THE PRODUCTION OF
CAUSTIC SODA SOLUTION
FROM TRONA

Thesis

by

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THE PRODUCTION OF CAUSTIC SODA FROM TRONA

This problem concerns itself with the possibility of producing a reasonably pure concentrated caustic soda solution using trona as a starting material. It involves a carbonation process, purification of raw material and causticization with lime. Since soda ash costs a little less than three times what trona costs, the process has good commercial possibilities.

Trona is a double carbonate of sodium whose formula has been given by Lunge and others a $Na2CO3NaHCO3H2O$. It is a white crystalline solid which loses CO_2 easily and is decomposed in solution at about 21°C. into the two carbonates and water. It has been made in the crystal form in the laboratory. The largest supply of the salt is at Owen's Lake in California. This lake has no outlet and is fed by the Owen's River which brings down large quantities of the carbonates each year. In 1898, Lunge calculated the amount of trona in and around the lake to be 50 million tons. The lake water is not yet saturated so that a system of solar evaporation is used. The material from the evaporators is sacked and shipped under the name of Owen's Lake trona.

Methods of Analysis

In order to have some basis on which to work it was necessary to obtain an analysis of the raw trona. In 1922, W.J. Beman worked on the same material toward the same end by the Löweg process. His analysis showed the absence of appreciable amounts of potassium so that all salts are considered sodium compounds.

Since most of the acid constituents are carbonates of both normal and acid carbonate form, a method was found that would show the amounts of these quickly and accurately. A modification of the method given in"Quantitative Analysis" by Treadwell and Hall, was used. Five grams of the material was dissolved in water and diluted to exactly 500 cc. in a standard volumetric flask. Twenty cc. portions were then pippetted to an Erlenmeyer flask and five drops of phenolphthalein indicator added. Since sodium bicarbonate is neutral to phenolphthalein all the red color is due to the normal carbonate. Very dilute standard hydrochloric acid is then measured into the solution until the red color just disappears. At this point the normal carbonate has all been changed to the bicarbonate. Methyl orange indicator is added and the solution reititrated until neutral. In the first titration it is essential that no CO_2 be lost. As a safeguard against this, the acid is added very slowly and the point of the burette is held under the surface of the liquid.

Unless the acid is added very slowly and the normality is less than 0.3 N, it is very difficult to obtain reproducable results. The method also serves as a means of determining the relative amounts of the two carbonates, in which case the strength of the acid is not necessarily known.

The chloride content was determined by gravimetric analysis using silver nitrate as a precipitant according to the method outlined by Blaisdale in his "Quantitative Analysis". Several volumetric schemes were tried in an effort to obtain an analysis quickly but no satisfactory results were obtained. The gravimetric method consists essentially in preparing a solution of known amounts of material, precipitating the chloride with silver nitrate from the solution made acid with nitric acid, boiling the mixture in order to coagulate the precipitate, filtering onto asbestos in Gooch crucibles of known weight and weighing after drying to 200°C.

The other more important constituent is sulphate. Gravimetric methods were also followed in this case. Gooch filters consisting of asbestos in the ordinary Gooch crucible were prepared and ignited in a blast lamp. After cooling in a dessicater, they were carefully weighed. To a boiling, acid solution of the material, a hot saturated solution of barium chloride was added in sufficient quantity to be sure that the barium was in slight excess. The precipitate was allowed to stand over night. The supernatant liquid was decanted and the precipitate washed into the funnel. After drying at 110° until all the water had been driven off, the crucibles were again ignited, cooled in a desiccator and weighed.

Using the above outlined methods, the following analysis was obtained:

Total carbonates	74%
Na_2CO_3	41%
$NaHCO_3$	33%
NaCl	4.2%
Na_2SO_4	9%

No attempt was made to determine the amount of water contained or the quantity of insoluble matter present, both of which were considerable.

Need of Purification

It depends entirely on what uses of the caustic produced what impurities are allowable in it. In the case of soap manufacture, there would be no objection to the presence of chlorides. However, in order to have a generally marketable product, standard requirments must be met with regard to the purity of the caustic.

The only practicable method devi~~d~~sed was simply washing the very soluble impurities from the relatively insoluble sodium bicarbonate. Since the total carbonate content was over half normal carbonate, this portion had to be converted into the acid form. Two general methods of carbonation were tried, the wet and the dry.

