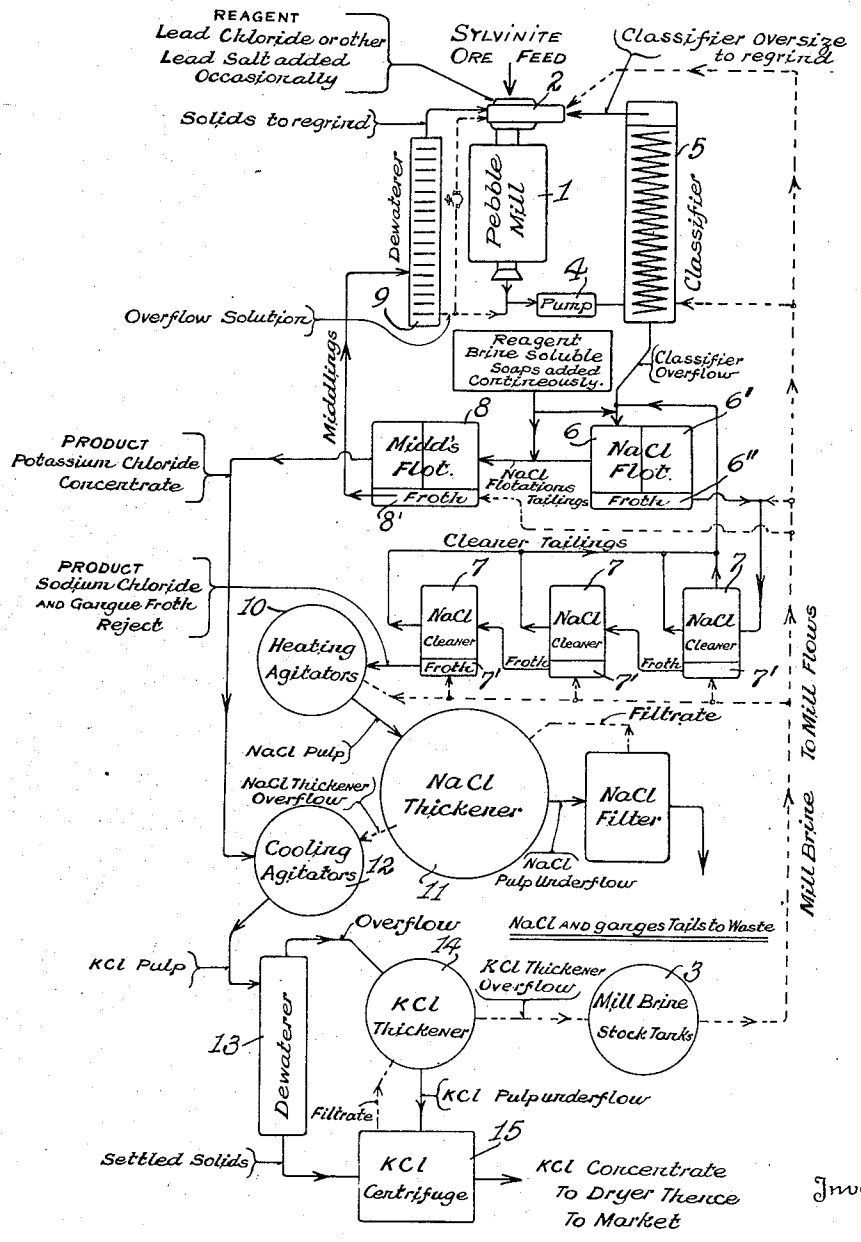
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SELECTIVE FLOTATION OF SODIUM CHLORIDE FROM SYLVINITE ORES

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SELECTIVE FLOTATION OF SODIUM CHLORIDE FROM SYLVINITE ORES

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This invention relates to a process for separating soluble and valuable constituents from sylvinite ores and the product or products to be obtained by such process, and the present application is in part a continuance of my co-pending applications Serial Nos. 755,576, filed December 1, 1934; 755,577, filed December 1, 1934; 11,059, filed March 14, 1935; and 28,983, filed June 28, 1935.

Sylvinite ores consist mainly of sodium chloride and potassium chloride crystals, together with small amounts of other mineral matter such as iron and manganese oxides, calcium and magnesium minerals, clays and the like. Sodium chloride and potassium chloride crystals in the ore are found as distinct crystals, with a more or less amount of the two crystals intimately associated together. Both are soluble in water, but with different rates of solubility with respect to the temperatures of the solution. Both are floatable by the froth flotation process in a saturated water solution of the sylvinite ore, but each requires a different reagent, or reagent combination, to produce flotation. In the present invention advantage is taken of the differences in rate of solubility and flotation properties to effect separation between the two salts.

The invention has for its object to obtain potassium chloride in a practically pure form and sodium chloride also in a pure form, or, if desired, said chlorides without the elimination of the foreign matters of the ore.

