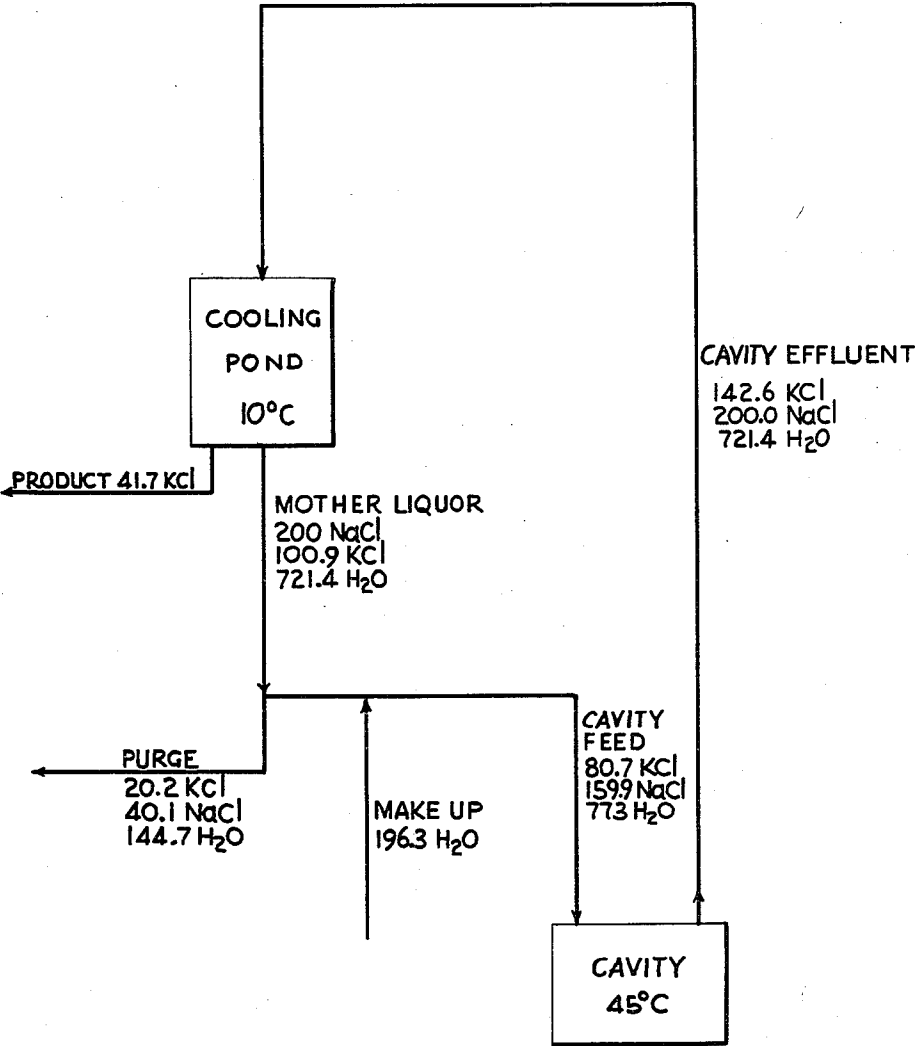


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SOLUTION MINING METHOD
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SOLUTION MINING METHOD

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The present invention relates to the manufacture of potassium chloride. It more particularly pertains to mining potassium chloride from subterranean deposits.

Typically, potassium chloride is obtained by mining subterranean deposits of saline materials, including potassium chloride. Many of these subterranean deposits, e.g., the deposits in the Carlsbad, New Mexico area, are in the form of horizontal layers or strata occurring at depths of 300 to 3000 feet or possibly deeper. In the main, commercial mining is directed to the recovery of potassium chloride from those deposits in which the potassium is available in sylvinite type ores, ores comprised principally of potassium chloride and sodium chloride.

Sylvinite deposits are typically mined by shaft, room and pillar type of mining very much analogous to ordinary shaft type coal mining. This type of mining requires provision of suitable access to the subterranean ore deposit and excavating ore in solid form. The solids are brought to the surface and then treated to separate potassium chloride from other ore components, notably sodium chloride. This separation is accomplished, for example, by flotation and classification systems utilizing their selective wettability.

