

May 14, 1929.

W. E. BURKE ET AL

1,712,787

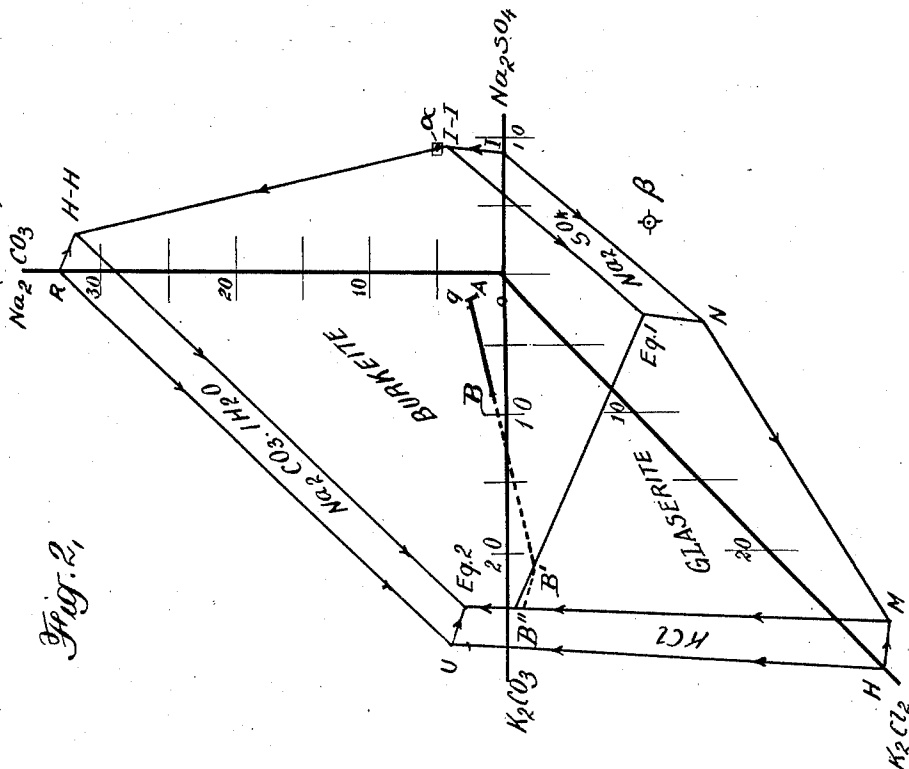
CONCENTRATION OF BRINES

Filed Feb. 6, 1924

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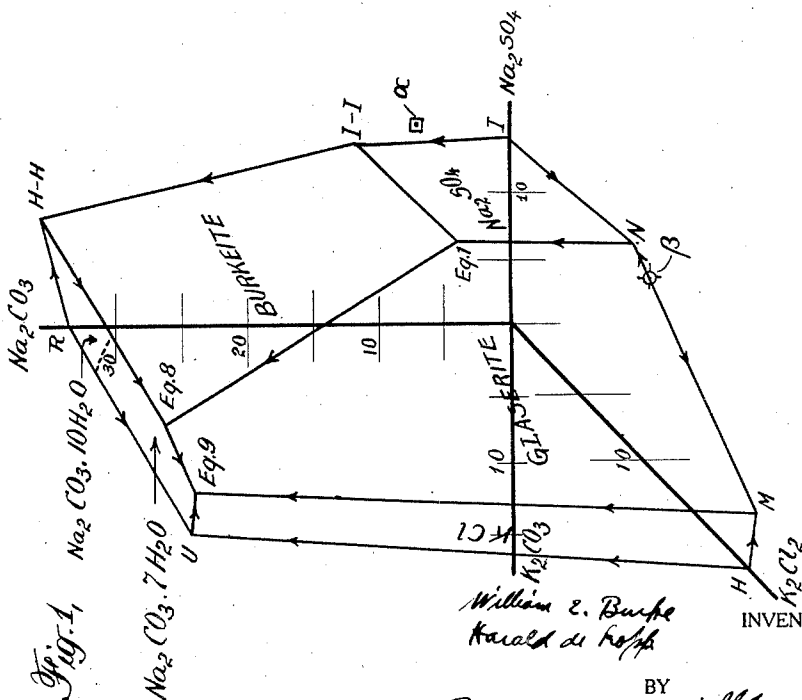
SYSTEM
Na-K-SO₄-Cl-CO₃
saturated at 57°C (134°F) with NaCl

