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[54] BENEFICIATION OF CLAY-CONTAINING SYLVINITE ORE

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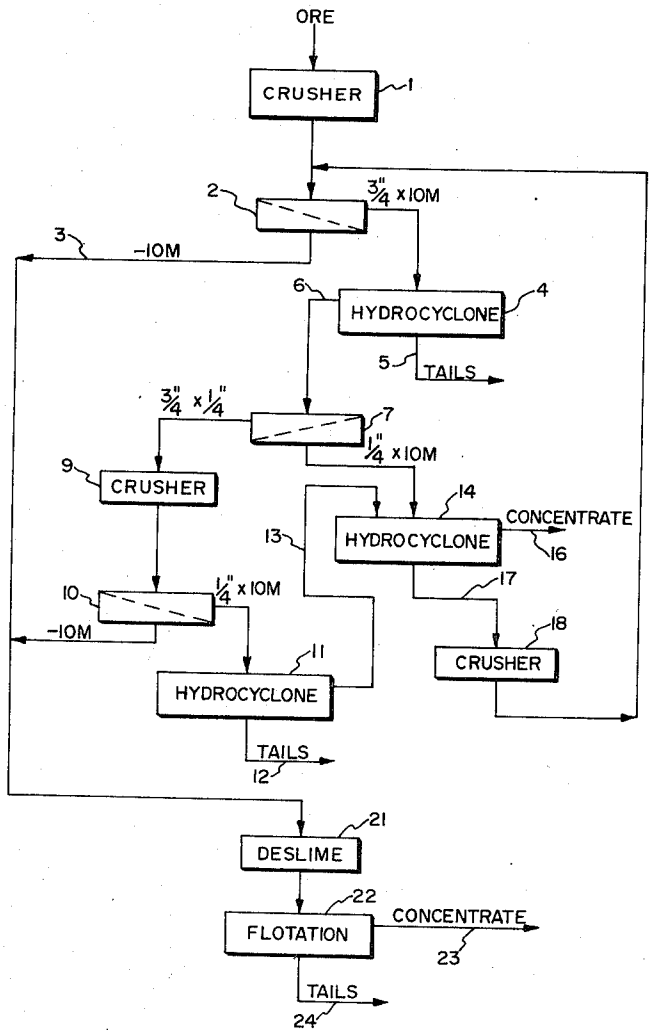
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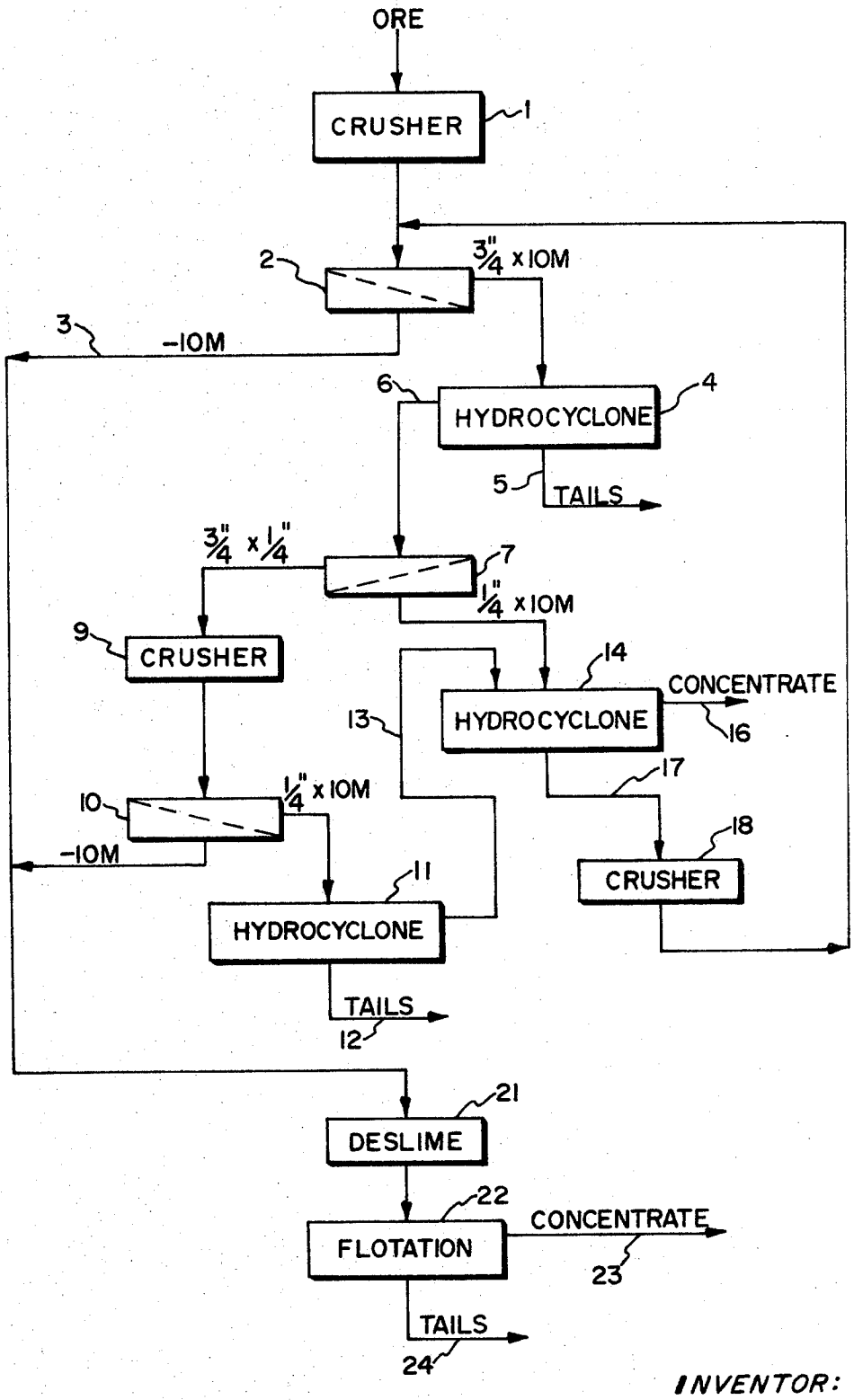
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[57] **ABSTRACT**

