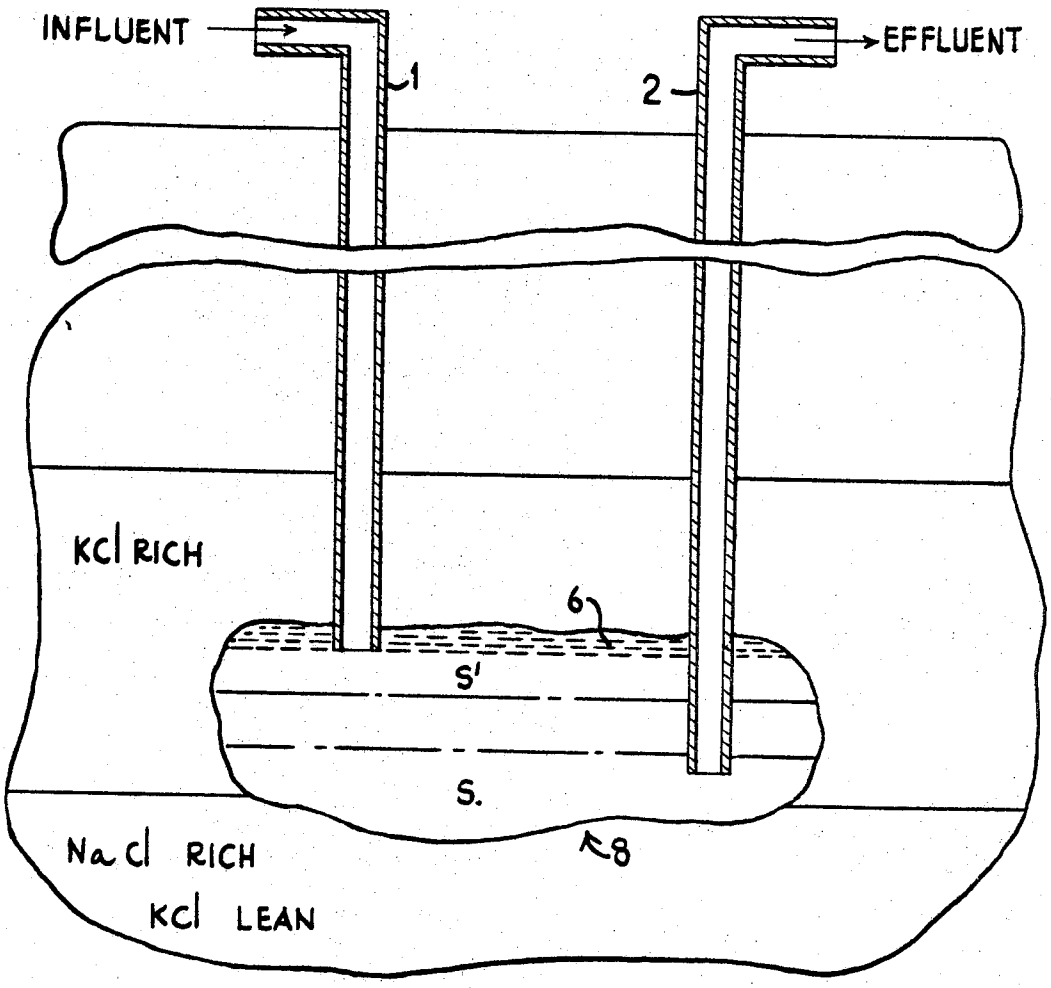
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METHOD OF SOLUTION MINING POTASSIUM CHLORIDE

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METHOD OF SOLUTION MINING POTASSIUM CHLORIDE

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ABSTRACT OF THE DISCLOSURE

Potassium chloride is recovered from a subterranean deposit by solution mining techniques. The solution mining cavity contacts at least one KCl-rich stratum. The cavity floor contacts a KCl-lean stratum. A concentrated zone of cavity solution is maintained adjacent the floor of the cavity. The ratio of KCl to NaCl in this concentrated zone is maintained higher than the ratio of KCl to NaCl in the KCl-lean stratum. Cavity effluent is withdrawn from the lower portion of the cavity. The ratio of KCl to NaCl in the effluent is greater than the corresponding average ratio in the deposit being mined. Often the ratio of KCl to NaCl in the effluent is greater than the corresponding ratio in the KCl-rich stratum.

This application is a continuation of applicants' copending application Ser. No. 646,431, filed June 15, 1967, now abandoned, which application is a continuation of application Ser. No. 446,370, filed Apr. 7, 1965, now abandoned.

