Sept. 8, 1964 J. B. DAHMS ET AL 3,148,000

SOLUTION MINING OF POTASSIUM CHLORIDE

Filed Feb. 28, 1962

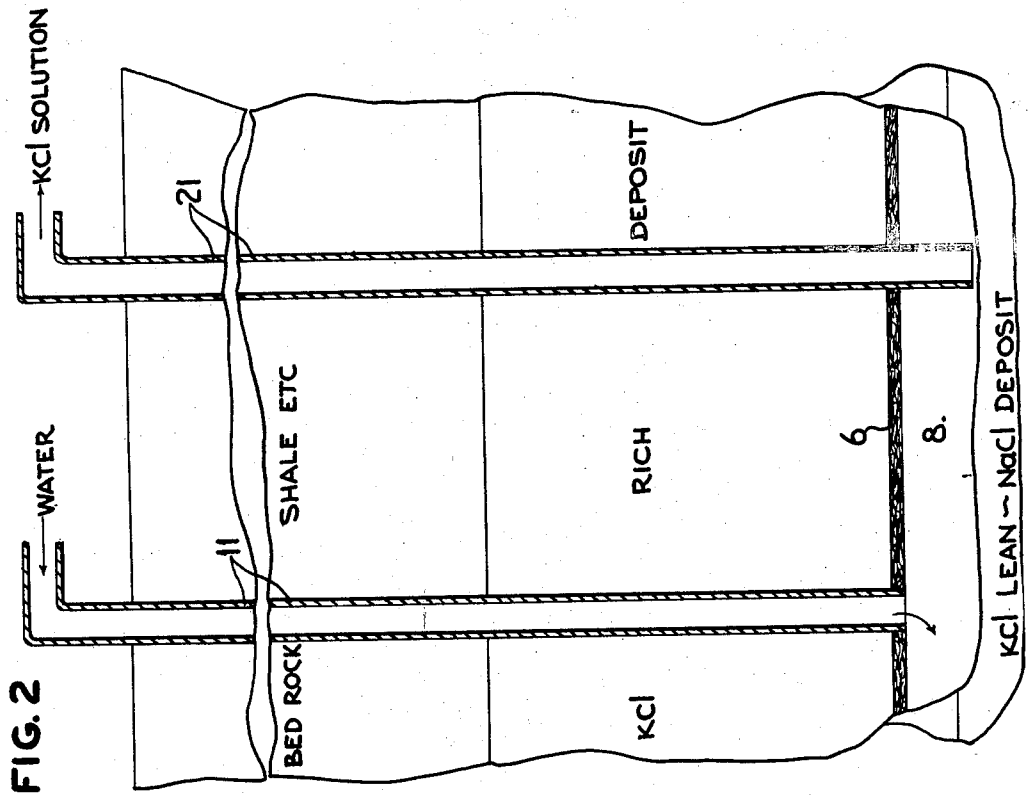


FIG. 2

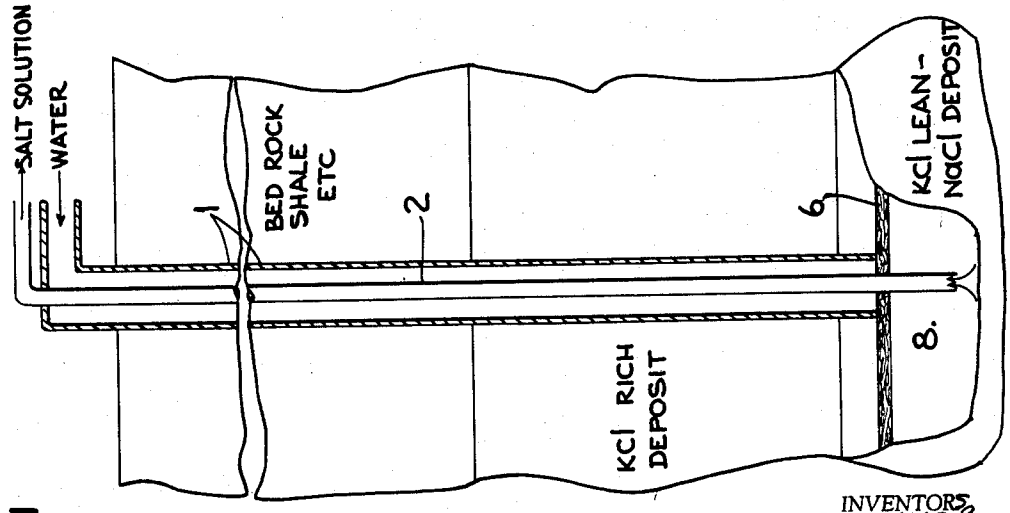


FIG. 1

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United States Patent Office 3,148,000 Patented Sept. 8, 1964

3,148,000

SOLUTION MINING OF POTASSIUM CHLORIDE

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Filed Feb. 28, 1962, Ser. No. 176,271
2 Claims. (Cl. 299—5)

This invention relates to a novel method of mining potassium chloride deposits.

Potassium chloride usually occurs in mineral deposits closely associated with sodium chloride. In many cases, potassium chloride exists in admixture or in combination with sodium chloride in the form of potassium chloride-rich strata. Often, potassium chloride-rich strata (containing 15 to 60 percent by weight of KCl based upon the total weight of KCl and NaCl in the strata) are disposed immediately above other strata lean as to potassium chloride, that is, containing less than 15 percent KCl by weight based upon the weight of NaCl and KCl contained therein, or which contain no substantial amount of potassium chloride but which are preponderantly sodium chloride. These mineral deposits usually contain other materials, generally clays and salts such as calcium sulphate, magnesium sulphate and the like in small quantities, typically, about 2 to 15 percent.

Subterranean deposits of potassium chloride and sodium chloride of this type frequently are very deep. For example, Canadian deposits of this character are often found 3,000 feet or more below the surface of the ground.

Although some KCl has been produced from natural brines or from sodium chloride brines, as a practical matter substantially all of the potassium chloride recovered from underground is obtained by shaft, room and pillar type of mining in which the potassium chloride-containing mineral is removed in solid state from the deposit and carried to the surface where it is treated by special techniques to separate potassium chloride.