Wet Carbonation

The trona was dissolved in as little water as possible, below 70°C. The temperature was raised no further because it has been shown that sodium bicarbonate loses carbon dioxide at that temperature in appreciable amounts. The solution was then filtered warm to remove the insoluble matter, largely sand and other silicate materials. The filtrate was then cooled and carbonated at the same time. Carbonation was effected by bubbling carbon dioxide through a jet in the solution. The carbonated solution showed marked supersaturation. Even upon cooling to as low as 0°C., violent agitation was required to precipitate the bicarbonate. It then came down in varying forms, but on standing for a short time was easily filtered and was mostly crystalline.
A preliminary run showed a yield of 45 grams of bicarbonate from 100 grams of raw trona. This is only about 56% efficient.

The next modification tried was the use of a saturated salt solution as a solvent for trona and then following the same procedure as before. Saturated salt solution dissolved only 6 grams of trona per 100 cc. of solution when warmed to 50°C. and continually stirred. A precipitate formed in the vessel as the trona went into solution. The salt solution was carbonated but with practically the same difficulties as before. The solubility of the bicarbonate was cut down and was easier to precipitate but there was a correspondingly smaller amount of it in solution, so that supersaturation was still a hindrance.

Because of the low efficiency of the process and the necessity of the use of heat and subsequent cooling to 0° or lower, this process was abandoned for the present in favor of the dry carbonation.

Dry Carbonation

A reference was found in Lunge stating that unhydrated normal sodium carbonate will combine with equimolal quantities of carbon dioxide and water to form two mols of the bicarbonate. From the formula assigned to trona it would appear as if there were enough water present for the reaction. This was tried by running carbon dioxide into a mass of the trona crystals. There was no appreciable absorption of the gas. Obviously it was necessary to add water.

In order to carry out this process an apparatus was set up as shown in Fig. 1.

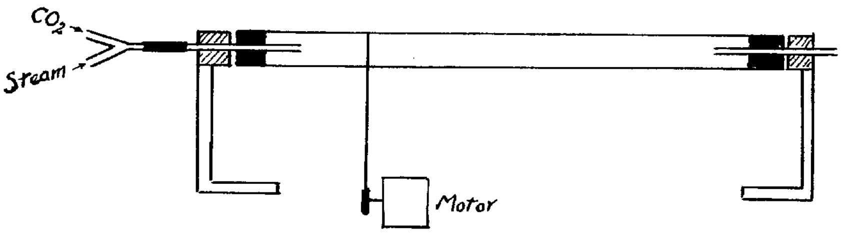


Fig 1.

Carbon dioxide was generated in a Kipp generator and mixed with steam in an ordinary T tube. The reaction tube was set in motion and the mixed gases sent in at a moderate rate. The solid did not completely absorb the gases as there was a considerable volume lost thru the exit tube. After a short time the reaction began and could be followed from one end of the tube to the other by the "hot spot". In one place the tube was several degrees higher than it was an inch on either side of the spot. Difficulty became apparent during the first run when the material was removed from the tube. It had formed an extremely hard cake on the walls of the tube and apparently was impervious to gas flow.

In run #1, 50 grams of trona was placed in the revolving tube. Carbon dioxide was generated from an excess of marble chips and 100 cc. of 6N HCl.