This invention relates to a novel method of solution mining. It more particularly relates to solution mining of potassium chloride.

Potassium chloride usually occurs in mineral deposits closely associated with sodium chloride. In many cases, potassium chloride exists in admixture with sodium chloride in the form of deposits comprising a plurality of strata of varying composition. A potassium chloride-rich stratum typically contains from about 15 to about 50 percent or more by weight KCl based upon the total weight of KCl and NaCl in the stratum. These mineral deposits usually contain other substances, e.g., clays and salts such as calcium sulfate, magnesium sulfate, magnesium chloride and the like. These salts are usually present in small quantities, typically about 2 to about 15 percent.

Subterranean deposits of potassium chloride and sodium chloride of this type frequently are very deep. For example, Canadian deposits of this nature are often found more than 3,000 feet below the surface of the earth. Typical deposits are characterized by a plurality of zones of varying NaCl and KCl composition. In the solution mining of these deposits, a solution mining cavity is normally established adjacent the lower part of a KCl-rich stratum, i.e., a zone containing an average composition in excess of about 15 percent KCl on the aforestated basis. The cavity is generally in substantial contact with a lower zone vertically disposed beneath the KCl-rich zone. This lower zone is usually rich in NaCl but relatively lean in KCl, i.e., contains less than about

15 percent KCl on the aforestated basis. Thus, a portion of the extraction surface of the cavity is in contact with extractable material of unacceptable ore grade.

The influent to a solution mining cavity is typically either substantially pure water or a dilute aqueous solution of KCl and/or NaCl. Thus, a typical feed or influent to a solution mining cavity normally ranges from 0 to about 10 grams per liter KCl and from 0 to 30 grams per liter NaCl. More highly saturated feeds are employable although less desirable.

When the feed is introduced to the cavity, it tends to dissolve KCl and NaCl from the cavity walls in substantially the proportion in which they exist in the formation. Because a substantial percentage of the cavity surface comprises material relatively lean in the product mineral, i.e., KCl, there is a tendency for the cavity solution to dissolve more NaCl than is desirable. Thus, the effluent from the cavity tends to be relatively richer in NaCl than would be expected were the entire cavity surface composed of KCl-rich material.

This invention teaches a method whereby the ratio of KCl to NaCl in the effluent from a cavity which contacts both a KCl-rich and a KCl-lean zone in a deposit of the nature described is higher than the corresponding average ratio existing in the ore contacted by the cavity. The average KCl/NaCl ratio of a deposit, zone, or stratum is readily determined by averaging the ratios found in foot sections of a core sample taken therefrom.

In the practice of this invention, a layer of KCl-rich solution is established and maintained at the bottom of the cavity to contact the KCl-lean zone. This KCl enriched layer of solution has a reduced capacity to extract and hold in solution NaCl. The cavity solution above this KCl-rich layer is kept relatively unsaturated with respect to both salts. Thus, both salts are readily extracted from the KCl-rich ore zone. It has been found that even when substantially pure water is fed to a solution mining cavity in which the conditions hereinbefore described are maintained, the effluent from the cavity usually contains KCl in a significantly higher ratio with respect to NaCl than exists in the KCl-rich zone in the deposit even though a substantial portion of the cavity surface is in contact with material which is relatively lean in KCl. In any event, the practice of this invention results in effluents containing an increased proportion of KCl.

Although the precise mechanism responsible for this improvement is not fully understood, the procedures which result in the improvement have been consistently effective. The invention will be more readily understood with reference to the accompanying drawing which illustrates a typical solution mining cavity communicating with two cased bore holes.

Referring to the drawing, cavity **8** is in contact with a KCl-rich deposit. The lower part of the cavity is in contact with an NaCl-rich, KCl-lean deposit. A layer of immiscible nonsolvent material **6**, typically hydrocarbon oil, floats on the top of the cavity to control the rate of rise of the cavity roof through the KCl-rich deposit and encourage horizontal expansion of the cavity. Other nonsolvent fluid, e.g., air, are operable. Liquids inert to the cavity solutions are preferred.

Conduit **1** terminates near the top of cavity **8** and is the influent or feed hole. The effluent conduit **2** terminates near the bottom of the cavity. In practice, solvent (in-

cluding water and dilute aqueous solutions of NaCl and/or KCl) is fed to cavity 8 through cased bore hole 1. The solvent flows into the upper portion of the pool of cavity solution. The cavity solution contacting the face of the cavity dissolves KCl and NaCl from the deposit. Substantially concentrated NaCl-KCl solution is withdrawn from the lower part of the cavity through bore hole 2.

