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PROCESS OF TREATING SALT MIXTURES.

No Drawing. Application filed December 13, 1918. Serial No. 266,606.

To all whom it may concern:

Be it known that I, FREDERICK WILLIAM HUBER, a citizen of the United States of America, residing at Riverside, in the county of Riverside and State of California, have invented certain new and useful Improvements in Processes of Treating Salt Mixtures, of which the following is a specification.

The present invention relates to the treatment of salt mixtures, such as occur in nature, and also such as are produced as by-products in some of the saline industries and elsewhere, which mixtures contain, as the principal ingredient, sodium chlorid or sodium sulfate, or a mixture of both, together with relatively small amounts of potassium chlorid or sulfate or both.

A saturated solution of sodium and potassium chlorids per 100 parts of water, contains: 30.6 parts of NaCl and 13.9 parts of KCl., this being at ordinary room temperature, say, 15 to 20° C. A solution containing potassium chlorid, sodium chlorid and potassium sulfate, and saturated for all three of these salts contains, per 100 parts of water, approximately 32.2 NaCl, 10.1 KCl, 4.7 K_2SO_4, this likewise being at about 15 to 20° C.

Accordingly, if a saturated solution of sodium chlorid is passed through, or is allowed to stand in contact with a mixture of solid salts consisting principally of NaCl and relatively small amounts of KCl or K_2SO_4, or both, a portion of the potassium salts will be dissolved, without dissolving any appreciable amount of NaCl, and such a solution can, if desired, be passed through successive batches of such mixed salt, until the same becomes substantially saturated with the potassium salts.

Instead of starting with a concentrated or saturated solution of sodium chlorid, I can start with a solution containing a small amount of potassium salts, or a small amount of sodium salts or a solution saturated with salt (NaCl) and containing a small amount of potassium salts, or, if desired, I can start with pure water but, of course, if the starting liquor is not saturated with sodium salts, it will take up the same from the solid material under treatment.

The solution of sodium and potassium salts, produced according to any of the above processes, can then be concentrated at or near the boiling temperature, until a density of 32 to 33.5° Be. (measured hot) is reached, during which operation sodium chlorid, and perhaps also sodium sulfate, will separate in solid phase, and can be removed in any convenient manner.

Having obtained, by any of the methods above referred to, a hot solution, substantially saturated with both sodium chlorid and potassium chlorid, either with or without some potassium sulfate, the liquor can be drawn off from the precipitated sodium salts, and can be allowed to cool, whereupon potassium chlorid (potassium chlorid and sulfate), in a high state of purity will crystallize. The mother liquor can then be returned to the evaporator and further concentrated, until it again becomes substantially saturated hot, with potassium chlorid (or chlorid and sulfate), during which operation sodium chlorid (perhaps mixed with sulfate) will be precipitated from the liquor, and can be conveniently raked out, but only relatively small quantities of potassium compounds will separate therewith.

In a different modification of the process, the hot solution obtained by any of the processes above described, and containing both sodium and potassium salts, especially in cases where sulfate predominates in the liquor, and where the liquor is saturated or substantially so, with respect to potassium, the liquor can be run into a hot concentrated solution of sodium sulfate, and this liquor can then be allowed to cool, during which operation glasserite, will at first crystallize, and this may be followed by a second crop of crystals of a double sulfate of sodium and potassium $x\ K_2SO_4\ y\ Na_2SO_4$ containing less potassium sulfate than glasserite. Successive batches of crystals can be produced from this mother liquor until a product containing potassium in amount equal to about 80 to 90% of the theoretical potassium content of glasserite is crystallized, whereupon this mother liquor can be again returned to the evaporator mixed with solution from any of the above described leaching processes.

In another form of execution of the process, magnesium sulfate solution may be used in place of sodium sulfate solution, in this part of the process. In using $MgSO_4$ solution, the potassium chlorid present is converted into sulfate, and this with sodium sulfate (either initially present or produced

from NaCl by interaction with $MgSO_4$) will form glasserite or a mixture of glasserite and K_2SO_4), or if less K_2SO_4 is present x K_2SO_4 y Na_2SO_4 (containing less potassium than does glasserite) might be formed and separate.

In a preferred form of operation of the present process, I start in with several, say, four or more, hoppers located at different levels, each filled with the crude sodium salts containing a small amount of potassium salts. To the uppermost of these hoppers is added fresh water, or a solution of sodium chlorid or other sodium salt solution, which may be of any desired concentration which is substantially free from potassium compounds, or at any event, is far below the point of saturation with potassium compounds. This liquor and salt are allowed to stand in contact with each other preferably at atmospheric temperature, with or without agitation until the liquor is substantially saturated with sodium chlorid, during which operation substantially the whole of the potassium content of the salt will be dissolved, but the resulting solution will be still far below its saturation point with respect to potassium salts. This liquor is then drawn into the next succeeding hopper, and allowed to stand therein until it has dissolved a considerable part, at least, of the potassium compounds contained in the salt therein, after which it may pass through several more of such hoppers containing the solid salts, until it leaves the last hopper substantially saturated with both potassium and sodium chlorids and with sulfates also if the same be present in the mixture. This solution is then run into a "salting evaporator," in which it is concentrated to the degree above referred to, during which operation sodium chlorid separates out, perhaps mixed with sodium sulfate. The remaining hot liquor is run from the evaporator into either the crystallizing vats in which the potassium chlorid (chlorid and sulfate) crystallizes out, or is run to the tank in which it is mixed with the hot sodium sulfate liquor.

The sodium sulfate employed in the process may, if desired, be the native sodium-sulfate, and the original starting material may, if desired, be a crude sodium chlorid containing a small amount of potassium chlorid, together with some sulfates, as produced in the recovery of potassium compounds from cement kiln flue gases, for example, as produced in accordance with the process of my co-pending application No. 235,992 filed May 22, 1918.

The crude sodium chlorid produced in the said process varies more or less, but has, on a particular date, had about the following composition:—

$NaCl$	95 %
Na_2SO_4	2.5%
KCl	1.8%
K_2SO_4	.6%

I find that with such a mixture, and by repeated leaching as above described, starting with fresh water, the end liquor contained approximately 6% of K_2O (as chlorid and sulfate) and was suitable for running into the evaporator.

What I claim is:

A process of treating a mixed salt consisting largely of sodium chlorid and containing smaller amounts of potassium compounds, which comprises systematically leaching the same with an aqueous liquid until such liquid has removed the major part at least, of the potassium compounds, and removing a part of the sodium chlorid and water from the liquor to leave the same substantially saturated with potassium compounds, adding the same to a solution of sodium sulfate and crystallizing therefrom a double sulfate of potassium and sodium.

In testimony whereof I affix my signature.

FREDERICK W. HUBER.