Generally stated, the invention consists in first preparing a saturated solution in water of the constituents of the sylvinite ore, which mainly consist of sodium chloride and potassium chloride, and dissolving in said saturated solution lead and/or bismuth so that the solution shall be a solution of sodium and potassium chlorides and lead or bismuth. This solution is the flotation liquid, and there is introduced into this solution sylvinite ore in a finely divided condition, thus forming a pulp, and the sodium chloride particles of this pulp, as well as the gangue that may be present, are separated from the pulp by flotation. The specific gravity of sodium chloride is 2.2 while the specific gravity of potassium chloride is 2, and in order to float off the sodium chloride a selective reagent or reagents is or are employed to cause air bubbles, produced in the solution in any suitable manner, to float sodium chloride and gangue particles of the pulp to the surface of the said solution without affecting the potassium chloride, or if affecting it, to retard or depress flotation thereof. The reagent employed consists of any fatty acid (or as the equivalent thereof a derivative or derivatives of a fatty acid or mixtures thereof) which is capable of being dissolved in said solution and which is capable of causing flotation of the sodium chloride and gangue in said solution. It is particularly pointed out, as indicated above, that fatty acids (or derivatives of fatty acids) employed must be such as are capable of being dissolved in said solution of the ore and also capable of causing flotation of sodium chloride and gangue in the solution, such for example as oleic acid, cocoanut oil soap, palm kernel oil soap, resin soap and the like. There are certain fatty acids and derivatives of fatty acids which are insoluble in such a solution, and/or are incapable of causing flotation of sodium chloride in said solution, and such are not included in the class of fatty acids or derivatives of fatty acids to be employed as a reagent. It is to be expressly understood that the term "fatty acid" as used in this description and the claims is intended to include not only fatty acids strictly as such, but also any derivative or derivatives of fatty acids which are soluble in a saturated solution of sodium chloride and potassium chloride containing lead dissolved therein and capable of causing flotation of the sodium chloride and gangue in said solution.

Furthermore, when a straight saturated solution of potassium chloride and sodium chloride has its temperature reduced, potassium chloride promptly crystallizes out, but when lead and/or bismuth are dissolved in and form a part of said solution, potassium chloride will not materially crystallize out of said solution, even with material cooling of the solution and standing for an hour or more, unless potassium chloride in solid form is present in the solution to act as "seed," and even then the potassium chloride crystallizes only on the "seed" and not to any substantial extent on the surfaces of pipes, containers and other parts. The result of this is that clogging of the pipes, etc., is avoided by the presence of the lead and/or bismuth in the solution. Another advantage lies in the fact that corrosion of iron surfaces by the solution is almost entirely prevented. The proportion of lead in the solution may vary. From 1.2 to 1.6 grams per liter of solution may be employed, but preferably from 1.8 to 1.9 grams per liter of solution is employed.

And, furthermore, it will be found that potassium chloride concentrate produced by the process herein set forth is covered with a film of a

sufficiently water repellent character to prevent material caking of the potassium chloride in transit or in storage, whereas potassium chloride heretofore produced, due to its water absorbing character, has been found to solidify in cars or the holds of ships to such a degree that it often had to be blasted out, and this makes it necessary for the product to be ground when the same is employed as an addition to fertilizers.

When, as in the present case, there is always present sufficient sodium chloride and potassium chloride to saturate the solution with these two salts, a rise in temperature will result in an increased percentage of potassium chloride and a decreased percentage of sodium chloride in the saturated solution, as indicated by the following table:

Degrees F.	KCl	NaCl
	Per-cent	*Per-cent*
50	8.7	20.9
60	9.6	20.6
70	10.4	20.2
80	11.3	19.9
90	12.2	19.5
100	13.0	19.2
110	13.9	18.9
120	14.7	18.5
130	15.5	18.2
140	16.4	17.9
150	17.3	17.6

This is a well recognized fact and it will be noted that the percentage of potassium chloride in the saturated solution increases as the temperature rises while the percentage of sodium chloride decreases, and that the former increases more rapidly than the latter decreases; and conversely, on a drop in temperature, the percentage of potassium chloride in the saturated solution decreases more rapidly than the percentage of sodium chloride increases in said solution. Advantage is taken of this phenomena in the process of the present invention to aid in effecting the separation of the constituents of sylvinite ore by properly varying and controlling the temperature at various stages of the process. Thus, at one stage care is taken to maintain during that stage an approximately constant temperature of the flotation pulp to the end that the liquid phase will neither dissolve nor deposit out of solution the soluble constituents of the ore; at another stage of the process the temperature of the flotation pulp is raised to cause potassium chloride in the solid phase to enter into solution in the liquid phase; at still another stage, the temperature of a flotation pulp product, containing a saturated solution of the ore constituent as a liquid phase and undissolved potassium chloride as a constituent of the solid phase, is reduced to cause potassium chloride to be deposited out of the liquid phase into the solid phase; furthermore, by raising the temperature of a sylvinite ore flotation pulp product to cause potassium chloride to pass into solution in the liquid phase, then separating the liquid phase from the solid phase, and then reducing the temperature of said separated liquid phase, potassium chloride is caused to separate therefrom. Preferably said reduction of temperature of the said separated liquid phase is in the presence of seed crystals of potassium chloride. Thus, before cooling, said separated liquid phase may be mixed with another flotation pulp product that has been enriched in potassium chloride in the solid phase, to act as seed on which the potassium chloride crystallizes out on lowering the temperature of the mixture. By enriching a flotation potassium chloride concentrate as a solid phase having some sodium chloride associated therewith and then cooling the same in the presence of a warm saturated solution of the sylvinite ore as a liquid phase, sodium chloride is dissolved from the solid phase and enters into solution in liquid phase, and potassium chloride deposits out of the liquid phase into the solid phase.