Fig. 2,



SYSTEM
Na-K-SO₄-Cl-CO₃
saturated at 20°C (68°F) with NaCl

Fig. 1,



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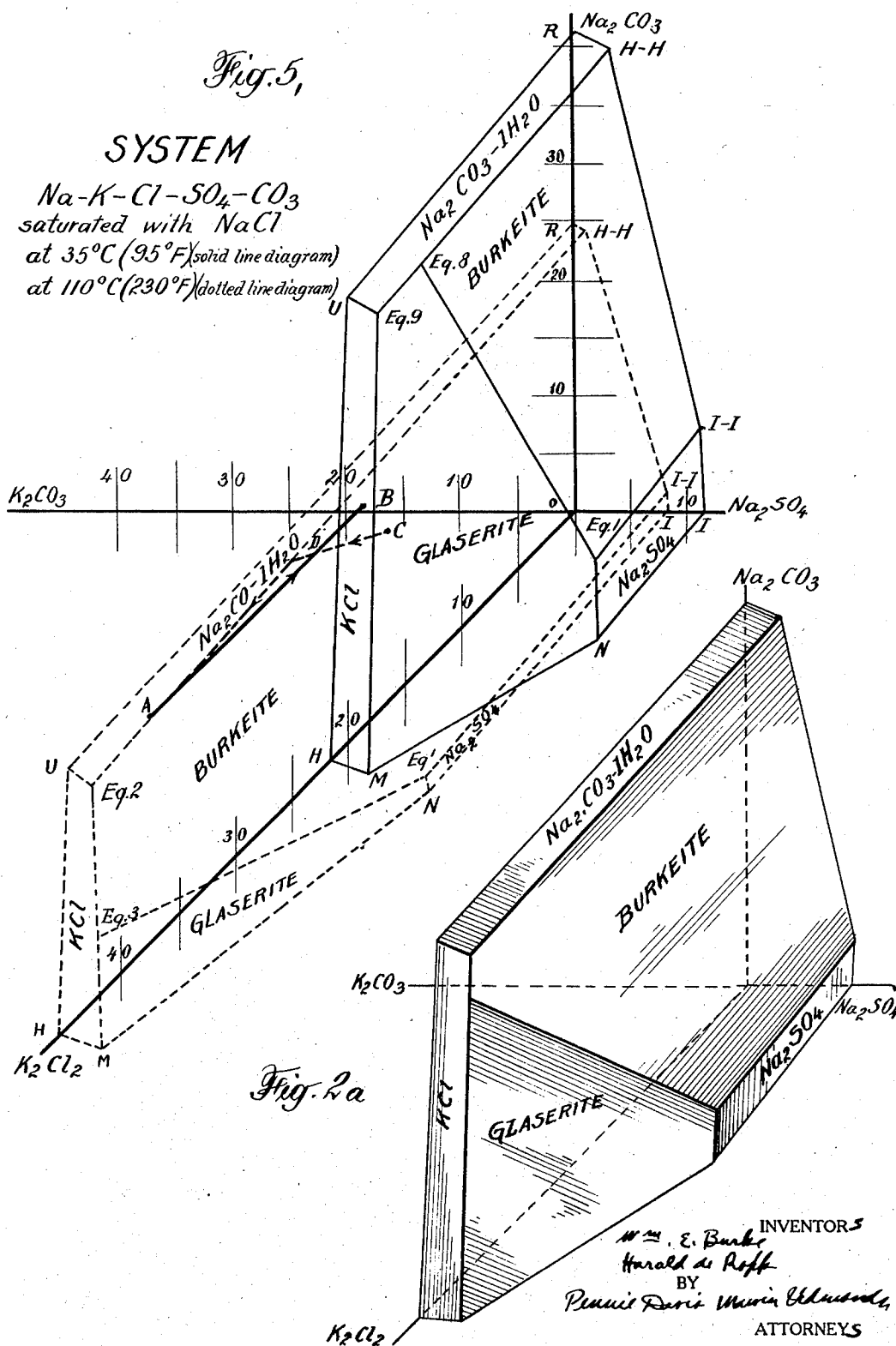
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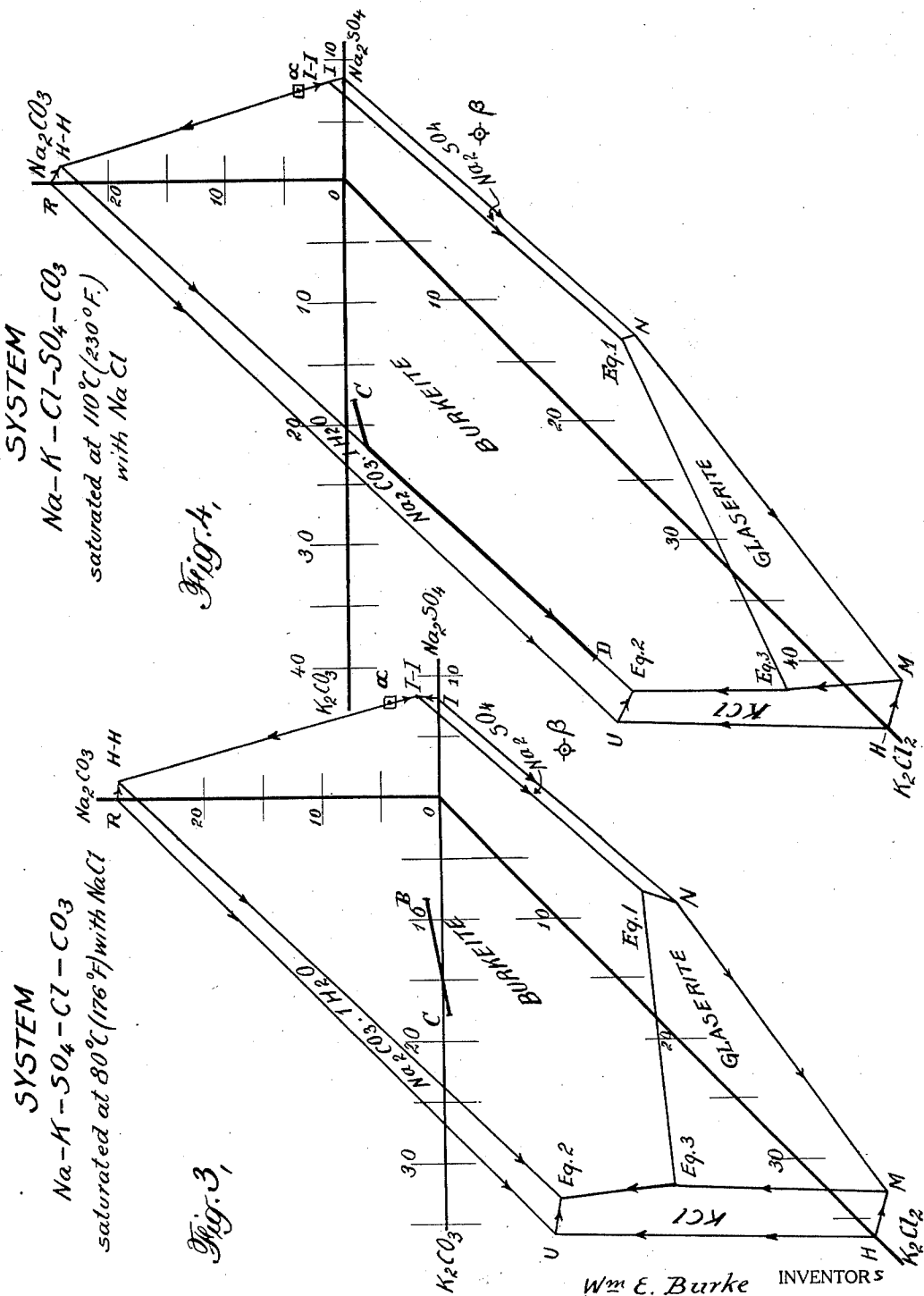
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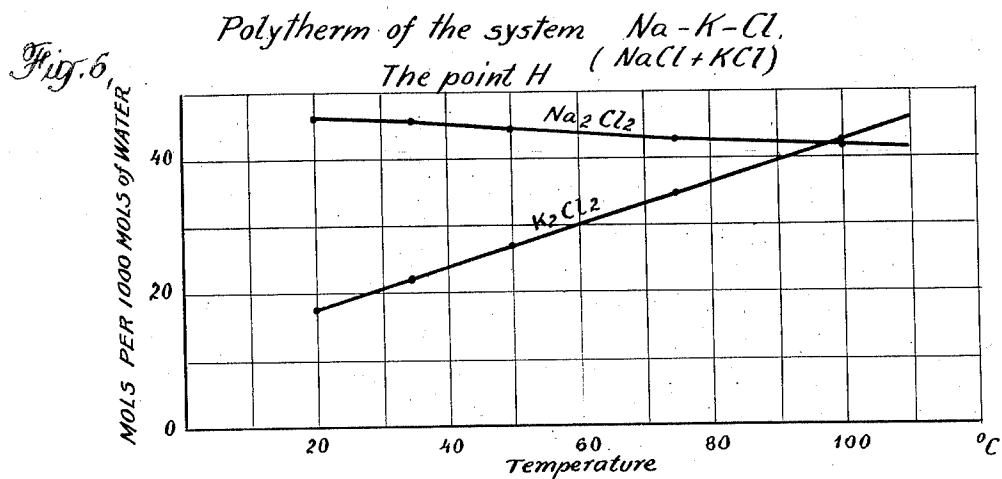
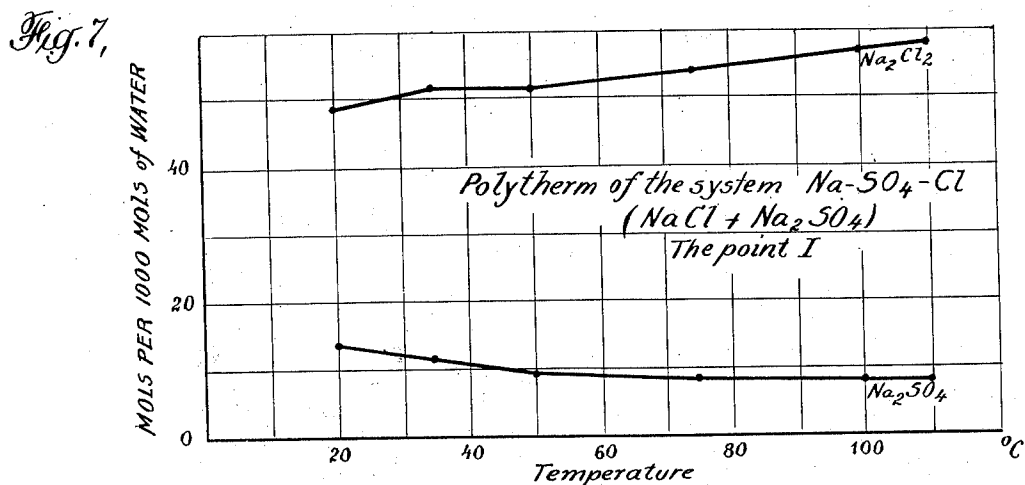
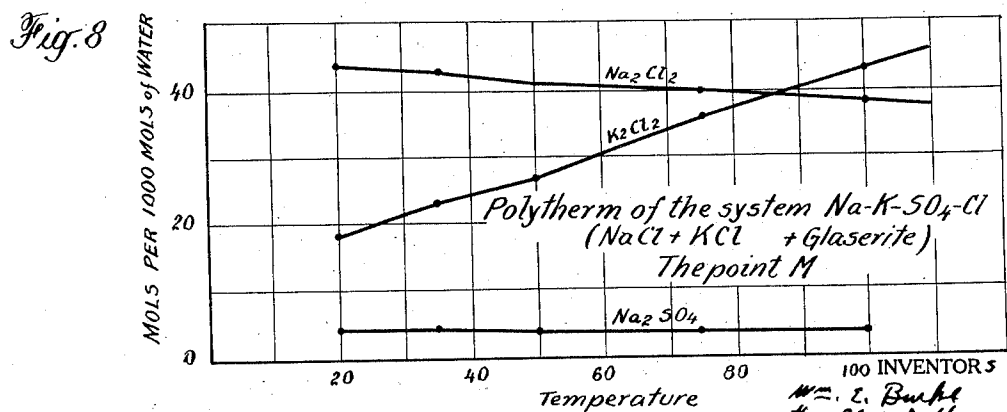
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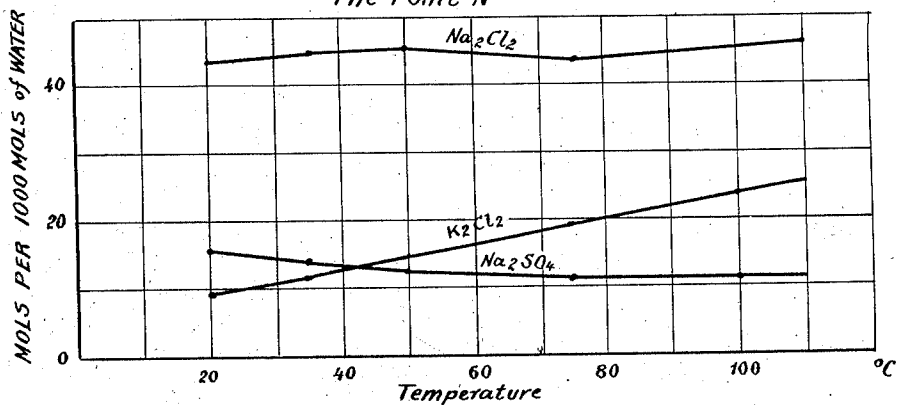
CONCENTRATION OF BRINES

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8 Sheets-Sheet 5

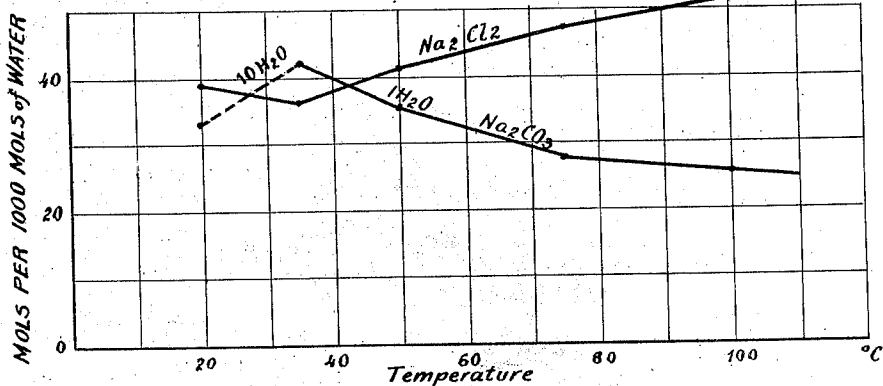
Polytherm of the system. $\text{Na}-\text{K}-\text{SO}_4-\text{Cl}$
($\text{NaCl}+\text{Na}_2\text{SO}_4+\text{Glaserite}$)
The Point N

Fig. 9,



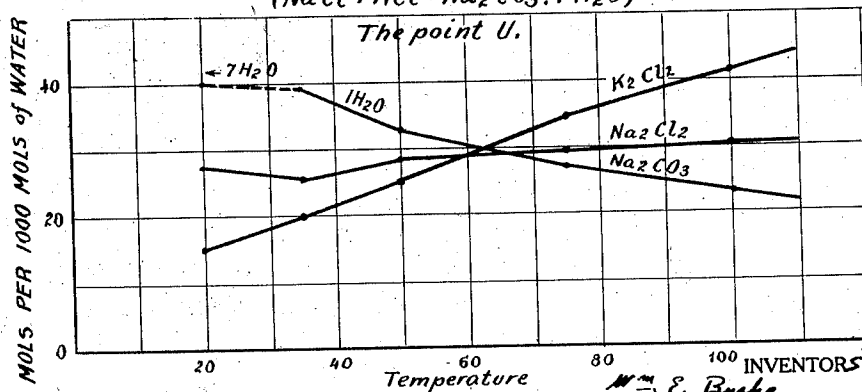
Polytherm of the system. $\text{Na}-\text{Cl}-\text{CO}_3$
($\text{NaCl}+\text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}$)
The Point R.

