An Investigation on the Production of Sodium Thiosulfate from Trona

Thesis

by

Charles Fisher Ritchie

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The manufacture of motion pictures is one of the largest industries in California. Thruout the fabrication of the entire film many chemicals are employed. Materials used by the photographer have heretofore been manufactured almost exclusively in the east. The large firms there have developed the production of fine photographic chemicals to such a degree as to make successful competition by young firms on the Pacific coast virtually impossible. There exists, however, a good market for the cheaper materials whose initial costs are low as compared with their freight charges from New York to Los Angeles.

The most outstanding material in this class is sodium thiosulfate or hypo. Vast quantities of this chemical are consumed here annually. An examination of the availability of the raw materials on this coast and in New York is interesting. The two raw materials are sulfur and soda ash. Sulfur, which is produced in Louisiana and Texas, should be shipped by water as cheaply to this coast as to the New York market. We may obtain crude soda ash in the form of Trona from Owens Lake at a price comparable to soda ash on the east coast. Hence, we find the raw materials market in a very favorable condition for the production of heavy chemicals in direct competition with the eastern manufacturers. This work was undertaken in view of developing a process for the production of hypo from trona thru the laboratory and semi-works scale and to apply the knowledge so gained to the design of a plant.

The fundamental reactions of the process as exemplified by any text on inorganic chemistry are:

$$Na_2CO_3 + SO_2 = Na_2SO_3 + CO_2$$

$$Na_2SO_3 + S = Na_2S_2O_3$$

Trona, an impure mixture of Na_2CO_3, $NaHCO_3$ is produced by the solar evaporation of the saline waters of Owens Lake. Besides Na_2CO_3 and NaHCO there are also present small amounts of Borates, chlorides, sulfates, and silica.

The materials of vital interest to the process are Na_2CO_3, $NaHCO_3$, $Na_2B_4O_7$ and water.

Analysis of Trona.

A representative sample of crude trona was crushed and ground and placed in an air tight container for future use. It was found that the material, containing about 15% of water, could be very satisfactorily ground in a disc pulverizer.

Total Alkali. A weighed (4. grams) portion of the ground trona was dissolved and made up to 250 cc. A 25 cc. portion was titrated with standard HCl, using methol orange as an indicator. The 0.1N HCl was standardized against analytical Na_2CO_3 (Kahlbaum) using methol orange; the liberated CO_2 being boiled off just previous to reaching the end point.

Borates. To a 25 cc. portion of the above solution of trona the exact amount of standard HCl found in the above to be required to neutralize was added. The solution was boiled under a reflux condenser for several minutes to expel the CO_2. The vapors are condensed in order to prevent the loss of boric acid which is volatile with steam. The condenser was washed down and 35 cc. of glycerine, neutral to phenolphthalein, was added. The resulting solution was titrated to colorless with standard NaOH solution, using phenolphthalein as an indicator. From the net amount of standard NaOH found necessary to neutralize the final glycerine solution, the amount of $Na_2B_4O_7$ was calculated.

The NaOH used was prepared from Baker's stick NaOH. The $\overline{\overline{CO_3}}$ was removed with $BaCl_2$. The excess Ba^{++} was then removed with Na_2SO_4; c.p. chemical being used thruout. Upon standardizing the resulting NaOH solution against the standard HCl solution, using phenolphthalein and methol orange, two distinctly different ratios were obtained. Methol orange was titrated to a yellow and phenolphthalein to colorless. Tests showed that the Na_2SO_4 used did not cause the discrepency. The time being short, it was decided to recognize these ratios in the case of the two indicators and to forego further investigation on the subject.

Bicarbonate. Analyses for bicarbonate were found to be very unsatisfactory. The spot plate method of the Solvay Process Company was tried, but was not applicable in 0.1N solutions.