It will thus be seen that by proper control and variation of temperatures during the process, effective separation of the potassium and sodium chlorides in sylvinite ores is facilitated.

When potassium chloride and sodium chloride are dissolved in water in the presence of sylvinite ore there is formed a solution saturated both wth respect to sodium chloride and potassium chloride, and it is this saturated solution with lead and/or bismuth also dissolved therein that is employed in the flotation of the sodium chloride and gangue. Inasmuch as the finely divided particles of the sylvinite ore are introduced into a solution saturated with respect to the constitutents of the ore, the ore thus introduced in the solution remains in solid form, and the mixture of this solution (having lead and/or bismuth dissolved therein) and finely divided ore constitutes, and will hereinafter be referred to as, the pulp.

The flotation step may be carried out in any suitable flotation apparatus, and preferably it is carried out in a plurality of flotation cells associated in series, in which cells the ratio of ore to solution may be varied. Thus, in the first flotation cell a large portion of the sodium chloride, and gangue if present, may be floated out while still leaving in the pulp some of the sodium chloride, and this remaining chloride is removed by a repetition of the flotation process in the succeeding cells, to the end that the solid residue in the final cell is a nearly pure potassium chloride, together with small quantities of iron oxides and manganese oxide.

It has been found that the flotation froth passing from the several flotation cells carries not only sodium chloride (in solid form) but also more or less of potassium chloride (likewise in solid form), and in order to effect a complete recovery of all the potassium chloride of the ore it is necessary that this potassium chloride, associated with the sodium chloride froth, be also recovered. When the temperature of the solution carrying the sodium chloride froth, with its associated potassium chloride, is raised, the amount of potassium chloride capable of being dissolved in the heated solution will be largely increased over that dissolved at a lower temperature; whereas the amount of sodium chloride that will be held in solution by such heated solution will be decreased, as indicated in the above table. Advantage is taken of this to pass the potassium chloride that is thus associated with the sodium chloride in the flotation froth into solution and afterwards to recover the same from this enriched solution. To this end, the saturated solution carrying the sodium chloride froth from the flotation cells is first heated under agitation, and then while still heated, sodium chloride is permitted to settle out of the solution. After separating the settled sodium chloride from the solution, the solution is cooled in the presence of solid potassium chloride. The solid potassium chloride affords "seed" upon which potassium chloride carried in the heated solution, referred

to above, will crystallize out upon cooling, and such solid potassium seed may be derived from the flotation cells or otherwise. The result of this is that nearly all of the potassium chloride contained in the sylvinite ore under treatment is recovered.

The sodium chloride that is settled out of the heated solution and separated therefrom, as indicated above, may be purified and free from moisture and is then ready for sale or other disposition.

The potassium chloride sludge, which is the pulp remaining from the above sodium chloride flotation and is freed from the sodium chloride, has the liquid separated therefrom in any suitable dewaterer, which liquid, with more or less finely divided solid potassium chloride that may be left therein, is passed to a potassium chloride thickener, while the body of the thickened sludge is transferred from the dewaterer, together with the settled solids from the thickener, to a centrifuge where the product is dewatered and prepared for drying.

The several steps of the process above described will be understood from a reference to the accompanying flow sheet in which 1 indicates a grinding mill, which is preferably a pebble mill, it being essential to avoid any class of grinding mills that present polished iron surfaces, since the lead or bismuth in the saturated solution would be precipitated out of the solution if brought in contact with polished iron surfaces. 2 indicates a suitable feeder for delivering the ore to the mill, and 3 indicates a tank containing the lead-sodium chloride-potassium chloride solution, saturated as to the latter two. From this tank the solution is transferred through conduits indicated by the dotted lines, to the several flotation cells and other parts of the apparatus, including the pebble mill 1. The crushed ore from the pebble mill 1 is delivered, preferably by a pump 4, to any suitable classifier 5, where the finer particles suitable for treatment in the flotation process are separated from the coarser particles. The coarser particles are returned from the classifier to the mill 1 through the feeder 2, while the finer particles are delivered to the initial flotation cell 6, where, being in suspension in the saturated solution of constituents of the sylvinite ore containing lead, they form a pulp. A suitable reagent or reagents in the form of fatty acids (or derivatives of fatty acids as equivalents thereof) such as oleic acid, cocoanut oil soap, palm kernel soap, resin soap or the like, that are soluble in the potassium chloride-sodium chloride-lead solution and which are capable of floating sodium chloride and gangue matter in such solution, are continuously added to the flotation pulp at any suitable point or points in the flotation operation. The amount of the reagent added may vary under different conditions, but it has been found that about four pounds of the fatty acid (or equivalent derivatives thereof) per ton of ore treated is usually required. The reagent employed must be one that is soluble in the solution and also capable of causing flotation of the sodium chloride and gangue. During the practice of the process the fatty acids or derivatives of fatty acids will be consumed, and hence a continuous supply of such reagent must be added during the flotation operation. It is to be noted, however, that while there is constant consumption of the flotation reagent, to wit, fatty acids or derivatives of fatty acids, there is no such consumption of the constituents, to wit, sodium chloride, potassum chloride and lead, of the flotation solution. The concentration of the potassium chloride and sodium chloride constituents of the solution are practically constant throughout the series of operations at any given temperature, though there may be small mechanical losses of the potassium chloride and sodium chloride over long periods of operation which are automatically replenished by the ore. The concentration of the lead constituent of the solution remains constant regardless of variation in temperature, though there may be a slight mechanical loss of the lead of the solution over long periods of operation which is compensated for by suitable occasional additions of the lead or bismuth to the solution. It is to be noted that the fatty acid reagent is consumed during the operation of the process, the amount consumed being dependent upon the amount of sodium chloride per ton in the ore being treated, whereas the lead in the solution is not consumed and the amount in said solution remains constant.