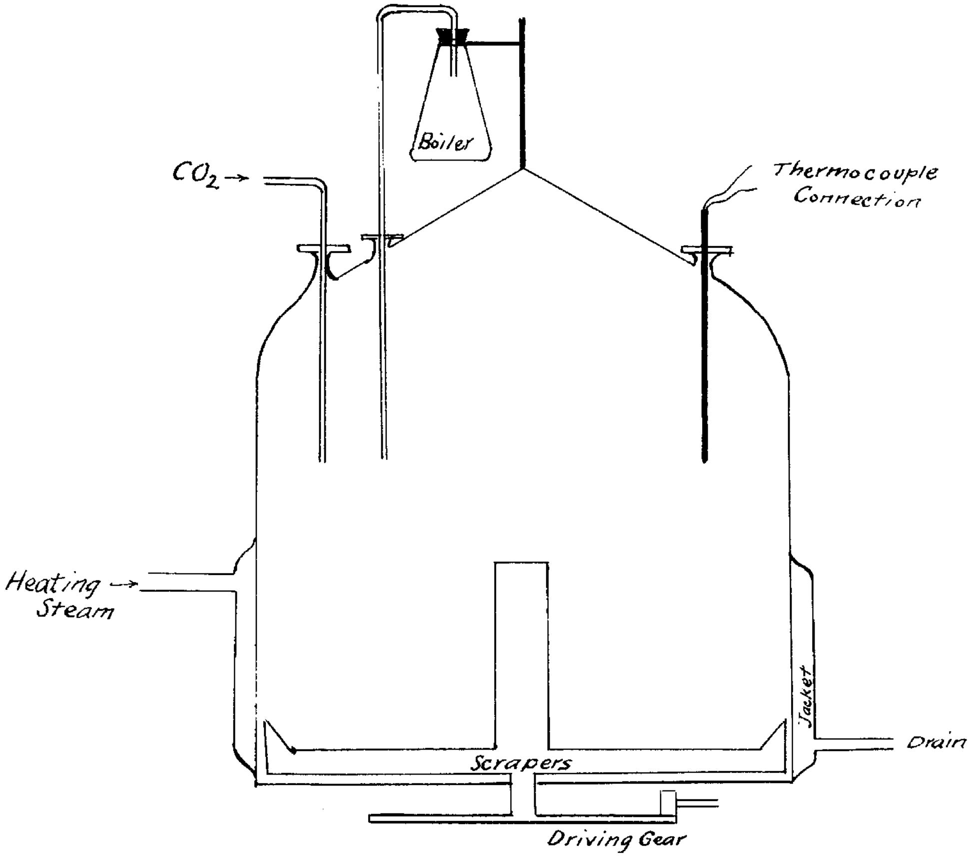
Twenty-five cc. of water was sent into the apparatus as steam. An analysis of the product showed only 90% of the total carbonates in the raw material. This was due to the addition of waterwhich was not entirely eliminated before sampling. The two carbonates were divided: 33% $Na_2CO_3$and 40% $NaHCO_3$. Calculation showed that only 26% of the CO_2 produced was retained in the solid and that a large excess of water was used. The results of this run were better than those of the wet method but unsatisfactory for use in a commercial scheme.

In the next run a different method was used. In order to maintain equimolal quantities of carbon dioxide and water the gas was bubbled through water held at a constant temperature at which the vapor press- of water equalled a half atmosphere. This temperature was calculated to be 80°C. No attempts were made to economize on gas as the rate of flow was fairly rapid and the carbonation extended over about three hours. In order to break up the cake which formed on the surface of the tube a number of steel rollers were intoduced. They did not accomplish their purpose after the cake had once been started. The results of this run showed the normal carbonate to be present as 17% of the total 74% of carbonates. This therefore, showed a decided improvement on any previous run.

The next run was the final small scale experiment and was carried out in practically the same way as those preceeding but with better control on the amount of water that was mixed with the gas. The temperature of the bath surrounding the flask through which the gas was bubbled seldom rose above 70°. The cake in the tube formed as before but was not nearly so hard and tenacious. Results of this run showd 90% conversion of the normal carbonate to bicarbonate. The success of this run may be attributed to the fact that the tube was heated by an improvised steam jacket consisting of a piece of stove pipe surrounding the reaction tube. Steam was blown into the space between and the reaction was accelerated to such an extent that the time taken for this run was less than either of the others and yet the conversion was practically complete.

The only piece of large apparatus approximating the conditions expected in specially designed carbonators that was available, consisted of a steam jacketed vacuum crystallizer, fitted with scrapers. A diagram of the complete set up is shown in Fig. 2. Steam was piped to the jacket and the temperature read by thermocouples. Carbon dioxide was introduced through a water trap which was kept at 75°. The gas was provided from a cylinder. During this run there was a leak in the

Fig 2.



Jacketed Crystallizer Used as a Carbonator which was not located so that no control of the pressure within the machine was possible.

After heating the inside up to the desired temperature of 60°C., the heat of the reaction and the entering steam kept the temperature at that point and even raised it two or three degrees. Under these conditions the gas was passed in for a period of 6 hours. The sample used was 25 pounds of trona put through a Braun Chipmunk jaw crusher. Seven pounds of carbon dioxide was used. It was apparent that water was being carried over by entrainment so that it did not enter the reaction space as vapor but as liquid. Since the material caked very easily if wet, the whole interior of the machine was found to be coated with a hard layer of the carbonated trona. Analysis showed that 96% of the normal carbonate had been converted to bicarbonate. This part of the process would have been satisfactory had it not been for the inconvenience of removing the finished product.

In the first run the material accumulated on one of the agitators and left the other idle. To obviate this difficulty twice as much material was used for a charge. Since the excess water was known to be causing the caking, two inlets were used, one for steam and one for carbon dioxide. The steam was generated in a graduated flask so that control could be kept on the rate of steam consumption. The carbon dioxide entered directly through another opening. This time the pressure was under control and served as a means of showing the speed of the reaction by the rate in which the gas was absorbed. During most of the run a pressure of one hal**f** inch of mercury was kept. This varied because it was impossible to keep step with the changing conditions with the crude controls on the gas flow.

