June 13, 1939. R. CROSS 2,161,800

MINING POTASH

Filed April 10, 1937 2 Sheets-Sheet 1

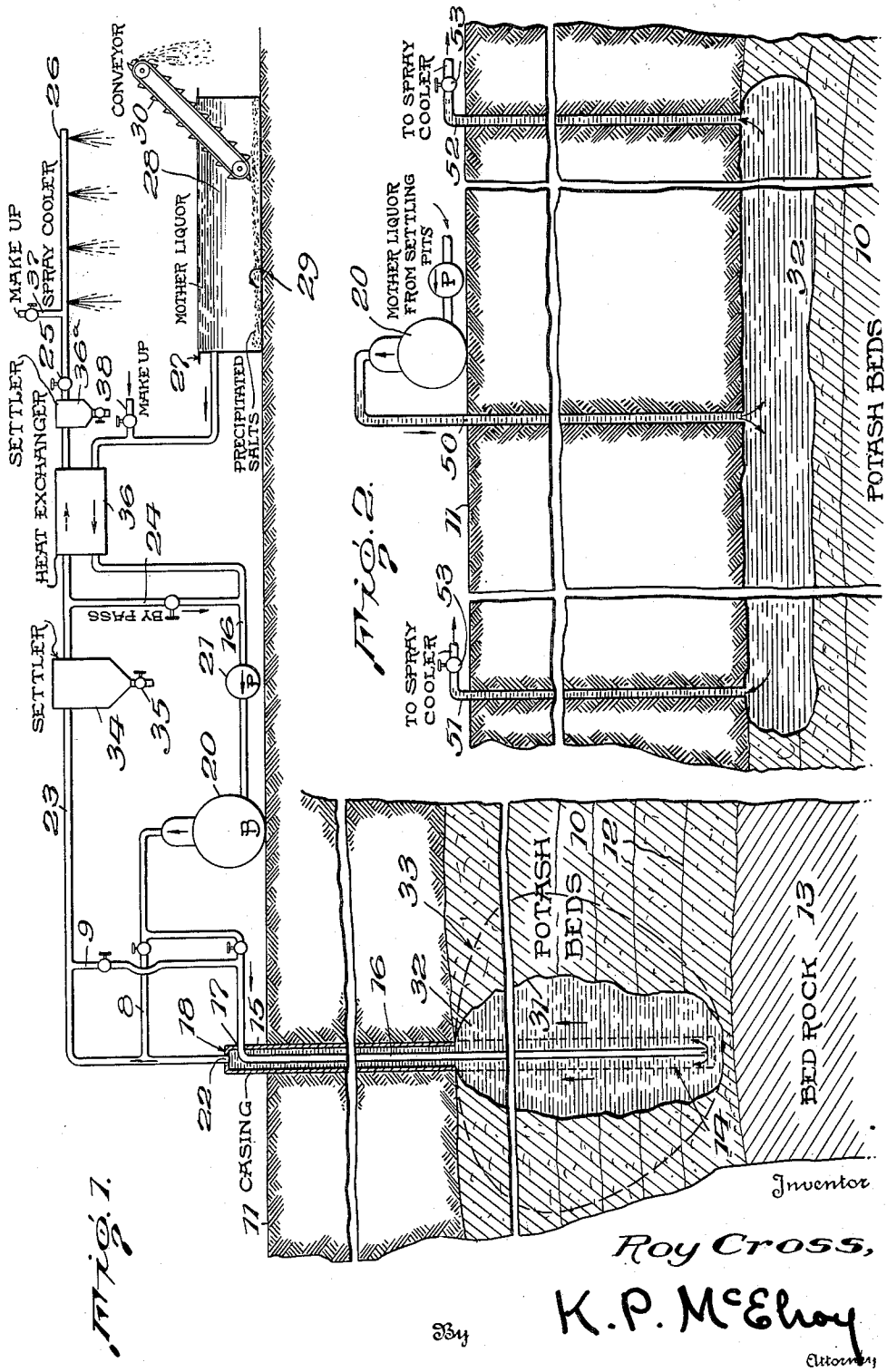


Fig. 1.

