

- [54] **ELECTROSTATIC SEPARATION OF POTASH ORES**
[75] Inventors: **Robert Berthon**, Wittelsheim, Haut-Rhin; **Michel Bichara**, Richwiller, Haut-Rhin, both of France

[73] Assignee: **Mines de Potasse d'Alsace S.A.**, Mulhouse, France

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[52] **U.S. Cl.**..... **209/9; 209/127**
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[58] **Field of Search** 209/9, 11, 127, 4, 128-130

[56] **References Cited**
UNITED STATES PATENTS
2,450,720 10/1948 De Vaney 209/166

2,762,505 9/1956 Lawver 209/9
2,927,010 3/1960 LeBaron 209/9 X
3,008,573 11/1961 Gross 209/127 X
3,063,561 11/1962 Snow 209/127 X
3,477,566 11/1969 Autenrieth..... 209/9

FOREIGN PATENTS OR APPLICATIONS

583,176 12/1946 United Kingdom..... 209/127

OTHER PUBLICATIONS

Ind'l. & Eng. Chem., 32, No. 5, Electrostatic Sep. of Solids, Ralston, pgs. 600-604.

Primary Examiner—Frank W. Lutter

Assistant Examiner—Robert Halper

[57] **ABSTRACT**

For recovering an enriched KCl fraction from potash ores by electrostatic separation, the ore is conditioned with a reagent comprising an aliphatic amine of 8 - 22 carbon atoms and an ammonium salt of a lower aliphatic carboxylic acid, e.g., laurylamine and ammonium acetate.

14 Claims, No Drawings

ELECTROSTATIC SEPARATION OF POTASH ORES

BACKGROUND OF THE INVENTION

This invention relates to a process for the beneficiation of potash ores, and in particular to an electrostatic process for the recovery of enriched fractions of potassium chloride from ores, such as sylvinite.

It is known that ores can be electrostatically separated into their constituents if such constituents have been previously differentially charged. For example, in the case of sylvinite ores which comprise more or less intermingled crystals of sylvite and halite (as well as insoluble and sometimes soluble impurities), the electrostatic method permits the concentration of the desired potassium chloride. But ordinarily, in order to obtain a satisfactory degree of separation, the differences between the charges induced on the ore components must be accentuated by subjecting the ore to a prior conditioning step.

Thus, it has been proposed to submit the potash ore to thermal conditioning (up to 300°–700° C, for example) before subjecting it to electrostatic separation, the latter being thereafter performed at a much lower temperature, e.g., between about 40° and 220° C. Apart from the fact that the high temperature thermal conditioning treatment is expensive, it has been observed that the results obtained differ greatly from one ore to another and that in all cases the major portion of insoluble impurities remain in the concentrate enriched in potash.

Another type of process often recommended comprises conditioning the potash ore with a chemical agent before the electrostatic separation. Agents most often used are organic acids having an aliphatic, cycloaliphatic, aromatic or hydroxy-aromatic radical, salts or esters of such acids, the molecule of which can also contain other carboxylic groups and/or sulfonic groups. Other type of surface active agents can also be employed, in particular, long chain aliphatic amines, especially amines obtained from mixtures of fatty acids prepared from natural products (tallow, coprah oil, fish oil, etc.) However, all of these various conditioning chemical agents present the same disadvantage. When the electrostatic separation is conducted after chemical conditioning, as well as after thermal conditioning, the insoluble materials of the treated ore tend to follow the potash constituent and end up in the final concentrate.

To cope with this drawback, it has also been proposed to perform a magnetic separation on the final concentrate obtained from electrostatic separation in order to clean the concentrate by removing at least a fraction of the insoluble materials contained therein. According to still another method, the ore is preheated between 120° and 175° C before its chemical conditioning to limit the detrimental effect of insoluble impurities. These various methods, however, require an additional step, which obviously increases the cost of the final product.

SUMMARY OF THE INVENTION

Thus, it is an object of this invention to provide a simple and economical process which avoids an accumulation of insoluble materials in the concentrate from the electrostatic separation.

Another object is to improve the efficiency of the separation.

Upon further study of the specification and claims, other objects and advantages of the present invention will become apparent.