Commercial operations are generally limited to recovering potassium chloride from subterranean deposits no deeper than about 3500 feet. The costs of sinking deeper shafts and assuring adequate support apparently are prohibitive. Consequently, deeper deposits extremely rich in potassium chloride, some of which are found at depths of 6000 feet or more, have not been mined to the extent that their potassium chloride content might otherwise justify.

Moreover, even the present expedients of dry mining potassium chloride ore deposits involve high capital investments, both because of the equipment and expenses involved in sinking and maintaining shafts and the methods required to separate selectively the potassium chloride from other components.

In accordance with the present invention, recovery of potassium chloride from subterranean ore deposits is accomplished without recourse to shaft type mining, and accordingly, without the inherent disadvantages of such mining. In addition, flotation and classification systems for selectively separating potassium chloride from mined ores are circumvented. Much of the costly equipment and mining techniques attendant to the recovery of potassium chloride by shaft mining and selective separation of potassium chloride from the mined ore are unnecessary. Both lower capital investments and operating costs are consequently possible. Efficient mining of subterranean ore deposits which might otherwise remain unmined due to the limitations of shaft mining is made possible.

According to this invention, the above enumerated benefits as well as other advantages are attained in the mining of potassium chloride by a method which includes charging water (including dilute aqueous salt solution) into a cavity of a subterranean ore deposit, dissolving in the aqueous charge both potassium chloride and sodium chloride, removing the resulting salt solution from the subterranean cavity, cooling this salt solution to separate selectively solid potassium chloride, returning the resulting mother liquor after appropriately adjusting its sodium

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and potassium chloride content to a subterranean cavity, dissolving both potassium and sodium chloride from the deposit therein and repeating the steps by which a portion of the solution's potassium chloride content is separated. In this solution mining of potassium chloride, liquors recycled to the salt cavity typically have their degree of unsaturation with respect to both potassium chloride and sodium chloride such that while in the cavity the solution will dissolve from the deposit these two salts in approximately the ratio they are present in the deposit. Thus, in most operations, solution of potassium chloride and sodium chloride from the ore deposit is such that both salts are removed from the deposit simultaneously and without appreciable selectivity.

Avoiding preferential solution of potassium chloride from the deposit is a material and distinctive facet of the present mining methods. Although the relative solubilities of potassium chloride and sodium chloride in water permit the selective solution of potassium chloride from subterranean deposits to thereby reduce the burden of recirculating or disposing of considerable sodium chloride, such selective solution has, nevertheless, been found to be disadvantageous. Among other things, selective solution of the potassium chloride limits the portion of the deposit which may be mined. Only a small fraction of a substantial deposit of goodly thickness may, as a rule, be mined. On the other hand, by avoiding selective solution of potassium chloride according to the present invention, a much greater proportion of the deposit may be mined. Considering the expense incurred in establishing a subterranean cavity for mining a deposit, the ability to deplete substantially the deposit is most important.

In the typical performance of this invention and the mining of potassium chloride from potash deposits of the type normally encountered, a hole is sunk into the subterranean strata of potassium minerals. Such strata may lie at a depth of as much as 7000 feet or more and may be several hundred feet thick. The hole is usually sunk to a point immediately adjacent the uppermost level of the strata of potassium minerals. It is then cased down as far as the upper portion of the potash mineral strata. A pipe is then sunk down through the casing (usually concentrically therewith) to a point below the lower level of the potash strata. If necessitated by the nature of overbearing or underbearing strata, expedients may be taken to insure the cavity is limited to the KCl ore strata and to avoid collapse of the cavity. Through the annulus provided between the casing and pipe (or through the central pipe in reverse circulation) aqueous medium is passed into the potash bed where a cavity is established. In the cavity, both potassium chloride and sodium chloride are dissolved in the medium which medium is ultimately removed through the pipe to the surface.

Alternatively, the circulation of appropriate aqueous media into and out of the cavity may be accomplished by providing two or more cased holes in communication with the cavity. Through one cased hole, water unsaturated with respect to potassium chloride and sodium chloride is passed into the cavity while the solution in which such salts from the deposit have dissolved is withdrawn from another hole in communication with the same cavity. Any of a number of holes may accordingly be sunk to mine an extensive subterranean deposit, capping and uncapping the holes as necessary.