Fig. 10,



Polytherm of the system. $\text{Na}-\text{K}-\text{Cl}-\text{CO}_3$
($\text{NaCl}+\text{KCl}+\text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}$)
The point U.

Fig. 11,



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Fig. 12,

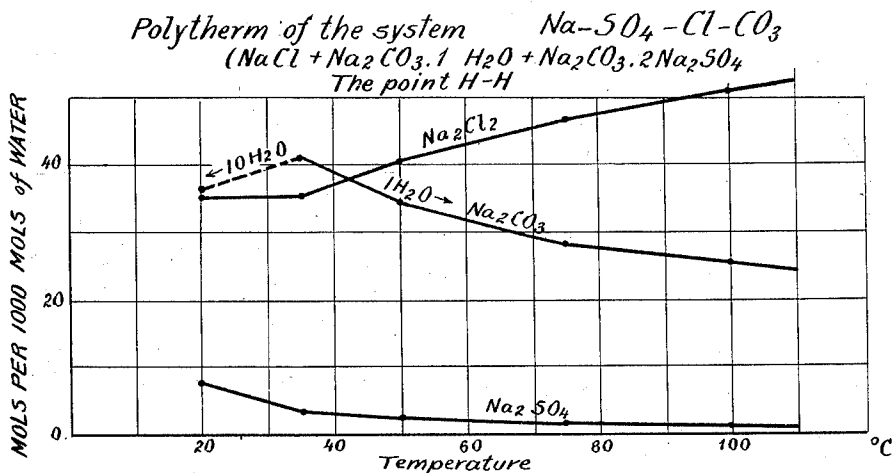


Fig. 13,

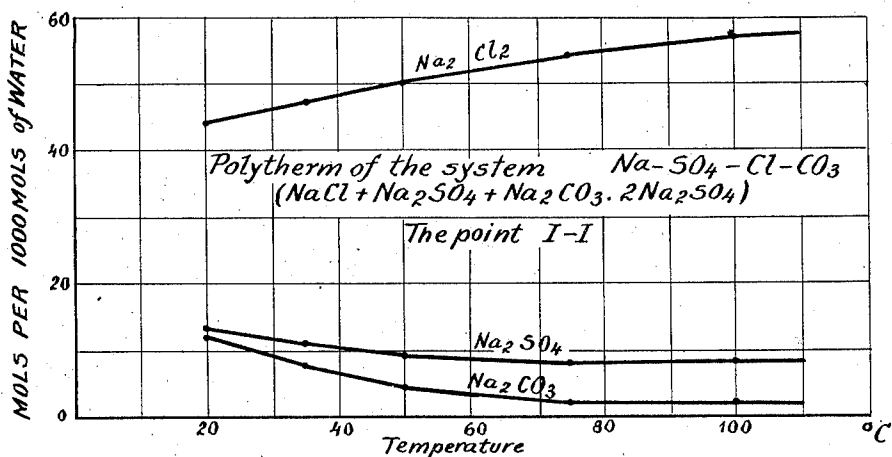
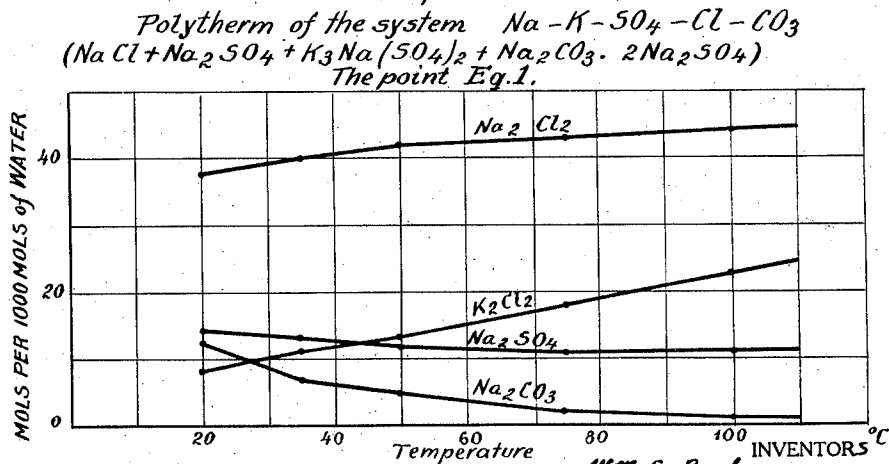


Fig. 14,



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Fig. 15,

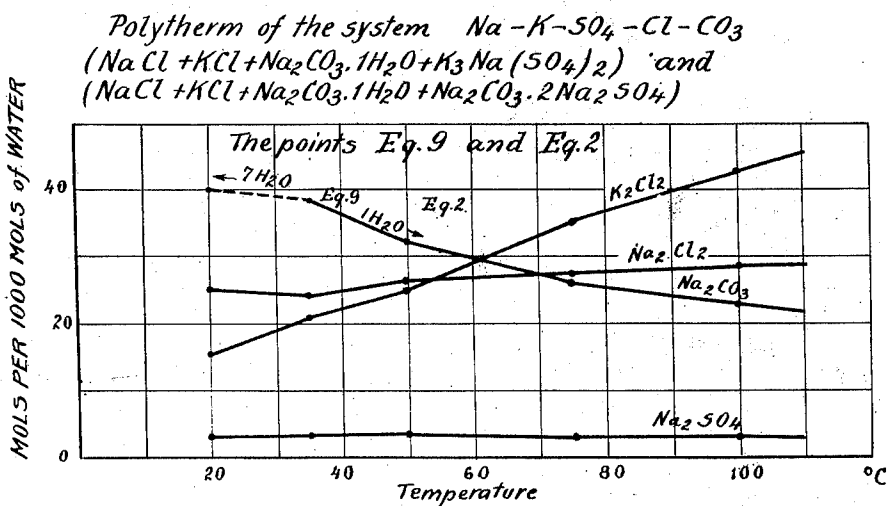
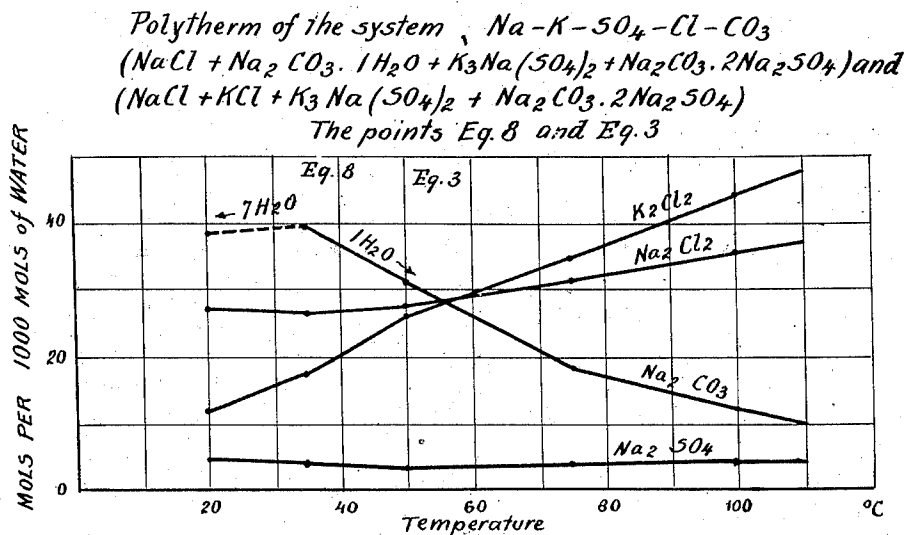


Fig. 16.



