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[54] **BENEFICATION OF A CLAY CONTAINING SYLVINITE ORE**

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[52] **U.S. Cl.** **241/20,** 209/17, 209/172

[51] **Int. Cl.** **B02c 21/00**

[58] **Field of Search** 209/2, 12, 166, 17, 209/172, 172.5; 241/20, 24; 23/89, 38, 42

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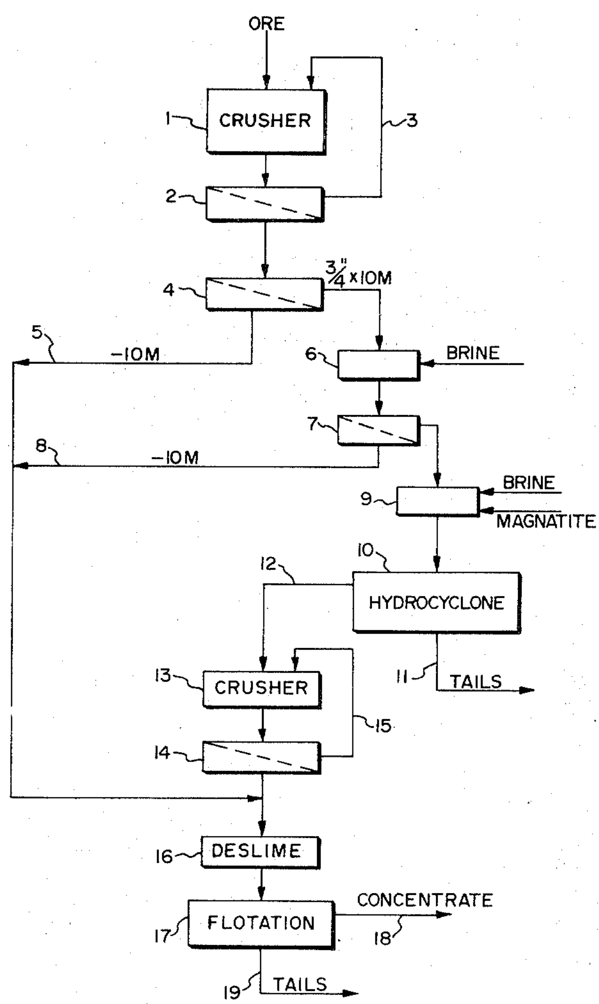
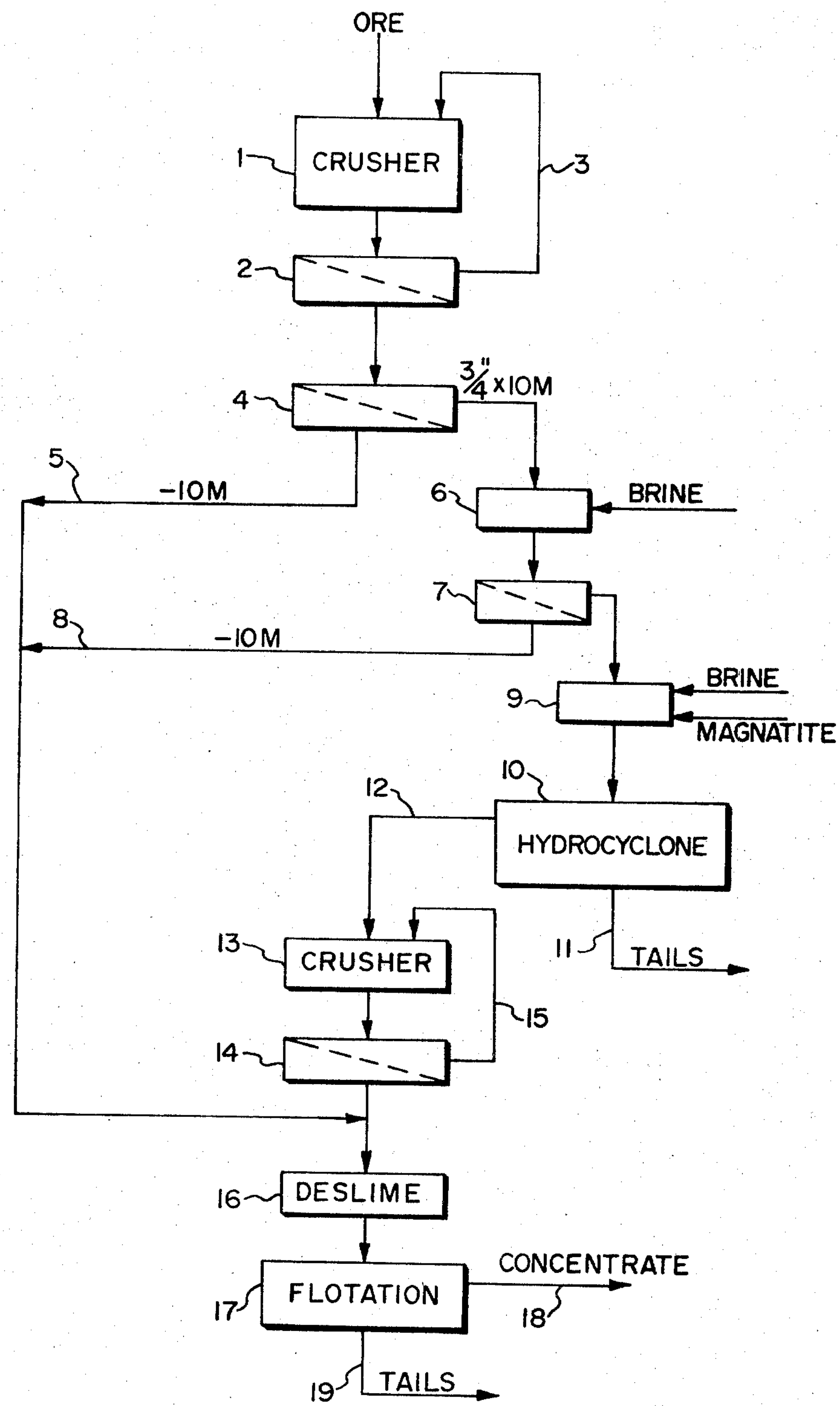
[57] **ABSTRACT**

