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PROCESS OF FLOTATION FOR SYLVINITE ORES

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This invention relates to improvements in the separation of potassium chloride from sodium chloride and associated impurities as they occur in the mineral sylvinite by flotation. It relates more particularly to the use, as a flotation reagent or collector, in such a process, of carboxylic acids derived from oxidized petroleum, and more particularly to the use of the neutralized fraction in which are concentrated the acids having from 7 to 11 carbon atoms.

The mineral sylvinite is a valuable source of potash. It consists principally of a mixture of potassium and sodium chloride, with small percentages of iron and such foreign matter as clay in varying, usually small, amounts. One method of removing the potassium chloride from the sodium chloride and associated impurities is by flotation, the raw ore, which contains around 40% potassium chloride and 60% sodium chloride, with traces of iron, clay, etc., being ground and then floated in a rougher-middle-cleaner cell installation, using a saturated brine as a carrier and medium. In one process being commercially used, the sodium chloride, together with the slime is removed in the froth, while the potassium chloride, along with much of the iron, is concentrated in the underflow from the cleaner cell, whence it goes to a centrifuge for drying and further treatment. The purity of the recovered potassium chloride usually runs around 97-98% the plant, and a purity of less than 95% is regarded as inadequate separation. The brine, after removal of the sodium chloride and potassium chloride, is recirculated to minimize the amount of the potassium and sodium chlorides which are dissolved in the carrier fluid.

In accordance with the present invention, potassium chloride is separated from the sodium chloride, clay, etc., with the use of a saturated brine as a medium or carrier in a closed cycle, following substantially the same procedure now used, and with the use of a reagent consisting of carboxylic acids derived from petroleum by an oxidation process and containing 7 to 11 carbon atoms in the carbon-linked chain, or a suitably derived fraction in which these acids are concentrated or predominant. Advantageously, a fraction consisting primarily of the C₇ to C₉ acids, with minor amounts of higher and lower acids and associated impurities, is used. Such acids may be used as such, or may be used in the form of sodium, potassium or other salts, although the use of the alkali metal salts is advantageous. Along with such acids as the col-

lector or flotation reagent, it is advantageous to use a relatively small amount of a lead compound and a conditioning agent, such as the commonly used cresylic acid, as the separation of the potassium chloride from the sodium chloride is greatly facilitated by the addition of such materials along with the flotation reagent.

The amount of flotation reagent which is required is relatively small, less than one pound of the reagent per ton of ore giving highly satisfactory results; but the amount will vary depending upon the coarseness of the grind of the ore, the purity desired in the separated potassium chloride, etc.

The use of these reagents in this flotation operation has a number of important advantages. It permits the coarser grinding of the crude ore while obtaining effective separation, thus effecting a substantial decrease in grinding and similar costs. The reagent may, if used in sufficient amount, be so effective in the separation of relatively coarse feed as to permit feeding to the flotation apparatus an ore much coarser than the feed now used and yet enable the production of a highly purified potassium chloride.

When the new reagents are used, the amount of water which must be added along with the reagent is substantially less than that required to be added with the reagents now commonly used, both because the new reagents are substantially more soluble in water and because they give effective separation in much smaller amounts than is required with the reagents now used. This is an important advantage, because any addition of water results in the dissolving of more of the ore in the brine, and substantially increases either the operating losses or operating expenses, and because of the fact that water must be hauled, at considerable expense, to the mills in which sylvinite is processed.

The reagents used in accordance with the invention may be prepared by oxidizing such petroleum distillates as kerosene, and separating from the resulting products a fraction in which the carboxylic acid having from 7 to 11 carbon atoms are concentrated. For example, a Pennsylvania distillate of 45° A. P. I. gravity or kerosene may be oxidized by blowing with air, or oxygen, or oxygen-enriched air, at temperatures up to 155° C. and relatively high pressures with the use of a small amount of an oxidation catalyst such as manganese oleate, distilling the resulting mixture to remove some of the hydroxy and ketone acids, alcohols, poly-alcohols, ketones, ketone-alcohols, etc.,

neutralizing the remaining product, dissolving it in water to remove unsaponifiable matter and then regenerating the acids by the addition of mineral acids. After washing the resulting product with water, a mixture of straight and branched chain monocarboxylic acids, usually beginning with the C₇ acids, and containing greater or lesser proportions of associated impurities, is obtained. The resulting acidic mixture is fractionated, and the fraction containing the acids having from 7 to 11 carbon atoms is separated and used as the reagent in accordance with the invention. This fraction will, of course, contain a certain amount of impurities of the most diverse kind, including appreciable amounts of acids having more than 11 or less than 7 carbon atoms, lactones, hydroxy acids, esters, etc., and the effectiveness of the reagent may be considerably improved by further purification to obtain the acids having from 7 to 11 carbon atoms in a more pure form, but such further purification is not essential. These carboxylic acids include both straight and branched chain compounds, and form a complex mixture, which contains a number of constituents in addition to the carboxylic acids, e. g., lactones, alcohols, etc., but the exact nature of the mixture is not known. They differ from the straight-chain fatty acids having from 7 to 11 carbon atoms, as these straight-chain fatty acids are solid, at ice-box temperature, while the mixture of acids used as the reagent in accordance with this invention is liquid even at such temperature.