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CONCENTRATION OF BRINES

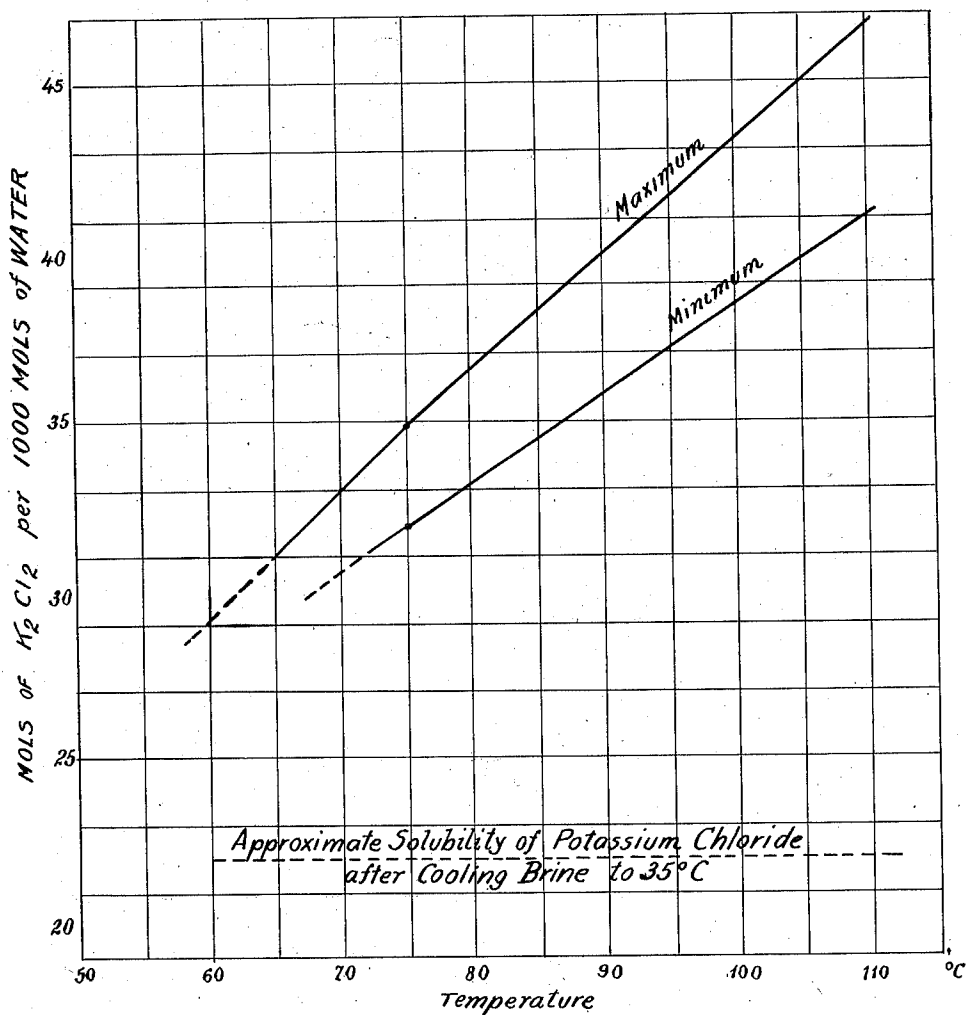
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Fig. 17

*Concentration of $K_2 Cl_2$ in Brine
To Prevent Precipitation of $Na_2 Cl_2$*



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CONCENTRATION OF BRINES.

Application filed February 6, 1924. Serial No. 690,946.

This invention relates to the treatment of brines such as are found in Searles Lake, California, and brines of similar composition, for the concentration of potassium chloride therein and the recovery of potassium chloride in a high state of purity from the concentrated brines.

Searles Lake brine is of complex composition, and consists mainly of the chlorides, sulphates, carbonates, and borates of sodium and potassium. It has heretofore been proposed to treat such brine for the recovery of potassium chloride, but in general, the yields of pure potassium chloride have been low, or where high yields have been obtained the potassium chloride has been impure. It is a primary object of the present invention to produce potassium chloride and borax from Searles Lake brine, and brine of similar composition, and obtain potassium chloride of a high degree of purity and with increased yield. The present invention enables an economical and high recovery of the potash content of the brines in the form of potassium chloride of a high degree of purity, while also enabling borax to be similarly recovered.

In order to avoid loss of potash during the concentration of the brine, it is necessary to prevent precipitation and loss of the potash in the form of insoluble salts during concentration. In order to obtain a high yield of potassium chloride, it is important that the concentration of the brine be carried to a high degree such as will permit the separation of substantial amounts of potassium chloride in a pure state on cooling. It is also important that the concentrated brine be of suitable composition, and the cooling carried out in such manner, that little or no salts other than potassium chloride will separate with the potassium chloride during the crystallization thereof on cooling. These desirable results have not heretofore been obtained during recovery of potassium chloride from brines of the character described; but they can readily be obtained by the process of the present invention and an economical and very high recovery of the potash content of the brines can thus be secured. A further marked advantage of the process of the present invention lies in the fact that suitable control

conditions with consequent uniformity of product may be readily and uniformly maintained under conditions of commercial operation.

One of the difficulties presented in the treatment of brines such as Searles Lake brine, containing the sulphates and chlorides of both sodium and potassium, is due to the tendency to form a double sulphate of sodium and potassium having the composition $\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$ or $\text{K}_2\text{Na}(\text{SO}_4)_2$. When such a brine is evaporated at temperatures above 4.4°C . this double sulphate, glaserite, which is much less soluble than potassium chloride, tends to saturate the brine so that the brine becomes saturated with respect to glaserite during concentration before it becomes saturated with respect to potassium chloride, with the result that concentration of the brine will cause precipitation of glaserite before the solution becomes saturated with potassium chloride. The precipitation of glaserite results in loss of potash in that form, from which it has not been readily recoverable. In order to avoid precipitation of glaserite during concentration at moderate temperatures, the concentration must ordinarily be stopped at a point short of that at which glaserite begins to form. If the concentration is stopped before glaserite begins to form, the brine will not be saturated with potassium chloride and only a low yield of potassium chloride can be obtained on cooling, while glaserite and sodium chloride may also separate in appreciable amounts along with the potassium chloride. If an attempt is made to obtain a higher concentration of potassium chloride or to saturate the brine with this salt, such further concentration is accompanied by a serious loss of potash as glaserite. The above conditions hold true at all temperature from 4.4°C . up to and above 100°C . when the brine contains no carbonate.

When the brine contains carbonates, however, we have found that under certain conditions, hereinafter pointed out, a double salt may be made to form, containing the carbonate and the sulphate of sodium, and having approximately the following composition: $\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$. It contains about 26.9% of sodium carbonate and 73.1% sodium sul-

phate, although in practice we have found the composition to vary slightly and to be somewhat higher in sodium sulphate and somewhat lower in sodium carbonate than is indicated by the formula. It is less soluble in hot than in cold solutions and on concentration of the brine separates without water of crystallization. We have named this double salt "Burkeite" and we will use this name for convenience in referring to this double salt in the present specification.

We have found that a potash brine of the class described, containing sulphates and carbonates, can be evaporated, under suitably chosen and properly regulated evaporating conditions, to high concentrations at lower temperatures and to saturation at higher temperatures with respect to potassium chloride without the formation of glaserite. We have found that the presence of carbonates may be utilized to cause formation and precipitation of Burkeite, with consequent decrease in the sulphate content of the brine, while preventing all formation of glaserite and while evaporating the brine to a high concentration or saturation with respect to potassium chloride. We have found that in a brine such as Searles Lake brine, the tendency towards formation of glaserite increases with decrease of temperature and that the tendency towards formation of Burkeite increases with increase of temperature. We have further found that the minimum concentration of carbonates necessary to prevent formation of glaserite is high at lower temperatures but that the necessary minimum concentration progressively decreases as the temperature of evaporation is progressively increased. A brine, such as Searles Lake brine, having a composition such that it cannot be evaporated to saturation with respect to potassium chloride at a lower temperature, as 50° C., without formation of glaserite, may, we have found, be evaporated to a high concentration or saturation with respect to potassium chloride by completing the evaporation at a suitable higher temperature. This higher temperature must be not lower than a certain minimum value which is determined by the composition of the brine, and the advantages and economy of our process are increased as the final temperature of evaporation is increased to 100° C. or higher. We have also found that at lower temperatures such a brine may be partially concentrated without formation of glaserite and loss of potash values, but that as the concentration progresses it is necessary to progressively increase the temperature of the brine in order to prevent such glaserite formation.

By carrying out the evaporation at progressively increasing and suitably chosen temperatures and completing the evaporation at a high final temperature, it is possible we have found, to make economical use of multiple effect evaporation and to thereby obtain a high final concentration with respect to potassium chloride at the high final temperature while at the same time preventing glaserite from precipitating at any point during the concentration. Although the evaporation may be completed at temperatures somewhat below 100° C. we have found it advantageous to finish the evaporation at temperatures of 100° C. or higher, for the reason that at these higher temperatures there is practically no possibility of glaserite formation and the concentration of the brines with respect to potassium chloride may be carried to a high degree, whereby a large and increased yield of potassium chloride may be obtained on the cooling of the concentrated brine. A further marked practical advantage of employing such high final temperatures, we have found, lies in the fact that whereas at lower temperatures the degree of concentration must be regulated within very narrow limits in order to obtain, without loss of the potash values, a concentrated brine from which pure potassium chloride can be obtained on cooling, at the above higher temperatures the permissible limits of concentration to avoid loss and contamination are considerably extended. The reason for this lies in the fact that, as will be further indicated, loss of potassium chloride occurs if concentration is carried beyond the point of saturation with respect to this salt, but that if the concentration with respect to potassium chloride is not carried beyond a certain minimum value at any given temperature, there will be an appreciable precipitation of sodium chloride together with the potassium chloride when the brine is cooled. At the higher temperatures there is an appreciable difference between these maximum and minimum values but at the lower temperatures they approach each other so closely as to make a suitable control of the evaporation a very difficult matter. Our process therefore avoids loss of potash during concentration, while nevertheless attaining a high degree of concentration and also avoids contamination of the potassium chloride on crystallization, while giving a high yield.

The present invention accordingly includes regulation and control of the concentration of the brine and of the temperature and composition of the brine during concentration with suitable removal of precipitated salts, so that sulphates will be removed as Burkeite along with sodium carbonate and the excess sodium chloride during concentration, and so that a concentrated brine can be obtained of proper concentration and composition to permit a high recovery of potassium chloride of high purity therefrom by cooling. It also includes rapid cooling of such concentrated brine in conjunction with such regulation and control so that the potassium chloride may

be separated and recovered practically free from borax.