Fig. 2.

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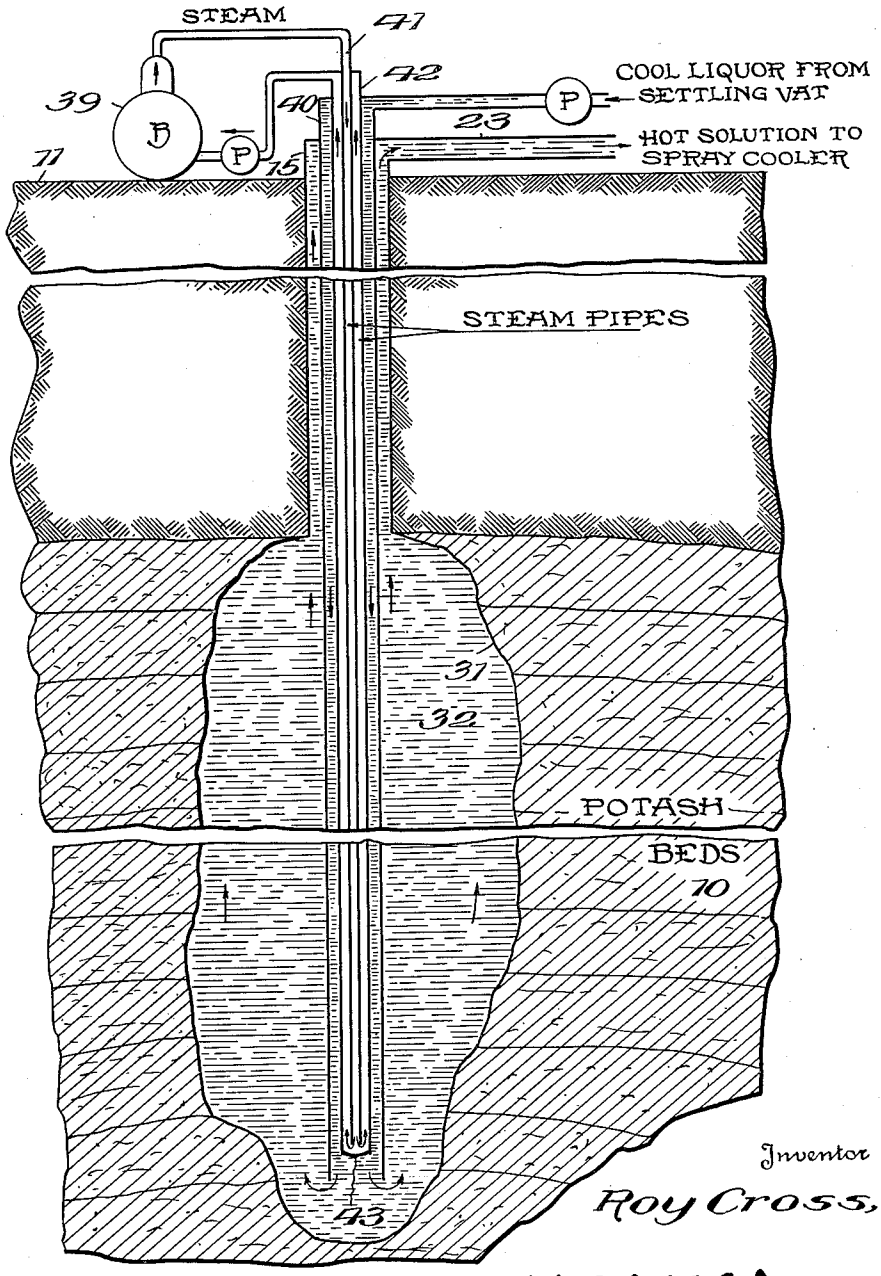
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Filed April 10, 1937 2 Sheets-Sheet 2

Fig. 3.