It was thought that the following method should prove satisfactory. To a 25 cc. portion of trona solution add a measured excess of standard NaOH, an excess of neutral $BaCl_2$ solution, and 35 cc. of neutral glycerine. Titrate the solution with HCl, using phenolphthalein as an indicator. Then, from the NaOH found to have been neutralized, the $NaHCO_3$ content of the trona may be calculated. Several analyses were made on this basis, but such widely varying results were obtained that the method was abandoned. It was found from trial analyses on a mixture of $NaHCO_3$ and Na_2CO_3 that the method described in Treadwell-Hall "Analytical Chemistry" (which is essentially the above analysis without the use of glycerine) gave very consistent results. If this analysis is employed in the presence of sodium borate, the $NaHCO_3$ will be reported low due to the formation of HBO_2. It was decided to titrate the trona samples by this procedure and to apply a correction for the small amount of $Na_2B_4O_7$ present.

Assuming that the trona consists of 1.2% $NaBO_2$ and that we have a .7 gram sample in 100 cc. of final solution, the concentration of BO_2^- would be 0.0013 molal. At change of color of phenolphthalein $(H^+) = 3 \times 10^{-9}$

$$\frac{(H^+)\ (BO_2^-)}{(HBO_2)} = K = 2 \times 10^{-9}$$

then $$\frac{(3 \times 10^{-9})\ (1.3 \times 10^{-3} - X)}{(X)} = 2 \times 10^{-9}$$

solving; $X = (HBO_2) = 0.00078$ molal.

Hence the concentration of HBO_2 at the change of color of phenolphthalein will be .00078 molal. Since the original concentration of BO_2^- was seen to be 0.0013 molal, it is evident that at the apparent end point the BO_2^- will have been 60% converted into HBO_2. In view of the nature of the analysis and of the relatively small error to be introduced by such assumptions, this procedure was adopted. The correction to be added to the amount of 0.109N NaOH used to neutralize the $NaHCO_3$ was 0.12 cc.

Water. Moisture was determined in the materials by heating a weighed sample on a sand bath for one to two hours at 250-300° C. and determining the loss in weight. This loss must represent the H_2CO_3 from the $NaHCO_3$, (the amount of which may be calculated) and the moisture.

The analyses showed the following for the composition of the trona:

Na_2CO_3	44.2%
$NaHCO_3$	37.1%
$Na_2B_4O_7$	0.9%
Water	15.2%
$NaCl, Na_2SO_4$ insoluble, etc. by difference	2.6%
	100.0%

In the process, as outlined, we shall acidify a solution of trona with SO_2. The two most vital points concerning the material are (1) its Na_2O content, and (2) the amount of water to be introduced by its use. This water consists of the moisture as reported in the above analysis and the water produced by the decomposition of the $NaHCO_3$. We may report the above analysis as:

Na_2O	39.8%
Available Water	19.2%
Foreign	41.0%
	100.0%

Method of Analysis of the Product.

In order to obtain comparative data on the amounts of hypo formed under different operating conditions, it is necessary that we have an analysis for sodium thiosulfate in the present of sulfite, bicarbonate, chlorides, etc. As a result of a survey of work done on this subject,* the following was accepted as a possible method of analysis:

The filtered product from a trial run is tested for $S^=$ with $HgCl_2$, in acid solution. An aliquot portion of the filtrate, containing about 10 grams of hypo, is removed and, if $S^=$ is absent, is made up to 250 cc. If $S^=$ is present, it is made slightly basic with 6 N NaOH, an excess of $Bi_2(CO_3)_3$ suspension added and digested for 15 minutes. The mixture is filtered and washed thoroughly and the filtrate and wash waters made up to 250 cc. To a 10 cc. portion of this solution, 10 cc. of freshly prepared NaCN solution is added, the vessel covered and heated on a water bath for an hour. The NaCN used should correspond to an excess of five times the amount required as shown by the equation

$$Na_2S_2O_3 + NaCN = NaSCN + Na_2SO_3$$

The solution is diluted to 200 cc. and the undecomposed NaCN titrated with standard $AgNO_3$ by the method of Liebig. From the amount of NaCN found to have been converted, the amount of $Na_2S_2O_3$ in the original sample may be calculated. The NaCN solution employed should be prepared just prior to its use, from the purest material obtainable. Its strength may be

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* Z. Anal. Chem. 46 (1907) 485, abs. J.Chem. Soc. 92 II (1907) 812
Chem. Ztg. 30 (1906) 58.Abs. J. Chem. Soc. 90 II (1906) 196.

determined by titrating a 10 cc. sample against standard $AgNO_3$ solution of a concentration of 0.1 normal or less. KI is added to the solution to facilitate the recognition of the first permanent turbidity. A solution of hypo was made up (about 0.5N) and standardized against the I_2 solutions of the quantitative analysis class, as well as against a standard solution, made up from a weighed amount of analytical (Kahlbaum) iodine; the two checking within 0.5%. Portions of this solution were run according to the proposed analysis. The results obtained for the concentration of the thiosulfate solution were about 4% higher than those found with the I_2 solution.