Because the lower part of the cavity is in contact with NaCl-rich, KCl-lean material, there is a tendency for the solution in the bottom of the cavity to dissolve substantial quantities of NaCl from the floor of the cavity thereby providing an effluent unduly rich with respect to NaCl. Although acceptable effluents may be recovered in this fashion, the economics of the system are adversely affected because the dissolving capacity of the solvent is wasted by extracting commercially undesirable ore.

The improvement of this invention is associated with maintaining a zone S of dense KCl-rich solution substantially concentrated with respect to both KCl and NaCl adjacent the floor of the cavity. Effluent is withdrawn from this zone at a point above the cavity floor. Zone S is sufficiently concentrated with respect to KCl to suppress dissolution of NaCl from the NaCl-rich stratum. Zone S is appreciably more concentrated with respect to KCl and NaCl than is the zone S' situated above zone S. Thus, the KCl-rich material adjacent zone S' is readily extracted into zone S'.

It has been found that by operating the solution mining cavity at appropriate flow rates, it is possible to provide a zone S of relatively stable composition containing appropriate amounts of NaCl and KCl. The desired flow rate depends upon a variety of factors including the precise composition of the specific deposits in which the cavity is located, the size and the shape of the cavity, the temperature in the cavity, the depth of the cavity floor and the composition of the influent or feed. In typical deposits presently being commercially mined, e.g., deposits containing about 25 to about 30 percent KCl, it has been found that a zone S containing about 32 pounds of NaCl and at least 10 pounds of KCl per 100 pounds of water desirably enhances the KCl content of the effluent. Even better results are obtained when zone S contains at least about 12 pounds of KCl per 100 pounds of water, preferably, zone S contains at least 27, usually above 29 pounds of NaCl per 100 pounds of water. The foregoing quantities are based on a cavity solution temperature of about 60° C. Thus, these quantities should be adjusted to take into account increased or decreased dissolving capacity of cavity solutions of higher or lower temperatures. It is normally preferred to operate the cavity at about, i.e., within about 10° C. of the formation temperature. The "formation temperature" is the temperature existing in the formation adjacent the cavity.

The appropriate range of flow rates required to establish and maintain the desired concentrations of KCl and NaCl in zone S is conveniently determined by sampling solution from zone S after operating at a chosen flow rate. An adjusted flow rate is then selected and zone S is again sampled. The procedure is repeated until the desired composition in zone S is achieved.

Zone S should be at least deep enough that the effluent conduit 2 is in contact therewith. Usually a depth of at least 1 foot is required. Zone S may extend up to about 90 percent of the height of the cavity. Preferably, zone S extends at least 10 percent, often 30 percent or more of the height of the cavity.

A noteworthy characteristic of the instant invention is that effluent withdrawn from bore hole 2 often is actually richer with respect to KCl than would be expected even if only the KCl-rich zone were extracted. Thus, e.g., a cavity located adjacent the lower portion of a stratum containing about 25 percent by weight KCl and in contact with a second stratum containing less than about 10 percent by weight KCl operated in accordance with this invention produced an effluent containing about 16 pounds of KCl and about 30 pounds of NaCl per 100 pounds of water in the effluent.

The solution of zone S should contain a higher ratio of KCl to NaCl than exists in the KCl-lean deposit adjacent the cavity floor. In this fashion, the concentration of NaCl in zone S is minimized. Thus, according to a preferred embodiment of this invention, the effluent is periodically analyzed for KCl and NaCl. If it is found that the effluent is not sufficiently concentrated with respect to KCl and/or NaCl, the rate of input of water into the pool may be decreased to allow sufficient residence time of the cavity solution to develop a more concentrated KCl solution. If the NaCl concentration of zone S is too high, the input rate may be temporarily increased to flush the NaCl-rich solution from the cavity and allow for the establishment of a solution relatively richer with respect to KCl. After the NaCl-rich solution is flushed from the cavity, the rate of input is usually decreased to establish a more concentrated KCl solution in zone S. The KCl concentration in zone S may be periodically adjusted by either decreasing or increasing the rate of input of water into the pool as needed. In any event, care is taken once the desired concentrations are established in zone S to avoid withdrawing effluent at too rapid a rate. In this fashion, zone S is maintained at a high concentration. The concentration of KCl in zone S should be at least 90, typically substantially above 100 often up to 200 or more percent of its saturated concentration. If the mineable deposit is relatively low grade, e.g., about 15 to about 20 percent KCl, the KCl concentration in zone S is often in excess of 150 to above 200 percent of its saturated concentration. The concentration in zone S is usually between about 100 and 150, typically between about 110 and 130 percent of the saturated concentration if the mineable deposit contains in excess of about 25 percent KCl.