Coarse clay-containing sylvinite is subjected to gravity separation and the overflow is divided into two portions by sizing at about one-quarter inch. The finer fraction is subjected to a gravity separation to provide a sylvite product while the coarser fraction is crushed to minus about one-quarter inch and then subjected to gravity separation to provide a sylvite concentrate which is subjected to another gravity separation to provide a sylvite product.

14 Claims, 1 Drawing Figure





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BENEFICIATION OF 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 ores.

Sylvinite ore such as that found in the Delaware arm of the Permian basin in the United States may contain from about 3 to about 7 percent or more of clay. Similar high clay ores are also found in France and Germany. In addition, sylvinite ore, such as that found in the Saskatoon region of Saskatchewan, may contain from about 5 to about 6 percent or more of clay.

Unfortunately, the degree of comminution required for liberation of ore values in a high clay ore provides a disproportionate amount of fine colloid clay particles commonly referred to as slimes which tend to clog the processing circuits and adsorb processing chemicals. Efforts to deslime high clay ores, such as by use of settling tanks, hydroseparators and the like, have not proven entirely satisfactory. As a consequence, the processing of clay-containing sylvinite such as that found in the Saskatoon region does not compare favorably economically with processing of low clay sylvinite.

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 ores containing at least about 3 percent clay and having a K_2O:clay ratio of less than about 5:1 comprising:

1. comminuting said sylvinite ore and sizing said ore to provide a fraction containing particles having a maximum size of from about three-fourth to about one-half inch and a minimum size of about 10 mesh;
2. subjecting said fraction of (1) 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 characterized by a K_2O:clay ratio of at least about 10:1 and halite and clay particles are removed as an underflow;
3. sizing said overflow fraction of (2) to provide a first fraction having particle sizes of less than about one-fourth inch and a second fraction having particle sizes greater than about one-fourth inch;
4. subjecting said first fraction of (3) to gravity separation in a media having a specific gravity of separation intermediate the specific gravity of sylvite and halite whereby an overflow sylvite concentrate is obtained;
5. comminuting said second fraction of (3) and sizing said fraction to provide particles having sizes ranging from about ¼ inch to about 10 mesh;
6. subjecting said comminuted particles of (5) to gravity separation in a media having a specific gravity of separation intermediate the specific gravity of sylvite and halite to provide a sylvite-containing overflow; and
7. subjecting said sylvite-containing overflow of (6) to gravity separation in a media having a specific gravity of separation intermediate the specific gravity of sylvite and halite whereby an overflow sylvite concentrate is obtained.