Comparison runs were made with and without $S^=$, having been present. The amounts of thiosulfate found in the cases where $S^=$ was present were seen to be about 4% lower than in the absence of $S^=$. This effect compensates the tendency of the analysis to give high results. A more thorough study of this analysis would be profitable. Since the available time was short and since at this stage of the process we were interested mainly in comparative results, it was decided to employ this procedure for analysizing the reaction products for $Na_2S_2O_3$.

Effects of Reagents upon Materials of Construction.

Hypo on steel. A piece of polished steel bar was placed in boiling hypo and allowed to stand for several days. The steel immediately turned black upon contact with hot hypo and the air. No pitting or corrosion was noticed when the surface was again polished. A test on the hypo after the treatment of the steel failed to show the presence of iron.

Trona on steel. A similar test was made, using a concentrated solution of trona. A discoloration of the polished surface was noted, but no pitting could be observed upon repolishing. Tests showed small amounts of iron present.

Sulfite on steel. A piece of polished steel bar was heated for several hours in a solution of Na_2SO_3. No immediate effects were apparent; the surface remaining bright. The material was allowed to remain in the solution for several days, producing a growth of sulfite crystals on the metal surface above the liquid. Upon cleaning the metal, a very decided pitting was noted, where there had been combined action of air and neutral sulfite.

Trona on enamel. A solution of trona was concentrated by intermittent boiling, over a period of several days, in a sample vessel of Elyria Enameled iron. No action upon the surface of the enamel could be seen.

Acid sulfite on enamel. A concentrated solution of acid sulfite was placed in the enameled dish for twenty-four hours. The acid sulfite was neutralized with trona, sulfur added and the mixture heated for several hours. No injury to the enameled surface could be noted.

Consideration of Working Conditions.

For a process in which a solid is to be obtained from solution, it is desirable that the amount of water entering into the process be as nearly a minimum as is consistent with other operations of the process. The other operations in this case are the saturating of the material with SO_2, stirring, cooking, filtering and crystallizing. As one extreme on the water problem, we have the possibility of producing sodium thiosulfate in such concentration that upon completion of the cooking operations, the ratio of anhydrous $Na_2S_2O_3$ to water shall be 158:90. Taking advantage of the fact that $Na_2S_2O_3 \cdot 5H_2O$ melts in its water of crystallization at 48° C., we might filter this concentrated solution hot, spread it onto a cold revolving iron drum and scrape off the solid as it cools. We could thus produce a sodium thiosulfate in small flaky chips which would be far more easily dissolved than the common crystaline form. Evaporators and their operating costs could be dispensed with in favor of this simpler and less expensive process. The most apparent difficulty to be encountered in such a scheme is the handling of a hot, concentrated syrup in filter presses. Crystalline sodium thiosulfate may be heated as high as 110° C.. and may even cool considerably below 48° C. without crystallization taking place. Even if the treatment of such a concentrated solution should prove feasible with commercial apparatus, there is always the possibility of having to chip hypo out of apparatus or to melt it out of pipe lines when the plant is suddenly shut down. The question of the purity of the product so produced is an important one. The extent to which the soluble unconverted matter and impurities of the raw materials would be carried into the final product can only be determined by experiment. It seems reasonable to expect a considerable quantity of such impurities. Whether these impurities would be detrimental to the utility or salability of the product can only be conjectured at this time.