The lead supplied to the solution is preferably in the form of lead chloride, lead nitrate, lead sulfate or lead acetate, or if bismuth is used, similar salts of bismuth, though other lead or bismuth salts may be employed. However, any means of dissolving lead in the solution may be employed, such for example as passing the potassium chloride-sodium chloride solution through a tumble mill containing lead bars or metallic lead in other forms. Lead salts are preferable however, because all known lead and/or bismuth salts are soluble in a saturated solution of potassium chloride and sodium chloride and may be, and preferably are, introduced into solution in the grinding mill.

There may be, and preferably there are, a plurality of original flotation cells, as shown for example at 6 and 6'. These flotation cells 6 and 6' are provided with suitable agitators whereby, with proper introduction of air, bubbles are formed in the pulp, and the effect of the reagents is to cause the sodium chloride to adhere to the bubbles which rise to the surface and are floated off in the shape of froth into the flotation trough 6''. It has been found that the froth thus delivered from the flotation cells 6 and 6' carries with it not only solid sodium chloride particles but also the gangue material of the ore and some solid particles of potassium chloride, and therefore, in order to effect a maximum recovery of all of the potassium chloride in the ore, steps are taken to separate this potassium chloride from the sodium chloride froth. To this end the froth is passed into one or more, and preferably a series (here shown as three) of so-called "cleaner" cells 7—7, which cells operate on identically the same principle as the original flotation cells 6 and 6'. The cells 7—7 float off the sodium chloride in the form of froth into the froth troughs 7'—7', to the end that the froth thus delivered from the last cleaner cell 7 is substantially free from potassium chloride, except certain small particles of potassium chloride which are intimately associated with particles of sodium chloride carried by the froth.

The pulp remaining in the flotation cells 6 and 6', after the sodium chloride has been floated therefrom, is passed from the cells 6, 6', directly to cells 8 technically known as "middling" cells. This pulp is composed largely of the flotation solution and solid potassium chloride, but there are almost invariably small particles of

sodium chloride attached to some of these particles of potassium chloride and these attached particles are floated to the surface in the cell 8 and delivered into the trough 8', additional fatty acids or derivatives of fatty acids as reagents being added at the cell 8. This insures flotation of substantially all the sodium chloride particles including those that may have some potassium chloride attached thereto. From the trough 8', the froth is delivered to any suitable dewaterer 9, where the solution of the froth is to a very large extent separated from the solid particles. These particles are delivered to the feeder 2 to be reground, while the solution is delivered through the pump 4 to the classifier and returns to the system.

The sodium chloride froth, with some potassium chloride intimately associated therewith, and which has been passed to the "cleaner" cells 7—7 is delivered from the last one of the "cleaner" cells 7—7 to a container 10 provided with means for heating its contents and also with means for agitating the same. This is technically known as a "heating agitator." The sodium chloride froth with the accompanying potassium chloride particles carries with it, of course, more or less of the flotation solution, but it may be, and frequently is, desirable to supply an additional amount of the solution to the heating agitator, and this is accomplished by withdrawing such solution from the stock tank 3 through conduits, indicated by dotted lines in the flow sheet.

When the temperature of the pulp in the heating agitator is raised, say 10 to 20° F., for example, the potassium chloride which is carried into the heating agitator in solid form by the froth from the "cleaner" cells 7—7 is dissolved, and this takes place notwithstanding the fact that the solution carrying the solid particles is saturated at a lower temperature. While the potassium chloride is dissolved, sodium chloride tends to pass out of solution as shown by the above table. When this is accomplished the pulp from the heating agitator is passed directly into the container 11 where it is maintained free from agitation and sodium chloride is thus permited to settle out. The temperature of the pulp is maintained in the container 11 at approximately the same as the temperature in the heating chamber 10, so that no potassium chloride crystallizes out of the solution.

