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SILICONE REAGENT FLOTATION

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This invention relates to the art of concentrating minerals by a flotation procedure and more particularly it relates to the concentration of a coarse sylvite fraction from a sylvite ore employing novel reagent combinations for the preferential flotation of the coarse mineral values.

Many commercial potash ores contain substantial amounts of potassium chloride, and in particular, the potash ore obtained from the Carlsbad area in New Mexico contains up to about 40% potassium chloride with the remainder being sodium chloride with minor amounts of other materials, such as insoluble matter which includes magnesium and calcium salts, light compositions, clay and other impurities. Froth flotation has become, generally, the standard procedure for the beneficiation of the potash ores, and in commercial practice a froth flotation of the ore ground to less than about 14 mesh or lower is the accepted procedure.

The maximum size of ore that may be beneficiated for one value is limited by the nature of the mineral, the flotation equipment and the reagents used for the beneficiation process. For sylvinitic ore which contains sodium chloride and potassium chloride, there must be a physical separation of the two compositions in order that beneficiation of one or the other ingredient might take place. Normally, a coarse grind of the ore will not completely liberate the potassium chloride from the sodium chloride particles, in other words, the particles resulting from the grind will contain portions of sodium chloride and potassium chloride effectively cemented together and particularly inseparable without further grinding, such particles being called middlings. A portion of middlings will react in a froth flotation process much the same as pure potassium chloride crystals, and in certain beneficiations will float with the potassium chloride thereby decreasing the grade of the beneficiated ore. By grinding a sylvinitic ore to a range of minus 6 to a minus 8 mesh, Tyler screen sizes, a substantial amount of the potassium chloride will be physically separated from the sodium chloride so that a high grade potassium chloride product may be obtained.

According to the present invention, applicants have discovered a novel reagent for use in beneficiating coarsely ground potash ore, having an average particle size substantially larger than is useful for conventional froth flotation processes. The ore may be efficiently and effectively dry milled and dry separated into relatively narrow particle size limits. The product of the beneficiating process according to the present invention is a high grade granular potassium chloride produced efficiently, at a low cost and in low cost equipment. The novel reagent of this invention is useful in a flotation process for coarse potassium chloride particles in the size range of about minus 8 to plus 14 mesh particle size range.

Included among the objects and advantages of the present invention is the provision of a novel reagent composition which provides an economical means for producing a clean, relatively large size granular potassium chloride

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product. By using the reagent of the invention, an inexpensive ore preparation may be utilized. The reagent combination provides means for producing a high grade product without utilizing fine grinding of the ore, and, therefore, provides a substantially reduced cost of beneficiating potassium chloride ores. The reagent of the present invention includes the combination of a fundamental collector for potassium chloride and a modifier for the collector. The collector for potassium chloride or sylvite is a well-known reagent and consists essentially of an aliphatic amine and/or salts thereof. A modifier according to this invention is a silicone fluid composition which completely mixes with amine composition.

The aliphatic amine collectors which may be used in the process are straight chain alkyl amines which are generally known to be useful as collectors for sylvite. Such alkyl amines generally have a carbon chain which extends from octyl to about octadecyl or even longer chains. In commercial practice the hydrocarbon chain is derived generally from animal fats and they obviously contain certain amounts of unsaturated chains such as oleic acid, etc. Amines prepared from beef tallow have been most widely used in the froth flotation field. Unsaturated acids in such beef tallow may by hydrogenation be converted to saturated acids for the amine reagent. The extent of hydrogenation or saturation determines the melting point of the composition and effectively determines the solubility of the amines produced from hydrocarbons. The amines used in froth flotation may be used individually or as combinations of various amines, and mixtures of amines need not necessarily consist of all saturated or unsaturated chains, but may obviously be a mixture of such amines to obtain the melting point or a solubility as desired. The amines are normally used as salts since the salts of the amines have greater solubility than the amines themselves. The most commonly used amine salt is the acetate, but the hydrochloride and like salts have been found effective. While such amines normally used in froth flotation are primary amines, there may be traces of secondary and tertiary amines and/or salts thereof.