Experiments showed that the least possible ratio between trona and water during its saturation with SO_2 was 1 : 1.5. This ratio was only possible when part of the water was added in successive portions as the gas was being introduced. The ratio of 1 : 2 was found to be the minimum where a batch process was employed. In all cases these figures are based on the assumption of the immediate saturation of the wetted trona. If the material is allowed to form the deca-hydrate, the mass becomes quite unworkable at these proportions. If this method of working with sludges is adopted, the saturation with SO_2 would have to be effected in kettles. This would be more complicated and costly than the use of wooden saturating towers which could be employed in the case of true liquids. Much difficulty is experienced with frothing in concentrated solutions, necessitating the use of oversize apparatus.

Upon the addition of sulfur and subsequent cooking, the mass was found to become very viscous, necessitating the further addition of water to permit the use of a power stirrer. Any reaction between materials in two different phases requires intimate mixing. Rapid stirring is essential in this process. The high power and attendant installation costs to be dealt with in the handling of concentrated materials will offset to a large extent the advantages to be gained by such a process.

A consideration of the above has led to the point of employing at least three parts of water to one part of trona. This is about five times the figure originally considered, which has been seen to be quite impracticable.

A more practicable plan is to treat a solution of trona with SO_2 in saturating towers, to boil the sulfite liquors so formed with sulfur in open kettles, filter, evaporate and crystallize.

Tests were made to determine the dilution necessary to prevent the precipitation of $NaHCO_3$ in the process of saturating the solution with SO_2. From a consideration of the amount of $NaHCO_3$ to be formed from the Na_2O content of the trona, it was shown that the maximum concentration was 18.5 grams of trona per 100 parts of water at 20° C. Such a solution was prepared and saturated with SO_2. No solid $NaHCO_3$ appeared. When 24 grams of trona was dissolved in 100 cc. of water and SO_2 passed in, a large precipitate of $NaHCO_3$ separated.

75 grams of trona was placed in 250 cc. of water and heated on a water bath for several hours. A small amount of trona remained indissolved. Further experiments showed the solubility of trona, so treated, to be 27 grams per 100 cc. of water. It was also found that, when this saturated solution was treated with SO_2 at 20° C., no $NaHCO_3$ separated out. A consideration of the composition of trona and its reaction with H_2SO_3 will serve to explain this phenomenon. When an excess of Na_2CO_3 is acidified with SO_2, the following reaction takes place:

$$2\ Na_2CO_3 + H_2SO_3 = 2NaHCO_3 + Na_2SO_3$$

From this reaction it is seen that one mol. of Na_2CO_3 produces one mol. of $NaHCO_3$. In the analysis of trona, we saw that it contained 44% Na_2CO_3 and 37% $NaHCO_3$. If 100 grams of trona be acidified, then we have 37 grams of $NaHCO_3$, plus 35 grams produced from the Na_2CO_3, or a total of 72 grams of $NaHCO_3$. However, if the trona solution be first boiled, the bicarbonate is decomposed;

$$4\ NaHCO_3 + heat = 2\ Na_2CO_3 + H_2O + CO_2$$

$$2\ Na_2CO_3 + H_2SO_3 = 2\ NaHCO_3 + Na_2SO_3$$

Hence, it is seen that the bicarbonate to be encountered is reduced by an amount equal to one-half the $NaHCO_3$ content of the original trona. The $NaHCO_3$ to be produced in a solution of 100 grams of boiled trona will be that coming from the Na_2CO_3 content, 35 grams, and one-half the amount originally present, 18.5 grams, or a total of 54 grams, as compared with 72 grams to be produced from a solution of "raw" trona.

From the above it is seen that the saving in water to be evaporated, by the use of boiled trona solution, is about 25%. In the design of a plant the heat from the sulfur burner might be utilized in treating the trona solutions. The added cost of a heat exchanger and wooden storage tanks is more than offset by the increased capacity of the plant to be gained in handling a 25% more concentrated liquor, as well as by the saving on evaporation charges. The question was thus raised as to the economy to be gained by utilizing waste heat in cooking the trona solution instead of in evaporating the 25% excess water at some later step. A consideration of the heats of formation, as given by the Landolt-Bornstein tables, of the substances involved should settle this point.

$$2\ NaHCO_3 + 20{,}800\ calories = Na_2CO_3 + H_2O + CO_2.$$

From the above it is seen that the heat necessary to decompose one mol. of $NaHCO_3$ is 10,400 calories. The heat required to convert the bicarbonate content of 100 grams of trona, will be 4,600 calories. In experiments it was found that a saturated solution of cooked trona (100 grams of trona in 375 cc. of water) could be saturated with SO_2 without precipitating bicarbonate. If 25% excess water (94 grams) be used in the case of raw trona, the heat required for its evaporation, from and at 100°C., will be approximately 50,000 calories. Hence, it is evident that a large saving of heat is made possible by pre-cooking the trona solution.