In a preferred embodiment of the invention −10 mesh particles resulting from comminution, such as the comminution of steps (1) and (5) above, are subjected to wet beneficiation, i.e., froth flotation or crystallization.

Since clays or insoluble slime-forming minerals tend to be softer than sylvite or halite, a disproportionate amount of colloid particles are formed when a high clay sylvinite ore is comminuted to liberation. This invention minimizes the difficulty presented by slimes by providing a process wherein coarsely comminuted ore is subjected to gravity separation which removes 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 is effective to substantially remove clay while depleting sylvite only to a very limited extent even though the ore is not comminuted to complete liberation.

The beneficiation of sylvinite by gravity separation is described generally in Canadian Pat. No. 792,819. The particular process of this invention is especially designed for the beneficiation of clay-containing sylvinite found in the Saskatoon region of Saskatchewan or in the Delaware arm of the Permian basin. Ore in the Saskatoon region of Saskatchewan generally will contain at least about 5 percent clay and generally from about 5 to about 6 percent or more of clay. The K_2O:clay ratio of the ore is less than about 5.5:1. Frequently, the ore will contain about 25 to about 30 percent sylvite as K_2O. Sylvinite found in the Delaware arm of the Permian basin (and comparable sylvinite found in France and Germany) 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. A typical ore may contain about 4 percent clay and about 17 percent sylvite as K_2O.

The ores to which the present invention is directed will also contain halite and may contain minor amounts of constituents such as polyhalite, kainite, keiserite, magnesium sulfate and/or leonite. Comminution to about one-fourth inch provides liberation of the sylvite constituent of Saskatoon ore and of sections of other clay-containing sylvinite ore such as that found in the Delaware arm of the Permian basin, and the like. The term liberation is employed herein to designate that degree of comminution which permits the ore to be physically separated into a sylvite concentrate having an analysis of 55% K_2O or more and containing at least about 80 percent of the sylvite K_2O values originally present in the ore. It will be appreciated that liberation of the sylvite constituent of specific clay-containing ore deposits within the region may vary somewhat from one-fourth inch.

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 the total K_2O:clay ratio of the overflow from the initial gravity separation will be at least about 10:1. The process is also desirably operated to provide −10 mesh material which is characterized by an overall K_2O:clay weight ratio of at least about 8:1 and preferably at least about 10:1.

It is preferred that the ore initially be crushed to about −¾ inch since about ¾ inch 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, unnecessary breaking up of the clay. While ores comminuted to

−¾ inch (particles ranging in size from about three-fourth inch) are preferred for the practice of this invention, advantageous results can also be obtained employing ores comminuted to about −½ inch, or to a maximum size intermediate of three-fourth inch and one-half inch. It will be appreciated that as the maximum size of comminution is decreased, increasingly more clay tends to be converted to slimes and that the maximum acceptable comminution will vary somewhat depending upon the precise ore being processed.

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 and to separation at one-fourth inch. 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 ¾ inch to 10 mesh, it is desirable that at least 30 percent of the particles have a size of about three-eighth 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. Drying generally may be accomplished at temperatures between about 150° F and about 700° F. Time of drying will obviously 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 inch × +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 liquid 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 media 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.

The overflow from the gravity separation will contain a major portion of the slyvite content of the ore and will be substantially diminished in clay content. This overflow, after removal of the heavy media, if desired, is sized to provide a first fraction having particles greater than about one-fourth inch and a second fraction having particles less than one-fourth inch. In effect, the second fraction contains ore with liberated mineral constituents while the first fraction contains unliberated ore.

The larger fraction is comminuted to about −¼ inch and sized to remove about −10 mesh material. The net result of this processing is to provide liberated ore particles having a size range from about ¼ inch to about 10 mesh which then is beneficiated by gravity separation as will be described in detail with reference to the attached drawing.

It is likely that sufficient −10 mesh material will be generated in the process to justify beneficiation of this material also. This material can be beneficiated readily by either conventional froth flotation or by conventional crystallization. The term "wet beneficiation" is employed herein to denote either froth flotation or crystallization.

In a conventional flotation beneficiation of −10 mesh particles, slimes can be removed in a hydroseparator, 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 molecular 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 KCl but saturated with respect to NaCl in order to solubilize KCl in the ore. Thereafter, the brine is cooled to deposit KCl crystals. Since the solubility of NaCl is not affected by temperature

changes in the same manner as KCl, the process is selective for the production of KCl crystals.