Potassium chloride and sodium chloride are dissolved from the deposit in the proportion they are found in the deposit, as by regulating the rate at which the aqueous media is circulated into and out of the cavity. The liquor is thus allowed to remain within the cavity until it is nearly saturated with both potassium chloride and sodium chloride. This may take some time. It is not unusual for

a quantity of circulating water or liquor to remain within a cavity for a period of several months.

After appropriate quantities of potassium chloride and sodium chloride have been dissolved from the deposit, e.g., the liquor in the cavity has reached operating equilibrium, it is withdrawn from the cavity, i.e., brought to the surface.

Equilibrium, e.g., the formation in the cavity of a saturated solution, is rarely attained because of economic considerations. More often than not, the solution withdrawn from the cavity is almost (e.g., 95 percent saturated) but not fully saturated with the chlorides. The exact degree of saturation (especially of potassium chloride) or how closely equilibrium is approached in the cavity is governed by economics.

After reaching the surface, the withdrawn liquor is cooled. The solubility of potassium chloride decreases with lower temperatures in the aqueous system and hence, potassium chloride precipitates upon cooling of the liquor. However, the solubility of sodium chloride does not decrease at cooler temperatures of the range here contemplated; usually sodium chloride is somewhat more soluble in the liquor. Thus, upon cooling, the potassium chloride selectively deposits out as solid which is not contaminated by the codeposition of sodium chloride. Small amounts of mother liquor which may adhere to the crystallized potassium chloride after separation from the mother liquor are not usually sufficient to contaminate significantly the potassium chloride. If desired, a goodly portion of such adhering mother liquor may be removed by mechanical means such as shaking of the potassium chloride or even by washing and centrifuging or filtering.

After separation of solid potassium chloride, the mother liquor is diluted sufficiently with water less saturated with the salts than the liquor to provide a solution having the capacity (a degree of unsaturation) to dissolve both potassium chloride and sodium chloride from the ore deposit in the proportion in which they are present in the deposit.

This is best accomplished by replacing with water essentially free of either chloride salt a portion of the mother liquor being introduced into the cavity. Thus, a stream of mother liquor removed from the cooling step is purged and an amount of water equivalent to the water removed by this purge is added to the returning mother liquor. By reference to the solubilities of potassium chloride and sodium chloride in aqueous solution, the weight ratio of the potassium chloride and sodium chloride in the deposit and the solution temperature prevailing in the deposit, the size of the purge stream (or degree of dilution) is readily calculatable, taking into account the content of the chloride salts in the recirculating mother liquor and change in cavity retention (e.g., increasing cavity volume due to solution of salts from the deposit).

This purge not only serves as the mechanism by which the mother liquor recirculated to the cavity is adjusted to the desired degree of unsaturation with respect to the two salts, but is an expedient by which sodium chloride is removed from the system and thus prevents buildup of sodium chloride in the recirculating mother liquor.

Since the solution of potassium chloride in an aqueous salt solution such as the recirculating mother liquor involves the absorption of heat, the temperature at which solution is accomplished within the cavity preferably is maintained by heating the feed; otherwise, the cavity would become progressively cooler. Such cooling, if permitted, increases the circulating rate and reduces process efficiency. When economically justified, increasing cavity temperatures (rather than maintaining them) may be practiced.

The following example illustrates the manner in which the present invention may be ideally performed:

Example I

In this example, potassium chloride is mined and re-

covered at the rate of 1000 tons per day from a subterranean sylvinitic deposit ranging up to 40 feet in thickness and approximately 5000 feet below the earth's surface. The deposit is comprised of approximately 57 percent potassium chloride and 43 percent sodium chloride by weight of these two chlorides. Other materials such as magnesium chloride are present in various portions of the deposit.

First, a suitable hole is sunk to provide for access to the strata of subterranean sylvinitic comprising the deposit. This hole provides access to the deposit and means for introducing and removing solutions from a cavity established in the deposit.

The drawing diagrammatically illustrates the mining of potassium chloride from this subterranean deposit. Numerical values are for tons per hour of material.

