Oct. 30, 1945. R. D. PIKE 2,388,009

SOLUTION MINING OF TRONA

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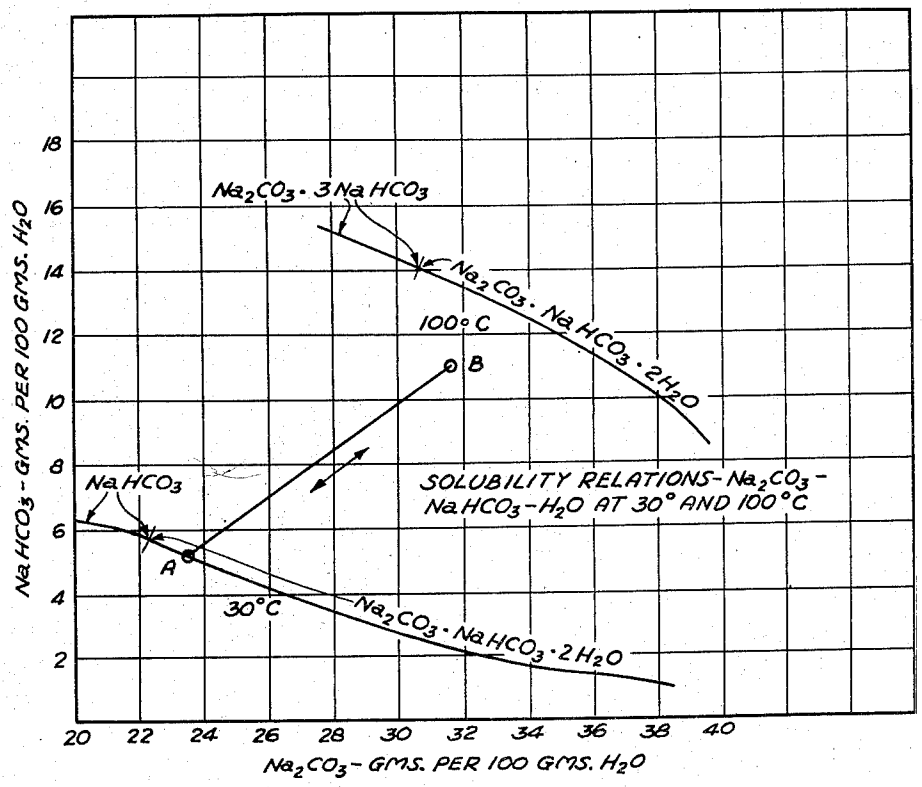
Fig. 1.



WITNESSES.
E. J. Maloney.
Fulton B. Flick.

INVENTOR.
ROBERT D. PIKE.

BY Brown, Critchlow & Flick
his ATTORNEYS.

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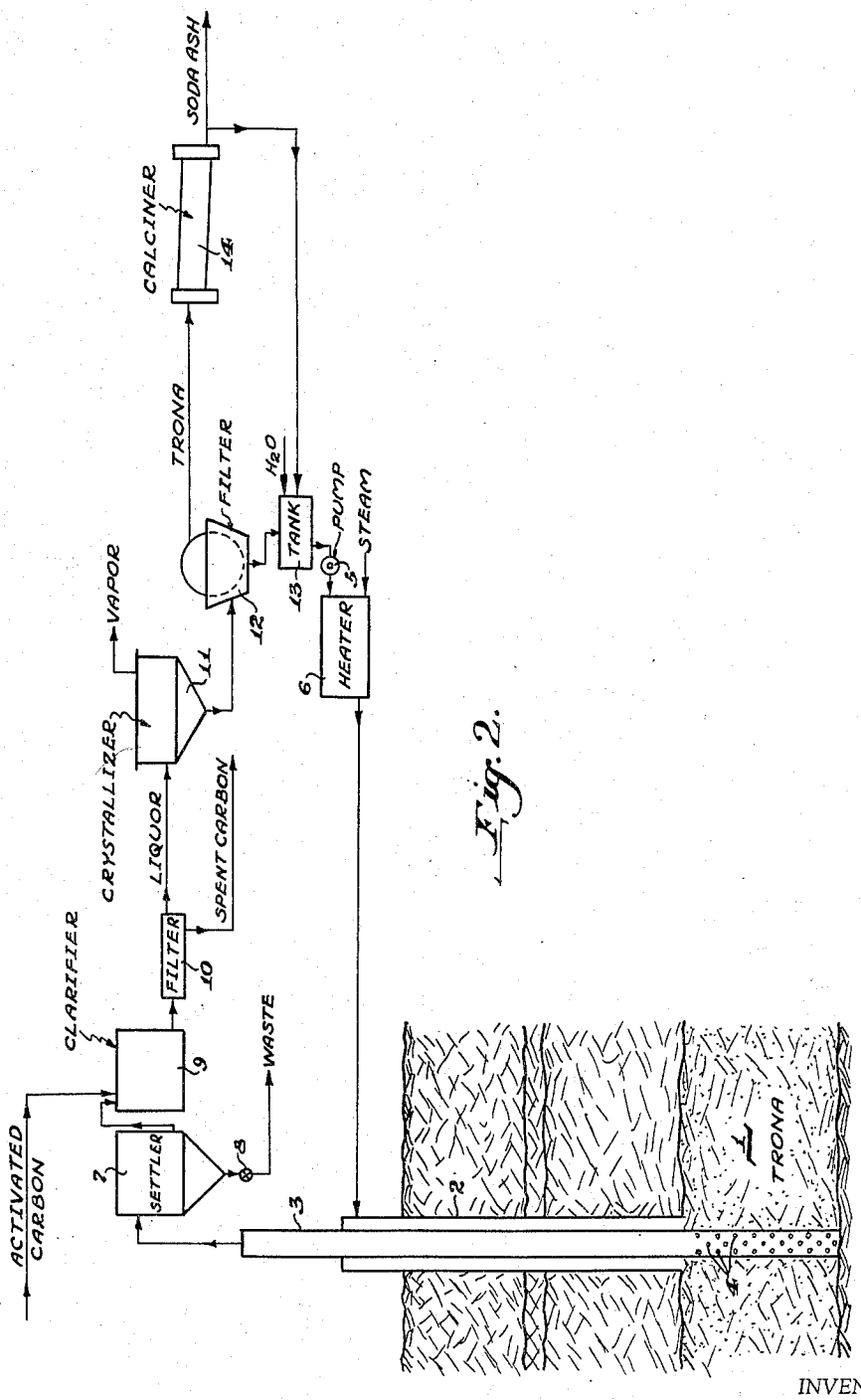