As used herein and in the claims, the term "saturated" denotes a solution which contains the same ratio of KCl to NaCl as the product stratum, i.e., a solution saturated with the ore of the deposit as opposed to a solution saturated with either KCl, NaCl or both. Thus, for example, a "saturated solution" produced by a cavity operating at about 60° C. in a product stratum which contains an average ratio of KCl to NaCl of 8 to 20 contains about 12.8 pounds of KCl and about 32.4 pounds of NaCl per 100 pounds of water.

Feed to the cavity is preferably sufficiently rapid to establish in zone S' relatively unconcentrated solution, e.g., about 30 to about 80 percent, preferably less than about 65 percent of the concentrations of KCl and NaCl in zone S. In this fashion, the rate of extraction of the KCl-rich ore adjacent S' is maintained at a high level.

The concentrations of zone S and S' are determined by sampling solution therefrom in accordance with well known techniques. Thus, a sampling vessel is lowered down the effluent casing to zone S and a sample collected. Zone S' is usually sampled by lowering a sampling vessel down the influent casing. Samples of both zones are taken along the axis of the bore hole.

We claim:

1. A method of recovering KCl from a subterranean deposit containing substantial amounts of NaCl and having a stratum therein rich in KCl disposed adjacent and above a stratum relatively lean in KCl which comprises establishing a cavity in the lower portion of said KCl-rich stratum, feeding solvent into the cavity and dissolving KCl and NaCl thereby forming a pool of solution within the cavity, withdrawing solution of KCl and NaCl from the lower portion of the cavity pool while minimizing reduction in the KCl:NaCl ratio of said pool through extraction of the KCl-lean stratum by establishing and maintaining a concentrated zone at the bottom of the pool of cavity solution, which zone contains at least 27 pounds of NaCl and at least 10 pounds of KCl per 100 pounds of water, said zone being in contact with the point of withdrawal of solution from said pool.

2. The method of claim 1 wherein the concentrated zone contains at least 12 pounds of KCl per 100 pounds of water.

3. The method of claim 2 wherein said zone contains at least 29 pounds of NaCl per 100 pounds of water.

4. The method of claim 1 wherein said zone contains at least 32 pounds of NaCl per 100 pounds of water.

5. The method of claim 1 wherein said zone contains at least 15 pounds of KCl per 100 pounds of water.

6. The method of claim 1 wherein said concentrated zone is at least one foot deep.

7. The method of claim 6 wherein said zone extends at least 10 percent the height of the cavity.

8. In the process of recovering KCl from an underground deposit having a KCl-rich zone containing NaCl overlying a deposit of NaCl which is lean with respect to KCl, the improvement which comprises establishing a cavity in the lower portion of the KCl-rich zone which cavity is in contact with the KCl-lean zone, feeding water into said cavity to establish a pool of cavity solution therein, withdrawing KCl-NaCl aqueous solution from the lower portion of the cavity slowly enough that the relative rates of water feed to the cavity and solution withdrawal from the cavity establish in the pool a zone of relatively lower concentration of KCl and NaCl in the upper portion in the cavity pool and a zone of relatively higher concentration of KCl and NaCl in the lower level of said pool, the concentration of solution adjacent the KCl-lean deposit being at least 29 pounds of NaCl and at least 10 pounds of KCl per 100 pounds of water and withdrawing KCl and NaCl solution from the zone of higher concentration, said KCl-NaCl solution withdrawn from said zone of higher concentration containing a larger proportion of KCl than exists in said KCl-rich deposit based upon the weights of KCl and NaCl in said deposit.

9. The method of claim 8 wherein the solution adjacent the KCl-lean deposit contains at least 12 pounds of KCl per 100 pounds of water.

10. A method of recovering KCl from a subterranean deposit thereof which also contains NaCl which comprises establishing a cavity in the deposit, feeding water into the cavity to dissolve both KCl and NaCl and to form a pool of solution in the cavity, holding the rate of withdrawal of solution sufficiently low to permit the concentration of the solution in a zone adjacent the cavity floor to attain at least 10 pounds of KCl and at least 29 pounds of NaCl per 100 pounds of solution, the ratio of KCl to NaCl being in excess of the average KCl-NaCl ratio in the deposit, feeding water into the cavity sufficiently fast to establish and maintain in an upper zone of said pool a second concentration of KCl and NaCl which is lower than that in the first zone and withdrawing solution from said first zone while feeding water to the pool sufficiently fast to hold the concentration of KCl and NaCl in the second zone lower than the concentration of the solution in the first zone.