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

In the drawing, ore is fed to crusher **1** which comminutes the ore to −¾ inch mesh. Typically, the crusher will have associated with it a screen for removal of oversize particles and facilities for the recycling of such particles to the crusher. The −¾ inch particles are fed to screen **2** for the removal of −10 mesh particles through line **3**. The larger fraction from screen **2**, consisting of particles ranging in size from ¾ inch to 10 mesh is fed to a gravity separator such as a hydrocyclone **4** wherein the media, desirably brine weighted with magnetite, has a specific gravity of separation in the range of about 2.10 to about 2.16 and preferably about 2.14. The underflow from the hydrocyclone is removed through line **5** and constitutes halite and associated clay. The overflow from the hydrocyclone is removed through line **6** and constitutes the sylvite-containing material.

It should be noted that the ancillary equipment normally associated with a hydrocyclone is not shown in the attached figure. Thus, for example, if the initial comminution and sizing are dry, the ¾ inch × 10 mesh fraction will be pulped with brine and magnetite to provide a slurry in heavy media. Similarly, weighting agents or heavy liquids are commonly removed from the hydrocyclone overflow and underflow streams by screening, brine washing or the like. In the event an intermediate stream containing heavy media or heavy liquids will be processed by further gravity separation, it may be possible to process the stream without intermediate removal of the heavy media or liquid. In such event, care must be taken not to upset the desired gravity in subsequent gravity separation due to uncontrolled carry over of heavy media or liquid from an earlier gravity separation.

While both brine and magnetite can be added in a pulper to provide the requisite media density, it is also possible to employ an initial pulping operation wherein the ore is pulped with brine and subjected to a sizing to remove any −10 mesh particles generated during pulping. The sized material will then be subjected to a second pulping operation in which magnetite and additional brine, if necessary, are added to provide the requisite specific gravity.

The overflow from hydrocyclone **4** is sized in screen **7** to provide a coarse fraction having particles ranging from about three-fourth to about one-fourth inch which are sent to crusher **9** wherein the ore is comminuted to about −¼ inch. The comminuted ore is sized on screen **10** to remove −10 mesh particles and the −¼ inch × 10 mesh particles are subjected to gravity separation in a gravity separator wuch as hydrocyclone **11** which desirably has an apparent gravity of separation of from about 2.10 to about 2.16 and preferably about 2.11. The underflow from hydrocyclone **11** is removed as tails through line **12**. The overflow concentrate from hydrocyclone **11** is sent through line **13** to a gravity separator such as hydrocyclone **14** wherein the specific gravity of separation is from about 2.02 to about 2.06 and desirably about 2.05. In effect, hydrocyclones **4** and **11** constitute "rougher" separations while hydrocyclone **14** constitutes a "cleaner" separation. Hydrocyclone **14** processes not only the concentrate from hydrocyclone **11** but also the −¼ inch × 10 mesh particles which are separated from the overflow concentrate of hydrocyclone **4**. This latter fraction is transmitted to hydrocyclone **14** through line **15** from screen **7**.

Hydrocyclone **14** provides an overflow sylvite product which is removed through line **16**. The underflow from hydrocyclone **14** is removed through line **17** and may have sufficient sylvite values to justify comminution in crusher **18** to −10 mesh and recycle to screen **2** or the stream can be subjected to wet beneficiation.

The −10 mesh removed from screen **2** through line **3** and the −10 mesh material removed from screen **10** through line **20** may be deslimed in hydroseparator **21** and thereafter subjected to cationic froth flotation in flotation circuit **22**. If desired, the streams can, of course, be deslimed separately. The flotation provides sylvite product **23** and underflow tails **24** containing predominantly halite. Instead of froth flotation, the −10 mesh material may be subjected to crystallization to provide a sylvite product.

While the attached flowsheet includes two rougher separators, **4** and **14**, the process can be conducted by recycling the particles from crusher **9** to hydrocyclone **4** either before or after 10 mesh particles are removed. If screen **10** is eliminated, the undersize (−10 mesh) is removed at screen **2** and the recycled liberated particles are then subject to gravity separation in hydrocyclone **4**.