After the separation of potassium chloride on cooling, the mother liquor can be further treated for the separation of borax and the remaining mother liquor may advantageously be returned and admixed with raw brine for further treatment in the process and for further recovery of potash and borax.

The process of the present invention is advantageously carried out in multiple effect evaporators, e. g. in triple effect evaporators, the raw brine, or the raw brine admixed with mother liquor, being pumped into the last or low temperature effect and from there being pumped through the remaining two effects in a direction countercurrent to that of the flow of steam through the system so that the final concentration is carried out at a high temperature.

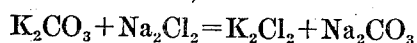
If Searles Lake brine of usual composition is subjected to evaporation at a temperature of about 50° C., the brine will become saturated with glaserite before it is saturated with potassium chloride, and if the brine is further evaporated to increase the concentration with respect to potassium chloride, loss of potash as glaserite will take place; while if the evaporation is stopped before the brine becomes saturated with glaserite, the yield of potassium chloride obtained on cooling will be low, and the potassium chloride will be impure.

We have found, however, that if the brine is evaporated at progressively increasing temperatures, as in a triple effect evaporator, and if the temperatures and compositions in the different evaporator pans are properly regulated, the brine can be concentrated to saturation or approximate saturation with potassium chloride without loss of potash as glaserite during concentration. If a triple effect evaporator is used, the three evaporating pans may advantageously be maintained at temperatures of about 57° C., 80° C., and 110° C., a proportionate part of the water being removed in each successive evaporating pan and a proportionate part of the salts other than potassium chloride and borax being removed in each pan.

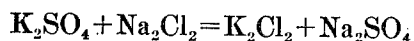
In order that the condition necessary for the formation of Burkeite and the removal of sulphates thereby during concentration of Searles Lake brine and other brines may be maintained, and the evaporation carried out to substantial completion in the manner indicated, we have determined, as a result of extended investigation, the solubility and equilibrium data required for controlling the evaporation. The results of our extended investigation are illustrated in a somewhat diagrammatic and conventional form in the accompanying drawings, in which Figs. 1 to 5, inclusive, are equilibrium diagrams or plane projections of space models which graphi-

cally illustrate the composition of all possible aqueous solutions of the sulphates, chlorides and carbonates of sodium and potassium, saturated with sodium chloride at the respective temperatures indicated, and which also illustrate the nature of the solid salts which will be precipitated by isothermal evaporation and concentration of any such possible solutions, and in which Figs. 6 to 16, inclusive, are temperature-concentration diagrams or polytherms which graphically illustrate the equilibrium conditions at the univariant points, such as H, I, Eq. 1 etc., in diagrams such as Figs. 1 to 5, inclusive, for any temperature between 20° C. and 110° C., and from which other diagrams for any temperature between these limits may be constructed. Fig. 2^A is a diagrammatic and conventional representation of Fig. 2 in another aspect. In these drawings, the points in the space diagrams are designated by the same reference characters as the polytherms from which they may be determined. The significance and use of these equilibrium diagrams and polytherms will be readily understood by anyone skilled in the art.

The conditions existing in a solution which contains several dissolved salts are such that these salts are not necessarily present in their original form. Accurately, the composition of a brine of the type with which we are concerned probably should be expressed in mols of Na, K, SO₄, Cl and CO₃, but for convenience, the composition of the solution in equilibrium with any specified solid salts may be expressed in terms of combined mols of K₂Cl₂, Na₂CO₃, etc. which has been done in this case. Moreover, because of the relations



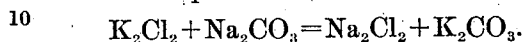
and



the composition of any solution in such systems may be correctly expressed in terms of four, or less, such combinations.

This method of expressing the composition of the various possible solutions has been adopted in the polytherms, where the compositions of the solutions in equilibrium with various solid salts are stated in terms of K₂Cl₂, Na₂Cl₂, Na₂CO₃ and Na₂SO₄. The curves on each polytherm figure represent the varying composition, with change of temperature, of a solution in equilibrium with the solid salts present at some one univariant equilibrium point. The equilibrium diagrams represent the limiting compositions of all possible aqueous solutions saturated with sodium chloride in the system Na, K, SO₄, Cl, CO₃, at some one temperature. They are projections of space models formed by plotting the univariant points for the desired temperature, as shown in the plane of the diagram, erecting at each point a perpendicular of which the length is proportion-

al to the total number of mols of Na_2CO_3 , K_2CO_3 , and Na_2SO_4 present in the solution at that point, and properly joining the ends of these perpendiculars. Neither the mols of Na_2Cl_2 nor of K_2Cl_2 are taken into account in determining the lengths of these perpendiculars, the former because they are not represented in the diagram and the latter in consequence of the relation



To locate the point Eq. 2 in Fig. 2 representing conditions at 57°C . for instance, we find from the polytherms of Fig. 15 that at this temperature this point represents a solution containing approximately 28 mols K_2Cl_2 , 3.5 mols Na_2SO_4 , 31 mols Na_2CO_3 and 27 mols Na_2Cl_2 per 1,000 mols of water. The composition of this solution may equally well be expressed as follows: 28 mols K_2CO_3 , 3.5 mols Na_2SO_4 , 3 mols Na_2CO_3 , and 55 mols Na_2Cl_2 . To locate this point we therefore measure 28 units to the left along the K_2CO_3 axis, then 3 units from this point in a direction parallel to the Na_2CO_3 axis, and then 3.5 units to the right from the latter point in a direction parallel to the Na_2SO_4 axis. This locates the point Eq. 2 on the plane surface of the diagram. To locate the point in the space model erect a perpendicular at this point having a length proportional to $28 + 3.5 + 3 = 34.5$ units. The other points are located in a similar manner. The space model is therefore formed by locating the various points Eq. 2, Eq. 3 U, R, etc., erecting the corresponding perpendiculars at these points, and properly connecting the ends of these perpendiculars. No perpendicular is erected at the point H since the solution at this point contains only Na_2Cl_2 and K_2Cl_2 .

Sodium chloride is not represented on the diagrams, because all the solutions represented are saturated with respect to this salt. Sodium tetraborate and sodium metaborate are not illustrated in the diagram because it has been found that the presence of these salts in an amount equivalent to 26 mols of B_2O_3 per 1000 mols of water, in the solutions represented by the diagrams, depresses the solubility of the sodium chloride somewhat, but produces no other marked change in the composition of the solution. Moreover, these diagrams represent equilibrium conditions which can be approached but not always attained in actual practice. Accordingly, although these diagrams are not strictly accurate in the presence of the borates, or under plant conditions, they are sufficiently accurate for practical purposes and indicate within fairly narrow limits the changes which will take place in the composition of a brine, and the salts which may be separated or redissolved, under any given set of conditions.

These or similar diagrams, therefore, in

conjunction with the data of the polytherms on which they are based, can be used in carrying out the process of the invention and enable the concentration and subsequent cooling of the brine to be regulated in the manner above described.

As above mentioned, the equilibrium diagrams of Figs. 1 to 5 inclusive, represent the composition of all possible aqueous solutions of the sulphate, chlorides and carbonates of sodium and potassium, saturated with sodium chloride at the temperatures indicated and containing an amount of sodium tetraborate not in excess of about 26 mols of B_2O_3 per 1000 mols of water. The space models, of which these diagrams are plane projections are constructed in the manner which has been described, and are bounded by the faces enclosed between the lines connecting the various points. Because of the relation between the different salts, the composition of any aqueous solution of the sulphates, chloride and carbonates of sodium and potassium, saturated with sodium chloride at the indicated temperature, may be represented by a point in the space within the space model. The limiting compositions at which the solution becomes saturated with respect to one or more salts and at which crystallization begins, are illustrated by the various faces bounding the space model and by the lines and points of intersection of these faces. Each limiting face represents all possible compositions of solution saturated with respect to the salt indicated and with respect to sodium chloride. Upon concentration at the indicated temperatures, the point representing the composition of the solution cannot pass outside of the space enclosed by these faces, but at saturation with any particular salt moves along the face corresponding to that salt which is being precipitated out.

Prior to saturation of the brine with respect to any salt other than sodium chloride, the point representing the composition of the solution will lie within the space bounded by the faces of the diagram; and, upon concentration, that is, water removal, the point will move in a straight line, away from the origin and only sodium chloride will be precipitated until it strikes one of the bounding faces. This will be apparent from the fact that the relative proportions of the other dissolved salts do not change, so long as water only is removed, until the point representing the composition reaches a boundary and precipitation of the salt then reaching saturation begins; after which the point will move upon this boundary face in a line governed by the change in composition, due to precipitation, until it strikes an edge of the face. It may then move upon this edge with simultaneous precipitation of the salts, or under certain conditions it may cross the boundary edge with precipitation of only sodium chloride

and the salt at saturation on the new face. The composition of the solution does not vary uniformly between the various equilibrium points and on the various crystallization areas. In order to represent exactly the compositions of all possible solutions these boundary lines and crystallization areas should be slightly curved, but for all practical purposes, the diagrams as shown are sufficiently accurate for use in the carrying out of the process of the invention.

It should be especially noted that the equilibrium conditions shown in these diagrams hold true only in brines saturated with respect to sodium chloride. Unsaturation with respect to this salt will alter the equilibrium relations of all the salts, sometimes to a very marked extent. In the practice of the invention it is necessary to maintain the brine saturated or nearly saturated with respect to sodium chloride during concentration. Brines which are deficient in chlorides but which contain the carbonates and sulphates of sodium and potassium can be concentrated by the process of the invention for efficient recovery of potassium chloride after addition of the necessary amount of sodium chloride. In the absence of sufficient chlorides to maintain the conditions shown in the equilibrium diagrams, and embodied in the process of the invention, serious loss of potash as glaserite may occur.

