

THESES 1922

- Alles, Gordon A A new acridine dye.
- Ames, Paul R The specific heat capacity of heavy petroleum products.
- Beman, Willard JF The Löwig process for caustic soda using trona as a raw material.
- Bridgeford, Frank R. A process for the utilization of pyrite ash.
- Burks, Jesse C Semi-works development of a germanium extraction process.
- Gillies, Robert W An attempt to dehydrogenate cottonseed oil.
- Knight, Alfred W Perchloric acid from ammonium perchlorate and oxides of nitrogen.
- Reynolds, Maynard S The utilization of a deposit of magnesite located near Porterville, California as a source of raw material for the manufacture of C.P. Epsom salts.
- Ritchie, Charles Fisher An investigation on the production of sodium thiosulfate from trona.
- Vesper, Howard G The preparation of carbon monosulphide and hydrocyanic acid by the use of activated carbon.
- Warner, Lester O The reaction between nitrogen and methane in the silent electric discharge.

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THE LÖWIG PROCESS FOR CAUSTIC SODA,
using
TRONA AS A RAW MATERIAL.

Thesis

by

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I Introduction

Caustic soda is one of the more important heavy chemicals and has wide industrial use. It would probably have greater use, if it were not for its high present cost.

Trona is a combination of Na_2CO_3 , NaHCO_3 , and H_2O . The formula to which it most nearly corresponds is $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$. There are large natural deposits of trona in various parts of the world. Large quantities are crystallized from Cwen's Lake, Inyo County, California, during the summer months. There are several plants around the lake for this purpose and the product is relatively cheap. This raw material offers the possibility of producing caustic soda at a lower cost provided a suitable process can be developed.

The quantities of the various salts in the brine have been estimated, in millions of metric tons, to be as follows: Na_2CO_3 - 46.6; NaHCO_3 - 11.08; Na_2SO_4 - 19.4; NaCl - 51.5; KCl - 5.53; $\text{Na}_2\text{B}_4\text{O}_7$ - 3.55.¹

II Previous Work

There have been two methods used for making NaOH from Na_2CO_3 . The most used method is by causticizing with $\text{Ca}(\text{OH})_2$. The other method has had very limited use and is known as Löwig's process.

The following description of Löwig's process is from Lunge² (British patents 7364 of 1882, 591 of 1897, 4227 of 1897, and 1974 of 1887).

¹Chemical and Metallurgical Engineering, 24 (1921) 683-8.
See also: Lunge, Sulfuric Acid and Alkali, vol. 2, part 1, 71-7.
Jour. Am. Chem. Soc., 28 (1906) 1164-70.

²Sulphuric Acid and Alkali, vol. 2, part 2, 821-3.
See also: Jour. Soc. Chem. Ind., 2 (1883) 280.
16 (1897) 1015.

An intimate mixture of sodium carbonate and ferric oxide, when exposed to a bright red heat, expells CO_2 and sodium ferrite (NaFeO_2) is formed, which is quickly decomposed by hot water into NaOH and Fe_2O_3 . The Fe_2O_3 must be pure, especially free from alumina and silica, and is used as a granular powder. The heating is done in two stages, the first being at a cherry-red heat for $\frac{3}{4}$ of an hour, which prepares a mass held together by fused sodium carbonate - it is then powdered, well mixed, and heated in a muffle for another $\frac{3}{4}$ of an hour, by which time all of the CO_2 should be driven off. The melt is dark green, heavy, hard and of a sandy and grainy texture. The mass is then washed with cold water to remove soluble impurities, after which the NaOH is leached out with hot water at a temperature of $70-80^\circ \text{C}$. The leaching takes about a half hour. On cooling, a few flakes of Fe_2O_3 settle out. The Fe_2O_3 can be used over and over again. The process immediately yields a caustic solution of specific gravity 1.32 - 1.38. Löwig³ later found that the process is practicable only with a very pure soda, the impurities preventing an intimate contact of the Na_2CO_3 and Fe_2O_3 , and their fusion prevents the escape of CO_2 . It is necessary to remove the CO_2 or the reaction would soon be stopped by the atmosphere of the pure CO_2 .

Precipitated Fe_2O_3 is not suitable for the process, since it yields a ferrite difficult to extract, on account of the oxide being separated as a fine mud⁴.