Provision of aqueous solution nearly saturated with both potassium chloride and sodium chloride in the initiation of this mining procedure involves charging water into the subterranean deposit through the hole. Usually, by allowing the water to dissolve into the strata, the cavity is established. After allowing the solution to attain operating equilibrium (e.g., about 95 percent saturation) with respect to the solution of the chloride salts, solution is withdrawn and treated in accordance with the cyclic process outlined in the drawing.

In the instant mining installation, the temperature of the solution in the cavity is about 45° C. Thus, the aqueous solution withdrawn from the cavity is at 45° C. and contains 197.75 pounds KCl and 277.25 pounds of NaCl per 1000 pounds of water. It is withdrawn from the cavity and brought to the surface at the rate of 721.4 tons per hour of water and respectively 142.6 tons potassium chloride and 200 tons sodium chloride per hour.

This solution is then discharged into an open cooling pond where through exposure to the prevailing ambient temperature of below 10° C. it is cooled to 10° C. The cooling pond is relatively shallow, having a liquid depth of 3 to 5 feet. Some 41.7 tons per hour of potassium chloride separates as solid. The resulting mother liquor in equilibrium with the conditions prevailing in the cooling pond is removed as a stream at a rate such that 721.4 tons per hour of water, 200 tons per hour of sodium chloride and 100.9 tons per hour of potassium chloride leave the cooling pond.

From this stream of mother liquor, a portion is separated as purge. This purge amounts to 144.7 tons per hour of water, 20.2 tons per hour of potassium chloride and 40.1 tons per hour of sodium chloride.

After being so purged, the stream of mother liquor is replenished with an amount of water essentially free of potassium and sodium chloride salts equivalent to that withdrawn from the purge, notably at the rate of 196.3 tons per hour of water (144.7 tons as replacement for purged water and 51.6 tons to account for increase in cavity size caused by dissolving the salts).

The resulting diluted mother liquor is then heated and recirculated as feed to the cavity. Thus, to the well an aqueous stream is fed at the rate of 773 tons per hour of water, 80.7 tons per hour of potassium chloride and 159.9 tons per hour of sodium chloride. This feed is then discharged into the subterranean cavity within the ore deposit and allowed to attain operating equilibrium conditions under the prevailing temperature within the cavity. This provides additional saturated aqueous solution of potassium chloride and sodium chloride for withdrawal from the cavity and recirculation to the cooling pond and ultimately for reintroduction into the cavity.

Ore is in this manner dissolved from the deposit at the hourly rate of 72.1 tons potassium chloride and 54.4 tons sodium chloride. Due to increase in size, the cavity retains 10.2 tons potassium chloride, 14.3 tons sodium chloride and 51.6 tons water per hour.

In mining potassium chloride according to the pro-

cedure of this example, it will be appreciated the operation is conducted in continuous fashion. There is sufficient holdup time provided both in the cooling pond and well so that the required degree of saturation is attained and the circulating liquors are of a composition substantially as described.

The solid potassium chloride which settles out on the cooling pond is removed by mechanical equipment such as scrapers. Depending upon the desired purity of potassium chloride, the so-separated potassium chloride may or may not be further treated. Since as it is separated from direct contact with the mother liquor potassium chloride will normally contain some accrued mother liquor, it may be advantageous to remove at least free moisture.

Moisture can be removed by allowing the potassium chloride when separated from the main body of mother liquor to stand open to atmospheric conditions. Should a substantial portion of the mother liquor adhere to the potassium chloride, the solid potassium chloride may be separated from such adhering liquor using conventional equipment. This product may also be dried.

While the precise temperatures of the solution within the cavity and in the cooling pond are mentioned in the foregoing example, the mining of potassium chloride in accordance with the present invention is not limited only to the use of such temperatures. Nevertheless, the temperature differential between the temperature of solution in the well and in the cooling pond is preferably at least about 20° C. and more preferably between 30° C. and 50° C. This does not preclude cooling to lesser extents. However, the large volumes of circulating liquor involved in mining commercially economic tonnages of potassium chloride mitigate against too little cooling.

Frequently, it is convenient if possible to utilize temperatures normally attained by the solution in the cavity. Temperatures at which the solution is formed (taking into account the heats of solution) may be between 35° C. and 55° C. Even higher formation temperatures may be employed by heating the cavity feed more than necessary to offset the negative heat of solution of potassium chloride. In any event, the temperature of the aqueous saturated solution withdrawn from the cavity is rarely above 75° C. or below 25° C.