A substantial reduction in water to be evaporated can be realized in the process by the further saturation of the sulfite to acid sulfite and subsequent neutralization of the resulting solution with a calculated amount of trona. The great disadvantage of this system lies in the fact that acid sulfites are more injurious to materials of tower construction, either wood or iron, than are neutral sulfites. The procedure also produces a rapid evolution of CO_2, which tends to cause the materials to froth out of their containers. In trial experiments on this procedure, it was found that the powdered trona, when stirred into the acid sulfite liquors, showed a very great tendency to cake. This caked material redissolved very slowly.

There is also a considerably decreased efficiency of absorption of SO_2 when the solution of trona is run to the acid sulfite instead of to the neutral sulfite. A weighed amount of trona and water were placed in a flask fitted with an intake tube for SO_2 and a $CaCl_2$ tube through which the evolved CO_2 was allowed to escape. SO_2 was introduced and the gain in weight noted. It was found to be almost impossible to obtain better than a 98% conversion of the sulfite to bisulfite, even with the concentrated gas from a SO_2 cylinder. The economy on evaporation and the increased capacity of the plant, to be gained by the use of such a system, must be carefully checked against the increased cost of towers, appliances to prevent frothing, and the caking of the solid matter, as well as the loss of absorption efficiency on SO_2. The available time being short, it was decided to treat a concentrated (cooked) solution of trona with SO_2, heat with an excess of sulfur, and examine the yields produced.

Time of heating and the effect of the acidity of the sulfite liquors are of vital interest in the commercial production of hypo. An indicator was desired which would give a fairly accurate indication of the condition of the sulfite liquors. The following considerations served to define the characteristics desired in such an indicator.

100 grams trona in 375 cc. of water when converted to Na_2SO_3 produced a solution containing 200 grams of Na_2SO_3 per liter (1.6 molal). Let us assume the ionization of such a solution to be 50%.

$$\frac{(H^+)\ (SO_3^=)}{(HSO_3^-)} = K = 5 \times 10^{-6}$$

If we assume the indicator to change (a) when 0.1% and (b) when 0.5% of the sulfite has been converted to the acid sulfite, we have:

(a) $$\frac{(H^+)\ (.8)}{(.0016)} = 5 \times 10^{-6}$$

$$(H^+) = 10^{-8}$$

(b) $$\frac{(H^+)\ (.8)}{(.008)} = 5 \times 10^{-6}$$

$$(H^+) = 5 \times 10^{-8}$$

An examination of the characteristics of the more common indicators showed litmus and rosalic acid changing color at $(H^+) = 10^{-7}$ which is as near the desired (H^+) as is possible to obtain.

Results of Trial Runs.

It was decided to make trial runs under constant conditions of dilution and varying conditions of acidity and to note the yields produced with varying time of heating.

A one liter distilling flask was fitted with a mercury seal stirring apparatus. The side neck of the flask was bent upward thru 90° and attached to a reflux condenser. 100 grams of trona was dissolved in 375 cc. water and the solution saturated with SO_2 until a 10 cc. portion (boiled to expel the CO_2) showed only a slight pink with rosalic acid. This solution was shown to contain $NaHCO_3$ by its effervescence when treated with a solution of H_2SO_3. The solution was placed in the distilling flask with 35 grams of sulfur (an excess of 75%). The mixture was heated on a water bath and kept vigorously stirred by a small, direct connected, fan motor, equipped with a rheostat to control its speed.

After heating one hour, the material was removed from the flask, suction filtered, and the volume and temperature of the filtrate noted. A portion of this filtrate was taken for analyzing. The remainder, together with the sulfur, was replaced and heated for another hour; when another sample was removed. Four such samples were taken.