Referring now to the "middling" cells 8, the pulp from these cells, the solid part of which is practically pure potassium chloride with possibly some solid sodium chloride associated therewith, is passed directly from the cells 8 to a cooling agitator 12. In this cooling agitator the temperature is maintained at approximately that of the entire system other than that in the tanks 10 and 11. After the sodium chloride particles have been settled out of the heated solution in the thickener tank 11 and separated therefrom, this warm solution is also passed into the cooling agitator 12 where it comes in contact with the concentrate particles of potassium chloride that have been delivered from the middling flotation cells 8. These particles act as "seed" upon which the potassium chloride in the solution from the thickener tank 11 crystallizes as the result of the lower temperature in the cooling tank, the contents of this latter tank being agitated during the operation. A further result of the lower temperature in the cooling agitator 12 is that any small amount of sodium chloride particles carried from the cell 8 with the potassium chloride concentrate pass into solution, so that the solid part of the pulp passing from the cooling agitator 12 to the dewaterer 13, as hereinafter described, consists of approximately pure potassium chloride. It is here to be noted that, due to the use of the potassium chloride-sodium chloride-lead solution, the temperature in the cooling agitator and elsewhere in the system may be very materially lowered (anywhere through a range of fifteen degrees F.) without causing any material amount of potassium chloride to be crystallized out unless potassium chloride in solid form is introduced thereinto to form the seed for the crystallization. One of the highly beneficial results of this is that though the potassium chloride-sodium chloride-lead solution may be materially cooled (i. e. through a range of fifteen degrees F.) in passing through pipes and other parts of the apparatus, no material amount of potassium chloride will be crystallized out of solution; and, furthermore, destructive corrosion of iron pipes or containers is avoided. This is in marked contrast to the destructive corrosion which occurs when a lead-free brine solution, such as potassium chloride-sodium chloride-solution, is employed. With the sodium chloride-potassium chloride-lead solution it will be found that when a plant is first started, employing iron pipes and containers, there will soon collect on the pipes and containers a thin coat of lead deposited out of the solution, which coat of lead protects the iron from corrosion and other destructive action. This, of course, results initially in some loss of lead from the solution, which is compensated for by a suitable addition thereto. It will be seen that this very materially reduces the depreciation and repair costs of the plant.

The temperature of the pulp having been sufficiently lowered in the cooling agitator 12, the same is passed to a dewaterer 13 in which the solution carrying finely divided particles of potassium chloride is largely removed from the mass of potassium chloride solids and then passed to a potassium chloride thickener 14. The solution thus removed from the dewaterer and passed to the thickener 14 will carry, as indicated above, more or less fine particles of potassium chloride with it, and these are permitted to settle out in the thickener 14, after which the solution thus freed from the potassium chloride is passed into the stock tank 3.

From the dewaterer 13 and the thickener 14 potassium chloride solids, having a small amount of solution associated therewith, are passed to a centrifuge 15 wherein nearly all of the remaining amount of the solution is removed and passes by way of the thickener 14 to the stock tank 3. The centrifuging removes nearly all of the solution from the potassium chloride, but there remains a very small amount of such solution attached to the potassium chloride particles, and this solution contains sodium chloride which it is essential to remove from the potassium chloride particles, if the potassium chloride is to be entirely free from sodium chloride. Accordingly, the centrifuged potassium chloride particles are subjected to a washing operation and thus freed from the sodium chloride contained in the original solution. To accomplish this washing without loss of any potassium chloride, and to assure the removal of the sodium chloride, the solids in the centrifuge 15 are washed with a saturated solution of potassium chloride. If perchance there are any stray particles of sodium chloride with the potassium chloride in the centrifuge 15,

this saturated solution of potassium chloride will dissolve them without dissolving any of the potassium chloride, and furthermore, the saturated solution of the potassium chloride acts as a means of washing the potassium chloride in the centrifuge free from any of the original solution which contains sodium chloride. If desired, water may be used as the washing medium, in which case the water will become saturated with potassium chloride shortly after it comes in contact with the material. This washing is preferably effected in the centrifuge 15, and this washing solution, as well as any of the original solution, passes from the centrifuge 15 to the thickener, 14, where any solid potassium chloride is settled out and the solution is then returned to the system by way of the stock tank 3.

While as illustrated in the flow sheet, the heating agitator 10 is shown as separate from the cleaner cells 7—7 this heating of the pulp may, if desired, be effected in one or more of the cleaner cells 7—7. Moreover, it will be recognized that inasmuch as the middlings flotation cells 8 are at a lower temperature than that maintained in the heating agitator (or if preferred, in the heated cells 7), the overflow from the sodium chloride thickener 11 may be discharged directly into the middlings flotation cells 8, where the function above indicated as pertaining to the cooling agitator 12 will take place. In this case it will be understood that cooling means will be provided in connection with the middlings flotation cells 8, from which cells the potassium chloride solids with the solution is passed directly to the dewaterer 13.

While the invention has been described in connection with a flow sheet, setting forth in detail certain arrangement of the flotation cells, heating and cooling agitators, thickeners, etc., it will be appreciated by one skilled in the art that various changes and modifications in the arrangement thereof may be made without departing from the spirit of the invention as herein set forth, and it will be understood that such flow sheet is merely for the purpose of illustrating the invention, and not for the purpose of defining the limits thereof, reference being had to the appended claims for this purpose.