Heretofore, recovery of potassium chloride by extracting deposits of potassium chloride from subterranean resources with water has not been of commercial importance. Various problems are encountered in establishing a proper cavity suitable for the extraction of KCl. In addition, crystal formation of sodium chloride on the cavity wall seriously hampers extraction of KCl.

This invention provides an improved method of recovering potassium chloride from a natural deposit containing potassium chloride. According to this invention, a cavity is first established in the deposit by feeding water thereto. The cavity is increased in size by reducing the water pressure therein thereby causing its roof to collapse. In this fashion, a large surface area of potassium chloride-rich ore is provided within the cavity. Thus, the rate of recovery of potassium chloride from the cavity is substantially increased.

It is herein provided a process for the mining of potassium chloride from a subterranean deposit regardless of its content therein. Thus, it is now possible to remove KCl in effective and commercial amounts even though it is present in the deposit in amounts of from .1 to 15 percent or more, basis combined weight of sodium chloride and potassium chloride contained within said deposit.

The aforementioned difficulties are overcome by the process of this invention which involves sinking a cased bore hole through a potassium chloride-rich deposit (wherein the potassium chloride content is typically 5 to 60 percent, preferably 15 to 60 percent, based upon the weight of KCl and NaCl in the deposit) into a sodium chloride-rich deposit disposed below the KCl-rich deposit, typically containing less than 5 percent (though may

range as high as 15 percent) by weight of KCl, basis weight of KCl and NaCl in the deposit. A cavity is established in the NaCl-rich deposit by extraction with water. On proper adjustment of extraction, the cavity is enlarged and its roof is raised to contact the potassium chloride-rich deposit. The water pressure in the cavity is then reduced to a pressure low enough to cause collapse of the cavity's roof, thereby depositing a portion of the KCl-rich strata to the floor of the cavity in the form of particles. Water extraction of the salts in the cavity is continued to remove KCl from the facing of the cavity and the particulate salt portion distributed on the floor of the cavity.