11. The process of claim 10 wherein the concentration of KCl and NaCl in the solution in said second zone is held below 80 percent of the concentrations of KCl and NaCl in said first named zone.

12. The process of claim 11 wherein the concentration of the solution in said second zone is held below 65 percent of the concentrations of KCl and NaCl in said first named zone.

13. The process of claim 10 wherein the solution withdrawn from said first zone is periodically analyzed for KCl and NaCl and the rate of input of water into the pool is correlated with said analysis to maintain the desired concentrations of NaCl and KCl in said first zone.

14. The process of claim 10 wherein the deposit includes a KCl-rich stratum disposed above a KCl-lean stratum and the concentration of KCl in the first-named zone is established at about 90 percent the concentration of KCl in a solution saturated with the ore of the KCl-rich stratum to contain the KCl:NaCl ratio existing in the KCl-rich stratum.

15. The process of claim 14 wherein the concentration of KCl in said first-named zone is between 100 and 130 percent of said saturated concentration.

16. The process of claim 14 wherein the concentration of KCl in said first-named zone is between 100 and 200 percent of said saturated concentration.

17. The process of claim 16 wherein the stratum being mined contains at least 25 percent by weight KCl based on the KCl and NaCl in the stratum and the concentration of KCl in the first-named zone is between about 100 and 160 percent of said saturated concentration.

18. The process of claim 17 wherein the concentration of KCl in said first-named zone is between about 110 and 130 percent of said saturated concentration.

19. In the method of recovering KCl from a subterranean deposit containing substantial amounts of NaCl and having a KCl-rich stratum disposed adjacent and above a stratum relatively lean in KCl by establishing a cavity in contact with said KCl-lean and said KCl-rich strata, feeding solvent into the cavity and dissolving KCl and NaCl thereby forming a pool of solution within the cavity and withdrawing effluent from the cavity pool, the improvement which comprises enhancing the KCl:NaCl ratio in the effluent while minimizing reduction in the KCl:NaCl ratio of said pool through extraction of the KCl-lean strata by establishing and maintaining in contact with the point of withdrawal of effluent a concentrated zone extending from the bottom of the pool and containing at least 10 pounds of KCl and at least 27 pounds of NaCl per 100 pounds of water.

20. The method of recovering KCl from a deposit containing substantial amounts of NaCl and having therein a stratum relatively rich in KCl disposed above a stratum relatively lean in KCl from a solution mining cavity in contact with both said strata which comprises feeding solvent into the cavity to dissolve KCl and NaCl thereby to form a pool of solution within said cavity, establishing and maintaining in contact with a withdrawal point of effluent in said pool a concentrated zone and withdrawing effluent from said concentrated zone in said pool of solution while maintaining the ratio of KCl:NaCl in said effluent higher than the corresponding ratio in said deposit while operating the cavity to establish and maintain a higher ratio of KCl:NaCl in the cavity solution in contact with the KCl-lean stratum than the corresponding average ratio which exists in the KCl-lean stratum.

21. A method of recovering KCl from a subterranean deposit thereof which contains NaCl which comprises establishing a cavity in the deposit, feeding solvent into the cavity to dissolve both KCl and NaCl and to form a pool of solution in the cavity, holding the rate of withdrawal of solution sufficiently low to permit the solution in a zone adjacent the cavity floor to attain a KCl to NaCl ratio in excess of the average KCl:NaCl ratio in the deposit, feeding solvent into the cavity sufficiently fast to establish and maintain in an upper zone of said pool a second concentration of KCl and NaCl which is lower than that in the first zone and withdrawing solution from said first zone while feeding solvent to the pool sufficiently fast to hold the concentration of KCl and NaCl in the second zone lower than the concentration of solution in the first zone.

22. The method of recovering KCl from a deposit which also contains NaCl from a cavity in the deposit which comprises feeding solvent into the cavity to dissolve KCl and NaCl thereby to form a pool of solution within said cavity, establishing and maintaining in contact with a withdrawal point of effluent in said pool a concentrated zone having a ratio of KCl:NaCl higher than the corresponding ratio in said deposit while establishing and maintaining in said pool above said concentrated zone a solution having a concentration of KCl and NaCl lower than the concentration of KCl and NaCl in

said concentrated zone and withdrawing from said concentrated zone a solution containing KCl and NaCl having a ratio of KCl:NaCl higher than the corresponding ratio in said deposit.

23. The method of claim 22 wherein aqueous solvent is fed to said pool above said concentrated zone to maintain a zone less concentrated than said concentrated zone.

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