³ See also: Jour. Soc. Chem. Ind., 7 (1888) 122.

⁴ Jour. Soc. Chem. Ind., 2 (1883) 280.

The article on British Patent No. 4364⁵ states that soluble impurities removed by the cold wash are " Na_2SO_4 , NaCl , Na_2CO_3 , etc."

It was decided to try the Löwig process for several reasons. The Löwig process yields a solution of specific gravity 1.32 - 1.38; the lime process a specific gravity of 1.075 - 1.100. A much purer product is secured by the Löwig process for the common impurities in NaOH made by the lime process (NaCl , Na_2SO_4 , etc.) are removed by the cold washing. The main disadvantage with the Löwig process is, apparently, that of the heat required.

III Experimental

A qualitative analysis⁶ of an average sample of trona showed:

Na^+	large amount
K^+	none
Ca^{++}	small amount
CO_3^-	large amount
SO_4^-	about 1% (estimated as SO_4^-)
Cl^-	about 2% (estimated as Cl^-)
B_4O_7	possible trace

There was a relatively small amount of dirt, insoluble in acid.

In all succeeding work the trona was dried over conc. H_2SO_4 .

Sulfate was determined gravimetrically. A known weight of trona was dissolved in water, acidified with conc. HCl , heated to destroy HCO_3^- and CO_3^- , filtered to remove insolubles, and finally the sulfate was calculated as SO_4^- and results were 1.98% and 1.92%.

⁵ Jour. Soc. Chem. Ind., 6 (1887) 438.

⁶ Method of A. A. Noyes, Qualitative Analysis, 8th edition.

The insoluble material in the sulfate determination was filtered thru previously dried and weighed filters. The filter papers and residues were dried and weighed. The insoluble matter thus found was 1.36% and 0.53%.

Na_2CO_3 and NaHCO_3 were determined by the following procedures. Total alkali was determined by adding an excess of standard HCl to a solution of the sample, boiling to drive off CO_2 and then titrating the cold solution with standard base for excess acid, using methyl orange as an indicator⁷. To determine NaHCO_3 an excess of standard base was added to a solution of the sample. The carbonate was then precipitated with BaCl_2 and filtered off. The excess base was then determined using standard HCl with phenolphthalein as indicator. This method was not entirely satisfactory as a few very fine particles of BaCO_3 would come thru the filter and were not removed by repeated filtration. Boiling before filtration did not help. However, the same amount of these particles seemed to be present after the end-point was reached as when the titration with the acid was started. Na_2CO_3 is calculated by difference between total alkali and NaHCO_3 .

The determination of Cl^- volumetrically⁷ consists of adding ferric ammonium sulfate to the solution and a few drops of standard KCNS to impart a red coloration. Standard AgNO_3 is added until the solution is decolorized and then a few additional drops are added. The AgCl is filtered off and the filtrate and washings are titrated with KCNS for excess AgNO_3 . Several analyses gave widely divergent

⁷ Method from Solvay Bulletin No. 3.

results. It was then found that the coloration disappeared before all of the chloride had been precipitated. This method was therefore rejected because of the difficulty of determining whether or not all the Cl^- had been precipitated without adding a large excess of AgNO_3 . It was thought that K_2CrO_4 would be a better indicator.

The first run was made using 19 grams trona and 27 grams commercial Fe_2O_3 . The mixture was placed in an iron crucible and heated with Tirril burners for 25 minutes. Judging by the appearance there seemed to have been a small conversion to sodium ferrite, leaving much unconverted carbonate. The mass was heated at a higher temperature for an additional hour, at the end of which the conversion appeared much larger. The mass was then removed from the crucible (it was found necessary to use a hammer and steel spatula to loosen the material), pulverized and placed on an asbestos suction filter and washed with 30 cc. cold water. Hot water (40 cc.) was then passed thru the filter with apparently no effect. The mass was transferred from the filter to a beaker, the hot filtrate added and heated for 25 minutes at a temperature of 70-95° C. and then refiltered thru asbestos. The filtrate contained a small amount of Fe_2O_3 . Repeated filtering thru quantitative filter papers did not entirely remove it. The filtrate was diluted to 100 cc. and portions were analyzed for total alkali and for NaOH , Na_2CO_3 being obtained by the difference. Total alkali was determined by titrating with standard HCl using methyl orange as indi-