The extent of cooling is sufficient to cause separation of an economically appropriate proportion of the potassium chloride from solution. Thus, selection of a specific cooling temperature depends upon various objectives. Usually, the solution is cooled to between 0° C. and 25° C. Lower temperatures are useful with the general proviso that solution freezing is avoided.

In a preferred embodiment of the present invention, separation of KCl solid from the solution is accomplished by discharging the solution into a pond exposed to atmospheric cooling temperatures. Cooling is effected by allowing the solution in this open pond to reach as low a temperature as is commensurate with ambient atmospheric conditions, liquor throughput and pond area. To this end, a pond having considerable surface exposed to the atmosphere is employed. Preferably, the pond is less than 10 feet deep and ideally but 2 to 3 feet in depth.

In climates which are not cold enough to permit cooling in open ponds, it is, of course, possible although less economical to rely upon other expedients. It is also possible to augment and/or accelerate cooling to atmospheric conditions by heat exchange technique using a coolant, or by utilizing recognized techniques for enhancing the effectiveness or rate of cooling. For example, atmospheric cooling may be accelerated and even improved by aerating pond liquors. Thus, liquor in the pond may be sprayed upwardly into the atmosphere and allowed to cool as it returns.

For best results, the saturated aqueous solution withdrawn from the cavity should be free of solid sodium

chloride. Should some solid sodium chloride be present it may be advisable to remove it mechanically before cooling. However, since the solubility of sodium chloride increases with decreasing temperature, a goodly amount of undissolved sodium chloride can be tolerated in the liquor removed from the cavity.

One important feature in the present process involves recycling to the cavity as feed an unsaturated aqueous solution of KCl and NaCl having the capacity to dissolve both sodium chloride and potassium chloride in a weight ratio corresponding approximately to the weight ratio of the salts in the ore deposit. By virtue of this, there is substantially no selective solution. This is important because it is found that selective solution of potassium chloride will all too rapidly result in reducing the rate at which this salt at the cavity interfaces may be dissolved. Ultimately, the solution of potassium chloride becomes negligible and, for all practical purposes, the cavity loses its value as a source of potassium chloride.

In the present invention, the recirculation of mother liquor from the cooling step to the cavity is an integral component of the process' economic feasibility. To so utilize the mother liquor and dissolve both salts within the cavity in the weight ratio they are present in the deposit involves dilution with water of the mother liquor. In accordance with a preferred embodiment hereof, the mother liquor is appropriately prepared for return to the cavity by first separating a substantial portion as purge and thereafter adding an amount of water equivalent to that removed by the purge plus the increase in cavity retention due to its increase in size. The precise volumes of purge and makeup water obviously will vary, depending upon the potassium chloride and sodium chloride content of the mother liquor and deposit. By reference to these chloride salt contents of the mother liquor, the ratio of potassium chloride and sodium chloride in the deposit, the solubility of these two salts at the cavity temperature, and variation in cavity retention, it is possible to determine the proper composition of the feed to insure that it fulfills the requirements of dissolving both salts from the deposit in the weight ratio they are found in the deposit.

Dilution of the mother liquor with water essentially free of KCl and NaCl is preferred. Obviously, however, dilution with water less concentrated with respect to KCl and NaCl than the purge (or mother liquor) is operable.

Any sylvinite type deposit may be mined in accordance with this procedure. Such deposits are principally KCl and NaCl in composition, but may contain various other solubles and even insolubles. Mining is usually limited to deposits containing at least 15 percent, more usually 25 percent, by weight of KCl. Whenever solubles are present which alter the solubilities of NaCl and KCl in water, their effect is considered in providing the circulating brine at desired conditions of saturation and unsaturation following the general principles herein described.

While the instant method of mining potassium chloride has been described with particular reference to the use of a single hole and cavity, it will be appreciated that a multiplicity of holes and cavities are not precluded. For example, by interconnecting a cavity to two holes it is possible to feed unsaturated solution through one hole in communication with the cavity and withdraw saturated solution from another hole connected to a different portion of the cavity. Use of two holes in this manner avoids loss of heat due to heat exchange between feed and withdrawn liquors. Alternatively, the mother liquor properly diluted may be fed to a cavity other than the cavity from which the mother liquor is initially derived, as for example, when the original cavity is taken out of operation and mining with a new cavity is commenced.