Coarse, unliberated, clay-containing sylvinite is subjected to gravity beneficiation to remove significant amounts of halite and clay. The sylvite-containing overflow, having a reduced clay content, may be comminuted and subjected to wet beneficiation.

12 Claims, 1 Drawing Figure





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BENEFICATION OF A CLAY CONTAINING SYLVINITE ORE

DESCRIPTION OF THE INVENTION

This invention relates to the beneficiation of sylvinite ores and more particularly to the beneficiation of clay-containing sylvinite.

Sylvinite ore, such as that found in the Delaware arm of the Permian basin, may contain from about 3 to 7 percent or more of clay. Unfortunately, the degree of comminution required for liberation of ore values provides a disproportionate amount of fine colloidal particles commonly referred to as slimes which tend to clog the processing circuits, adsorb processing chemicals and reduce K_2O recoveries to unacceptable levels. Efforts to deslime high clay ores, such as by the use of settling tanks and the like, have not proven entirely satisfactory and, as a consequence, substantial sylvinite ore bodies remain untapped.

It is one object of this invention to provide a process for the beneficiation of high clay sylvinite ores.

It is a further object of this invention to provide a process wherein a substantial portion of the clay is removed with coarse halite.

It is another object of this invention to provide a process wherein a substantial portion of the clay is removed before the sylvinite is finely comminuted.

The present invention contemplates a process for beneficiating clay-containing sylvinite ore having a clay content of at least 3 percent and a K_2O:clay ratio of not more than about 5:1 comprising:

1. subjecting an unliberated sylvite fraction of said clay-containing ore containing particles having a maximum size of from about three-fourths inch to about one-half inch and a minimum size of from about one-fourth inch to about 10 mesh to gravity separation in a media having a specific gravity of separation intermediate the specific gravity of sylvite and halite whereby sylvite-containing particles are removed as an overflow fraction having a K_2O:clay ratio of at least about 10:1 and halite and clay particles are removed as an underflow fraction;
2. comminuting said overflow fraction to at least -1/4 inch; and
3. wet beneficiating said comminuted particles.