The application of the equilibrium data to the process of the present invention will be illustrated by specific graphic illustrations of the changes which take place in the composition of the brine during concentration by evaporation. We will use the equilibrium diagrams of Figs. 2, 3, and 4 showing the solubilities at 57°, 80° and 110° C. for this purpose. The origin O represents a brine saturated with sodium chloride but containing no other dissolved salt. Point A of Fig. 2 represents the original composition of a brine such as Searles Lake brine containing sulphates, chlorides and carbonates of sodium and potassium in solution but saturated with respect to sodium chloride only. Until this brine becomes saturated with respect to some other salt during evaporation, the increasing concentrations of the other dissolved salts will be in proportion to their original concentrations. The point representing the composition of this solution at any moment during evaporation will therefore move along the prolongation of the line OA until the point *q* is reached, at which point the solution is saturated with respect to sodium chloride and the salt represented by this face, in this case Burkeite.

During concentration by isothermal evaporation a solution in depositing its content gradually varies its composition away from that of a solution which is saturated with the substance being deposited and which con-

tains nothing but this substance. Such a solution in this case is represented by point α , the crystallization starting point for Burkeite. With further concentration, therefore, the composition of this solution will be represented by points along the line *q*—B lying in the Burkeite face and drawn from the point *q* through and away from the crystallization starting point for Burkeite. As the point representing the composition of the solution moves along this line, sodium chloride and Burkeite will be precipitated by crystallization. The crystallization paths of any other solutions saturated with respect to sodium chloride and Burkeite would likewise lie in the Burkeite face along lines drawn through and away from the point α .

With continued evaporation at 57° C. the point representing the composition of the original solution A would move along the line *q*—B—B' until it reached the edge of the glaserite face at point B'. Precipitation of glaserite would begin at this point and with further evaporation, provided no solid Burkeite were left in contact with the solution, the crystallization path would lie in a line drawn through B' in a direction away from the glaserite crystallization starting point β until the brine became saturated with respect to potassium chloride at point B''. Further evaporation would then give solutions having compositions represented by points lying along line M—Eq. 2 until the point Eq. 2 is reached, which is the crystallization end point. When this point is reached, no change in the composition of the solution will be caused by further evaporation but simultaneous precipitation of Burkeite, potassium chloride, sodium chloride and sodium carbonate monohydrate will take place.

It will be noted that under these conditions it is impossible to obtain a brine saturated with respect to potassium chloride without first causing formation and precipitation of the glaserite, with consequent loss of potash. If the brine should contain a higher concentration of sodium carbonate relative to the concentrations of the other constituents than is indicated for the point A, this point will be moved in a direction parallel to the sodium carbonate axis, or along the slope of the Burkeite face if Burkeite saturation is reached, to some higher position on the diagram representing the increased sodium carbonate concentration. With a sufficiently high concentration of carbonate, it can be seen that the crystallization path drawn from α through the new saturation point corresponding to point *q* will strike the edge of the sodium carbonate face instead of striking the edge of the glaserite face. Evaporation of such a brine would cause precipitation of only sodium chloride, Burkeite and sodium carbonate monohydrate until the brine be-

came saturated with respect to potassium chloride, but Searles Lake brine does not contain sufficient sodium carbonate to permit of such concentration during evaporation at a temperature of 57° C.

In the practice of our invention, however, we avoid the formation of glaserite through suitable regulation of the temperatures of evaporation and the amount of evaporation taking place at any one temperature. If evaporation indicated in this diagram is not continued to the point at which the brine becomes saturated with respect to glaserite but is stopped at some point such as B, no such precipitation of glaserite will occur. In the practice of our invention we ordinarily employ a triple effect evaporator; pass the mixture into the third or low temperature effect, in which the composition of the mixture is represented by point A, and continue the evaporation in this effect only until such a point as B is reached. The brine, from which precipitated salts have been removed, is passed into the second evaporator pan, in which the conditions are approximately as shown by Fig. 3 for 80° C. The concentration taking place in the second effect is represented by the crystallization path B—C lying in the Burkeite face at this temperature. Whereas continued evaporation at the lower temperature would have caused formation and precipitation of glaserite, it may be readily seen by comparison of the two diagrams that the area of the glaserite face is greatly decreased at the higher temperature and that the area of the Burkeite face greatly increased, so that at this higher temperature a much higher concentration of potassium chloride may be obtained before any formation of glaserite can occur. Fig. 4 showing equilibrium conditions at 110° C. indicates conditions existing in the first or high temperature effect of a triple effect evaporator. Reference to this figure shows that continued concentration of the brine represented by point C in the preceding figure will, at this higher temperature, cause concentration and crystallization along the line C—D with precipitation of only Burkeite, sodium carbonate monohydrate and sodium chloride until the brine becomes saturated with respect to potassium chloride. As may readily be seen the solubility of potassium chloride at this higher temperature is much greater than for either of the lower temperatures and the amount of potassium chloride which can be recovered by chilling of the brine to a given lower temperature is correspondingly increased. By such suitable evaporation at progressively increasing temperatures we have avoided all formation of glaserite and loss of potash, have obtained a brine highly concentrated with respect to potassium chloride, and have gained these desirable results while employing multiple ef-

fect evaporation and obtaining the great economy and efficiency which is thereby made possible.

By reference to Fig. 1, showing equilibrium conditions at 20° C., it will be noted that the crystallization end point Eq. 9 is in equilibrium with potassium chloride, sodium carbonate, heptahydrate, sodium chloride and glaserite. Since this point is in equilibrium with glaserite rather than with Burkeite, it is impossible under any conditions to concentrate the brine at this temperature until it becomes saturated with respect to potassium chloride, without also causing saturation with respect to glaserite. The highest concentration with respect to potassium chloride which can be obtained at this temperature without loss of potash, as glaserite, during concentration of brines similar to Searles Lake brine is therefore represented by the point Eq. 8. This point can only be reached, however, without loss of potash, as glaserite, when the brine contains high concentrations of sodium carbonate. A similar condition exists at all temperatures up to about 50° C. and in order to obtain saturation of Searles Lake brine with potassium chloride without separation of potash as glaserite final evaporation must in any case be effected at this or a higher temperature. The amount of carbonate naturally present in Searles Lake brine is insufficient to permit of saturation with potassium chloride without loss of potash, as glaserite at this temperature, however, and such saturation can be attained only through addition of substantial amounts of sodium carbonate to the brine or by completing the evaporation at substantially higher temperatures in the manner which has been indicated above. Preventing the formation of glaserite by completing the evaporation at higher temperatures, as carried out in the practice of our invention, is much easier and more economical than adding sodium carbonate.

In the actual evaporation of Searles Lake brine in multiple effect evaporators, according to this invention, the brine, temporarily, may not be completely saturated with sodium chloride. At ordinary temperature, Searles Lake brine is saturated with sodium chloride and also saturated or nearly saturated with Burkeite. On warming to the temperature of the first effect into which the brine is introduced, 57° C. for example, the solubility of the sodium chloride increases and that of Burkeite decreases. Warming alone without any removal of water will, therefore, precipitate Burkeite and render the brine unsaturated with respect to sodium chloride. Initially, for a brief interval, the brine in the low temperature effect will accordingly be saturated with Burkeite but not with sodium chloride. Similar solubility changes may take place in the brief interval during which brine is transferred between succeeding ef-

fects. This condition is only temporary, however, and saturation with sodium chloride is quickly restored. In continuous operation, where brine is introduced into the evaporators continuously or intermittently in small amounts, this condition can be ignored.

The foregoing illustrations have graphically represented the manner in which our equilibrium data may be used as a guide in determining suitable conditions under which concentration may be carried out. More accurate determination of the limiting conditions governing concentration at different temperatures may be obtained by calculation from the data of the polytherms. Our equilibrium diagrams and data may be equally well used to determine the changes which will take place in the composition of concentrated brines during cooling and to determine suitable conditions under which a high yield of pure potassium chloride may be economically obtained by cooling. Similarly, the data can be used to determine the necessary composition of the concentrated brine in order that during suitable cooling only the desired changes will take place and that only potassium chloride will be precipitated. It is obvious that concentration of the brine cannot be carried beyond the point at which it becomes saturated with respect to potassium chloride. As has been previously stated, however, the concentration must be carried at least to a certain minimum value, for if this is not done there will be a precipitation of sodium chloride and under certain conditions, glaserite together with potassium chloride when the brine is cooled. For any given temperature of evaporation, the minimum permissible concentration with respect to potassium chloride above which no sodium chloride will precipitate on cooling to say 35° , and below which concentration such precipitation of sodium chloride will take place, may readily be determined by means of our equilibrium data.

The conditions which exist during final concentration of a brine at 110° and cooling to 35° , for example, may be followed by reference to Fig. 5, which shows equilibrium diagrams for these two temperatures superimposed upon each other. Point C represents the initial composition of a typical brine entering the high temperature evaporator pan. With further evaporation the point representing the composition of the brine will move along the line C—D, with precipitation of sodium chloride and Burkeite, and from D along the line D—Eq. 2 with precipitation of sodium chloride, Burkeite, and sodium carbonate monohydrate until the crystallization end point, Eq. 2, is reached, or until evaporation is stopped at some point such as A. After evaporation is stopped and the solid salts which have been precipitated are removed, if the brine is cooled to 35° C. its com-

position will change, chiefly through deposition of potassium chloride, until it reaches equilibrium at some point, such as B, in the potassium chloride saturation face of the solid line equilibrium diagram for 35° . The changes which take place in the composition of the brine during such evaporation and cooling may be readily calculated from the data of our polytherms and will be briefly illustrated in the following example.