In the practice of this process, a bore hole is drilled through the potassium chloride-rich strata or deposit and downwardly into the zone in which the potassium chloride concentration is low, i.e., below 15 percent based upon the weight of KCl and NaCl, or is substantially non-existent and where the sodium chloride is comparatively high. At this point, water or an aqueous solution which is unsaturated as to sodium chloride is caused to flow down the cased hole either through a pipe disposed in the well or through the concentric area within the hole but outside the pipe, and sodium chloride is extracted from the potassium chloride-lean, sodium chloride-rich strata to establish a cavity in the manner well-known to the art of extracting sodium chloride from subterranean deposits.

In order to cause the cavity to grow laterally, a water-immiscible inert fluid, which may be air, nitrogen or like inert gas, but preferably a liquid which has a density lower than that of water at the temperature of operation, such as mineral oil, crude or refined petroleum oil, or like hydrocarbon oil, is fed into the cavity in order to establish a thin layer at the roof thereof. This causes the cavity to expand laterally as water is fed thereto and the sodium chloride dissolved in aqueous sodium chloride solution withdrawn from the cavity.

On development of the cavity in the sodium chloride-rich strata located below the potassium chloride-rich deposit to a size of at least 100 feet in diameter and in contact or close to contact with the potassium chloride-rich strata deposit, the water pressure in the cavity is reduced until roof collapse results. It will be readily appreciated by those skilled in the art that the required reduction in pressure to cause roof collapse depends upon the diameter of the cavity, the depth from ground surface to the cavity roof and the distribution of impurities within the ore comprising the immediate roof of the cavity. This reduction in pressure can readily be accomplished to whatever degree required by pumping fluid from a hole communicating with the cavity, thus reducing the height of the fluid within the hole. As a result, collapse of the roof is effected causing particles of the potassium chloride-rich strata to be deposited in the cavity.

The significance of the process of this invention resides in providing in the cavity a surface area of potassium chloride-rich ore which heretofore was unavailable for extraction purposes. This allows for considerable latitude in the mode of extraction. For example, potassium chloride may be more selectively extracted as opposed to the extraction of a mixture of NaCl and KCl in the proportion in which they occur in the deposit. As a result, the cost of recovery of KCl is substantially reduced.

Heretofore, selective solution mining of KCl has been impaired by the decrease in the rate of solution of KCl in the deposit. This decrease is caused by the accumulation of sodium chloride crystals in the pore spaces on the wall of the cavity which prevents reasonable flow rates of the selective extractant (typically saturated NaCl brine) through the pores. These pores are formed as

a result of selective extraction where only the KCl is leached from the cavity wall thereby leaving a spongy facing of NaCl. There proceeds, throughout this spongy facing, constant dissolution and precipitation of NaCl so that in a short time, NaCl crystals plug up the pores.

The process of this invention averts this difficulty by providing a large enough surface area that regardless of the amount of NaCl crystal accumulation on the particles or wall of the cavity, reasonable rates of KCl recovery are obtainable. Furthermore, if and when NaCl crystal formation does impair productivity, the roof of the cavity may again be collapsed thereby providing sufficient and productive surface are in the cavity.

It is within the contemplation of this invention to employ water free of NaCl and/or KCl or water partially or fully saturated with sodium chloride for extracting KCl from the deposit. Preferably, the NaCl content of the aqueous solution is in excess of 50 percent by weight of the NaCl content of a corresponding saturated solution. When partial or fully saturated sodium chloride solution is employed, it is possible to selectively extract potassium chloride to the significant exclusion of NaCl. When such a selective extraction operation is employed, the necessity of separating NaCl from the cavity brine during the product recovery steps is substantially removed (typically eliminated). This reduces the high cost attendant with evaporting procedures conventionally employed for separating NaCl from KCl.