The sylvinite to which the present invention is directed frequently requires comminution to about −10 mesh (Tyler) for liberation of K_2O values. The term liberation is employed herein to designate that degree of comminution which permits the ore to be physically separated into s sylvite concentrate having an analysis of 55 percent K_2O or more and containing at least about 80 percent of the sylvite K_2O values orginally present in the ore. While sections of ore will liberate at sizes larger than 10 mesh, a practical process for the beneficiation of the high-clay sylvinite such as that found in the Delaware arm of the Permian basin must accommodate ore that liberates at about 10 mesh if froth flotation is to be employed effectively. Somewhat similarly, if crystallization is employed, a practical process mush accommodate ore that requires comminution to about minus one-fourth inch for effective crystallization.

Since clays tend to be softer than sylvite or halite, a disproportionate amount of colloid particles or insoluble slime-forming minerals are formed when a high-clay sylvinite ore is comminuted sufficiently to permit

wet beneficiation. This invention avoids the difficulty presented by slimes by providing an initial separation of coarsely comminuted ore. It has been determined that comminution of the sylvite to about minus one-half inch and preferably to about minus three-fourths inch provides material that can be subjected to gravity separation to remove some halite and a significant amount of the clay present. In this regard, it has been noted that the clay is predominately associated with the halite and that an initial gravity separation is a feasible way to remove both coarse halite and clay. Importantly, the initial gravity separation does not substantially deplete the sylvite content even though the ore has not been comminuted to liberation.

The gravity separation of low-clay sylvinite ores that liberate at relatively coarse sizes (e.g., three-eighths inch) has been practiced in Canada and is described in Canadian Patent No. 792,819. No instance is known, however, in which a gravity separation comparable to that described herein has been suggested for the beneficiation of clay-containing sylvinite ore. The process of this invention is particularly designed for sylvinite found in the Delaware arm of the Permian basin. Comparable sylvinite is also found in France and Germany. Such ore generally will contain at least about 3 percent clay and generally from about 3 to about 7 percent or more of clay. Such ores have a K_2O:clay ratio of only about 5:1 or less. Frequently, the ore will contain from about 12 to about 22 percent sylvite as K_2O. The ore also contains halite and may contain minor amounts of polyhalite, kainite, keiserite, langbienite and/or leonite. A typical ore may contain about 4 percent clay and about 17 percent sylvite as K_2O.

The term "clay" as employed herein embraces not only true clay minerals such as montmorillonite, kaolin and atta pulgite but also other slime-forming water-insolubles such as dolomite, silica and the like. These materials all form troublesome colloids or semi-colloids and, therefore, behave much like true clays in the processing circuit. All of the materials termed "clays" are water insoluble minerals that tend to form slimes.

This invention permits at least about 35 percent of the clay present in the initial ore to be removed in the initial gravity separation. Generally, at least about 35 percent of the halite present in the initial ore will also be removed. Under preferred operating conditions at least about 50 percent of the clay initially present in the ore will be removed. In many cases, at least 50 percent of the halite will also be removed. In the preliminary separation, less than about 12 percent sylvite need be lost. Generally, process conditions such as degree of comminution, gravity for separation, and the like, will be chosen so that K_2O:clay ratio of overflow from the gravity separation will be at least about 10:1. It is also desirable for the total K_2O:clay ratio of the fraction subjected to wet beneficiation will be at least about 8:1 and preferably at least about 10:1.

It is preferred that the ore initially be crushed to about three-fourths inch since such particles are the largest that feasibly can be beneficiated in a gravity separator such as a vortex separator for the purposes of this invention. Comminuting only to −¾ inch mesh avoids, to the maximum extent, unneces-sary breaking up of the clay. While ores comminuted to three-fourths inch (particles ranging in size from about three-fourths inch) are preferred for the practice of this invention, advantageous results can also be obtained employing ores comminuted to about one-half inch, or to a maximum size intermediate of three-fourths inch and one-half inch. Inasmuch as increasingly more clay tends to be converted to slimes as the maximum size of comminution is decreased, the maximum acceptable comminution will vary somewhat depending upon the precise ore being processed.