During evaporation at 110° C. from D toward Eq. 2 the concentration of the brine with respect to potassium chloride will increase, with respect to sodium carbonate and sodium sulphate will change but slightly, and the solubility and concentration of sodium chloride will steadily decrease. If evaporation is stopped at any point A between D and Eq. 2 and after separation of the precipitated salts the brine is cooled to 35° C., the solubility of the potassium chloride will decrease, causing crystallization and precipitation of this salt. The solubility of sodium carbonate and sodium sulphate increases, but in the absence of their solid salts the concentration cannot increase. During cooling the point representing the composition of the brine will therefore move along a line A—B parallel to the K_2Cl_2 axis until equilibrium at the lower temperature is reached at B. During this cooling, the solubility of the sodium chloride, which is shown in the complete data of the polytherms but not on the diagrams, may or may not decrease, to cause crystallization and contamination of the potassium chloride, depending on the extent to which the evaporation has been carried. For any position of the point A at which evaporation is stopped, between the limits D and Eq. 2, the corresponding values of B, after cooling to 35° , will not be greatly changed. A solution evaporated to any value A between these limits will therefore, on cooling to 35° C., reach a final composition B which is not very far from constant. It has been said that the solubility of sodium chloride decreases during evaporation from D toward Eq. 2. At D the brine will hold more sodium chloride, and at Eq. 2 will hold less, than can be held in solution at the more or less constant corresponding positions of B. In the first case, cooling will cause a decrease in sodium chloride solubility and objectionable precipitation; in the second case, cooling from Eq. 2, there will be an increase in solubility. At some position of A between the limits D and Eq. 2, therefore, the solubility of sodium chloride at the higher temperature, 110° C., will be the same as after cooling to 35° C. and in this case precipitation of sodium chloride to contaminate the potassium chloride obtained on cooling will just be prevented. This value of A can readily be calculated from the data of the polytherms, and represents the minimum concentration, to a value be-

tween which and the concentration represented by Eq. 2, the brine should be evaporated in order to obtain on cooling a potassium chloride salt free from sodium chloride.

Therefore, if evaporation of the brine is carried out under the suitable conditions which have been indicated until its composition is represented by some point between the minimum value A and the crystallization end point Eq. 2, the concentrated brine may then be cooled to 35° C. to give a high yield of potassium chloride free from sodium chloride. If separation of borax from the brine until after the potassium chloride has been removed is suitably prevented by rapid cooling as described below, the potassium chloride which separates from such a concentrated brine on cooling will be of very high purity. We have found that if the final evaporation is carried out at a temperature of 110° C., the maximum possible concentration representing saturation with respect to potassium chloride at this temperature is nearly 47 mols per 1000 mols of water and the minimum concentration to prevent separation of sodium chloride on cooling as indicated above is only slightly over 41 mols. These maximum and minimum values are indicated for various temperatures of concentration in Fig. 17.

It will be noted that as the temperature of evaporation is decreased from 110° C., the maximum and minimum values approach each other. At the higher temperature there is a fairly wide range within which concentration can be stopped without having caused saturation and precipitation of potassium chloride on the one hand, and without causing separation of sodium chloride when the brine is cooled, on the other hand. This safe working range becomes smaller and smaller, however, at the lower temperatures of evaporation.

The curves of Fig. 17 show very clearly the advantages gained in our process by completing the evaporation at a final high temperature. As the final temperature of evaporation is increased, it is possible to attain greatly increased concentrations with respect to potassium chloride and greatly increased yields of potassium chloride on cooling, and at the same time the permissible range of concentration within which the evaporation can be suitably stopped is increased to a considerable extent. Concentration at a final temperature of 110° C. followed by cooling to 35° C., for example, gives more than double the yield over concentration at a final temperature of 70° C. followed by cooling to 35° C. This is of great advantage in the commercial operation of the process, because of the increased yield and because limitations of mechanical and analytical control of the evaporation make it difficult, if not impos-

sible, to always carry the concentration exactly to the point of saturation with potassium chloride.

In order to promote the crystallization of pure potassium chloride and prevent borax from separating with it on cooling of the concentrated brine; it is important to cool the brine very rapidly, in not over two to three hours for example, and preferably much less, from the higher to the lower temperature. In practice, ordinarily it is carried from about 110° to about 30°. By rapid cooling in this way no appreciable amount of borax crystallizes out because of its slower crystallizing tendency. The borax remains in super-saturated solution and can afterwards be separated from the mother liquor by slower crystallization. We have found that the presence of sodium borates in moderate quantities does not appreciably affect the behavior of the other salts during concentration, and does not interfere with the separation of pure potassium chloride during suitable rapid cooling. On standing, however, for a further period of time the borax will crystallize out and can be recovered as one of the valuable products of the process. If the borate content of the concentrated brine is equivalent to not over 7 or 8% of sodium tetraborate, it is possible to produce potassium chloride, containing less than 0.5% borax by the method above described, and this figure may be materially reduced by operating under favorable conditions such as decreased concentration of borates in the concentrated liquor and more rapid cooling.

In the continuous operation of the process, the mother liquor, from which potassium chloride and borax have been largely removed by crystallization, may be advantageously returned to the process, together with certain wash liquors which will be further indicated, and admixed with the raw brine for further recovery of potassium chloride and borax. Such return of mother liquor and wash liquors will correspondingly modify the composition of the brine entering the evaporator, but this change in the composition of the brine is not ordinarily great enough to necessitate material change from the control conditions as outlined. Compared with the raw brine alone, the concentration of a mixture of mother liquor and wash liquor will ordinarily be higher with respect to sodium carbonate and potassium chloride. An increase of concentration with respect to potassium chloride alone increases the tendency towards formation of glaserite during evaporation. The increase of concentration with respect to sodium carbonate tends to reduce the tendency towards formation of glaserite and it will further be found that under normal conditions the crystallization paths of the feed liquor obtained by mixing raw brine, mother liquor and wash liq-

uors will not be greatly different from those indicated in Figs. 2, 3 and 4. As may be readily seen from study of the diagrams, however, a large return of wash liquors containing a high concentration of potassium chloride alone will increase the tendency towards formation of glaserite, particularly in the initial low temperature evaporation. Such unduly large return of potassium chloride liquors should therefore be avoided. By carrying out our process as indicated herein, however, we gain the advantages of economically evaporating the brine to a high concentration of potassium chloride, while preventing all loss of potash salts during concentration, and obtain a concentrated brine which, in the further step of suitable rapid cooling, gives a large yield of pure potassium chloride practically free from sodium chloride and borax, and we still further return the mother liquor for ultimate recovery of the potassium chloride and borax which remain dissolved therein at the end of each cycle.

The practice of our invention may be illustrated by the following specific example of procedure followed in treating Searles Lake brine of normal composition for the recovery of pure potassium chloride and borax. It will be understood that in actual operation of such a process it is difficult, if not impossible, to maintain absolutely uniform conditions and obtain theoretical efficiencies because of the limitations of mechanical equipment. Washing of crystallizers may give liquors high in potash which is best recovered by mixing the liquor with the mother liquor and raw brine fed to the evaporators and which will therefore slightly alter the composition of the mixed brine. Scaling of evaporator or cooler tubes may affect the efficiencies at various points in the process. These, and other factors, make an absolutely uniform control difficult, if not impossible, to attain in the commercial operation of the process. The following example, however, illustrates the process which is indicated by out data to be best suited to the economical commercial treatment of Searles Lake brine and which should be approached as closely as possible in actual operation. It is one of the marked advantages of our invention, however, that because of our comparatively exact knowledge of the limiting conditions under which the various steps in the process may be suitably carried out we have been enabled to choose normal operating conditions which permit the greatest possible latitude and ease of control. Efficient operation of our process on a commercial scale may therefore be carried out more readily and economically than has been possible in other processes which, in order to produce even low yields of satisfactorily pure potassium chloride, require that the operations be controlled within impractically narrow limits.

In the preferred practice of our invention as applied to Searles Lake brine, the volume of mother liquor remaining at the end of each cycle is such that by mixing one part of mother liquor with about 2.7 parts of raw brine, the process may be made completely cyclic, and this proportion of mother liquor and raw brine is regularly combined in the mixed brine which is fed to the evaporators. A typical analysis of raw Searles Lake brine is as follows:

	Grams.
Water	100.0
KCl	7.3
NaCl	25.3
Na ₂ SO ₄	10.3
Na ₂ CO ₃	7.7
Na ₂ B ₄ O ₇	2.5

A complete cycle of the process, assuming a producing of 100 tons of potassium chloride and neglecting mechanical losses, which may vary, is indicated below:

Raw brine and mother liquor are mixed in the proportions indicated in the following tabulation, and give the mixture which is further indicated below, and which is fed to the low temperature evaporator pan of a series of three evaporators operating in multiple effect:

	339,000 gals. raw brine.	143,000 gals. mother liquor.
Water	Tons. 1,370	Tons. 563
KCl	100	88
NaCl	346	80
Na ₂ SO ₄	141	9
Na ₂ CO ₃	105	70
Na ₂ B ₄ O ₇	32	

It will be noted that the amount of borates in the mother liquor is not indicated. In the operation of the process, a part of the tetraborate is converted to the metaborate and accumulates in the mother liquor. This difficulty is overcome by periodically discarding mother liquor or by reconverting metaborate in the plant liquor to tetraborate by any suitable method.

Mixture to low temperature evaporator—
532,000 gals.