It will also be understood that fatty acids, and derivatives of fatty acids, as well as mixtures of these are equivalents, provided only that they are soluble in a saturated solution of the sylvinite ore having lead and/or bismuth dissolved therein and are capable of floating the sodium chloride and gangue, and the term "fatty acid" used in the claims is intended to include any and all such derivatives and mixtures.

It will also be understood that, if desired, the ore may be subjected to dry grinding and the product of such grinding then introduced into a saturated solution of the ore having lead and/or bismuth dissolved therein.

It will be found that the potassium chloride secured as the result of the process herein described is not the ordinary white, chemically refined potassium chloride. On the contrary, it is granular in form and of a pinkish color due to small amounts of iron oxide and manganese oxide in the sylvinite ore which remain with and color the potassium chloride obtained as a product. Furthermore, it will be found that the grains of this product after drying are water repellent and will have little or no tendency to cake or adhere together as a result of absorbing moisture. This is a matter of particular importance, since potassium chloride heretofore produced is deliquescent, and as a result it tends to cake in bags in storage or in warehouses or holds of ships during transportation, and renders it necessary that the same be ground or otherwise pulverized to put it into condition for use as fertilizer.

This water repellent condition is due to the fact that the granules of potassium chloride produced by the present invention are coated with insoluble lime and magnesium soaps resulting from the combination of the fatty acid reagents employed and the lime and magnesium salts occurring in small amounts in the sylvinite ore. This favors the absorption of oils which are sometimes added in controlled amounts (under 1% by weight) before, during or after drying to increase the water repellent properties, and by this means controlled repellent characteristics may be maintained in the final product. Mineral oils or fractions thereof, such as fuel oil or kerosene; animal oils, such as red oil or oleic acid; or vegetable oils, such as cotton seed oil or cocoanut oil may be used.

What is claimed is:

1. The process of separating potassium chloride from sylvinite ore which consists in removing the sodium chloride content of the ores by flotation in a saturated solution of the ore, then raising the temperature of the flotation froth and the solution carrying the same under agitation, whereby potassium chloride particles carried by the froth are dissolved in the solution and sodium chloride is thrown out of solution, then permitting sodium chloride to settle out of the solution and separating it therefrom while maintaining the elevated temperature of the solution, then lowering the temperature of said solution in the presence of solid potassium chloride carried in a saturated solution of the ore, whereby potassium chloride is crystallized out of the solution, then separating the potassium chloride from the main body of the solution while leaving it still moistened thereby, and then washing the moist potassium chloride with a saturated solution of potassium chloride to remove sodium chloride carried by the original saturated solution of the sylvinite ore.

2. The process of separating potassium chloride from sylvinite ores which consists in removing the sodium chloride content of the ores by flotation in a saturated solution of the ore, then raising the temperature of the flotation froth and the solution carrying the same under agitation, whereby any potassium chloride particles carried by the froth are dissolved in the solution and sodium chloride is thrown out of solution, then separating sodium chloride in the solid phase out of the solution while maintaining the elevated temperature of the solution, then lowering the temperature of said solution in the presence of solid potassium chloride carried in a saturated solution of the ore, whereby potassium chloride is crystallized out of solution, then separating the solution from the potassium chloride crystals and returning the saturated solution to the system.

3. In a process of treating sylvinite ores, including an initial separation of sodium chloride and gangue constituents from potassium chloride constitutents of sylvinite ore, the steps of heating the separated sodium chloride and gangue constituents in the presence of a saturated sodium chloride potassium chloride solution to dissolve any adhering potassium chloride subjecting the heated matter to gravity settling, re-

moving the settled solids from the treatment, mixing the clarified solution of the settling operation with the separated potassium chloride constituents, cooling the mixture to induce precipitation of potassium chloride in the solution, and then separating the precipitated solids from the solution.

4. In a process of treating sylvinite ores, including an initial separation of sodium chloride and gangue constituents from potassium chloride constituents of sylvinite ore, the steps of heating the separated sodium chloride and gangue constituents in the presence of a saturated sodium chloride potassium chloride solution to dissolve any adhering potassium chloride, subjecting the heated matter to gravity settling, removing the settled solids from the treatment, mixing the clarified solution of the settling operation with the separated potassium chloride constituents, cooling the mixture to induce precipitation of potassium chloride in the solution, then separating the precipitated solids from the solution, and returning the separated solution to the initial treatment stage of the process.

5. In a process of treating sylvinite ores, including an initial separation of sodium chloride and gangue constituents from potassium chloride constituents of sylvinite ore, the steps of heating the separated sodium chloride and gangue constituents in the presence of a saturated sodium chloride potassium chloride solution to dissolve any adhering potassium chloride, subjecting the heated matter to gravity settling, removing the settled solids from the treatment, mixing the clarified solution of the settling operation with the separated potassium chloride constituents, cooling the mixture to induce precipitation of potassium chloride in the solution, subjecting the cooled matter to gravity settling, separating the settled solids from the solution, and returning the solution of this separation to the gravity settling treatment.