The minimum size of the ore particles will vary somewhat depending upon the particular ore being processed and the type of wet beneficiation to be employed for the undersize material. The term "wet beneficiation" as employed herein contemplates either froth flotation or crystallization. Froth flotation requires substantial liberation of the mineral constituents of the ore and, therefore, the minimum particle size will be about 10 mesh if froth flotation is employed for the wet beneficiation of undersize particles. In the event that crystallization is employed for wet beneficiation of undersize particles, the minimum particle size of the ore subjected to gravity separation may be as large as one-fourth inch since particles of about −¼ inch effectively can be beneficiated by crystallization. In very high-clay ores or in ores in which a substantial number of particles fall within the −¼ inch × 10 mesh size range, it may be desirable to select a minimum size less than about one-fourth inch (i.e., between about one-fourth inch and 10 mesh) even if crystallization is employed for wet beneficiation.

For ease of presentation, the practice of the invention will be described hereinafter with reference to the processing of a −¾ inch × +10 mesh ore fraction. The mesh sizes referred to herein are standard Tyler mesh sizes.

The process of this invention readily can be carried out employing standard equipment well known in the art. For example, either wet or dry comminution may be employed in the practice of this invention, and suitable apparatus includes a ball mill, hammer mill, rod mill, impact crusher, or the like. Such equipment will provide particles ranging from a selected maximum size downward. Since it is desirable to maintain as much clay as possible in the larger fraction, comminution is preferably maintained at a minimum consonant with the size requirement for the ore.

In a preferred embodiment wherein froth flotation is employed and ore particles have sizes ranging from three-fourths inch to 10 mesh, it is desirable that at least 30 percent of the particles have a size of about three-eighths inch or larger and it is particularly desirable for at least about 60 percent of the particles to be about three-eighths inch or larger.

In one embodiment, this invention contemplates drying mine run ore or coarse crushed ore to remove free water from the clay and thereby provide a clay somewhat less susceptible to slime formation. Dryng generally may be accomplished at temperatures between about 150° and about 700°F. Time of drying will, of course, vary depending upon the temperature. In a typical drying step, ore may be maintained at about 350°F for about 10 to 20 minutes.

Comminution will, of course, provide some fines which may interfere with the gravity separation by altering the specific gravity of the medium or by interfering with the separation of weighting agent from the ore particles. Accordingly, the comminuted ore is sized employing hydrocones, rake classifiers, screens, or the like to remove at least the −10 mesh fraction. The −10 mesh fraction may be deslimed and beneficiated by conventional flotation or crystallization techniques as will be discussed more fully below.

The −¾ × +10 mesh fraction is subjected to gravity separation employing a liquid that has a gravity intermediate the gravity of halite (approximately 2.17 at 20°C) and sylvite (approximately 1.99 at 20°C). Typical vessels employed for gravity separation include cones, classifiers, drum-type vessels or vortex separatory vessels such as hydrocyclones. In order to minimize generation of clay particles during handling the ore, it is advisable to avoid abrasive conditions during the pulping of the ore in the heavy media.

The liquid media employed for the gravity separation may be either a so-called "heavy media" or a so-called "heavy liquid." A heavy media is a suspension of a weighting agent, or a mixture of weighting agents, in a brine which is preferably substantially saturated with respect to the sylvinite feed. Ferrous media, such as magnetite and/or ferrosilicon, are preferred weighting agents because of their commercial availability, low cost, ease of recovery and cleaning by magnetic means, and ability to form a fluid medium of the predetermined specific gravity in the brine. The ferrous media are usually used as substantially all minus 100 mesh particles. These are very readily suspended in the brine and the resultant suspension is self-sustaining with the moderate agitation produced by recycling the suspension in the normal operation. Halogenated hydrocarbons and mixtures thereof are suitable for use as heavy liquids. Illustrative of such halogenated hydrocarbons are methylene bromide (specific gravity of 2.49) and methylene chlorobromide (specific gravity of 1.92). Fluorine substituted and iodine substituted alkyl compounds may also be used.