The aliphatic amines are relatively insoluble in water and have not by themselves had extensive use in the potash industry. By adding sufficient amount of such amine in water about a 3% by weight suspension may be made. The emulsions may best be prepared from aliphatic amines by heating to melt the same and then pouring the melted amine into water containing sufficient acid to neutralize a desired portion of the amine to make a salt. In a preferred form, utilizing a 3% mixture of the amine, sufficient acid is added to neutralize about 30% of the amine to produce an emulsion which is medium heavy in consistency but is readily added to the brine of the ore.

The modifier for the amine collector to produce a reagent combination according to the present invention is a silicone fluid which has a very definite attraction to the collector but is not attracted to potassium chloride or sodium chloride crystals. The silicone fluid modifier may vary in viscosity, depending on the degree of polymerization, the configuration of the end groups, and the character of the polymer as to whether it is cyclic or linear in structure. Such silicones are water insoluble but may be soluble in an organic solvent. The silicone fluids which may be used are organosiloxanepolymers and include dimethyl silicones, phenyl silicones, methyl hydrogen silicones, and the like. Silicone fluids having viscosities of 20, 100, 500 and 1000 or more centistokes at 100° Fahrenheit have been found very effective. The phenyl silicones are more resistant to higher temperatures. All of the silicones are very effective, however, the very high water

repellancy of the phenyl silicones makes them effective at very low rates of consumption.

The silicone fluid composition must be water insoluble, and they must be attracted to the amine. Contact angles of coated surface provides a comparison of effectiveness. Measurement of such contact angles is known procedure, and it includes measuring the angle of a bubble of water or air in contact with a coated surface. A drop of water on an amine coated surface or a bubble of air in water on an amine coated surface has a contact angle of 62°. Adding a silicone to the amine coated surface increases the contact angle which shows that additional water repellancy has resulted. By adding a 100 cs. viscosity silicone to the amine surface, the contact angle was increased to a 92-94° range; adding a 500 cs. viscosity silicone to amine coated surface increased the contact angle to a 95-98° range; and adding a 1000 cs. viscosity silicone to the amine coated surface increased the contact angle to a 96-99° range.

Obviously, from the foregoing, organosiloxane polymers which are insoluble in water are intended in the instant process since the purpose of the addition of the organosiloxane polymer is to increase the bubble angle and thus increase bubble attachment for floating coarse sizes of the desired mineral values.

The spreading of a drop of a silicone on an amine coated surface is, also, a measure of the effectiveness of the reagent, as it is an indication of attraction of the modifier to the amine. The spreading is measured by the angle of contact of a drop of modifier placed on an amine coated surface. Crude oil shows an angle of 28½°, coal tar creosote No. 4 produces an angle of 27°, while 100 cs., 500 cs., and 1000 cs. silicones produced angles of 9°, 10½°, and 11½° respectively.

The reagent of the present invention may be made by dissolving the amine collector and modifier in a menstruum or solvent and then dispersed throughout a pulp of the ore so as to film the particles of potassium chloride for flotation. The compositions of the reagent combination are physically and chemically compatible at the temperatures of use. While it is not necessary that the components of the combination be mixed in such ratios as to obtain a true solution in a solvent, it is preferable that the reagent be fluidized for easy and effective distribution in the pulp.

The preparation of potassium chloride or sylvite ore for the flotation using reagent of the present invention is simply and easily accomplished. Coarsely ground sylvite ore, which has been selected for coarse ore flotation, is screened to avoid oversize particles and the fine undersize particles. The ore in the size range of minus 6 to plus 14 mesh is separated from the oversize and undersize particles and is washed with a clean brine to remove as much of the clay slimes and the fine particles adhering to the coarser particles as is practical. One important advantage in using selected coarse material, which is substantially larger than ore ground for conventional froth flotation processes, is that most of the clay is easily and effectively removed by washing, elutriating or decanting ore with clean brine. This clean pulp which is substantially deslimed ore generally need not be treated with a clay binding agent. Some ores seem to benefit from a clay binding agent, and, therefore, in a few cases such an agent may be used. Amine flotation using an auxiliary or clay binding agent is well known, and such clay binding reagents as starch, dextrans, modified starches, glucosans, mannogalactans, pentosans, uronic acid polymers, metallic hydroxides, and the like are well known. The ore is drained of the brine to make a damp, drained ore. The reagent combination of the invention is mixed with the damp ore and is then thoroughly mixed. The mixing or conditioning is completed in a short time, and the ore is then ready for beneficiation. The ore is subjected to a flotation treatment in equipment which is capable of handling the coarse ore with a minimum of scrubbing

and grinding of the particles and without a froth or frothing in the flotation cell.