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 Saskatoon region of Saskatchewan containing 260 parts of K_2O and **60** parts clay is comminuted and sized to provide a ¾ inch × 10 mesh fraction. Approximately 700 parts of the ore was −¾ inch × +10 mesh, while the remaining 300 parts was −10 mesh. The ¾ inch × 10 mesh fraction is beneficiated in a "rougher" hydrocyclone at a 2.14 specific gravity of separation. The gravity separation reject approximately 375 parts containing 47 parts of clay (78 percent of clay originally present) and 18 parts of K_2O. The overflow concentrate (approximately 360 parts) from the gravity separation contains 160 parts K_2O and 5 parts clay and is screened at ¼ inch. The + ¼ inch fraction (about 122 parts containing about 38 parts K_2O and about 2 parts clay) is crushed to − ¼ inch and recycled to the initial sizing operation. The − ¼ inch fraction is subjected to a second beneficiation in a "cleaner" hydrocyclone at a 2.04 specific gravity of separation. The cleaner hydrocyclone provides 178 parts of overflow product containing 103 parts K_2O (58% K_2O) and 1 part clay. The cleaner hydrocyclone also provides 60 parts of middlings (underflow) containing 19 parts K_2O and 2 parts clay for wet beneficiation.

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

TABLE 1

	Total Parts	Wt. K_2O	% Clay	Ratio K_2O:Clay
Mine Run Ore	1000	26	6	4.5:1
Rougher Tails	375	4.8	12.5	
Rougher Concentrate	360	44.5	1.4	32:1
Cleaner Concentrate	178	58	0.6	103:1
Total Feed to Wet Beneficiation	447	31	2.7	11.6:1

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

Since variations of this invention will be apparent to those skilled in the art, it is intended that the invention be limited only by the scope of the appended claims.

I claim:

1. A process for beneficiating clay-containing sylvinite ores containing at least about 3 percent clay and having a K_2O:clay ratio of less than about 5:1 comprising:

1. comminuting said sylvinite ore and sizing said ore to provide a fraction containing particles having a maximum size of from about 1 to about ½ inch and a minimum size of about 10 mesh;
2. subjecting said fraction of (1) 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 characterized by a K_2O:clay ratio of at least about 10:1 and halite and clay particles are removed as an underflow;

3. sizing said overflow fraction of (2) to provide a first fraction having particle sizes of less than about one-fourth inch and second fraction having particle sizes greater than about one-fourth inch;
4. subjecting said first fraction of (3) to gravity separation in a media having a specific gravity of separation intermediate the specific gravity of sylvite and halite whereby an overflow sylvite concentrate is obtained;
5. comminuting said second fraction of (3) and sizing said fraction to provide particles having sizes ranging from about ¼ inch to about 10 mesh;
6. subjecting said comminuted particles of (5) to gravity separation in a media having a specific gravity of separation intermediate the specific gravity of sylvite and halite to provide a sylvite-containing overflow; and
7. subjecting said sylvite-containing overflow of (6) to gravity separation in a media having a specific gravity of separation intermediate the specific gravity of sylvite and halite whereby an overflow sylvite concentrate is obtained.

2. A process according to claim **1** wherein said ore is sized to provide particles having a maximum size of about three-fourth inch.

3. A process according to claim **1** wherein said ore is sized to provide particles having a maximum size of about one-half inch.

4. A process according to claim **1** wherein said gravity separations employ heavy media as the liquid media.

5. A process according to claim **1** wherein said gravity separations employ a heavy media of brine and magnetite and are vortex separations.

6. A process according to claim **1** wherein said ore is heated to remove free water prior to comminuting.

7. A process according to claim **1** wherein the undersize from comminution is subjected to wet beneficiation.

8. A process according to claim **7** wherein said wet beneficiation is froth flotation.

9. A process according to claim **7** wherein said wet beneficiation is crystallization.

10. A process according to claim **7** wherein the composite K_2O:clay ratio of said undersize is at least about 8:1.

11. A process according to claim **7** wherein the composite K_2O:clay ratio of said undersize is at least about 10:1.

12. A process according to claim **1** wherein the comminuted particles of step (5) are subjected to further gravity separation by recycling to the gravity separation of step (2).

13. A process according to claim **1** wherein the underflow from the gravity separation of (7) is comminuted and recycled to the gravity separation of (2).

14. A process according to claim **1** wherein the undersize from comminution and the underflow from the gravity separation of (7) are subjected to wet beneficiation.

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