The terms "circulating gravity" and "specific gravity of separation" will be used herein in accordance with the general usage in the art. Thus, "circulating gravity" means and refers to the actual density of the separating medium, while "specific gravity of separation" means and refers to the apparent density of the separating medium based on the separations which can be made with it in a specific separating vessel. When the separatory vessel used is one in which the path taken by the individual particles is determined only by their respective specific gravities, such as a conventional cone, classifier or drum-type vessel, the circulating gravity and specific gravity of separation will be the same. In such instances, the separating medium (either circulating or in the separation vessel) will have a specific gravity intermediate the specific gravities of the sylvite and halite. However, when a vortex separatory vessel is employed as in the preferred embodiment of this invention, use is made of centrifugal forces which are many times greater than gravity. In such instances, a given heavy media may itself have a specific gravity, i.e., a circulating gravity, of less than the gravity of either halite or sylvite but may produce a separation in a vortex vessel such as a hydrocyclone between the sylvite and the halite because the forces in the vessel provide a heavier specific gravity of separation. For example, a circulating gravity of 1.85 may provide a medium in the vortex vessel that has the characteristics of a 2.1 specific gravity. The specific gravity of separation of such a heavy media would then be said to be about 2.1. The relationship between circulating gravity and specific gravity of separation will vary somewhat depending upon the apparatus and operating conditions but is readily within the skill of the routineer. Specific gravities of separation ranging from about 2.05 to about 2.15 are particularly preferred for the practice of this invention.

The overflow from the gravity separation will contain a major portion of the sylvite content of the ore and will be substantially diminished in clay content. The underflow from the gravity separation will contain halite and clay. The overflow, after removal of the heavy media, may be comminuted to −10 mesh to liberate the ore values and beneficiated by conventional flotation techniques or may be comminuted to about −¼ inch and beneficiated by crystallization.

In conventional flotation benefication of −10 mesh particles, slimes can be removed in a hydro-separator, the deslimed ore reagentized with a cationic flotation agent, and the fraction subjected to froth flotation. Suitable cationic flotation agents include aliphatic amines, such as n-lauryl amine; and high mo'ecular weight aliphatic amines containing about 14 to 20 carbon atoms and their water-soluble addition salts, as well as quaternary ammonium salts, as for example, octadecylamine acetate, hexadecylamine hydrochloride, and the like. The conditioned ore is finally fed into a suitable flotation vessel, which usually consists of a battery of units in parallel or in series. The flotation is effective to remove as an overflow concentrate a substantial amount of the sylvite content of the fine fraction together with some of the halite. The flotation concentrate is dried and sent to storage. The underflow tail from the flotation operation, predominating in halite and containing a minor amount of sylvite, is removed and discarded as waste.

In a conventional crystallization process, ore is contacted with heated brine unsaturated with respect to KC1 but saturated with respect to NaC1 in order to solubilize KC1 in the ore. Thereafter, the brine is cooled to deposite KC1 crystals. Since the solubility of NaC1 is not affected by temperature changes in the same manner as KC1, the process is selective for the production of KC1 crystals.

As indicated earlier, the individual technique and apparatus for comminuting, screening, gravity separation, and flotation are known to the art. Gravity separation of sylvinite is described in U.S. Pat. No. 2,590,756 and Canadian Pat. No. 792,819; flotation beneficiation of sylvinite is described in U.S. Pat. No. 2,968,525, and U.S. Pat. No. 2,984,348, as well as many others; a vortex gravity separator is described in U.S. Pat. No. 2,917,173; and removal of weighting agent from ore particles is described in U.S. Pat. No. 2,998,882.

The accompanying drawing is a diagrammatic flow sheet illustrating a preferred embodiment of the process of this invention.