Fifty pounds of trona were carbonated with 13 pounds of carbon dioxide and 4 pounds of water. No test could be obtained for sodium carbonate, showing complete conversion to the bicarbonate. In this run the material came from the machine in small round pellets averaging about 1/8" in diameter. It showed no further tendency to form a cake except on the flat surfaces of the iron where a comparitively loose coating was found.

The results of this run show beyond a doubt that with proper control of water added, trona can be carbonated on a large scale. There appears to be no reason why a long rotary carbonator would not be successful. Provisions for heating do not have to be elaborate because after the reaction has once been well started its own heat keeps the material up to the proper temperature. Moisture control would be a neessity, otherwise, the rolling action of the kiln-like carbonator would hot be enough to keep the trona from coating the walls and forming a solid cake. The last run in the vacuum crystallizer showed that it was possible to control the amount of water added until there was little or no tendency for caking.

The source of carbon dioxide offers some problems. The raw trona is 33% $NaHCO_3$ and 40% Na_2CO_3. After carbonation it is practically all changed to the bicarbonate. For the purpose of causticization a given amount of lime will produce twice as much NaHO from Na_2CO3 as it will from $NaHCO_3$. Therefore, between the carbonation and the causticization a heater can be placed which will drive off all the CO_2 held in the form of bicarbonate and leave the normal carbonate to react with the lime. Using this source of CO_2 the larger part of the gas required is provided for. The remainder can be obtained from either a burner or from limestone kilns. If the size of the plant warranted, a lime kiln would probably be used to produce the CaO used in causticization. The gas derived from either burning or from the lime kiln has the disadvantage that it is contaminated with nitrogen and carbon monoxide to say nothing of the possibility of some volatile material from the fuel. For this reason, it would probably be advantageous to carbonate in two steps. First with the impure gas and then finish with the pure CO_2 from the bicarbonate reduction.

Washing

Since the sodium bicarbonate is relatively insoluble as compared with the compounds which are impurities in this case, it should be possible to wash from the bicarbonate the chlorides and sulphates which render it of less value. Twenty-five grams of the completely carbonated trona were put into a Buchner funnel and washed with 25 cc. of pure water. Vacuum was applied and 22 cc. were drawn out of the mass. The solid showed a medium test for chlorides by use of silver nitrate. The same procedure was followed in a second trial.. This time the liquid was put through three times, being drawn off each time by vacuum. After this 10 cc. of pure water was put through. The solid showed no test for either chloride or sulphate.

After the first large scale run, a washer was constructed as shown in Fig. 3.

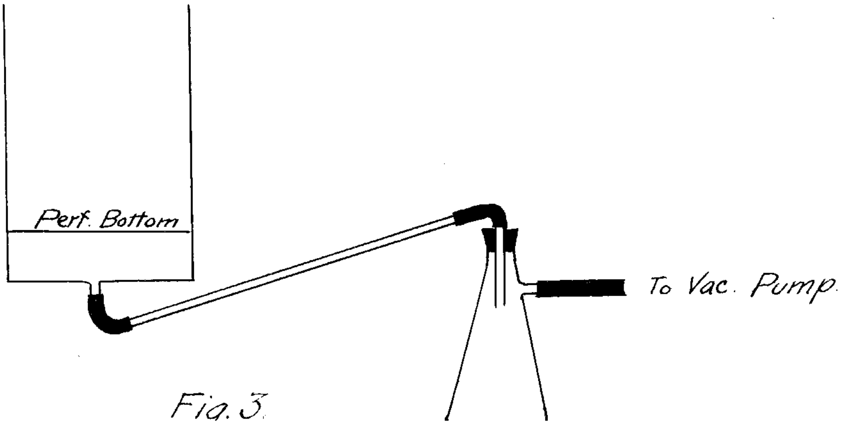


Fig. 3

It was constructed by soldering a false bottom onto a can after perforating the upper bottom. Material was put into the can until the cake was about 4 inches thick. Water was added a little at a time until a liter had gone into the solid. About half of this volume wad drawn off by vacuum and put through twice more. Two hundred fifty cc. of pure water was then put in and the vacuum applied. Tests of the solid showed marked chloride content.