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MINING POTASH

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10 Claims. (Cl. 262—3)

This invention or discovery relates to mining potash; and it comprises a method of winning potassium compounds from underground potash beds, which comprises establishing and maintaining a body of cyclically circulating superheated saline liquor unsaturated with respect to potash in contact with such beds forming a hot-walled cavity, withdrawing therefrom hot liquid containing potash salts in solution, releasing pressure and lowering temperature on the withdrawn liquor to cause precipitation of potash salts, removing said salts, and replenishing the underground body of superheated liquor by reheating the motor liquor remaining after precipitation of the potash salts and forcing it back into the bed; all as more fully hereinafter set forth and as claimed.

In western Texas and New Mexico there occur, over a wide area, subterranean beds of saline minerals, including potash salts. The beds are of varying thickness, are approximately horizontal and occur at depths of 300 to 3000 feet or more. The potash occurs as the chloride in sylvinite (KCl, NaCl) and, in much larger amounts, as a sulfate in polyhalite

$$(2CaSO_4.MgSO_4.K_2SO_4.2H_2O).$$

Many of the beds, however, contain indefinite mixtures of complex salts containing potassium, calcium and magnesium. In addition to chlorides and sulfates there are minor proportions of iodides, bromides and other substances. The mineral beds often occur as thin streaks or layers separated by shale.

In recovering potash from these deposits, most attention has been paid to sylvinite. This mineral can be mined by methods analogous to those used in coal mining, and the potash can be won from the granulated mineral by simple solution methods; sylvinite being readily soluble in water. Polyhalite, on the other hand, has not been externally mined, partly because of the difficulty of recovering potash from this almost insoluble mineral.

Only the shallower and roller potash beds have been mined, because of the cost of sinking deep shafts. There are deep deposits of minerals containing substantial proportions of potash which have remained untouched. And there are many strata of high potash content which are so narrow as to be unprofitable to mine in the dry way.

It is extremely old to recover salt (NaCl) from underground deposits through wells by pumping out brine and replenishing the well cavity with water. In this operation the water is at ordinary temperature, the solubility of salt being about the same at all practical working temperatures. This simple procedure is equivalent to merely dissolving or washing out the salt, and while attractive, it is not readily applicable to potassiferous salts for several reasons. For one thing potash contained in complex salts like polyhalite is attacked but slowly by water at any temperature.

According to the present invention I provide a process capable of economically mining deep-lying potash deposits; deposits too deep for ordinarily mining methods and containing such refractory minerals as polyhalite.

I have discovered that underground beds of potash salts yield relatively rapidly to the action of hot water, particularly at a temperature of 200° C. or more, giving a saline liquor or brine rich in potash compounds. Even at 100° C. substantial amounts of potash are brought into solution. But I also find that the action is one requiring time for the brine to come to any definite composition. In any cavity in a saline deposit it is a rare occurrence that there is a surface exposure of only one salt. This requirement for time to permit equilibration is particularly true with deposits including polyhalite. In attacking polyhalite by superheated water, there is a first solution of some components, a liquid phase being produced not of the same composition as the solid phase. Rearrangement in the brine follows both as regards the liquid phase and the solid phase; new equilibria are established within the liquid phase and between the contacting liquid and solid phases. The composition of the brine changes. In some measure this is true in all hot water extractions of potassiferous beds.

I have further discovered that even better results can be obtained in some cases by attacking the subterranean beds with a superheated solution of NaCl or $CaCl_2$, in which case successive equilibria take place resulting in the building up of a KCl concentration in the liquid phase at the expense of the solid phase. If the liquid be now removed from contact with the mineral, say polyhalite, and cooled to a temperature at which KCl crystallizes out, the KCl removed, and the mother liquor or brine reheated and sent back into renewed contact with polyhalite, the former equilibria once more recur; there is a preferential solution of KCl with some redeposition of NaCl. Sodium chloride, in typical brines produced under the invention, is even less soluble at high temperatures than at low temperatures.