In the drawing, ore is fed to crusher **1** which comminutes the ore to −¾ inch. The crushed ore is fed to screen **2** for separation of oversize and return of oversize through line **3** to crusher **1**. The −¾ inch fraction is then fed to screen **4** which separates a −10 mesh fraction therefrom. That fraction, having its ore values liberated, is set through line **5** to hydro-separator **16** for desliming and then to flotation beneficiation **17**. If desired, crystallization can be substituted for flotation beneficiation or a combination of the two can be employed.

The ¾ inch × 10 mesh fraction is sent to pulper **6** wherein it is gently mixed with brine saturated with respect to the ore components. Since some fine particles may be generated in the pulping step, the suspension is optionally sent to screen **7** where additional −10 mesh particles are removed. Those particles may be sent through line **8** to hydro-separator **16** and flotation beneficiation **17**. The ¾ inch × 10 mesh pulped ore from screen **7** is sent to pulper **9** wherein additional brine and weighting agent (e.g., magnetite) are added to provide a heavy media having the requisite specific gravity of separation in hydrocyclone **10**.

The ore is subjected to gravity separation in hydrocyclone **10**. The underflow **11** from the gravity separation will contain halite and a significant proportion of the clay originally present in the ore. The overflow **12** will contain sylvite and will be characterized by a clay content substantially diminished from the clay content of the original ore. The weighting agent is removed from both streams such as by screening followed by a brine wash, or the like and preferably is recycled to the pulping operation.

The sylvite-containing overflow from hydrocyclone **10** is sent to crusher **13** wherein it is crushed to −10 mesh to liberate sylvite from halite. The material from the crusher is screened on screen **14** and oversize (i.e., +10 mesh) is recycled to the crusher through line **15**. The −10 mesh from the crusher may be combined with the −10 mesh material separated earlier in the process and subjected to desliming in a hydraseparator **16**. Thereafter, the liberated particles are subjected to flotation **17** to provide sylvite concentrate **18** and halite tails **19**.

While the attached figure depicts a two-stage pulping process, pulping can be accomplished in a single stage with the elimination of an immediate screen. Moreover, it will be appreciated that, if desired, the −10 mesh streams may be processed separately and it may prove desirable to at least deslime these fractions separately. Similarly, crystallization may be substituted for flotation **17** or a combination of the two can be employed.

The following example is included for illustrative purposes only and is not intended to limit the scope of the invention.

EXAMPLE 1

One thousand parts of sylvinite ore from the Delaware arm of the Permian basin containing 170 parts of K_2O and 40 parts clay is comminuted and sized to provide a ¾ inch × 10 mesh fraction. Approximately 800 parts of the ore was −¾ inch × + 10 mesh while the remaining 200 parts was −10 mesh. The ¾ inch × 10 mesh fraction is beneficiated in a hydrocyclone at a 2.14 specific gravity of separation. The gravity separation rejects approximately 434 parts containing 24 parts of clay (60 percent of clay originally present) and 8 parts of K_2O. The overflow concentrate (approximately 366 parts) from the gravity separation is crushed to −10 mesh and combined with the undersize from the initial sizing operation and deslimed. The deslimined −10 mesh fraction is then subjected to cationic froth flotation to provide a 60 percent K_2O concentrate. The process provides an overall K_2O recovery of about 87 percent.

The analysis of the mine run ore and the various fractions is shown in Table 1 below.

TABLE 1

	Wt. % K_2O	Clay	Ratio K_2O:clay
Mine Run Ore	17	4	4.25:1
Gravity Tails	2	6	
Gravity Concentrate	35	2	16:1
Total Feed to Desliming	29	3	10:1

The K_2O content noted above, and employed throughout this specification, refers to the potassium values present in the ore as sylvite.

While the invention has been described with respect to a vortex separation in which all the coarse ore is processed, it will be appreciated that the coarse fraction can, for example, be divided into two parts (e.g. −¾ × ½ inch and −½ inch × 10 mesh) and each processed separately at the specific gravity of separation best suited for that fraction. Since other variations of the invention will be apparent to those skilled in the art, it is intended that this invention be limited only by the scope of the appended claims.