Fig. 2.

INVENTOR.
ROBERT D. PIKE.

BY Brown, Critchlow & Flick
his ATTORNEYS.

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SOLUTION MINING OF TRONA

Robert D. Pike, Pittsburgh, Pa.

Application October 19, 1943, Serial No. 506,841

5 Claims. (Cl. 23—38)

This invention relates to the mining of trona, especially by solution methods, and a major object of the invention is to provide a method of recovering trona from underground solid deposits which is simple, easily performed and efficient, and which results in a trona that is easily and cheaply converted into soda ash of acceptable commercial purity.

The invention will be described with reference to the accompanying drawings in which the graphs of Fig. 1 represent solubility relationships which are applied in the practice of the invention, and Fig. 2 is a flow sheet illustrating the preferred practice of the invention.

There has been discovered by core drilling in the Green River formation near Green River, Wyoming, a vast deposit of the mineral trona which in its pure state has the empirical formula $Na_2CO_3.NaHCO_3.2H_2O$. The soluble portion of this deposit, which averages at least about 95 per cent of the formation, is almost pure trona although typical analyses indicate that its content of the normal carbonate is slightly greater than corresponds to the empirical formula. Chlorides and sulfates occur only in traces, and the iron content is extremely low but is present, at least to a considerable extent, in the remains of organisms such as *Artemia salina*. The purity of this trona deposit would thus render it an ideal source of soda ash but the bed, which averages about 12 feet in thickness, occurs at a depth of about 1500 feet and is overlaid by well compacted sedimentary deposits. Mining of that formation by usual methods would, therefore, involve the sinking of deep shafts with the expense attendant upon it and upon manual mining methods.

In accordance with the the present invention a well is driven into the trona formation for the purpose of passing into it a brine of such composition and at such a temperature as to be capable of dissolving the trona in the bed. The resultant pregnant solution is then withdrawn and subjected to changed conditions to cause trona to be crystallized from it. The crystallized trona is recovered and the impoverished brine is then recirculated to the well to repeat the cycle.

In accordance with the invention there is used a brine which is capable of congruently dissolving trona i. e., a brine in which trona is dissolved and from which trona may be crystallized as such and without metathetical or other alteration of the trona constituents. Most suitably the brine contains sodium carbonate and bicarbonate, and preferably it contains substantially more of the normal carbonate than of the bicarbonate.