According to the invention, I form a hot-walled cavity in the potash bed, by forcing into the

bed, through a well, a superheated current of liquid, which at the beginning may be plain water, but becomes a saline solution. Superheated water, kept in the liquid phase by heavy pressure, at temperatures up to 200° C. and above, attacks potash minerals even when they are of a type ordinarily considered insoluble (e. g. polyhalite). The rise of solubility of most potash salts with temperature is very rapid; much more so than with most other salts; sodium salts for example. Accordingly, the superheated water takes up a substantial proportion of potash salts, and less amounts of other salts. The circulating current gradually forms a cavity, the walls of which are at a high temperature, and becomes saturated with salts. In the course of time thermal and chemical equilibria are established. The cavity walls reach a constant, high temperature, and the dissolved saline content of the circulating liquor is in equilibrium with the undissolved minerals. At this stage the system is a closed system substantially in equilibrium. The circulating liquid body is saturated with salts and is at approximately constant temperature throughout. Instead of water, I sometimes use superheated NaCl or $CaCl_2$ brine in establishing circulation.

I now break the circulation by releasing pressure and temperature on the liquor at the surface of the earth. That is, the superheated liquor coming up through the wall is passed through a reducing valve or the like, and sprayed into the air. Upon this release of pressure, some of the water flashes into water vapor or steam, and droplets of cooled liquor fall into a pit or tank, forming a cool lake. Potash salts crystallize out at once, as their solubility is low at ordinary air temperatures, leaving a mother liquor retaining other salts in solution. Some of the potash salts remain dissolved, and almost all the other salts remain in solution since they are almost as soluble at air temperatures as at high temperatures. The deposited potash salts are removed mechanically.

The mother liquor remaining after deposition of the potash salts is now capable, upon being reheated, of dissolving more potash salts. It is now pumped under high pressure into a boiler and heated to a high temperature. The superheated liquor is forced down the well, into the cavity. The liquor is unsaturated with respect to potash salts but saturated as regards other salines. It is allowed to remain in contact with the cavity long enough for potassium salts to be dissolved until equilibrium is again substantially attained, and the hot concentrated liquor is withdrawn and treated as before.

The process involves establishment and maintenance of a dominant pool of superheated saline liquor filling the cavity and tending to come into thermal and chemical equilibrium with the minerals forming the cavity walls. Some of the pool liquor is continually withdrawn, to be cooled and relieved of some of its potash content, and the pool is continually being replenished, by addition of superheated, mother liquor unsaturated as regards potassium salts. The pool liquor is continuously tending toward equilibrium with the saline beds, and the addition of heated unsaturated liquor continually tends to unbalance the equilibrium. The time factor is of considerable importance; it is better not to remove the brine as fast as it forms without giving it time to stabilize. The dominant pool is of magnitude sufficient to allow withdrawals and replenishments to average out.

The higher the temperature the higher the yield, and I ordinarily heat the water to as high a temperature as is conveniently practicable. Sometimes, as when the more soluble salts are being mined, I employ lower temperatures than those mentioned; temperatures as low as 100° C. This gives less yield, but saves on heating costs, and lessens depreciation of equipment. In all case the temperature, and the rate of circulation, are adjusted according to the character and proportion of salts crystallized out in the cooling step.

In the accompanying drawings I have shown diagrammatically a mining system within the purview of the invention.

Fig. 1 is a diagrammatical view of my invention applied to a single well in a potash bed.

Fig. 2 is a modified form of the invention shown in Fig. 1, showing how my invention may be applied to a plurality of wells when desired to run the potash solvent from one well to another.

Fig. 3 is a second modification to the invention shown in Fig. 1 in which a steam heater 43 is shown added to the single well of Fig. 1, but which heater could be added to any, or all, wells of Fig. 2 as desired.

Referring to the drawings, the system is shown applied to a typical potash field as encountered in the southwestern part of the United States, with beds 10 of various potash minerals which may be several hundred feet thick and lying at a depth of as much as 2000 to 3000 feet from the surface of the ground 11. The potash minerals occur as strata of varying thickness separated by shale or the like indicated at 12. Underneath is bed-rock 13. In the beginning, a well is sunk substantially to the bed-rock horizon, as indicated in short-dashed lines at 14, and is cased off as by a casing 15 down as far as the potash deposit. A pipe 16 is sunk down through the casing with an outlet 17 close to the bottom of the potash beds. The casing is closed at the top as at 18. In beginning operations in the field, first water or brine is injected into a heater or boiler 20 by a pump 21, is heated in the heater and is forced down the central pipe 16. Liquid flows up between the central pipe and the well bore, issuing from the top of the casing at 22 and is withdrawn through a pipe 23. In the beginning, this water is simply recirculated from pipe 23 to pipe 16 through a valved bypass 24. In the course of time, the walls of the well cavity are heated and material is dissolved, thus beginning to form an enlarged cavity somewhat as indicated at 31. Valved bypasses 8 and 9 between pipes 16 and 23 allow the circulation to be reversed if desired. After a time thermal and chemical equilibria are established. I now begin recovering potash. Bypass 24 is closed and the hot concentrated liquor issuing from the well is passed through a reducing valve 25 to a spray cooler 26 arranged above a settling vat or pit 27. The liquor is thus cooled by evaporation and falls as droplets, forming a lake 28. Potash salts are deposited out and collect on the bottom as at 29, whence they are withdrawn by scraping means (not shown) and a conveyor 30. The spray cooler is designed to bring the liquor to about weather temperature or below. The mother liquor contains some of the potash and all the dissolved salines. It is passed in heat exchange relation with the hot liquor in pipe 23, as indicated at 36,

is forced by pump 21 into the heater and reheated to temperatures of 200° C. or thereabouts and is then sent back into the well. The cavity contains a body or pool of liquor, 32, which is at high temperature. It tends to come into chemical and thermal equilibria with the surrounding minerals. Portions of it are continually being withdrawn and unsaturated solution is continually being added to it, which tends to unbalance the equilibria. The rate of circulation is made such that the liquor withdrawn is substantially saturated. Saturation takes some time. Ordinarily, a given unit quantity of circulating liquor will remain in the cavity at least one or two hours.

It is sometimes desirable to force the heated mother liquor down between the casing and the central pipe, and withdraw the concentrated liquor through the central pipe. This has the advantage of obviating deposition of salts in the upper portion of the tubing. But the way first described is usually better.

In the course of time the cavity becomes enlarged, say to the size indicated in long-dash lines at 33. When the cavity becomes quite large, I sometimes find it convenient to sink another well spaced from the original well, so as to have a lateral circulation. In this case, the superheated brine or water is forced down one well and the concentrated liquor is withdrawn from the other well. Any desired number of wells can be used. Fig. 2 shows such an arrangement, heated mother liquor being forced down a central well 50 and saturated solution being withdrawn through output wells 51 and 52 spaced from the input well. Throttle valves 53 are provided, so that the flow from the output wells can be equalized. In cases where it is impossible to establish a lateral circulation naturally, the output wells can be drilled directionally (in a way known per se) so as to slant towards the bottom of the input well. It is convenient to provide four output wells in a square, with the input well at the center. Fig. 2 shows the input well and two of the output wells.

The liquor coming up from the cavity is often more or less contaminated with mud, silt, sand, etc., and it is usually best to provide a closed settling chamber as indicated at 34, wherein the sludge may settle out of the hot liquor prior to passage to the spray cooler. Sludge may be removed through a sump outlet 35. A similar settler 36a is provided just before the spray cooler, as shown.

Some water is evaporated and lost in the spray cooling, and I accordingly add make-up water or brine as required through an inlet 38 to the mother liquor prior to going to the heat exchanger and heater. Water can also be added at this point to make up for any dissipation in the underground bed. Make-up water can also be added to the liquor prior to the spray cooling if desired, a valved inlet 37 being provided as shown.

The heater can be any suitable type of high pressure heater, and in the southwestern United States can conveniently be heated by natural gas, which occurs in regions adjacent the potash deposits. The heater, as well as the other apparatus elements which handle the circulating liquors, should be made of materials adapted to resist corrosion by the hot brines. The heater should be of a type adapted for easy cleaning, since some of the salines may deposit out from the liquors being heated, forming scale. Heaters constructed in a way similar to cracking stills, with detachable return bends giving access to the interior of the tubes for scraping, are useful.

In Fig. 3 I have shown a modification of the invention in which the boiler is arranged to heat the liquor by indirect heat exchange, and which obviates scaling difficulties. The boiler is shown at 39. In this modification four concentric pipes are provided; the well casing 15, a pipe 40 for liquor, and two steam pipes 41 and 42. Pipes 41 and 42 may extend part way down the well, or clear to the bottom, as shown, and pipe 42 is capped at 43. In operation, high pressure steam is forced down and up the inner pipes, as indicated by the arrows, and liquor is circulated down pipe 40 and up between pipe 40 and the casing. The liquor is heated in its downward course. The boiler and steam tubes form a closed system and use plain water. Heat transfer media which give higher temperatures than water at the same pressure can be employed.

While the process has been described using a spray cooler, other cooling means can be employed. Sometimes sufficient cooling can be had merely by running the brine issuing from the well, into a wide, shallow pool exposed to the atmosphere.

In the preliminary step of heating up the potash deposits in the vicinity of the well bore, it is sometimes convenient to use steam instead of hot water. Superheated steam is injected down the central pipe 16 and condenses on the walls of the well cavity. The cavity walls can be heated much faster by steam than by circulating hot water.

In using NaCl brine as the circulating liquid, the NaCl stays mostly in solution when the liquor is cooled to deposit potash salts; a little may be deposited out with the potash salts due to the fact that the liquor is concentrated somewhat by loss of water in the evaporating step. This may be avoided by adding sufficient water to the liquor before it enters the sprays, to make up for loss of water by evaporation. The same considerations apply to certain other salts taken up by the brine, e. g. calcium sulfate and magnesium sulfate; which salts are even less soluble in superheated water or brines than in cold water or brines. These salts redeposit to some extent in the subterranean cavity. The advantage of using NaCl is that it attacks polyhalite and similar refractory minerals aggressively. However, in such procedure the potash is recovered as chloride (KCl; sylvite). Where recovery as sulfate is desired it is better to use plain water if this is otherwise economical. Calcium chloride is even more aggressive than NaCl and is useful where the potash minerals are markedly refractory. In some cases I use CO_2 in attacking the potash minerals, CO_2 gas and water being pumped down the well under heavy pressure. At the high hydrostatic pressure existing in deep wells (e. g. about 66 atmospheres at the bottom of a 2000 foot bore), the CO_2 solution is quite aggressive. At the top of the ground CO_2 is recovered from the liquor by release of pressure, and sent back into the well.

The circulating solution brings up various salts, and if it is desired to recover other compounds than potash, the heating and cooling temperatures, and the degree of concentration of the liquor, are adjusted accordingly. Other saline deposits besides potash can be mined.

In mining potash from the New Mexican beds, bromides and iodides build up in the circulating liquor. From time to time, the liquor can be treated, for instance with chlorine and steam to displace the bromine and iodine; these sub-

stances being recovered in elemental form by fractional condensation.

As stated, I have found that in a saturated solution of NaCl and KCl in contact with excess salts (sylvinite), the concentration of NaCl is actually somewhat less at high temperatures than at ordinary temperatures. Thus, the solubilities of NaCl and KCl under such conditions at temperatures of 70° F. and 200° F. are as follows (grams per 100 ccm. of solution):

	NaCl	KCl	Total	Specific gravity
At 200° F.	21.7	26.3	48.0	1.33
At 70° F.	26.4	12.0	38.4	1.28

What I claim is:

1. A method of winning potassium compounds from underground potash beds, which comprises establishing and maintaining a body of superheated saline liquor, unsaturated with respect to potash, in contact with such beds to form a hot-walled cavity, maintenance being of a time sufficient to dissolve potash, withdrawing liquor from said body containing potash salts in solution, cooling the withdrawn liquor to cause precipitation of potash salts therefrom, removing said precipitated salts, reheating to a superheated condition the mother liquor remaining after precipitation of the potash salts, and sending it back into the cavity to replenish said body of liquor.