To attain these objects, prior to electrostatic separation, the potash ores are conditioned with an ammonium salt of a lower aliphatic carboxylic acid and an aminated reagent comprising at least one primary or secondary aliphatic amines of 8–22 carbon atoms or salts thereof.

Indeed, it has been unexpectedly observed that by association of an ammonium salt such as ammonium formate, acetate or oxalate with the known aminated reagent, there occurs a reversal of charge polarity between sylvite and halite during ore electrification, but such a reversal does not take place for insoluble impurities. As a result, the insoluble materials tend to preferentially follow halite, and, accordingly, a concentrate poorer in insoluble materials is obtained without any additional treatment.

DETAILS OF THE INVENTION

The lower aliphatic carboxylic acid portion of the ammonium salt preferably comprises 1–4, preferably 1–3 carbon atoms, and the salt can be monobasic or polybasic depending on the number of acid groups in the acid, all acid groups being completely neutralized.

Although the ammonium salt is somewhat effective when added to the ore in form of an aqueous solution, it is preferably used in solid form, for not only is it more efficient in this latter form, but the drying of the ore at about 100° C becomes unnecessary. Consequently, for subsequent treatment, the ore can be heated to lower temperatures, e.g., 50° to 90° C.

As aliphatic amines, primary or secondary, saturated or unsaturated amines having from 8–22 carbon atoms can be used as well as salts of such amines as, for example, acetate or hydrochloride. Among the amines which can be used, those prepared from commercial fatty acids, either pure or technical grade, are perfectly suitable, such as laurylamine, palmitylamine, stearylamine or oleylamine. Lower purity products, for example, amines produced from naturally occurring fatty acid mixtures or those found in industrial residues or by-products, such as fatty amines of coprah, tallow, various animal or vegetable oils, can also be used. The fatty amines coming from petroleum chemicals are also suitable. For further information regarding these amines and amine salts, and other matters, reference is directed to applicants' application entitled "Electrostatic Upgrading of Potash Ores," filed concurrently herewith.

These amines can be used either as they occur, that is to say, in solid or liquid form, depending on their molecular weight, or dissolved in an organic solvent having no effect on the electrostatic separation, such as hexane, benzene, or trichlorethylene. It is advisable to avoid the use of aqueous solutions or dispersions of these amines, to impede the formation of ore agglomerates and the splitting of the clay-like materials which would otherwise coat the ore particles, thereby inhibiting the separation of valuable constituents. Furthermore, as already said for ammonium salt, the addition of water requires the ore to be dried at about 100° C, whereas it is possible to operate at much lower temperatures by using a low boiling organic solvent.

The amine reagent and the ammonium salt can be added to the ore together or separately. This addition

can take place in any type of equipment wherein a uniform distribution of reagents on ore particles can be obtained, for example, a mixer, a rotary drum, etc.

The quantity of amine reagent is generally about 50 – 500 g/t (grams per metric ton) of ore and the quantity of ammonium salt about 100 – 1,000 g/t of ore. Within these ranges, a man skilled in the art can select the optimum proportions for the particular ore by a few routine tests.

Other preferred compounds of the amine and ammonium salts not mentioned in the following examples include but are not limited to: all of the fatty amines such as the amines commercially available from Armour and Company under the trade name "Armeens" can be used, and preferably those containing less than 16 carbon atoms. The corresponding amine acetates sold under the trade name "Armac" are also suitable. Although ammonium formate, oxalate and acetate are more advantageous due to their relatively lower cost, ammonium salts of the acids such as propionic, malonic, butyric, isobutyric and pivalic can also be associated with any of the cited amines.

For practicing the invention, the ore is comminuted in a conventional manner, but preferably dry comminuted in order to avoid an additional drying of the ore. Comminution must be sufficient to liberate the various ore constituents, and in any case, it is advisable that the particle size does not exceed about 2 mm (9 mesh Tyler). It is also advantageous to select a comminution method which produces a relatively low proportion of very fine particles (< 150 mesh Tyler).

After the addition of reagents to the suitably comminuted ore, the latter is electrically charged, for example, by contact electrification. This charging can be conducted either in a rotary drum or in a vessel where the ore is maintained in fluidized state by means of hot air. The operation is performed at about 50° – 100° C in order to dry the ore or remove the organic solvent used during the conditioning step.