In addition to providing increased product ore surface area in the cavity in the form of particles, roof collapsing causes rapid expansion of the cavity. This makes available greater cavity wall surface area for extraction of KCl. As a result, larger quantities of extractant may be fed to the cavity thereby increasing productivity of the mining operation.

Moreover, this increased surface area available for extraction means that reasonable rates of KCl recovery are obtainable from deposits extremely low in KCl content. The process of this invention increases the potentials of KCl mineral deposits heretofore considered undesirable.

During extraction of the salts from the cavity, water pressure in the cavity typically ranges from 0.4 to 1 pound per square inch, preferably from .42 to .52 pound per square inch, per foot of depth from ground surface to the base of the cavity. On reduction of the water pressure in the cavity up to partial or essentially complete removal of water or brine therefrom, the roof of the cavity will totally or partially collapse. Preferably, water pressure is reduced by 50 percent or more. The effect of roof collapse is noted by the increased salt concentration, particularly KCl concentration, in the brine received from the well.

Decrease of water or brine pressure in the cavity can be achieved by reducing or discontinuing water flow to the cavity and increasing the withdrawal rate of brine from the cavity through an outgoing hole.

Collapsing of the cavity is generally effected when the roof of the cavity is at the base of the potassium chloride-rich strata. It is possible, on the other hand, to cause collapse of the cavity when the roof thereof is, e.g., within 10 feet of the potassium chloride-rich strata.

On many occasions, the lower sodium chloride-rich strata is separated from the potassium chloride-rich strata by a layer of clay. It is possible, under these circumsances, to develop the cavity in the sodium chloride-rich strata to achieve contact with this clay layer, that is, the clay lever forms the roof of the cavity. At this point, the water pressure within the cavity is reduced and the layer of clay is collapsed to allow for immediate contact with the potassium chloride-rich strata. Further collapse of the cavity's roof upon contact with the potassium chloride-rich strata is then possible.

Control of the collapsing of the roof of the cavity can be achieved by employing the maximum water pressure in the cavity capable of allowing roof collapse. In this way it is possible to maintain a more regulated feed of particulate KCl-rich mineral to the floor of the cavity. As a rule, it is best to stage the roof collapsing at a rate equivalent to the maximum KCl concentration recoverable from the cavity.

Thus, it is possible to deposit only a small particulate portion of the KCl-rich strata to the floor of the cavity. On further extraction of the cavity on increasing water pressure in the cavity, an increase in the KCl concentration of the brine withdrawn from the cavity will be noted. Repeated water pressure reductions, each followed by increase in water pressure, may be effected until there is obtained a maximum concentration of KCl in the brine obtained from the well. Extraction should then be continued to the point where a slight decrease in the KCl concentration is noted in the brine during the run. This decreased KCl concentration should be less than the highest KCl concentration of the brine after collapse but more than the KCl concentration of the brine normally obtained from the cavity prior to collapse of the cavity roof. Once such a decrease is noted, the pressure is maintained at normal extraction values to prevent further roof collapse within the cavity until the KCl concentration in the brine begins to show a value approaching that of brine obtained prior to roof collapse.

This process is diagrammatically illustrated in the accompanying drawings. FIGURE 1 shows a typical cavity being developed below the mineable deposit. FIGURE 2 shows a preferred embodiment with two cased bore holes communicating with a subterranean cavity. As shown in FIGURE 1, a bore hole suitably fitted with a casing **1** is drilled through the bed rock into the subterranean deposit, through the potassium chloride-rich layer and and into the potassium chloride-lean, sodium chloride-rich layer. The potassium chloride-rich layer may have the following approximate composition:

	Percent by weight
KCl	15 to 40.
Water insoluble clay	About 1 to5.
Calcium sulfate	1 to 5.
Water soluble calcium and magnesium salts, such as $MgCl_2$, $MgSO_4$ and $Ca(HCO_3)_2$	About 2.
NaCl	Remainder.