Where a reference is made in the specification to a coarse ore or coarse product, it is intended that the material designated has a major portion of its content in particle sizes substantially larger than 14 mesh, and is less than 6 mesh. While the minus 6 plus 14 mesh product may be considered typical coarse product, it may be recognized that even coarser products may be utilized.

In using the term brine in this specification it is intended to mean the solution in which the potassium ores are introduced for the wet treatment of such ores. Such a brine would usually be saturated with respect to one or more of the soluble constituents of ore, and obviously the brine concentration or content may be changed in a plant circuit as the ore suspended in the pulp changes.

In co-pending applications Serial No. 526,720, for Beneficiation of Potash Ores filed August 5, 1955, and in application Serial No. 595,500 for Method and Apparatus for Flotation Concentration in Coarse Size Range filed July 2, 1956, there is described effective and efficient equipment for flotation of coarse particles of potash ore.

Ore prepared as described above is then conditioned with the flotation reagent. The flotation reagent may be prepared by mixing Armeen HTD (manufactured by Armour and Company) which is a distilled grade of hydrogenated tallow amine, heating to about 50° C. and combining with water and acid with agitation to form about a 3% solution of the amine. The amine is then added to a drained ore and thoroughly mixed therewith. A silicone polymer in the desired amount is mixed with the treated ore and thoroughly mixed or conditioned therewith. The conditioned ore is then passed to a flotation cell where streams of a mixture of brine and air agitate the ore so that the particles of potassium chloride so coated float very easily and are literally ejected from the brine solution. The air and brine currents, as described in the above identified co-pending applications, keep the pulp agitated, and any air bubbles in the brine which reach the surface break immediately so that the surface of the brine is substantially froth free, and the particles of sylvite float on the free surface of brine. Complete flotation action is completed in about fifteen seconds to produce a high grade, granular product.

In a series of tests using 0.06 pound of a hydrogenated tallow amine per ton of ore, three silicone fluids of 100 cs., 500 cs., and 1000 cs. viscosity were used in amounts of 0.76, 0.86, and 0.99 per ton of ore, and the flotation produced tailings of 5.3, 6.0 and 6.8% KCl respectively. For coarse flotation, as set forth in co-pending application, 595,500, the practice is to accept the higher grade tailings so as to secure a higher grade product. The tailings may be retreated to recover additional potash in cleaner cells and leaving a low grade tailings.

Flotation tests indicate that silicones may be used in amounts as low as 0.04 pound per ton of ore, for a first stage flotation, and produce a very high grade product. It thus appears that the silicones are far more effective than other materials which usually are required in pounds per ton.

The following is a summary of flotation tests using the indicated amount of silicone and amine, on a potash ore containing about 40% potassium chloride.

Reagent Rates in lbs./ton		Percent KCl in Products	
Silicone	Amine	Concentrate	Rougher Tailings
0.04	0.10	95.5	15.0
0.12	0.10	93.1	10.2
0.20	0.10	93.1	5.7
0.20	0.06	95.2	9.4
0.04	0.18	95.0	10.0

To express the foregoing summary of flotation steps and previous description with reference to particular mesh size, reagents, ore, and results, the following table is here presented:

concentration of the mineral value in the floated concentrate, the improvement which comprises conditioning such a pulp with an amine reagent, and then conditioning the treated pulp with a water insoluble silicone fluid com-

