or chloride salt of sodium comprising floating the soda ash from the salt mixture in a saturated aqueous solution of said salts of the mixture containing cresylic acid as a flotation reagent.

2. The method of claim 1 wherein the salt mixture contains sodium sulfate.

3. The method of claim 1 wherein the salt mixture contains sodium chloride.

4. The method of claim 1 wherein the salt mixture contains both sodium chloride and at least one sulfate salt of sodium.

5. The method of claim 4 wherein the sulfate salt of sodium is in the form of salt cake.

6. The method of claim 4 wherein the sulfate salt of sodium is in the form of burkeite.

7. The method of claim 4 wherein the sulfate salt is sodium sulfate or burkeite and the residual sodium chlo-

ride and sulfate salts are separated by floating the sulfate salts from the sodium chloride in a saturated aqueous solution of said salts containing a flotation reagent selected from the group consisting of naphthenic acid and its alkali metal salts, straight chain amines and acetates thereof, and hydrocarbon sulfates and sulfonates.

8. The method of claim 4 wherein the sulfate salt is sodium sulfate and the residual sodium sulfate and sodium chloride are separated by floating the sodium chloride from the sodium sulfate in a saturated aqueous solution of said salts containing an amine flotation reagent selected from the group consisting of branched chain amine acetates and branched chain diamine acetates.

9. The method of claim 4 wherein the sulfate salt is Glauber's salt and the residual sulfate salt and sodium chloride are separated by floating the sodium chloride from the sulfate salt in saturated aqueous solution of said salts containing a flotation reagent selected from the group consisting of naphthenic acid and its alkali metal salts, straight chain amines and acetates thereof, and hydrocarbon sulfates and sulfonates.

10. The method of claim 1 wherein the soda ash of the mixture is in the form of trona.

11. A method for the froth flotation separation of a salt mixture containing soda ash, burkeite and sodium chloride, comprising floating the burkeite and soda ash from the sodium chloride in a saturated aqueous solution of said salts containing a flotation reagent selected from the group consisting of naphthenic acid and its alkali metal salts, straight chain amines and acetates thereof, and hydrocarbon sulfates and sulfonates, and then separating the resulting floated mixture of burkeite and soda ash by floating the soda ash from the burkeite in a saturated aqueous solution of these salts containing cresylic acid as a flotation reagent.

12. A method for the froth flotation separation of a salt mixture containing burkeite, soda ash, salt cake and sodium chloride, comprising floating the burkeite, soda ash and sodium chloride from the salt cake in a saturated aqueous solution of said salts containing a branched chain fatty amine as the flotation reagent and then separating the resulting floated mixture of soda ash, burkeite and sodium chloride by the method defined in claim 11.

13. A method for the froth flotation separation of a salt mixture containing burkeite, soda ash, salt cake and sodium choride, comprising floating the burkeite, soda ash, and sodium chloride from the salt cake in a saturated aqueous solution of said salts containing a branched chain fatty amine as the flotation reagent and then separating soda ash from the resulting floated mixture of burkeite, soda ash and sodium chloride by floating the soda ash from a saturated aqueous solution of the salts of said floated mixture containing cresylic acid as a flotation reagent.

14. A method for the froth flotation separation of sodium carbonates from a mixture of sodium chloride, trona, and sal soda, comprising grinding the mixture to minus 28 mesh, suspending the ground mixture in a saturated aqueous solution of the soluble components of said mixture, adding cresylic acid as a flotation reagent, and obtaining a flotation product consisting essentially of trona and sal soda.

15. A method for the froth flotation separation of trona from a mixture of salts containing burkeite, trona, and sodium chloride, comprising floating the trona from the burkeite and sodium chloride in a saturated aqueous solution of said salts containing cresylic acid as a flotation reagent.

16. A method for the froth flotation separation of burkeite and trona from sodium chloride, comprising floating the burkeite and trona from the sodium chloride in a saturated aqueous solution of said salts containing an alkali metal naphthenate as a flotation reagent.

17. A method for the froth flotation separation of burkeite and trona from sodium chloride, comprising floating the burkeite and trona from the sodium chloride in a saturated aqueous solution of said salts containing a flotation reagent selected from the group consisting of naphthenic acid and its alkali metal salts, straight chain amines and acetates thereof, and hydrocarbon sulfates and sulfonates.

18. A method for the froth flotation separation of burkeite, trona, and sodium chloride from a mixture containing salt cake, burkeite, trona, and sodium chloride, comprising floating the burkeite, trona, and sodium chloride from the salt cake in a saturated aqueous solution of said salts containing a branched chain amine acetate as a flotation reagent.

19. A method for the froth flotation separation of sodium chloride from sodium sulfate, comprising floating the sodium chloride from the sodium sulfate in a saturated aqueous solution of said compounds containing an amine flotation reagent selected from the group consisting of branched chain amine acetates and diamine acetates.

20. A method for the froth flotation separation of salt cake from sodium chloride, comprising floating the salt cake from the sodium chloride in a saturated aqueous solution of said materials containing at least one flotation reagent selected from the group consisting of naphthenic acid and its alkali metal salts, straight chain amines and acetates thereof and hydrocarbon sulfates and sulfonates.

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