The solubility relationships that are made use of in practicing this invention with such a brine are as explained in my copending application Serial No. 385,092, filed March 25, 1941, now Patent No. 2,346,140, granted April 11, 1944, of which the present application is a continuation-in-part. Fig. 1 is a duplicate of Fig. 1 of that application. In that drawing the lower graph represents the composition of brines of sodium carbonate and bicarbonate at about 30° C., and the upper graph represents the relationships at about 100° C., and both graphs show compositions which are saturated with reference to sodium sesquicarbonate (trona). A brine saturated with sequicarbonate as shown by the lower graph is brought into contact with a body of natural trona which is to be recovered from the formation. By increasing the temperature the brine will dissolve the soluble matter from the trona, and upon cooling the resultant solution trona, or sodium sesquicarbonate, will be crystallized from it. Thus, a brine corresponding to the point A of the lower graph will contain, per hundred grams of water, approximately 5.4 grams of sodium bicarbonate and 23.4 grams of sodium carbonate. Upon heating this brine above 30° C. and contacting it with trona the composition of the solution will change along the line A—B, and upon cooling the resultant solution to 30° C. sodium sesquicarbonate will be crystallized out with progressive impoverishment of the solution with respect to sodium carbonate and bicarbonate. This action occurs along line A—B until the point A is reached, when the brine is reheated and used for further treatment of the trona bed.

The process may be described in greater detail with reference to Fig. 2, which is illustrative of its preferred embodiment. As shown there, the trona formation 1 is penetrated by a well which comprises an outer casing 2 that reaches at least to the upper level of the bed, and a tube 3 which is disposed concentrically within the casing 2 and which extends substantially to the bottom of the deposit. The portion of tubing 3 which is within the trona formation is provided with a plurality of perforations 4. Brine of appropriate composition, as indicated above, is passed by a pump 5 through a heater 6 and thence is forced, under the action of pump 5, into the trona deposit through the annular space provided between casing 2 and tubing 3. The brine supplied to the formation may advantageously be one which is in equilibrium with trona as the solid phase from about 20° to 40° C., and in passing through heater 6 it is brought to a temperature such that when

it comes into contact with the trona 1 it will be at a temperature substantially above the equilibrium temperature of the brine with respect to solid trona, which in this case is about 20 to 40° C., so that when it reaches the trona formation the brine will be capable of readily dissolving the trona congruently to form a pregnant brine which passes through the perforations 4 and is withdrawn through tube 3 for treatment to recover trona from it. The pump 5 is of sufficient capacity to maintain a suitable flow through the well in this manner, for example, at least 100 gallons per minute which, operating in accordance with Fig. 1, should result in production equivalent to about 50 tons of soda ash per day using brine that enters the well at a temperature of at least about 100° C.

The pregnant brine leaving the well will carry with it insoluble matter in suspension which should, of course, be removed to avoid contamination of the crystallized trona. To this end the pregnant brine is passed to a settling tank 7 provided with a blowdown valve 8 through which the insoluble sludge may be passed to waste. The iron contained in this trona is in a form which becomes colloidally dispersed and which is difficult to remove by ordinary methods. It may be removed readily, however, in accordance with the procedure described and claimed in my aforesaid copending application, in accordance with which the solution is intimately contacted with an adsorbent, most suitably activated carbon. Thereby the iron content of the pregnant brine is virtually eliminated. As applied to the present process, the partly clarified brine passes from settling tank 7 to a clarifier tank 9 where it is agitated with a charge of activated carbon that is subsequently removed in a suitable filter 10. To avoid premature deposition of trona in an impure state, the operations just described are preferably carried on in a closed system with the well, i. e., without reducing the pressure and without substantial cooling of the brine as it leaves the well.

The fully clarified brine is then ready for the crystallization step. In the embodiment shown it passes from filter 10 to one or more vacuum crystallizers 11 which, in effect, act as evaporators by utilizing the sensible heat of the liquid to effect evaporation by application of reduced pressure, which also results in a marked reduction of the temperature of the liquid. In short, the sensible heat of the liquid is converted into the latent heat of evaporation. Thus the brine becomes supersaturated with respect to trona and causes it to be crystallized congruently. The crystallized trona and mother liquor then pass to a filter 12. The mother liquor from the filter passes to a tank 13 and thence is recycled to the well by pump 5 as described above. The trona cake from filter 12 may be used as desired, e. g., by passing it to a calciner 14 where it is converted to soda ash.

The trona recovered in this manner is of high purity as evidenced by the fact that soda ash made by calcining it is pure white and shows upon analysis no chlorides or sulfates, about 0.01 per cent of insoluble matter, and 0.0008 per cent of iron. Washing of the trona crystals upon the filter is therefore ordinarily unnecessary but the crystallized trona will, in that case, remove water in the form of adherent mother liquor. This loss is compensated for by make-up water added to tank 13. Such removal of mother liquor will progressively remove sodium carbonate from the recycled brine but this may be corrected by the occasional addition to tank 13 of soda ash from calciner 14.