cator. NaOH was determined by precipitating the carbonate, filtering off, and titrating for NaOH using standard HCl with phenolphthalein as indicator.⁸ The analysis showed 5.6% Na_2CO_3 and 0.98% NaOH. The result for Na_2CO_3 was calculated as a percentage of the Na_2CO_3 which would be present if all the sodium were in that form. The result for NaOH was calculated in a similar manner. In the analysis given above this means that 5.6% of the total sodium was present in the hot leach as Na_2CO_3 , and 0.98% was present as NaOH. This left 93.38% ($100 - 5.6 - 0.98$) of the total sodium unaccounted for. It may have been in the cold wash or it may have remained with the Fe_2O_3 residue. All the results in the following analyses are given on this basis. It might be said here that, in this and all succeeding runs (unless noted), a clear filtrate was obtained when the precipitated BaCO_3 was filtered off for the NaOH analysis. Qualitative tests showed the presence of appreciable amounts of Cl^- and $\text{SO}_4^{=}$.

The second run was made using larger quantities of trona and commercial Fe_2O_3 - 30 grams trona, 33 grams Fe_2O_3 (10% excess over theoretical). The mixture was placed in a crucible and heated as in the previous run for 45 minutes. There seemed to be but little conversion and practically no tendency to fuse. The second heating of the mass was for one hour. This time a Meeker burner was used and the crucible and burner were surrounded by asbestos forming an air bath which gave a much higher temperature. Judging by appearance, a fair conversion was obtained - also there seemed to

have been some fusion during the second heating. The mass was transferred to a beaker, 55 cc. of cold water was added and allowed to stand over night. After filtering thru asbestos the filtrate had a little Fe_2O_3 which was filtered out thru a filter paper, the resulting filtrate being clear and having a yellow color. On standing for some time a precipitate settled out which on filtering was found to be light yellow in color. The filtrate was still yellow. Analysis showed the solution to have 7.7% NaOH and 23.0% Na_2CO_3 . Hot water was passed thru the filter. No appreciable change was seen in the amount of the precipitate but the water, on analysis, showed 0.07% NaOH and no Na_2CO_3 . After analyzing the cold wash water some of it was heated to boiling for several minutes. A light yellow crystalline precipitate settled out and the yellow color remained in the solution. The mixture, after the cold wash was filtered off, was transferred to a beaker, 45 cc. of hot water was added and kept at a temperature of 80-95° C. for 40 minutes and was then filtered. The filtrate was freed from Fe_2O_3 by a second filtration (thru paper) and analyzed. The analysis showed 3.2% NaOH and 3.3% Na_2CO_3 .

At this point references were found indicating that the natural iron oxide should be used. However, the third and fourth runs were made with the commercial Fe_2O_3 , to see what effect, if any, strong heating of the Fe_2O_3 before use would have on the results. The Fe_2O_3 used in run No. 3 was strongly heated in a muffle furnace for 35 minutes before use, whereas that used in run No. 4 was

not heated. In these runs, and the succeeding ones, shallow iron pans, rather than iron crucibles, and a muffle furnace, having a suction draft to remove the gases formed, were used. In other respects, these runs were similar to No. 2. Analysis for total alkali in the hot leaches showed 3.6% in No. 3 and 7.7% in No. 4.

While waiting for some red haematite to arrive a couple of runs were made using heated limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). The limonite was crushed and heated in a muffle furnace to a bright red for $1\frac{1}{2}$ hours. The heating changed the limonite from a yellowish brown color to a dark red. Thirteen grams of trona were used with 15 grams of the heated limonite, corresponding to 10% excess Fe_2O_3 , on the assumption that all of the water had been driven off from the limonite. The mixture was heated at a low red for 45 minutes, was pulverized, and heated for 40 minutes at a high red heat. Cold water (45 cc.) was added to the mixture and it was allowed to stand over night. The cold wash water was filtered off thru asbestos and then filtered thru paper to remove a little Fe_2O_3 . The filtrate came thru clear and was yellow in color, but on standing became cloudy. A second filtration cleared the solution but it again became cloudy on standing. The cloudy solution was acidified with HCl, which removed the cloudiness and left a clear yellow solution. A little KCNS was added giving a deep red coloration. The yellow residues on the filter paper were apparently insoluble in hot water but dissolved readily in dilute HCl and gave a deep red coloration with KCNS. The yellow coloration was apparently due to colloidal iron.