2.7 brine	1.0 Mother liquor.
Water	1,873 tons.
KCl	188 tons.
NaCl	426 tons.
Na ₂ SO ₄	150 tons.
Na ₂ CO ₃	175 tons.
Na ₂ B ₄ O ₇	

The combined brines, having a volume of approximately 532,000 gallons, are fed into the low temperature pan of a triple effect evaporator, or the pan which has the highest vacuum and the lowest temperature. In this pan the temperature is maintained at ap-

proximately 57° C. and the following work will be effected during the time that the brine is evaporated in this pan:

Removed by evaporation, 366 tons water.

- 5 Removed by precipitation—Burkeite 101 tons, NaCl 60 tons.

From this evaporator pan approximately 444,000 gallons of brine will be transferred to the pan at next higher temperature. In this pan the temperature is maintained at approximately 80° C. and the following work will be effected during the time that the brine is evaporated in this pan:

Removed by evaporation, water 478 tons.

- 15 Removed by precipitation—Burkeite 63 tons, NaCl 136 tons.

From this pan there will in turn remain 318,000 gallons of brine which are transferred during the operation of the cycle to the high temperature pan. In this pan the temperature is maintained at approximately 110° C. and the following work will be effected during the time that the brine is evaporated in this pan:

- 25 Removed by evaporation, 517 tons of water.

Removed by precipitation—Burkeite 30 tons, NaCl 150 tons, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ 61 tons.

From this pan there will in turn remain 163,000 gallons of concentrated liquor of suitable composition for recovery of potassium chloride and borax by suitable cooling. This liquor will contain approximately the following:

	Tons.
35 H_2O -----	503
KCl-----	188
NaCl-----	80
Na_2SO_4 -----	9
Na_2CO_3 -----	70
40 $\text{Na}_2\text{B}_4\text{O}_7$ -----	60

In order to obtain pure potassium chloride from cooling of concentrated brine, it is absolutely essential that all other salts which have been precipitated during the course of the evaporation should be completely removed, and that the concentrated brine shall contain no solid salts in suspension. In order to effect such a complete removal of all precipitated salts during evaporation, we use salt traps for collecting such salts from each evaporator pan. These are so arranged that the brine from each pan is circulated through one of these traps where, due to slow circulation, the suspended salts are practically completely precipitated, after which the clear brine is largely returned to the same pan from which it was drawn. A part of the brine from the lower temperature pan, however, is passed on to the next evaporator pan as required to maintain suitable level in each pan. Two or more of these salt traps are used for each evaporator pan in order that one may remain in operation while the other is being emptied of precipitated salts, whereby continuous evaporator opera-

tion is maintained. Before emptying these salt traps, the precipitated salts are washed with raw brine for removal of the concentrated brine contained therein, such wash liquors being returned to the mixed liquors for further evaporation and recovery of their contents. Through proper use of such salt traps it is possible to obtain a concentrated liquor such as has been described above, which contains no suspended salts and from which pure potassium chloride, and substantially pure borax, may be obtained by suitable cooling.

Rapid cooling is carried out in order to bring the temperature down to approximately 30° C. within less than three hours. By means of such rapid cooling, in the absence of solid borax salts, crystallization of potassium chloride only will take place, the brine remaining in a condition of supersaturation with respect to borax. When the brine has reached the lower temperature and crystallization of the potassium chloride is practically complete, the cooled mixture of potassium chloride crystals and liquor is pumped into a settling tank and allowed to stand for about 20 minutes. At the end of this period, the clear liquor is sent to cooling tanks for further cooling and the sludge remaining in the bottom of the settling tank is sent to the centrifuges.

In the centrifuges, potassium chloride crystals are separated from most of the accompanying liquor and then washed with water to free them from the remaining liquor. The liquor and wash water mixture from the centrifuges is added to the liquor decanted from the settling tanks and sent to the cooling tanks. The potassium chloride salts are removed from the centrifuges and sent to the storage piles. These salts contain all the potassium chloride recovered in the process.

The combined liquor from the potash settling tanks and centrifuges is brought down to a temperature of about 20° C. in the cooling tanks and then transferred to storage vats where the sodium tetraborate, with respect to which the solution has been supersaturated, slowly crystallizes out. After this crystallization, which may take twelve hours or more, is completed, the mother liquor is allowed to drain off into a sump where it is mixed with raw brine for return to the process cycle. The remaining sludge, which consists principally of borax but contains considerable quantities of potassium chloride and mother liquor, is sent to a hot dissolver where it is heated to boiling with a sufficient quantity of water added to bring the sodium tetraborate concentration down to about 20%. The liquor is passed hot through a pressure filter and then cooled to about 40° C. in a crystallizer with agitation. The borax which separates is passed, together

with the borax mother liquor, to settling tanks. After a period of settling the clear liquor is decanted and the borax sludge dropped to centrifuges for removal of the remaining liquor, with a final wash in the centrifuges. No further purification of the borax is necessary. Decanted and wash liquors are returned to the process.

We claim:

1. An improvement in concentrating brines containing carbonates, sulphates and chlorides of sodium and potassium, which are substantially saturated with sodium chloride and contain less than the amount of sodium carbonate necessary to saturate the brine, which consists in evaporating the brine to a concentration less than that at which formation of glaserite begins, increasing the temperature and continuing the evaporation.

2. An improvement in concentrating brines containing carbonates, sulphates and chlorides of sodium and potassium, which are substantially saturated with sodium chloride and contain less than the amount of sodium carbonate necessary to saturate the brine, which consists in evaporating the brine above about 49° C. to a concentration less than that at which formation of glaserite begins and more than that below which sodium chloride will separate on cooling.

3. An improvement in concentrating brines containing carbonates, sulphates and chlorides of sodium and potassium, which are substantially saturated with sodium chloride and contain less than the amount of sodium carbonate necessary to saturate the brine, which consists in evaporating the brine above about 49° C. to a concentration less than that at which formation of glaserite begins and continuing the evaporation at a higher temperature to a concentration more than that below which sodium chloride will separate on cooling.

4. An improvement in concentrating Searles Lake brine, which consists in evaporating the brine in triplicate effect evaporators, first at a temperature of about 57° C., then about 80°, and finally about 110° C., transferring the brine to each successively higher temperature effect before formation of glaserite begins at the prevailing temperature and concentration, and evaporating the brine in the final effect to a concentration of more than about 41 mols of K_2Cl_2 per 1000 mols of water.

5. An improvement in concentrating Searles Lake brine, which consists in evaporating the brine in triple effect evaporators, first at a temperature of about 57° C., then about 80°, and finally about 110° C., transferring the brine to each successively higher temperature effect before formation of glaserite begins at the prevailing temperature and concentration, and evaporating the brine in the final effect to a concentration of

more than about 41 mols of K_2Cl_2 per 1000 mols of water and less than about 47 mols of K_2Cl_2 per 1000 mols of water.

6. An improvement in concentrating Searles Lake brine, which consists in concentrating the brine by evaporation at a final temperature of about 110° C. to a concentration of more than about 41 mols of K_2Cl_2 per 1000 mols of water.

7. An improvement in concentrating Searles Lake brine, which consists in concentrating the brine by evaporation at a final temperature of about 110° C. to a concentration of more than about 41 mols of K_2Cl_2 per 1000 mols of water and less than about 47 mols of K_2Cl_2 per 1000 mols of water.

8. An improvement in recovering potassium chloride from brines containing carbonates, sulphates and chlorides of sodium and potassium, which are substantially saturated with sodium chloride and contain less than the amount of sodium carbonate necessary to saturate the brine, which consists in evaporating the brine above about 49° C., to a concentration less than that at which separation of potassium salts begins and cooling the concentrated brine to a temperature at which sodium chloride is at least as soluble as at the final evaporation temperature.

9. An improvement in recovering potassium chloride from Searles Lake brine, which consists in evaporating the brine in triple effect evaporators, first at a temperature of about 57° C., then about 80°, and finally about 110° C., transferring the brine to successive higher temperature effects before formation of glaserite begins at the prevailing temperature and concentration and cooling the concentrated brine to about 30° C.

10. An improvement in recovering potassium chloride from Searles Lake brine, which consists in evaporating the brine in triple effect evaporators, first at a temperature of about 57° C., then about 80°, and finally about 110° C., transferring the brine to successive higher temperature effects before formation of glaserite begins at the prevailing temperature and concentration, cooling the concentrated brine to about 30° C., separating potassium chloride, further cooling the brine to about 20° C. and separating borax.

11. An improvement in recovering potassium chloride from Searles Lake brine, which consists in concentrating the brine by evaporation at a final temperature of about 110° C. to a concentration of more than about 41 mols of K_2Cl_2 per 1000 mols of water, cooling the concentrated brine to a temperature at which sodium chloride is at least as soluble as at the final evaporation temperature, separating potassium chloride, further cooling the brine and separating borax.

12. An improvement in recovering potassium chloride from brines containing carbonates, sulphates, chlorides and borates of

sodium and potassium, which are substantially saturated with sodium chloride and contain less than the amount of sodium carbonate necessary to saturate the brine, which consists
5 in evaporating the brine above about 49° C. to a concentration less than that at which formation of glaserite begins, continuing evaporation at a higher temperature, cooling the concentrated brine to a temperature at which
10 sodium chloride is at least as soluble as at the final evaporation temperature, separating potassium chloride, further cooling the brine and separating borax.

13. An improvement in concentrating
15 Searles Lake brine, which consists in evapo-

rating the brine in triple effect evaporators, first at a temperature of about 57° C., concentrating to a point just below that at which glaserite is formed, then stepping up the temperature to 80° C., and continuing the concentration up to a point just below that at which glaserite is formed at this temperature, and finally stepping up the temperature to 110° C. and concentrating at this temperature to a point just below that at which
20 glaserite is formed.
25

In testimony whereof we affix our signatures.

HARALD DE ROPP.
WILLIAM E. BURKE.