Table I

Silicone	Lbs./ Ton	Cs. at 100° F.	KCl, Percent	Tons of KCl	Mesh Size of KCl	Amine	Lbs./ Ton	Conc., Percent KCl	Percent KCl in Rougher Tailings
Fluid organosiloxane polymers.....	0.04	100-1,000	40	1	-6 to -14	C N Armeen HDT..	0.10	95.5	15.0
Do.....	0.12	100-1,000	40	1	-6 to -14	do.....	0.10	93.1	10.2
Do.....	0.20	100-1,000	40	1	-6 to -14	do.....	0.10	93.1	5.7
Do.....	0.20	100-1,000	40	1	-6 to -14	do.....	0.06	95.2	9.4
Do.....	0.04	100-1,000	40	1	-6 to -14	do.....	0.18	95.0	10.0

It is thus readily apparent that any fluid organosiloxane polymer which is insoluble in water and has a 100-1000 cs. viscosity at 100° F. and which will be attracted to and form with an amine collector reagent a contact angle of from 92-99°, when used in an amount of about 0.04 to 0.20 lbs./ton of ore, is a very satisfactory reagent. The quantity of silicone reagent, as pointed out hereinbefore, may be as low as 0.04 lbs./ton of ore. Also, a range of from 0.06 to 0.18 lbs./ton of an amine is highly satisfactory for use in the process.

It is apparent from the above summary that the ratio of silicone to amine may vary over wide limits. Thus an effective separation may be produced on an economic balance depending on the cost of each reagent. A second flotation separation of the tailings may be performed to achieve a high recovery.

The silicone fluid modifiers of the invention are fluids in the viscosity range of about 100-1000 centistokes at 100° F., they are water insoluble and attracted to the primary amine collector.

While the invention has been described by reference to specific embodiments, there is no intent to limit the spirit or scope of the invention, except insofar as defined in the following claims.

We claim:

1. In a flotation treatment of a pulp having a potash value ore ground to flotation size therein and in which an amine collector composition is utilized for the concentration of the mineral value in the floated concentrate, the improvement which comprises conditioning such a pulp with such an amine and a small, effective amount of a water insoluble silicone fluid composition having a viscosity in the range of 100 to 1000 centistokes at 100° F. prior to its introduction into the pulp as a collector reagent to improve the concentrate and reduce the amine consumption.

2. A treatment according to claim 1 in which the silicone fluid composition is a methyl silicone.

3. A treatment according to claim 1 in which the silicone fluid composition is a phenyl silicone.

4. In a froth flotation treatment of a pulp having a potash value containing ore suspended therein and in which an aliphatic amine composition is utilized for the

position having a viscosity of 100 to 1000 centistokes at 100° F. prior to the flotation treatment of the pulp as a collector reagent for the mineral value whereby to improve the concentration of the mineral value and reduce the amine consumption.

5. In a flotation treatment of a pulp having undissolved sylvite therein and in which an aliphatic amine is utilized for the concentration of the sylvite in the floated concentrate, the improvement which comprises conditioning such a pulp with such an amine and a small, effective quantity of a water insoluble silicone fluid composition having a viscosity in the range of 100-1000 centistokes at 100° F. prior to the introduction of the pulp into a flotation treatment whereby to improve the concentration of the sylvite and reduce amine consumption.

6. A flotation treatment of sylvite according to claim 5 in which the silicone fluid composition is dimethyl silicone.

7. A flotation treatment of sylvite according to claim 5 in which the silicone fluid composition is methyl hydrogen silicone.

8. A flotation treatment of sylvite according to claim 5 in which the silicone fluid composition is phenyl silicone.

9. In a flotation treatment of pulp having undissolved sylvite therein and in which an aliphatic amine is utilized for the concentration of the sylvite in the floated concentrate, the improvement which comprises conditioning such a pulp with an effective amount of aliphatic amine reagent and substantially smaller amount of a silicone fluid composition prior to flotation treatment of the pulp, the silicone fluid being characterized by having a viscosity of a range of 100 to 1000 centistokes at 100° F. and being highly immiscible with water and being non-attracted to the mineral values in the pulp and being highly attracted to the amine, whereby to form a water repellant coating on the sylvite and to improve the concentration of the sylvite in the froth and to reduce the amine consumption.

References Cited in the file of this patent

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