6. In a process of treating sylvinite ores, including an initial separation of sodium chloride and gangue constituents from potassium chloride constituents of sylvinite ore, the steps of heating the separated sodium chloride and gangue constituents in the presence of a saturated sodium chloride potassium chloride solution to dissolve any adhering potassium chloride, subjecting the heated matter to gravity settling, removing the settled solids from the treatment, mixing the clarified solution of the settling operation with the separated potassium chloride constituents, cooling the mixture to induce precipitation of potassium chloride in the solution, subjecting the cooled matter to gravity settling, separating the settled solids from the solution, returning the solution of this separation to the gravity settling treatment, and returning excess solution of the gravity settling operation to the initial treatment stage of the process.

7. In a process of treating sylvinite ores, including an initial separation by a froth flotation treatment of the ores, of a froth concentrate consisting of gangue and sodium chloride present as halite from a non-floated residue of potassium chloride present as sylvite, the steps of cooling the flotation residue containing solid phases of sylvite suspended in a liquid phase which is a saturated solution of the ore, and then separating the liquid and solid phases of the cooled residue.

8. In a process of treating sylvinite ores, including an initial separation by a froth flotation treatment of the ores, of a froth concentrate consisting of gangue and sodium chloride present as halite from a non-floated residue of potassium chloride present as sylvite, the steps of cooling the flotation residue containing solid phases of sylvite suspended in a liquid phase which is a saturated solution of the ore, then separating the liquid and solid phases of the cooled residue, and returning the separated liquid phase to the froth flotation treatment.

9. The process of treating sylvinite ores, which comprises introducing sylvinite ore in finely-divided condition into a saturated solution of the ore to form a pulp, separating sodium chloride particles and gangue from the pulp by the action of a froth flotation reagent having a selective affinity therefor, purifying the potassium chloride content of the non-floated residue by subjecting the residual solids and solution thereof to a cooling action, separating the solution from the solids at the completion of the cooling operation, and washing the separated solids with a saturated potassium chloride solution to remove any adhering sodium chloride.

10. The process of treating sylvinite ores, which comprises introducing sylvinite ore in finely-divided condition into a saturated solution of the ore to form a pulp at a controlled temperature, separating sodium chloride particles and gangue from the pulp by the action of a froth flotation reagent having a selective affinity therefor, purifying the potassium chloride content of the non-floated residue by subjecting the residual solids and solution thereof to a cooling action, then separating the solids from the cooled solution, and returning the cooled solution so separated to condition the pulp of the flotation operation.

11. In a process of treating sylvinite ores, including the production of a pulp composed of sylvite as its solid phase and a saturated halite-sylvite solution as its liquid phase, which under ordinary conditions would deposit potassium chloride, the step of maintaining a substantially uniform phase relationship of the variably soluble values in the pulp under temperature variations by maintaining a lead compound dissolved in said solution.

12. In a process of treating sylvinite ores, including the production of a pulp composed of sylvite as its solid phase and a saturated halite-sylvite solution as its liquid phase, the step of maintaining a substantially uniform phase relationship in the pulp under temperature variations by dissolving bismuth in its liquid phase.

13. In a process of treating sylvinite ores, including the production of a pulp composed of sylvite as its solid phase and a saturated halite-sylvite solution as its liquid phase, the step of maintaining a substantially uniform phase relationship in the pulp under temperature variations by dissolving lead and bismuth in its liquid phase.

14. In a process of treating sylvinite ores, including the movement, across iron surfaces at a stage of the treatment, of a pulp containing sylvite in the solid phase and a saturated halite-sylvite solution in the liquid phase, the steps of dissolving bismuth in solution, and then causing bismuth to deposit out of solution onto the iron surfaces to form a protective coating therefor.

15. In a process of treating sylvinite ores, including the movement, across iron surfaces at a stage of the treatment, of a pulp containing halite in the solid phase and a saturated halite-sylvite solution in the liquid phase, the steps of dissolving bismuth in solution, and then causing

bismuth to deposit out of solution onto the iron surfaces to form a protective coating therefor.

16. In an ore treating process in which sylvinite ore in finely-divided condition in a saturated solution of the ore containing dissolved metal of the class consisting of lead and bismuth is treated for the separation of its sodium chloride and potassium chloride constituents, the improvement which comprises heating such a solution containing sodium chloride and some potassium chloride solids to dissolve the potassium chloride and crystallize sodium chloride, separating the solids from the solution, and then inducing crystallization of potassium chloride constituents of the solution so enriched in potassium chloride by reducing the temperature thereof in the presence of seed particles of potassium chloride.

17. A process for the recovery of valuable constituents of sylvinite ores, which comprises introducing sylvinite ore in finely-divided condition into a saturated solution of the ore to form a pulp, subjecting the pulp to a froth flotation treatment to separate its sodium chloride and potassium chloride constituents by selective flotation of sodium chloride, heating the sodium chloride of the froth concentrate to dissolve any associated potassium chloride, cooling the separated residue of flotation to dissolve any retained sodium chloride and to crystallize potassium chloride of the solution, separating the solution from the solids of the froth concentrate after heating, and separating the solids from the solution of the cooled residue.