The potassium chloride-lean or sodium chloride-rich deposit may have the following typical composition:

	Percent by weight
KCl	0 to 5.
Water insoluble clay	1 to 5.
Calcium sulfate	About 1 to 5.
Calcium and magnesium water soluble salts	About 1 to 2.
NaCl	Remainder.

There is then disposed a pipe **2** concentrically within the casing **1** of the hole. Water is then caused to flow down the hole in order to extract sodium chloride from the deposit. In the embodiment, as illustrated, the water is allowed to flow downwardly in the space between the pipe and the casing and substantially saturated sodium chloride is withdrawn from the lower part of the cavity as it is formed via pipe **2**. An immiscible fluid which has a density lower than that of water and which is insoluble in or immiscible with water (preferably hydrocarbon oil) is fed in small amounts (usually in amount up to about 10 pounds of such agent per cubic foot of salt withdrawn) into the hole along with the water. As a consequence, this fluid forms a protective layer **6** at the upper portion of the cavity **8** which is produced.

The amount of such fluid which is introduced should be enough to establish a layer of ½ to 8 inches at the top of the cavity in order to protect the roof thereof. This amount can be computed roughly by estimating the

approximate volume of the cavity from the number of tons of sodium chloride which is extracted from the cavity. Usually, about 0.1 to 2 pounds of hydrocarbon oil is fed per cubic foot of salts withdrawn.

In general, it is not necessary to drill into the sodium chloride-rich layer to any great depth. Usually extraction of sodium chloride from the sodium chloride-rich deposit is conducted at a level of 1 to 50 feet below the level of the potassium chloride rich deposit which it is ultimately desired to extract.

As a consequence of the operation, water is caused to flow rapidly into the hole and a solution of sodium chloride withdrawn therefrom, and the cavity enlarges laterally to a substantial size, for example, preferably 100 feet or more in diameter, while the roof of the cavity is in contact or close to contact with the KCl-rich deposit.

It is at this point that the water pressure or brine pressure within the cavity can be reduced to the aforementioned values causing a collapse of the cavity's roof. Thereafter the KCl extraction is conducted while controlling the level of the cavity roof so that it rises at a very gradual rate or at a rapid rate through roof collapse of the KCl-rich deposit in the manner described above.

According to a preferred embodiment of the invention, it is desired to effect extraction of potassium chloride through a pair of cased bore holes. Thus, it is more desirable to conduct the extraction by feeding water or a partially unsaturated aqueous solution down one hole and withdrawing the resulting KCl-sodium chloride brine from the brine pool from another hole. This is accomplished as diagrammatically illustrated in FIGURE 2. As shown therein, two holes, **11** and **21**, are drilled and developed substantially, as has been described above, by establishing cavities in the sodium chloride-rich deposit. Extraction of the sodium chloride solution from the sodium chloride-rich deposit is accomplished from one or from both of the holes until the cavity **8** has been caused to expand laterally to the point where it is in communication with both holes. There is then established a cavity **8**, as is diagrammatically shown in FIGURE 2. This cavity has a thin layer of the inert, immiscible fluid **6** comparable in character to the layer discussed in connection with FIGURE 1.

When the holes are in communication and have been raised to a point where the roof of the cavity is in contact with the bottom of the KCl-rich deposit, roof collapse can be achieved by reducing the water or brine pressure in the cavity, e.g., by adjustment of the water head in the incoming hole **11** and outgoing hole **21**. After the roof the cavity is collapsed, the water pressure is increased through hole **11** and potassium chloride-sodium chloride solution is withdrawn from hole **21**, usually from a level below that at which water is introduced through hole **11** and often at or near the bottom of the cavity but above the level where crystals or insoluble impurities have accumulated to an appreciable degree. Alternatively, a solution of sodium chloride and potassium chloride, which is unsaturated as to both sodium chloride and potassium chloride, may be fed down the hole.