It will be understood the purge stream may be dis-

carded as waste or treated further to recover one or both salts by one of a number of alternatives.

While the present invention has been described by reference to specific details of certain embodiments, it is not intended that the invention be construed as limited to such specific details except insofar as such details are recited in the appended claims.

We claim:

1. A method of mining potassium chloride from a subterranean deposit containing potassium chloride and sodium chloride which comprises dissolving with an aqueous medium these two salts from a tubterranean cavity in the deposit, removing so formed solution from the cavity, depositing solid potassium chloride from solution so removed from the cavity, separating mother liquor from solid potassium chloride, adjusting the potassium chloride and sodium chloride content of the mother liquor such that it is capable of dissolving further potassium chloride and sodium chloride in the weight ratio such chlorides are present in a subterranean ore deposit, feeding this aqueous medium to a cavity of a subterranean ore deposit, dissolving both potassium chloride and sodium chloride from the deposit in approximately their weight ration in the deposit to thereby form additional solution of potassium chloride and sodium chloride, removing from the cavity such aqueous solution and depositing from solution solid potassium chloride.

2. A method of mining potassium chloride from a subterranean deposit of potassium chloride and sodium chloride which comprises dissolving with aqueous medium in a cavity of a subterranean deposit these two salts to form an aqueous solution thereof, removing from the cavity such solution, cooling removed solution to deposit solid potassium chloride, separating mother liquor from the solid and returning to a cavity in a subterranean deposit mother liquor having its potassium chloride and sodium chloride content such that it is capable without substantial selectivity of dissolving potassium chloride and sodium chloride.

3. A method of mining potassium chloride from a subterranean deposit of potassium chloride and sodium chloride which comprises dissolving from the deposit these chloride salts with an aqueous medium to form an aqueous solution of these salts, removing such solution from the cavity, cooling the solution to deposit solid potassium chloride, separating mother liquor from the solid, adjusting the concentration of salts in the mother liquor so that it is capable of dissolving without substantial selectivity

from an ore cavity potassium chloride and sodium chloride and using such mother liquor to provide further aqueous medium for recovery of solid potassium chloride.

4. A method of mining potassium chloride from a subterranean deposit of potassium chloride and sodium chloride which comprises dissolving from the deposit these chloride salts with an aqueous medium to form an aqueous solution of these salts, removing solution from the cavity, cooling the solution to deposit solid potassium chloride, separating mother liquor from the solid, reducing the concentration of potassium chloride and sodium chloride in the mother liquor by dilution with water to provide a solution which upon being saturated within the cavity will dissolve both such salts in their weight ratio within the deposit, introducing the diluted mother liquor into a cavity to dissolve the salts and form further solution.

5. A method of mining potassium chloride from a subterranean deposit of potassium chloride and sodium chloride which comprises dissolving from the deposit these chloride salts with an aqueous medium to form an aqueous solution of these salts, removing solution from the cavity, cooling the solution to deposit solid potassium chloride, separating mother liquor from the solid, separating from the mother liquor a purge stream and diluting the resulting body with water to provide a solution which dissolves both such salts in their weight ratio within the deposit, introducing the diluted mother liquor into a cavity to dissolve the salts and form further aqueous solution.

6. A cyclic process of mining potassium chloride from a subterranean cavity in a deposit of potassium chloride and sodium chloride wherein an aqueous solution of the two salts is removed from a cavity within the deposit, cooled to deposit solid potassium chloride and mother liquor separated from solid potassium chloride is returned to a cavity to dissolve further salt which includes adjusting the concentration of sodium chloride and potassium chloride in the mother liquor returned to a cavity such that the chlorides dissolve therein in substantially the weight ratio they are present in the deposit.

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CERTIFICATE OF CORRECTION

Patent No. 3,058,729

October 16, 1962

James B. Dahms et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 12, for "tubterranean" read -- subterranean --; line 24, for "ration" read -- ratio --.

Signed and sealed this 31st day of March 1964.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

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Commissioner of Patents