I claim:

1. A process for beneficiating clay-containing sylvinite ore having a clay content of at least about 3 percent and a K_2O:clay ratio of not more than about 5:1 comprising:

1. subjecting particles of said clay containing sylvinite ore having sylvite in unliberated form and having a maximum size of from about three-quarters inch to about one-half inch and a minimum size of from about one-quarter inch to about 10 mesh to gravity separation in a liquid media having a specific gravity of separation intermediate the specific gravity of sylvite and halite whereby sylvite-containing particles are removed as an overflow fraction having a K_2O:clay ratio of at least about 10:1 and halite and clay particles are removed as an underflow fraction;
2. comminuting said overflow fraction to at least −¼ inch to liberate said sylvite; and
3 wet beneficiating said comminuted particles

2. A process according to claim **1** wherein said sylvinite ore particles range from about three-quarters inch to about 10 mesh, the overflow from the gravity separation is comminuted to about −10 mesh, and said comminuted particles are subjected to froth flotation.

3. A process according to claim **1** wherein said sylvinite ore particles range from about one-half inch to about 10 mesh, the overflow from the gravity separation is comminuted to about −10 mesh, and said comminuted particles are subjected to froth flotation.

4. A process according to claim **1** wherein said sylvinite ore particles range in size from about three-quarters inch to about one-quarter inch, the overflor from the gravity separation is comminuted to about −¼ inch, and said comminuted particles are subjected to crystallization beneficiation.

5. A process according to claim **1** wherein said gravity separation in a vortex separation.

6. A process for beneficiating clay-containing sylvinite ore having a clay content of at least about 3 percent and a K_2O:clay ratio of not more than about 5:1 comprising:

1. comminuting said ore to provide particles having a maximum size of from about three-quarters inch to about one-half inch;
2. sizing said ore particles at about 10 mesh to about one-quarter inch to provide an oversize fraction containing sylvite in substantially unliberated form and an undersize fraction;
3. subjecting the oversize from (2) to gravity separation in a liquid media having a specific gravity of separation intermediate the specific gravity of sylvite and halite whereby sylvite-containing particles are removed as an overflow fraction having a K_2O:-clay ratio of at least about 10:1 and halite and clay particles are removed as an underflow fraction;
4. comminuting said overflow fraction from the gravity separation of (3) to at least −¼ inch to liberate the sylvite; and
5. combining and wet beneficiating said undersize from (2) and said comminuted particles from (4), the composite K_2O:clay content of these fractions being at least about 8:1.

7. A process according to claim **6** wherein said sylvinite ore particles are comminuted to about three-quarters inch and are sized at about 10 mesh, said overflow fraction is comminuted to about −10 mesh and said fractions are subjected to froth flotation.

8. A process according to claim **6** wherein said sylvinite ore particles are comminuted to about one-half inch and are sized at about 10 mesh, said overflow fraction is comminuted to about −10 mesh and said fractions are subjected to froth flotation.

9. A process according to claim **6** wherein said sylvinite ore particles are comminuted to about three-quarters inch and are sized at about one-quarter inch, said overflow fraction is comminuted to about −¼ inch and said fractions are subjected to crystallization.

10. A process according to claim **6** wherein said ore is heated to remove free water prior to comminution.

11. A process according to claim **6** wherein said gravity separation is a vortex separation.

12. A process according to claim **6** wherein the composite K_2O:clay ratio of the fine particles is at least about 10:1.

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,750,963 Dated August 7, 1973

Inventor(s) William B. Dancy

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

Column 1, line 5, between "to" and "7", the word --about-- should be inserted; line 51, "s" should be --a--; line 62, "mush" should be --must--. Column 2, line 3, "sylvite" should be --sylvinite--; line 63, "unneces-sary" should be --unnecessary--. Column 4, line 63, "medium" should be --media--. Column 5, line 20, "mo'ecular" should be --molecular--; line 63, "set" should be --sent--. Column 6, line 31, "hydraseparator" should be --hydroseparator--. Column 7, line 53, "overflor" should be --overflow--. Column 8, line 5, "in" should be --is--.

Signed and sealed this 20th day of August 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents