Jan. 5, 1954

W. M. CROSS, JR

METHOD OF WINNING POTASSIUM CHLORIDE FROM UNDERGROUND DEPOSITS

2,665,124

Filed July 10, 1948

3 Sheets-Sheet 1

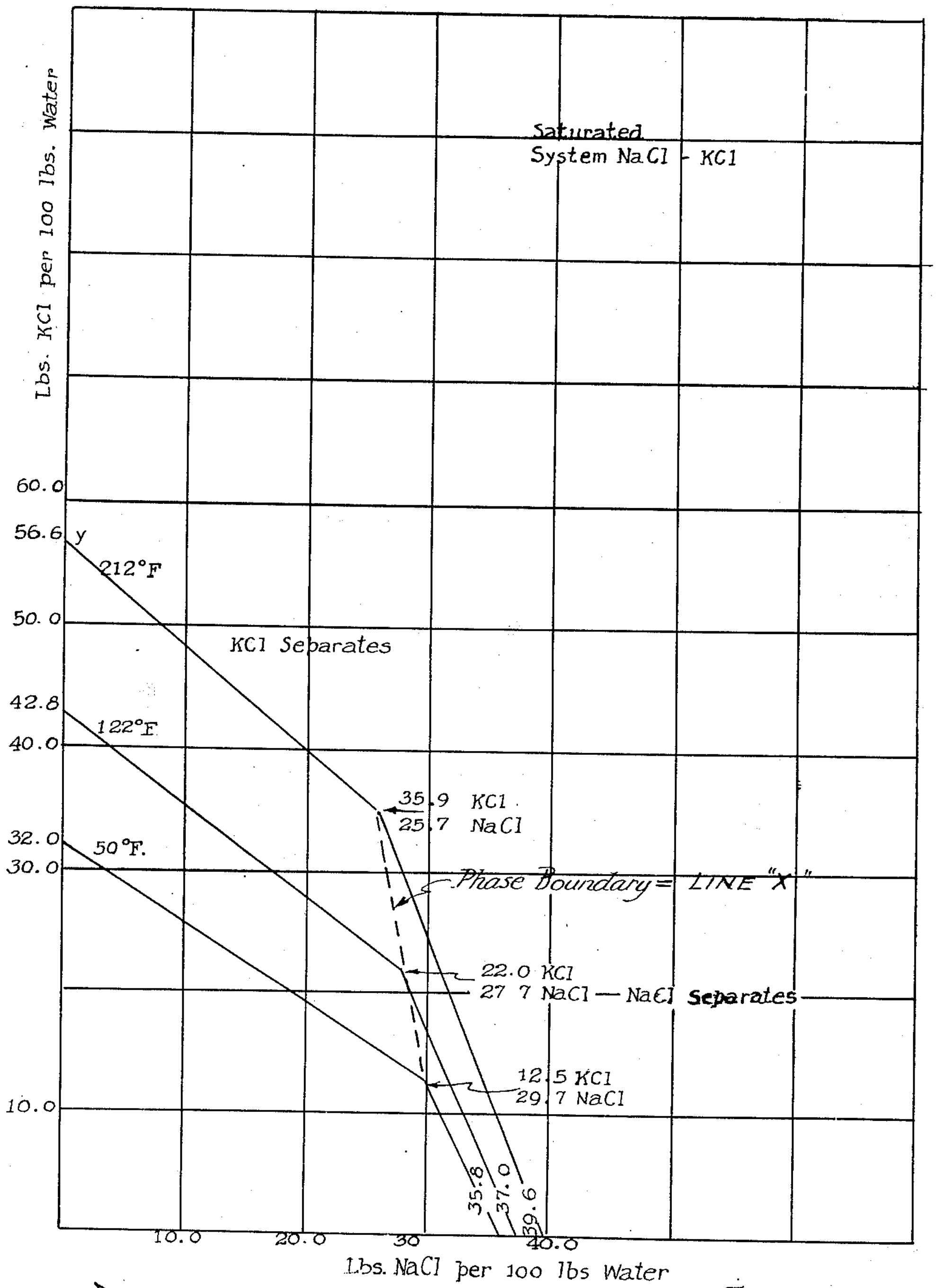


Fig. 1

Inventor
Walter M. Cross Jr.
By: Spencer Marzall Johnston & Cook
Attys

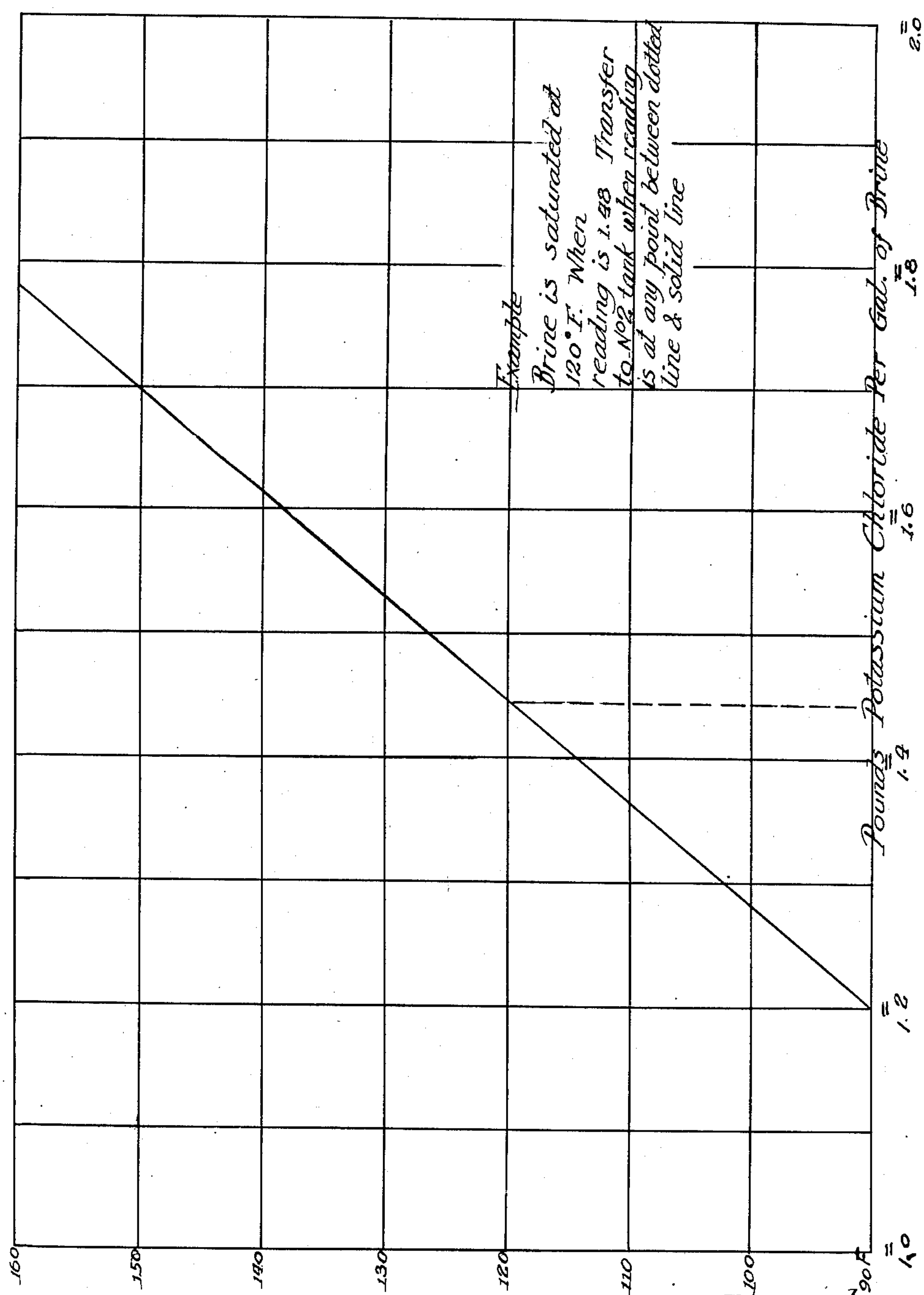


Fig.2

Inventor
Walter M. Cross Jr
By: Spencer, Marzall, Johnston & Cook
Attys

Jan. 5, 1954

W. M. CROSS, JR

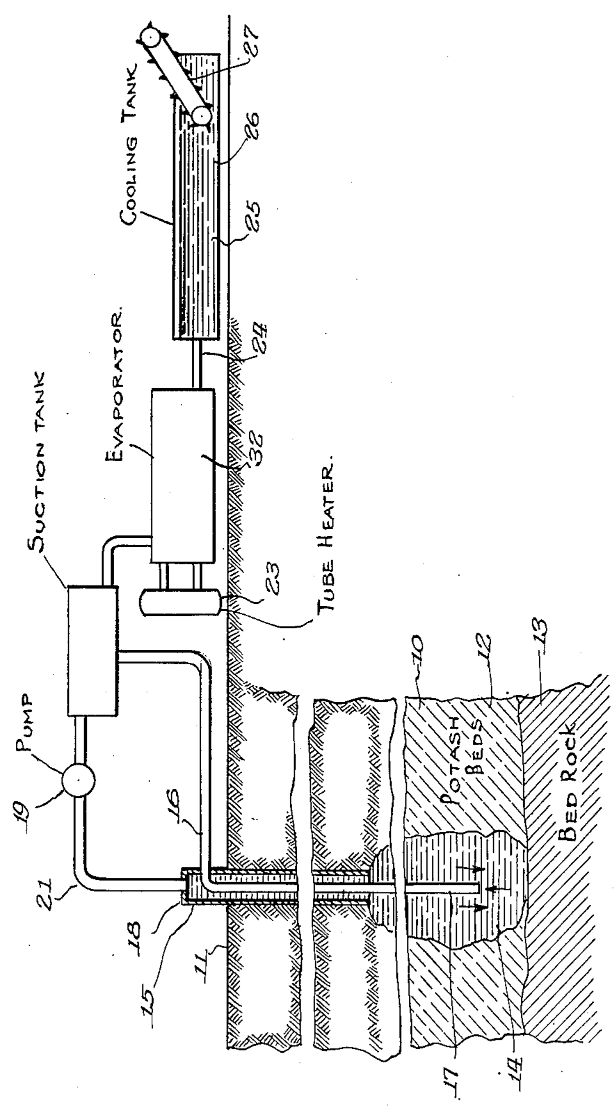
2,665,124

METHOD OF WINNING POTASSIUM CHLORIDE
FROM UNDERGROUND DEPOSITS

Filed July 10, 1948

3 Sheets-Sheet 3

Fig. 3.



Inventor
Walter M. Cross Jr
By: Spencer, Marzall, Johnston + Cook
Attys

Patented Jan. 5, 1954 2,665,124

UNITED STATES PATENT OFFICE

2,665,124

METHOD OF WINNING POTASSIUM CHLORIDE FROM UNDERGROUND DEPOSITS

Walter M. Cross, Jr., Kansas City, Mo., assignor to Kansas City Testing Laboratory, Kansas City, Mo., a corporation of Missouri

Application July 10, 1948, Serial No. 37,980

3 Claims. (Cl. 262—2)

1

This invention relates to an improved process of recovering potassium salts from brines and ores. More particularly this process pertains to a method of winning potassium compounds from underground potash beds, which comprises: establishing and maintaining in contact with such beds, a body of cyclically circulating saline liquor unsaturated with respect to potash; withdrawing therefrom liquid containing potash salts in solution, and evaporating the liquor until a suitable concentration of salts is obtained whereby potassium chloride may be precipitated upon cooling. The supernatant liquor may or may not then be returned to the system.

It is an object of this invention to enable solution mining as herefore conducted to be performed upon potash beds wherein the potassium chloride concentration is insufficient to warrant the economic operation of present mining methods. It is a further object of this invention to operate upon salt beds lean in potash by solution mining wherein the mining solution is cold. Solution mining processes as now conducted and particularly as described in Cross, U. S. 2,331,890 proceed on the basis 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. Such methods may even be operative so as to bring substantial amounts of potash into solution when hot water at or near 100° C. is circulated. Solubility, however, follows the general rule and is proportionate to temperature of the solvent used. This process requires much time before the circulating liquor attains any definite composition. This is readily apparent because it is a rare occurrence to find a saline deposit of only one salt. There is a period required for the solution to come to a definite equilibrium between the salts present and the concentration of liquid. Illustrative of this requirement for time to permit equilibration, and particularly so, is a situation where deposits of polyhalite are involved. Polyhalite is a salt of variant color corresponding to a formulae of $K_2SO_4.MgSO_4.2CaSO_4.2H_2O$. When pure it contains 15.6% K_2O; 6.6% MgO; 18.6% CaO; 53.2% SO_3; and 6.0% H_2O. In attacking polyhalite by superheated water, there is a first solution of some of the components comprising the polyhalite. The liquid phase so produced is not of the same composition as the solid phase (the material being dissolved). As further time elapses there is a realignment between the dissolving liquid and the saline deposit and the concentration of the brine being formed is rearranged. Eventually an equilibria of such rearrangement is achieved, and the liquid phase is stable with the solid phase. These facts are particularly true for langbeinite ($K_2SO_4.MgSO_4$).

The principal of such arrangement to reach an

2

equilibria is employed in other methods 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. At that point the KCl solution is removed, is cooled and KCl crystallized out.

The effectiveness of these methods is dependent upon the nature of the deposit mined. If the deposit is such that a solution rich in potassium compounds cannot be obtained, the rearrangement between the medium introduced to dissolve the saline deposit serves only to establish an equilibria whereby an undesirable salt is mined; only undesirable salts are brought into solution. This, for example, may occur where sylvinite is mined. The potash in sylvinite occurs as the chloride.

It therefore occurs that from time to time considerable sodium chloride is mined, which occurrence limits the operability of known potassium chloride solution mining methods. I have discovered that a circulating liquid in the form of cold water with subsequent evaporation to a suitable point may now be used to get saturation to the point achieved in hot water solution mining. Such cold water operation may be successfully employed where potash deposits are too lean to get satisfactory saturation of hot circulating saline solutions.

A typical effluent from a well wherein potash deposits are not too rich is of the following nature wherein the brine is 10.0 lb./gal.; the composition of such effluent may be:

	Pounds
Water	7
Sodium chloride	2.5
Potassium chloride	0.5

Potash may be recovered from an effluent as described in two ways. One is to evaporate it to dryness and obtain a mixture of 1 part potassium chloride and 5 parts sodium chloride. An offshoot of this method is to partially evaporate the mixture until sodium chloride is in sufficient concentration so as to give a mixture of at least one third potash when the brine has been evaporated to dryness. A mixture of this nature comprises a commercial manure salt. The second method is far superior. The brine is evaporated so as to drop out sodium chloride until the weight ratio of potassium chloride to sodium chloride in the liquor lies between 0.2 and 0.6. The ratio is a variant differing with the temperature of the evaporation tank. Thus at 50° F. the ratio would be 0.2 and at 212° F. it would be 0.6. The ratios 0.2 to 0.6 covers the practical operating range in my method. Other salts present may modify the successful operation range to some extent. Certain salts containing magnesium or sulphate may interfere badly with the possibility of concentrating to ratios above enumerated but this interference may be curbed. See my co-pending application Serial No. 36,271, filed June 30, 1948. For all ostensible purposes the range of 0.2 to 0.6 is substantially the most satisfactory limits of operation.

The ratio cited is the "phase boundary" of potassium chloride and sodium chloride. If at a given temperature there is not enough potassium chloride to satisfy the ratio of KCl/NaCl, both salt and potash will precipitate. The suitability of the method herein described is dependent upon the purity of potassium chloride required. A salt of high concentration of potassium chloride may be obtained by merely cooling at a ratio yielding the concentration of the two salts as may be desired.

Figure 1 is a curve showing the phase boundary, i. e. the point where at a given temperature KCl or NaCl will precipitate on cooling, depending upon which is in the ascendancy with respect to the ratio set out. To the left of the line X potash will precipitate upon cooling. In a deposit rich in potash operations are favorable to potash with respect to precipitation. But in mining deposits lean in potash, it is necessary to artificially create this condition in connection with mining from underground deposits of certain types because other methods are unsuccessfully operative. By this method we are thus able to produce high grade potash in a system of solution mining. The only other alternative is to evaporate to dryness and then wash the dried salt with a saturated solution of sodium chloride hot until the brine is of sufficient potash concentration to satisfy the ratio with subsequent cooling in order to precipitate the potash. An evaporation process of this nature is unsatisfactory because of increased cost and because it then becomes necessary to resort to batch operations with the elimination of a cyclic operation.

Figure 2 is a curve showing the amount of potassium chloride which must be present per gallon of brine at a given temperature in order to precipitate out potash upon cooling.

Figure 3 is a diagrammatical view of my invention as applied to a single well in a potash field. The beds **10** of various potash minerals 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 as 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 the operations of the system a pump **19** circulates water or brine from a suction tank **20** through pipe **21**. The salt containing liquor issues from the well through pipe **16** and into the suction tank **20**. From this circuit is bled 10 gal./min. into an evaporating tank **22**. The evaporator may be of the usual commercial type vacuum heater or a combination thereof. Brine is cycled from the evaporating tank through a tube heater **23** at 60 gal./min. and flashed back into the evaporating tank at 300° F. Evaporation of about 10 gal./min. results from the flashing operation. From the far end of the tank, brine is bled through pipe **24** into a cooling tank **25** at 10 gal./min. Potash precipitates and is collected on the bottom as at **26** whence they are withdrawn by a scraping means and a conveyor **27**. The supernatant liquor is then returned to the suction tank. Water or de-salted brine is supplied to the suction tank to maintain the volume of the system constant.

What I claim is as follows:

1. The method of winning potassium chloride from underground deposits sparse in potash content which comprises establishing and maintaining a body of cyclically circulating cold liquid capable of dissolving both sodium chloride and potassium chloride and unsaturated with respect to potassium chloride in contact with said deposits, withdrawing a portion of said liquid containing both sodium chloride and potassium chloride dissolved therein, heating said portion, evaporating an amount of said heated solution sufficient to raise the weight ratio of potassium chloride to sodium chloride in said solution to between 0.2 and 0.6, cooling said solution thereby to precipitate potassium chloride, and returning the supernatant liquid to said body of circulating liquid.

2. The method of winning potassium chloride from underground deposits sparse in potash content which comprises establishing and maintaining a body of cyclically circulating cold liquid capable of dissolving both sodium chloride and potassium chloride and unsaturated with respect to potassium chloride in contact with said deposits, withdrawing a portion of said liquid containing both sodium chloride and potassium chloride dissolved therein, heating said portion, evaporating an amount of said heated solution sufficient to raise the weight ratio of potassium chloride to sodium chloride in said solution to between 0.2 and 0.6, cooling said solution thereby to precipitate potassium chloride, removing said potassium chloride and returning the supernatant liquid to said circulating body of liquid.

3. The method of winning potassium chloride from sparse sylvinite ore deposits which comprises contacting said ore with a cyclically circulating body of cold liquid capable of dissolving both sodium chloride and potassium chloride and unsaturated with respect to potassium chloride, withdrawing a portion of said liquid containing both sodium chloride and potassium chloride dissolved therein, heating said portion above the boiling point of said solution, evaporating an amount of said heated solution sufficient to raise the weight ratio of potassium chloride to sodium chloride in said solution to at least 0.2 but not greater than 0.6 and cooling said solution thereby to precipitate potassium chloride, recovering said potassium chloride, and returning the supernatant liquid to said circulating body of liquid.

WALTER M. CROSS, Jr.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
874,906	Frasch	Dec. 24, 1907
874,907	Frasch	Dec. 24, 1907
1,288,592	Horney	Dec. 24, 1918
1,415,203	Stevenson	May 9, 1922
1,422,571	Harlow	July 11, 1922
2,331,890	Cross	Oct. 19, 1943

OTHER REFERENCES

"Solubilities of Inorganic and Organic Compounds" by Seidell, page 521, second edition, second printing, D. Van Nostrand Co. Inc., N. Y.