It will be understood from Fig. 1 that brines in equilibrium with trona at a temperature of about 30° C. (average of 20° to 40° C.) may be used, and that the brine is preferably heated so that when it meets the trona it will be at about 85° C. The longer the line A—B in Fig. 1, the greater the proportion of refined trona produced per cycle, and for this reason it is preferred to work with brines in the vicinity of point A, although any of the brines of the lower graph saturated with sesquicarbonate may be used. Thus, the brines used for treating trona and for recycling in accordance with the invention may contain per hundred grams of water from about 22 to 38 grams of sodium carbonate and from about 1 to 5.8 grams of sodium bicarbonate. The closer the point B comes to coinciding with the upper graph, the greater will be the amount of refined sesquicarbonate produced per cycle. However, as the point B approaches the upper curve the likelihood of loss of carbon dioxide, by decomposition of trona, increases. For this reason it is preferred to operate in a closed system and with the pregnant brine at a maximum temperature not much over about 100° C. The process may be carried out satisfactorily at about 85° to 100° C., which is my preferred practice, or even higher. Of course, with adequate maintenance of CO_2 pressure higher temperatures may be used. Likewise, the brine passed to the well may be of such composition as to be in equilibrium with trona at temperatures higher or lower than 30° C.

Other modifications are equally permissible without departing from the spirit of the invention. Thus, the pregnant brine may be merely cooled to obtain a crop of trona crystals, or it may be subjected to evaporation in other than vacuum crystallizers, the primary requisite being to alter the condition of the brine to effect crystallization of the trona which it has dissolved from the formation, which is accompanied by evaporation and cooling, either or both. Likewise, instead of using the single well shown in Fig. 2 the brine might be pumped into one or more input wells and caused to pass through the formation to a separate output well. The type of well shown in Fig. 2 is preferred, however, because the ingoing brine keeps the outcoming pregnant brine hot and thus presents premature trona crystallization.

According to the provisions of the patent statutes, I have explained the principle and mode of practicing my invention, and have illustrated and described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

I claim:

1. That method of producing soda ash from an underground deposit of Wyoming trona carrying organic matter and contained iron which comprises forcing into the trona formation under a pressure greater than atmospheric a heated cycling brine of sodium carbonate and sodium bicarbonate containing substantially more normal carbonate than bicarbonate and which is unsaturated with respect to trona and from which the dissolved trona may be crystallized congruently, withdrawing the pregnant solution from the formation, contacting the pregnant solution with an

adsorbent and thereby removing said organic matter and contained iron, separating the clarified solution from said adsorbent, crystallizing and recovering from the clarified brine refined sodium sesquicarbonate, calcining the crystallized sesquicarbonate to produce soda ash, and cycling the mother liquor from said crystallizing step to the formation.

2. A method according to claim 1 in which a portion of said soda ash is cycled to said mother liquor to maintain the ratio of normal carbonate to bicarbonate in the cycling brine.

3. A method according to claim 1 in which the cycling brine contains about 22 to 28 grams of sodium carbonate and 1 to 5.8 grams of sodium bicarbonate per 100 grams of water and is heated to at least about 85° C. as it is passed to the formation.

4. That method of producing soda ash from an underground deposit of Wyoming trona carrying organic matter and contained iron which comprises forcing into the trona formation under a pressure greater than atmospheric a heated cycling brine of sodium carbonate and sodium bicarbonate containing substantially more normal carbonate than bicarbonate and which is unsaturated with respect to trona and from which the dissolved trona may be crystallized congruently, withdrawing the pregnant solution from the formation, contacting the pregnant solution with an adsorbent and thereby removing said organic matter and contained iron, separating the clarified solution from said adsorbent, crystallizing and recovering from the clarified brine refined sodium sesquicarbonate with some of said brine adhering to the crystals, calcining said crystals with the adherent brine to produce soda ash, and cycling the mother liquor from said crystallizing step to the formation.

5. That method of producing soda ash from an underground deposit of Wyoming trona carrying organic matter and contained iron which comprises forcing into the trona formation under a pressure greater than atmospheric a heated cycling brine of sodium carbonate and sodium bicarbonate containing substantially more normal carbonate than bicarbonate and which is unsaturated with respect to trona and from which the dissolved trona may be crystallized congruently, withdrawing the pregnant solution from the formation, contacting the pregnant solution with an adsorbent and thereby removing said organic matter and contained iron, separating the clarified solution from said adsorbent, subjecting the clarified solution to vacuum crystallization and recovering refined sodium sesquicarbonate with some of the brine adhering to the crystals, calcining said crystals with adherent brine to produce soda ash, cycling the mother liquor from said crystallizing step to the formation, and cycling to said mother liquor a portion of said soda ash to maintain the ratio of normal carbonate to bicarbonate in the cycling brine.

ROBERT D. PIKE.