Potassium chloride absorbs heat when it is dissolved in water. To compensate for this, it is desirable that the temperature of the water or sodium chloride-potassium chloride solution fed down hole **11** be at least 10 to 100° F. higher than the temperature of the potassium chloride brine coming from hole **21**. By this means, heated solution is supplied to the pool of brine in the cavity **8** and thus undue cooling of this cavity is prevented.

As stated previously, one significant feature of this invention lies in its adaptability for the selective extraction of potassium chloride while leaving the essential sodium chloride content of the deposit remaining in the cavity. Thus, it is possible to employ, as the extractant, partially or totally saturated sodium chloride solution, typically an aqueous solution containing sodium chloride in amounts of from 50 percent by weight of total saturation up to total saturation. Advantageously, the brine solution employed for extraction, that is, the aqueous sodium chloride solution, may have a temperature ranging from 100 up to 300° F. As the temperature of the brine solution is increased, likewise is the extraction rate of potassium chloride.

It has been found that by providing a large surface area within the cavity by the deposition of particulate ores therein, the amount of extraction achieved through the selective method is equivalent to the best yields obtainable under other conditions yet is achieved without the deleterious effects from sodium chloride crystal formation over the facing of the deposit within said cavity and which normally would preclude the utilization of brine solution as an extractant.

In operation of this process, it is advisable to provide after collapse that the incoming or outgoing hole located near the zone of collapse terminates at the base of the cavity. This is particularly desirable in the case of the incoming hole which, as a rule, will be closer to the zone of collapse than the outgoing hole. If as a result of roof collapse the incoming hole is damaged then a new tubing can be inserted therein and driven close to the base of the cavity by known drilling techniques.

It will be understood that the process herein contemplated is subject to numerous variations. For example, the cavity used to commence dissolution of the potassium chloride may be formed by means other than extraction. Thus, a cavity may be excavated or formed by fracturing in the lower sodium chloride-rich layer or stratum or in the lower portion of the potassium chloride-rich stratum and then the roof of the cavity gradually raised to the potassium chloride-rich stratum by extraction and collapsing of the cavity roof as described above.

More than two cased holes may be installed in communication with a single cavity and operated as contemplated herein.

Although the present invention has been described with reference to specific details of certain embodiments thereof, it is not intended that such details should be regarded as limitations upon the scope of the invention, except insofar as included in the accompanying claims.

We claim:

1. In the method of recovering potassium chloride from a water-soluble subterranean stratum containing potassium chloride and sodium chloride by establishing a cavity in the stratum and feeding water to the cavity to dissolve potassium chloride from the stratum thereby forming a potassium chloride enriched solution which is withdrawn from the cavity, the improvement which comprises increasing the rate of recovery of potassium chloride from the cavity by alternately reducing the water pressure in the cavity sufficiently to cause collapse, within said water-soluble stratum, of the cavity roof thereby increasing the surface area of potassium chloride being contacted by the water and increasing the water pressure within the cavity to prevent further collapse of the cavity roof until there is obtained a maximum concentration of potassium chloride in the brine removed from the cavity, feeding water at increased pressure to extract potassium chloride until the concentration of potassium chloride in the brine decreases to approach the concentration of potassium chloride in the brine obtained prior to roof collapse and then again feeding water to the cavity alternately at reduced and increased pressure until there is obtained a maximum concentration of potassium chloride in the brine removed from the cavity.

2. In the method of recovering potassium chloride from a water-soluble subterranean stratum containing potassium chloride and sodium chloride by establishing a cavity in the stratum and feeding water to the cavity to dissolve potassium chloride from the stratum thereby forming a potassium chloride-rich solution which is withdrawn from the cavity, the improvement which comprises increasing

the rate of recovery of potassium chloride from the cavity by alternately reducing the water pressure in the cavity sufficiently to cause collapse of the cavity roof and increasing the water pressure within the cavity to prevent further collapse of the cavity roof until there is obtained a substantially increased concentration of potassium chloride in the brine removed from the cavity, and then feeding water into the cavity at increased pressure to extract potassium chloride to obtain a substantially increased

concentration of potassium chloride in the brine removed from the cavity.

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