The analysis of the cold wash water was not made. The hot leach showed, on analysis, 10.8% NaOH and 26.5% Na_2CO_3 . The hot leach solution was very slightly yellow and gave a test for iron.

The sixth run was similar to the fifth, reutilizing the Fe_2O_3 from the fifth run. After adding cold H_2O , the mixture stood for several days. Analysis showed (in percent):

NaOH			Na_2CO_3			Total alkali
cold wash	hot leach	total	cold wash	hot leach	total	
19.6	19.0	38.6	28.1	15.1	43.2	81.8

The cold wash was yellow in color and it was found that by boiling for 5 to 10 minutes, cooling and filtering, a clear, colorless solution could be obtained, which did not cloud up on standing.

The seventh and eighth runs were made at the same time and similar to the previous run. Red haematite (Fe_2O_3) was used in both runs. Run No. 7 used 10 grams C.P. Na_2CO_3 with 17 grams of haematite while run No. 8 used 14.5 grams trona (Na_2O content was the same as in the Na_2CO_3) and 17 grams haematite. A second hot leach of 2 hours duration was made to see if it would account for any more alkali. This second hot leach (and all subsequent leachings and washings) were made in a beaker, using an inverted 'T' stirrer driven by a small motor. This gave continual stirring instead of occasional stirring by hand as in previous runs.

The results of the analysis were:

	NaOH			
	cold wash	1st hot leach	2nd hot leach	total
No. 7 C.P. Na_2CO_3	2.4	37.5	0.0 ^x	39.9
No. 8 trona	0.8	33.0	0.7	34.5

	Na_2CO_3				Total Alkali
	cold wash	1st hot leach	2nd hot leach	total	
No. 7 Na_2CO_3	7.0	17.5	15.7 ^x	40.2	80.1
No. 8 trona	4.7	15.2	10.3	30.2	64.7

^x Probable loss due to spattering.

The ninth and tenth runs were made together - No. 9 using the Fe_2O_3 from No. 7 with C.P. Na_2CO_3 and No. 10 using the Fe_2O_3 from No. 8 with trona. The time for the cold wash was reduced to $\frac{1}{2}$ hour and the hot leach was lengthened from $\frac{1}{2}$ hour to 2 hours. Except for the conditions noted, the runs were made the same as the previous runs. The analyses on the runs were spoiled so that no results were obtained.

Runs No. 11 and No. 12 were made together and were made the same as No. 9 and No. 10. Run No. 11 used C. P. Na_2CO_3 with the Fe_2O_3 from No. 10. Both the cold wash and hot leach waters had to be boiled to free them from iron. Analyses for the runs showed:

	NaOH		
	cold wash	hot leach	total
No. 11 C.P. Na_2CO_3^x	0.3	20.4	20.7
No. 12 trona	13.4	41.7	55.1

	Na_2CO_3			Total Alkali
	cold wash	hot leach	total	
No. 11 C. P. Na_2CO_3^x	4.8	8.1	12.9	33.6
No. 12 trona	18.0	10.6	28.6	83.7

^x very small loss due to breaking bottom of iron pan while transferring to beaker after heating.

The solutions from runs No. 7 to No. 12 inclusive were tested qualitatively for chloride and sulfate. The Na_2CO_3 runs showed no sulfate and only a trace of chloride, due to the reagents or water. With the trona the hot leaches appeared to have about 0.1% each of chloride and sulfate (estimated as Cl^- and SO_4^{--}) while the cold wash waters in general showed from two to four times as much chloride and sulfate as the hot leaches.