These samples were analyzed as follows: The sample was made up to 250 cc., A 10 cc. portion was taken and the $S^{=}$ removed with $Bi_2(CO_3)_3$. The solution was filtered and the precipitate of Bi_2S_3 thoroughly washed. 10 cc. of KCN solution was added and heated for one hour. The excess KCN was determined with standard $AgNO_3$ according to the method of Liebig, using KI as an indicator. The washings from the Bi_2S_3 precipitate so diluted the $Na_2S_2O_3$ that practically no reaction ensued between it and the KCN. This difficulty was overcome by removing the $S^{=}$ from the original sample and making it up to 250 cc. with the wash waters. This analysis is given on page 6.

Time did not permit further trial runs on basic solutions. It may be stated, however, that the reaction between Na_2SO_3 and S had taken place to a considerable extent at the end of the first hour of heating, as evidenced by the fact that the sulfur residue filtered was found to weigh only about 14 grams. A similar run was made on a sample of trona which had been treated with SO_2 until slightly acid. The analysis on page 6 was applied to the product obtained after three hours heating. Three samples were analyzed. The amounts of the standard $AgNO_3$ solution required for each of these three samples varied widely. A mean of these showed a 70.8% yield of $Na_2S_2O_3$ from the original trona.

Experiments were made to determine the reasons for these varying results in analyses. Pure KCN was titrated against the standard $AgNO_3$, using varying amounts of KI indicator. The results obtained showed that the amount of KI used had no effect upon the end point.

Tests were made to determine the approximate degree of reversibility to be expected as the excess cyanide is removed from the final solution by titration. 20 cc. of 0.6 molal Na_2SO_3, corresponding to six times the amount to be formed from a sample of hypo upon analysis was added to the 275 cc. of solution of the completed analysis, containing the slight turbidity of AgI. After standing cold for one hour, none of this precipitate had dissolved, showing a non-reversal, under these conditions, of the reaction,

$$Na_2S_2O_3 + KCN = Na_2SO_3 + KSCN.$$

When heated for an hour, the precipitate was seen to redissolve, requiring about 2% more $AgNO_3$ to restore it. Hence, it was concluded that, under the conditions of dilution and temperature of the analysis , the reversion of the reaction to be encountered during titration would be negligible.

A consideration of the left hand member of the above equation shows that, in the case of **incomplete** conversion of the hypo, the error introduced upon titration with $AgNO_3$ is not only that produced by the action of the KCN, but also an effect produced by the dissolving of the end point precipitates by the hypo.

The method of analysis on page 6 had been previously tried and found applicable on solutions of pure hypo, so the assumption was made that it was applicable to the products of the trial runs. The excess of NaCN solution added is calculated on the basis of a 100% conversion of the Na_2SO_3 to $Na_2S_2O_3$. The analysis reaction between $Na_2S_2O_3$ and NaCN is reversible and may be expressed by the equilibrium equation

$$\frac{(SO_3^{=})\ (SCN^{-})}{(S_2O_3^{=})\ (CN^{-})} = K$$

Let us assume that the filtrate from the run contains only 50% of the calculated $S_2O_3^{=}$; the remainder consisting of unconverted $SO_3^{=}$. From a consideration of the above equation, we find that the concentration of $S_2O_3^{=}$ at equilibrium in this case must be less than in the case when the filtrate contains the calculated (100%) amount of $Na_2S_2O_3$.

This is seen to vindicate the assumption that the proposed method of analysis should be applicable to the analysis of reaction products.

However, the facts of the case have not, in the limited number of analyses made, been in accord with this assumption. Results of these analyses have been widely varying. It was concluded that, to continue the study of the process by means of trial runs, the method of analysis must be thoroughly studied and adapted to the conditions found in the filtrates.

Summary.

A study was made on the production of sodium thiosulfate from trona in view of its development thru the laboratory and semi-works scale to the design of a plant.

Methods of analysis were developed for the control of the process. Improvement of the analysis of the product was found necessary.

Action of the raw materials and the products upon materials of construction was studied.

A preliminary recommendation was made on the basis of this work.