The charged reagentized ore is then fed to the electrostatic separator. Although the process of this invention may be performed in a roll-type separator, a free-fall-type electrostatic device is generally preferred, inasmuch as the latter yields a higher output and a more efficient separation of fine particles. The field strength in this separator may vary from 2 to 6,000 V/cm but a strength of about 3,000 V/cm is generally sufficient to obtain good results. The separation can be accomplished between 50° and 100° C, preferably between 60° and 80° C, that is substantially at the same temperature as that of the electrical charging of ore particles. Therefore, it is advantageous that the ore does not cool down between these two steps and when severe climatic conditions or exploitation requirements are liable to cause a cooling of the treated ore, the latter must be heated just before it is fed into the separator. In any case, all convenient measures must be taken so that the desired ore temperature is maintained in the electrostatic separator.

The process of this invention yields perfectly good results even when the treated ore contains relatively large proportions of insoluble impurities, for example, about 4 – 5 percent. However, certain sylvinites contain much larger amounts of insoluble materials, which may reach 10 – 15 percent or more, and such ores have to be submitted to a preliminary treatment to reduce their impurity content to an acceptable value,

preferably by the method outlined in applicants' previously mentioned concurrently-filed application. That method gives an ore concentrate having an impurity content sufficiently low to allow the electrostatic separation of the present invention to be performed under satisfactory conditions. Furthermore, in addition to a reduced impurity content, the dry ore coming from the preliminary treatment already contains an aminated reagent suitable for the subsequent electrostatic beneficiation. Therefore, in most cases, it is sufficient to add the ammonium salt to the concentrate resulting from the preliminary treatment before feeding it into the charging apparatus.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the specification and claims in any way whatsoever.

EXAMPLE I

A sylvinites ore containing 22 percent K_2O and 8.5 percent insoluble materials, comminuted so that substantially all the particles have a size lower than 1.2 mm (14 mesh Tyler), was submitted to a preliminary electrostatic separation in the presence of laurylamine (200 g/t) and caprylic acid (50 g/t) according to the process of the French application PV No. 115,859. The concentrate resulting from this separation contained 21.4 percent K_2O and 3.9 percent of insoluble impurities.

In a first test, an aqueous dispersion of a conventional reagent comprised of the sodium salt of a C_{14-18} fatty acid mixture was added to a sample of the preliminary concentrate in proportion corresponding to 500 g of reagent per metric ton of ore. The conditioned ore was heated to about 100° C in a rotary drum through which a hot air stream was flowing. The electrically charged ore was then fed through a vibratory trough to a free-fall-type separator operating with a field strength of 3,000 V/cm, the ore temperature being about 70° C during the separation. After a single pass, three fractions were collected: a concentrate, a middling fraction and a residue containing respectively 40.7, 24.6 and 10.4 percent K_2O and 4.3, 5.4 and 3.5 percent of insoluble materials.

To another sample of the preliminary concentrate were added 500 g of solid ammonium acetate per metric ton of ore and the electrical charging was performed as above, but while heating at 60° C. All other conditions being the same as above, three fractions were collected: concentrate, middlings and residue containing respectively 50.0, 13.2, and 5.9 percent K_2O and 1.0, 3.2 and 6.3 percent of insoluble materials.

EXAMPLE II

A concentrate containing 21.2 percent K_2O and 4.5 percent of insoluble impurities was obtained by a preliminary treatment effected as in Example I but in the presence of peanut oil instead of caprylic acid.

Two tests of electrostatic separation were performed under the same conditions as in Example I from the preliminary concentrate, the first one as a control test without an ammonium salt and the second one in the presence of ammonium acetate. The results obtained were as follows:

	CONCENTRATE		MIDDINGS		RESIDUE	
	% K ₂ O	% insol. materials	% K ₂ O	% insol. materials	% K ₂ O	% insol. materials
CONTROL TEST	38.2	5.0	23.5	5.7	10.1	3.9
AMMONIUM ACETATE	57.9	1.4	22.0	5.6	3.3	5.8

These two examples show that the insoluble impuri-
ties tend to follow the residue containing essentially so-
dium chloride rather than the potassium chloride con-
centrate. It can be also observed that the separation se-
lectivity is notably improved.