As a small centrifugal was available, a run was made to see whether it would prove practical asa means of washing the material. Seven pounds of carbonated trona was added to enough water to form a thick sludge. This was put through the centrifugal and washed with about a quart of water. The solid, which was remarkably dry, gave a strong test for chloride. Since both of these methods failed and the laboratory experiment was successful, some difference in the conditions must have been responsible. The greatest difference was in the thickness of the cake being washed. In the laboratory experiment this cake was approximately $\frac{1}{2}$" in thickness and in the other two, much more than that. If a piece of apparatus could be devised to wash a large quantity of solid without forming a thick cake it ought to do the work. Such a machine is the rotary filter which runs continuously and forms only a thin cake. By specially designing the outlet ports, and mechanically controlling the wash water feed, it would be possible to use one of these filters with two different kinds of wash liquor. The sludge can be made up from a saturated solution of bicarbonate without seriously affecting the solubilities of the impurities in it. The first wash can be another saturated solution to be used only for that purpose, While the last wash should be pure water. Time and apparatus were not available for the large scale testing of this part of the process.

Causticizing

After the carbonated trona is washed free from the chlorides and sulphates, the wet cake which will be about 10% moisture, is run into a heater where the water and CO_2 from the $NaHCO_3$ is driven off. The gas is led back to the carbonators and Na_2CO_3 is left. At this point the product is identical with material being handled commercially at the present time. Further experimental work was therefore considered unnecessary and the following is an outline of possible operations to complete the production of caustic solutions. The first problem consists in getting the concentrations and proportions such that maximum yield is obtained in the shortest time using the least amount of CaO.

It has been found that concentrated carbonate solutions react faster with the lime but do not give as good yields. Lunge states that the optimum concentration for liquor to be causticized is one of 1.1 specific gravity. Such a solution contains 9.25% Na_2CO_3 and is approximately 2 normal. In an article* on the same subject it was stated that 2.5N solution reached equilibrium with the lime in ½ hour if well agitated. From these two statements it seems safe to assume the action to take about 40 minutes or an hour, if a slight excess of lime is used and the material well heated and agitated, using 2 normal solution of Na_2CO_3.

Apparatus has been designed to causticize continuously. It consists essentially of a series of agitated tanks through which the mud and solution are run in succession. Dorr thickeners are used as a first separation of solid and liquid. The nearly clarified liquor is filtered and run to the evaporators. The advantages of such a system are that a uniform solution is obtained and little attention need be paid to the

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*Le Blanc and K. Novotny "Z. anorg. Chem." 51 181-201.

outfit once it is started and regulated. Batch causticizers are commonly used. They are simply tanks fitted with agitators run mechanically or with steam jets. The lime is suspended in the tank in a grid to retain the large pieces. With these machines the process follows this general path: The carbonate solution of proper strength is put into the causticizer and brought up to boiling by steam heaters. The lime is then added always in the unslaked condition in order to utilize the heat of the reaction. After agitation from ½ to 1½ hours the suspension is allowed to settle for ½ hour. The clear liquor is drawn off by a swivel pipe and led to a settling tank where it is left perfectly quiet. The mud is agitated with enough water to form a sludge and again allowed to settle. The thin liquor is drawn off and used for the next run. After all these settling operations, the amount of solid in the liquid is so small that a filter press is practicable for separating the last of the suspension.

Concentration

The caustic solutions so produced are very dilute. They might be used as such if the demand and the supply were close enough together but for the purpose of shipping it is necessary to concentrate the solution. Many systems have been proposed and tried out. In a few cases the dilute liquor was used as boiler feed. This system proved successful as long as perfect control was kept on the boiler but careless operation caused great difficulty.

Multiple effect evaporators are generally used. Evaporation is carried on in these systems up to the point of concentration causing the precipitation of dissolved salts.

Summary

This process has been developed with the idea of using Owen's Lake trona as a starting material for the production of caustic soda solutions. The following results have been obtained:

1. The trona contains no impurity rendering it impractical for use in this process.
2. Trona can be converted to sodium bicarbonate by CO_2 and steam, quantitateively on a large scale, but requires careful regulation to prevent the product from absorbing too much water and becoming caked in the apparatus.
3. The chloride and sulphate content can be removed by washing after carbonation.
4. The produced material is the same as that used in industries already operating, so that the commercial application of the process is assured if the operations involved do not prove too expensive.

Acknowledgement

The writer wishes to thank Dr. W.N. Lacey, professor of Applied Chemistry at the California Institute, for his invaluable help and advice in gathering and putting together the data here set forth.

Bibliography.

Little material could be found on this subject, even on the widely practised commercial processes. The following literature was consulted:

Thesis--"The Löweg Process for Caustic Soda
using Trona as a Raw Material."
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"Sulphuric Acid and Alkali" by Lunge. 1909.

Several articles and analytical books noted in the text.