While, as pointed out above, the complex mixture resulting from the production of a fraction consisting predominantly of carboxylic acids having 7 to 11 carbon atoms forms a highly effective reagent, particularly when completely or partially neutralized, as with caustic soda, a corresponding fraction consisting predominantly of carboxylic acids having 7 to 9 carbon atoms, together with associated impurities and lesser quantities of higher and lower acids gives substantially better results, and hence forms reagents having important advantages over those formed from the less closely cut fraction.

The acid mixture may be used as such, or may be used in the form of alkali metal or other salts. The alkali metal salts appear to be more effective than the free acids or other salts.

The invention will be further illustrated by the following specific example, but it is not limited thereto.

Example.—Raw sylvinitic ore is crushed, wet ground in a ball mill, screened and then fed as a 30% pulp to flotation cells arranged as rougher, middle and cleaner cells. The reagent, prepared as above, in the form of the sodium salt, is added, in aqueous solution, to each of the cells, a small amount being added to the rougher cell, a larger proportion to the middle cell, and a small amount, slightly more than the amount in the rougher cell, being added to the cleaner cell. Usually, considerably less than a pound of reagent per ton of ore, for example, 0.6 pound of reagent per ton of ore, gives highly satisfactory results. A conditioning agent, such as cresylic acid, is advantageously added at each point where the flotation agent or collector is added. A lead salt, such as lead chloride, is advantageously added to the wet charge in the ball mill, approximately 2.0 grams of lead salt (calculated as lead) per gallon of brine being used. The lead salt acts as an activator or selectivity intensifier, and it may be added continuously or periodically, for example, three times a day, to adjust the lead content of the brine

to the 2.0 grams per gallon. The froth from the middle and cleaner cells is recycled through the rougher cell, the froth from which goes back to the refinery. The underflow from the rougher cell goes to the middle cell and the underflow from the middle cell to the cleaner cell. The underflow from the cleaner cell goes to a centrifuge, where the purified potassium chloride crystals are freed from accompanying brine. The brine is recycled through the ball mill.

I claim:

1. The process of concentrating potassium chloride from a sylvinitic ore by a flotation process which comprises using as a flotation reagent a material of the class consisting of acidic fractions of petroleum oxidation carboxylic acids in which acids having seven to eleven carbon atoms are concentrated and products resulting from at least the partial neutralization thereof.

2. The process of concentrating potassium chloride from a sylvinitic ore by a flotation process which comprises using as a flotation reagent a material of the class consisting of acidic fractions of petroleum oxidation carboxylic acids in which acids having seven to nine carbon atoms are concentrated and products resulting from at least the partial neutralization thereof.

3. The process as in claim 1, in which the flotation reagent is the specified acidic fraction with at least a part of the carboxylic acids converted to their alkali metal salts.

4. The process as in claim 1, in which the flotation reagent is the specified acidic fraction with at least a part of the carboxylic acids converted to their sodium salts.

5. The process as in claim 2, in which the flotation reagent is the specified acidic fraction with at least a part of the carboxylic acids converted to their sodium salts.

6. The process of concentrating potassium chloride from a sylvinitic ore by a flotation process which comprises using as a flotation reagent a neutralized acidic fraction of petroleum oxidation carboxylic acids in which acids having from seven to eleven carbon atoms are concentrated.

7. The process of concentrating potassium chloride from a sylvinitic ore by a flotation process which comprises using as a flotation reagent a neutralized acidic fraction of petroleum oxidation carboxylic acids in which acids having from seven to nine carbon atoms are concentrated.

8. The process of concentrating potassium chloride from a sylvinitic ore by a flotation process which comprises using as a flotation reagent the alkali metal salts of petroleum oxidation carboxylic acids having seven to eleven carbon atoms.

9. The process of concentrating potassium chloride from a sylvinitic ore by a flotation process which comprises using as a flotation reagent the alkali metal salts of petroleum oxidation carboxylic acids having seven to nine carbon atoms.

10. The process of concentrating potassium chloride from a sylvinitic ore by a flotation process which comprises using as a flotation reagent a mixture of petroleum oxidation carboxylic acids having seven to eleven carbon atoms.

11. The process as in claim 1, in which, in addition to the flotation reagent, cresylic acid is used as a conditioning agent.

12. The process as in claim 1, in which a lead salt is used in addition to the flotation reagent.

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