18. In an ore treating process in which sylvinite ore in finely-divided condition in a saturated solution of the ore containing dissolved metal of the class consisting of lead and bismuth is treated for the separation of its sodium chloride and potassium constituents, the improvement which comprises inducing crystallization of potassium chloride constituents of such a solution after separation of the sodium chloride and potassium chloride constituents of the ore by reducing the temperature of the solution in the presence of solid phases of potassium chloride, separating the solid and liquid phases, and then washing the separated solids with a saturated solution of potassium chloride to remove any adhering solution containing sodium chloride.

19. In a process of treating sylvinite ores in which sylvinite ore which under ordinary conditions would deposit potassium chloride, in finely-divided condition in a saturated solution of the ore is treated for the separation of the valuable constituents of the ore in a progressive movement through a plurality of treatment stages, the improvement which comprises dissolving lead in the said solution in a quantity sufficient to prevent potassium chloride from being precipitated out of the solution during its progressive movement when the temperature thereof is lowered as much as fifteen degrees Fahrenheit in the absence of seed particles of potassium chloride.

20. In a process of treating sylvinite ores in which sylvinite ore in finely-divided condition in a saturated solution of the ore is treated for the separation of the valuable constituents of the ore in a progressive movement through a plurality of treatment stages, the improvement which comprises dissolving bismuth in the said solution in a quantity sufficient to prevent potassium chloride from being precipitated out of the solution during its progressive movement when the temperature thereof is lowered as much as fifteen degrees Fahrenheit in the absence of seed particles of potassium chloride.

21. A process for the recovery of valuable constituents of sylvinite ores, which comprises introducing sylvinite ore in finely-divided condition into a saturated solution of the ore to form a pulp, separating the sodium chloride and potassium chloride constituents of the ore by a froth flotation treatment, subjecting the sodium chloride constituents so separated to temperature increases sufficient to induce dissolution of any adhering potassium chloride solids therein and crystallization of sodium chloride from the associated solution, subjecting the potassium chloride constituents so separated to temperature decreases sufficient to induce dissolution of any adhering sodium chloride solids therein and crystallization of potassium chloride from the associated solution, and separating the solids of each separation from the solution associated therewith.

22. A process for the recovery of valuable constituents of sylvinite ores, which comprises introducing sylvinite ore in finely-divided condition into a saturated solution of the ore to form a pulp, separating the sodium chloride and potassium chloride constituents of the ore by a froth flotation treatment, subjecting the sodium chloride constituents so separated to temperature increases sufficient to induce dissolution of any adhering potassium chloride solids therein and crystallization of sodium chloride from the associated solution, subjecting the potassium chloride constituents so separated to temperature decreases sufficient to induce dissolution of any adhering sodium chloride solids therein and crystallization of potassium chloride from the associated solution, separating the solids of each separation from the solution associated therewith and returning the solution so separated for reuse in the flotation treatment.

23. A process for the recovery of valuable constituents of sylvinite ores, which comprises introducing sylvinite ore in finely-divided condition into a saturated solution of the ore to form a pulp, subjecting the pulp to a froth flotation treatment to separate its sodium chloride and potassium chloride constituents by selective flotation of sodium chloride, heating the sodium chloride of the froth concentrate to dissolve any associated potassium chloride, separating the solution from the solids of the froth concentrate after heating, cooling the separated residue of flotation to dissolve any retained sodium chloride and to crystallize potassium chloride of the solution, introducing the solution separated from the froth concentrate into the cooling stage, and separating the solids from the solution of the cooled residue.

24. A process for the recovery of valuable constituents of sylvinite ores, which comprises introducing sylvinite ore in finely-divided condition into a saturated solution of the ore containing dissolved metal of the class consisting of lead and bismuth to form a pulp, subjecting the pulp to a froth flotation treatment to separate its sodium chloride and potassium chloride constituents by selective flotation of sodium chloride, heating sodium chloride of the froth concentrate to dissolve any associated potassium chloride, separating the solution from the solids of the froth concentrate after heating, cooling the separated residue of flotation to dissolve any retained sodium chloride and to crystallize potassium chloride of the solution, introducing the solution separated from the froth concentrate into the cooling stage,

and separating the solids from the solution of the cooled residue.

25. A process for the recovery of valuable constituents of sylvinite ores, which comprises introducing sylvinite ore in finely-divided condition into a saturated solution of the ore containing dissolved metal of the class consisting of lead and bismuth to form a pulp, subjecting the pulp to a froth flotation treatment to separate its sodium chloride and potassium chloride constituents by selective flotation of sodium chloride, heating sodium chloride of the froth concentrate to dissolve any associated potassium chloride, separating the solution from the solids of the froth concentrate after heating, cooling the separated residue of flotation to dissolve any retained sodium chloride and to crystallize potassium chloride of the solution, introducing the solution separated from the froth concentrate into the cooling stage, separating the solids from the solution of the cooled residue, and returning the solution so separated to the froth flotation treatment.

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