2. A method of winning potassium compounds from underground potash beds, which comprises establishing and maintaining in contact with such beds, a body of superheated aqueous solution of a compound selected from the class consisting of sodium chloride and calcium chloride, the solution being unsaturated with respect to potash, thereby disolving potash and forming a hot-walled cavity, withdrawing liquor from said body containing potash in solution as chloride, cooling the withdrawn liquor to cause precipitation of potassium chloride therefrom, removing the precipitated potasium chloride, reheating to a superheated condition the mother liquor remaining after precipitation of the potash salts, and forcing it back into the cavity to replenish said body of liquor.

3. A method of winning potash compounds from underground polyhalite beds, which comprises establishing and maintaining a body of highly heated saline liquor in contact with such beds for an extended period of contact so as to dissolve potash and form a hot-walled cavity, withdrawing liquor from said body containing potash salts in solution, cooling the withdrawn liquor to cause precipitation of potash salts therefrom, removing the precipitated salts, reheating the remaining mother liquor to a temperature of at least 200° C. under superatmospheric pressure and forcing it back into the cavity to replenish said body of liquor.

4. In the mining of subterranean potash minerals occurring in beds, the cyclic process which comprises establishing and maintaining a hot body of concentrated saline solution at a temperature of 200° C. or higher in such a bed, the hot saline liquor being withdrawn, cooled to deposit crystalline potash salts and reheated whereby it becomes unsaturated with respect to potash, and returned to maintain the temperature and replenish the body, the rate of circulation being sufficiently slow that the reheated liquor comes substantially into equilibrium with the bed minerals.

5. A method of winning potassium compounds from underground potash beds, which comprises establishing a body of super-heated saline liquor in contact with such beds to form a hot-walled cavity and dissolve potash, withdrawing liquor from said body containing potash salts in solution, cooling the withdrawn liquor to cause precipitation of potash salts therefrom, removing said precipitated salts, and maintaining said body of liquor in super-heated condition in contact with the potash beds, by supplying heat thereto and replenishing it with dilute liquor.

6. A method of winning potash salts from underground beds of relatively insoluble potash minerals, which comprises circulating an aqueous liquid heated to 200° C. or over at the surface of the earth, at a slow rate in contact with such beds to attack and dissolve salts and form a hot-walled cavity in the bed, withdrawing the hot solution thereby produced, cooling the solution to deposit potash salts, and reheating it to 200° C. or over and returning it to the beds in cyclic operation.

7. The method of winning potassium chloride from underground deposits of salts containing potassium which comprises sending into contact with such a deposit a body of superheated NaCl solution, removing and cooling the solution to crystallize out potassium chloride, reheating the solution to a superheated condition and returning the solution of NaCl in its super-heated state to the deposit for further attack thereon.

8. A method of winning potash salts from subterranean deposits, which comprises circulating downwardly into and through the deposits, superheated saline liquor unsaturated with respect to potash, at such rate as to provide an extended period of contact with a deposit, so as to take some of the potash therefrom, returning the hot solution upwardly, cooling the solution to a point sufficient to cause crystallization therefrom of at least some of the dissolved potash salts, reheating the solution to a superheated condition and again returning it to extended contact with the deposits.

9. The method of claim 8 wherein the subterranean potash deposits are largely sylvinite (KCl, NaCl) and the circulating aqueous liquor contains NaCl and KCl.

10. The method of claim 8 wherein the subterranean potash deposits are largely polyhalite ($2\ CaSO_4.MgSO_4.K_2SO_4.2\ H_2O$) and the aqueous liquor is reheated to at least 200° C. before it is returned to the deposits.

ROY CROSS.

CERTIFICATE OF CORRECTION.

Patent No. 2,161,800. June 13, 1939.

ROY CROSS.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 14, for the word "motor" read mother; line 42, for "externally" read extensively; line 45, for "roller" read richer; same page, second column, line 11-12, for "ordinarily" read ordinary; page 2, first column, line 31, for the word "wall" read well; page 4, first column, line 23, claim 1, for "of" read for; line 40, claim 2, for "disolving" read dissolving; same page, second column, line 47, claim 8, before "superheated" insert the article a; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 8th day of August, A. D. 1939.

(Seal)

Leslie Frazer,
Acting Commissioner of Patents.