There still seemed to be a considerable loss of alkali and an appreciable amount of the NaOH is obtained in the cold wash. It was thought that when working with large quantities it would be possible to cut down on the amount of cold wash water used with the result that the amount of NaOH removed by the cold wash might be decreased. Runs No. 13 and No. 14 were made together, run No. 13 using three times as much C.P. Na_2CO_3 as in No. 11 and run No. 14 using three times as much trona as in No. 12. The excess of Fe_2O_3 over theoretical requir-

ed was increased from 10% to 20%. Iron crucibles were used instead of shallow iron pans. Fifty cc. of water (same as for previous runs) was used for the cold wash. For the hot leach the water used was increased from 30 cc. to 70 cc. It was necessary to heat both cold washes and hot leaches to free them from iron. Analyses showed:

	NaOH			Total Alkali
	cold wash	hot leach	total	
No. 13 C.P. Na_2CO_3	1.0	7.5	8.5	
No. 14 trona	3.7	15.4	19.1	

	Na_2CO_3			Total Alkali
	cold wash	hot leach	total	
No. 13 C.P. Na_2CO_3	22.4	11.2	33.6	42.1
No. 14 trona	32.4	16.7	49.1	68.2

Qualitative tests on No. 14 showed considerable chloride and sulfate in the hot leach, but about one-quarter to one-half as much as there was in the cold wash.

Runs No. 15 and No. 16 were made the same as No. 14. Both runs used about 20 grams trona (No. 14 used 43 grams trona). Run No. 15 was heated for 2 hours, No. 16 was heated for 3 hours, whereas No. 14 was heated for 1 hour 26 minutes. Shallow iron pans were used in these runs. Considerable trouble was caused by the stirrers sticking while making the hot leaches so that the water was in contact with the mixture much longer than 2 hours. However,

the water was kept at 80-95° C. for only two hours. The cold wash waters were boiled several times, about 10 minutes each time, but that from No. 16 did not lose the yellow color due to the colloidal iron. At the end of 39 minutes (the total time of the boiling) the cold washes were filtered and the filtrate from No. 15 was then analyzed. The filtrate from No. 16 (still yellow in color) was boiled for an additional 9 minutes, cooled and filtered. The filtrate was still yellow. Previously 10 minutes was the maximum time required to free from the colloidal iron. Analysis of this solution was then made, after precipitating the carbonate (as BaCO_3) no trace of the yellow color could be seen in either the filtrate or the precipitate. Analyses of these two runs showed:

	NaOH				Total Alkali
	cold wash	1st hot leach	2nd hot leach	total	
No. 15	0.09	22.2	0.00	22.3	
No. 16	0.00	14.2	0.00	14.2	
No. 14 ^x	3.7	15.4	--	19.1	

	Na_2CO_3				Total Alkali
	cold wash	1st hot leach	2nd hot leach	total	
No. 15	8.5	9.6	19.5	37.6	59.9
No. 16	7.2	14.9	9.3	31.4	45.6
No. 14 ^x	32.4	16.7	--	49.1	68.2

^xRun No. 14 is given here for convenience.

In these two runs the BaCO_3 precipitate came repeatedly thru the filter as mentioned under the analysis of the trona for Na_2CO_3 and NaHCO_3 . A qualitative analysis showed for both No. 15 and No. 16, that practically all of the chloride was removed by the cold wash. In run No. 15, the cold wash removed from 2 to 4 times as much sulfate as was removed by the first hot leach, while in run No. 16, the cold wash removed from four to five times as much sulfate as the first hot leach. The second hot leach of both No. 15 and No. 16 showed a trace of sulfate.

IV Summary

The Lowig process has been studied with reference to its adaptation for use of trona as a raw material. The following conclusions have been reached:

1. Commercial Fe_2O_3 , which is obtained by calcining precipitated $\text{Fe}(\text{OH})_3$, is unsatisfactory for this process.
2. Limonite, heated before use, and red haematite give about the same results.
3. The cold washing, for the purpose of removing impurities, is unsatisfactory.
4. The hot leaching for the recovery of the NaOH would be satisfactory if the cold washing removed the chloride, sulfate, and carbonate.
5. Colloidal iron may be separated by boiling from 5 to 10 minutes, cooling, and filtering.

6. Such impurities as are found in the tronæ do not hinder the process as shown by comparative runs with C.P. Na_2CO_3 .

7. The conversion has been unsatisfactory, ranging from 19.1% to 55.1% in the experiments using tronæ and red hæmatite.

8. The process is impracticable without further work. If the conversion and cold washing can be improved the process would probably prove to be practicable.