EXAMPLE III

A sylvinite ore containing 18.2 percent K₂O and 5.2
percent of insoluble materials was comminuted so that
substantially all the particles have a size lower than 1.2
mm (14 mesh Tyler). The ore was conditioned in a
mixer with 100 g of laurylamine and 1,000 g of solid
ammonium acetate per metric ton of ore.

The conditioned ore was fluidized by means of a hot
air stream, thereby heating the ore temperature to
about 90° C, and simultaneously electrically charging
same. The charged ore was fed to a free-fall type separ-
ator with a field strength of 3,000 V/cm, and after a
single pass, there is obtained three fractions: (a) 26.7
percent by weight of potassium chloride concentrate
containing 58 percent K₂O and 1.5 percent insoluble
materials; (b) 6.3 percent of middlings at 14.4 percent
K₂O and 5.2 percent insoluble materials; and (c) 67
percent of a sodium chloride residue at 6.5 percent in-
soluble materials and containing only 1.7 percent K₂O.

EXAMPLE IV

Example 3 was repeated but ammonium acetate was
replaced by solid ammonium formiate.

Three fractions were thus collected: (a) 28.2 percent
by weight of potassium chloride concentrate, (b) 10.9
percent of middlings and (c) 60.9 percent of sodium
chloride residue. The composition of these fractions
was respectively 53.0, 16.2, and 2.9 percent K₂O and
2.5, 7.0 and 6.6 percent of insoluble materials.

The preceding examples can be repeated with similar
success by substituting the generically or specifically
described reactants and/or operating conditions of this
invention for those used in the preceding examples.

From the foregoing description, one skilled in the art
can easily ascertain the essential characteristics of this
invention, and without departing from the spirit and
scope thereof, can make various changes and modifica-
tions of the invention to adapt it to various usages and
conditions. Consequently, such changes and modifica-
tions are properly, equitably, and intended to be, within
the full range of equivalence of the following claims.

We claim:

1. In an electrostatic process for the beneficiation of
potash ore containing intermingled crystals of sylvite
and halite and insoluble impurities, the improvement
comprising conditioning said ore before electrostatic
separation with:

- an aliphatic amine of 8-22 carbon atoms, and
- an ammonium salt of a lower aliphatic carboxylic
acid of 1-4 carbon atoms whereby a concentrate is
obtained having a higher proportion of sylvite to
insoluble impurities.

2. A process as defined by claim 1, wherein said
amine is lauryl amine and said ammonium salt is ammo-
nium acetate.

3. A process as defined by claim 1 wherein said ali-
phatic amine is a straight chain amine.

4. A process as defined by claim 1 wherein said ali-
phatic amine contains less than 16 carbon atoms.

5. A process as defined by claim 1 wherein said ore
contains up to 5 percent of insoluble impurities.

6. A process as defined by claim 1 wherein the elec-
trostatic separation is conducted at 50°-100°C.

7. A process as defined by claim 1 wherein the pro-
portions are such that 1 metric ton of ore is conditioned
with 50-500 grams of said amine and 100-1,000 grams
of said ammonium salt.

8. A process as defined by claim 7, wherein said am-
monium salt is ammonium acetate, ammonium formi-
ate or ammonium oxalate.

9. A process as defined by claim 7, wherein said pot-
ash ore is sylvinite.

10. A process as defined by claim 7, wherein said
amine is lauryl amine and said ammonium salt is ammo-
nium acetate.

11. A process as defined by claim 1, wherein said am-
monium salt is ammonium acetate, ammonium formi-
ate or ammonium oxalate.

12. A process as defined by claim 3, wherein said am-
monium salt is employed in solid form.

13. A process as defined by claim 1, wherein said pot-
ash ore is sylvinite.

14. A process as defined by claim 13, wherein said
amine is lauryl amine and said ammonium salt is ammo-
nium acetate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3885673

DATED : May 27, 1975

INVENTOR(S) : Robert BERTHON et al

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

Claim 12, line 1, delete "3" and insert --11--

Signed and Sealed this

Twenty-first Day of September 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks