

# MANUFACTURE OF SODA

With Special Reference to  
the Ammonia Process

*A Practical Treatise*

By

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*IN MEMORIAM*

Professor Daniel Dana Jackson  
A Dear Friend and Kindly Teacher  
To Whose Inspiration I owed in  
Large Measure the Writing of this  
Second Edition of My Book

”



## GENERAL INTRODUCTION

### American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's *Handbuch der Organischen Chemie*, Richter's *Lexikon*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Abegg's and Gmelin-Kraut's *Handbuch der Anorganischen Chemie*, Moissan's *Traité de Chimie Minérale Générale*, Friend's and Mellor's *Textbooks of Inorganic Chemistry* and Heilbron's *Dictionary of Organic Compounds*, it often takes a great deal of time to coördinate the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing

to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

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### **SPECIAL ACKNOWLEDGMENTS**

**To Mr. Edward N. Trump and Mr. Z. G. Deutsch, both of whom have rendered valuable assistance in the preparation of the Second Edition, the author wishes to express his appreciation.**



## Foreword

The first edition of "Manufacture of Soda" was written in my home. I count it a privilege, therefore, to be asked by the author, whom I have known for almost thirty years, to write this Foreword to the Second Edition of his valuable contribution to chemical technology.

I know of no person so eminently fitted for writing on the subject as Dr. T. P. Hou. Dr. Hou is not only a scholar by training but also an engineer and technologist with years of experience in building up China's chemical industries. To him China owed the first and one of the largest alkali plants in the Far East. This was located in Tangku near Tientsin. When fighting began at the Marco Polo Bridge in July, 1937, just a short distance from the plant, it had attained a daily production capacity of some three hundred tons of soda ash, which was a good record on the Continent of Asia.

To him China also owed her new Synthetic Ammonia industry. Having established the alkali industry in North China, Dr. Hou turned to the great Yangtze Valley to erect the first and largest nitrogen fixation plant in China. Dr. Hou personally supervised the building of the four modern chemical plants at Hsiehchiatien near Nanking, which took three years to complete. In the summer of 1937, the plants were producing 150 tons of ammonia sulfate daily, and the Chinese farmers, sold on the new fertilizer, had booked orders a year ahead. Soon the War of Invasion broke out, interrupting the work.

I was so impressed with the transformation of the farming village of Hsiehchiatien into a humming industrial town, equipped with modern chemical machinery, that on one of my visits to my homeland I had the American Ambassador, Nelson T. Johnson, and the president of the Export-Import Bank, Warren Lee Pierson, accompany me on a tour of inspection. The statesman and the banker were both pleasantly surprised and impressed.

Time marched on . . . When bombs were falling thick and fast, and when his associates urged him to leave the plants, Dr. Hou said: "My duty to the farmer is to stay on the job. I want to see it through." Dr. Hou caught the last boat to leave Nanking with time to save nothing except a roll of blue prints of the plants. Dr. Hou's contributions are continuing, for far into the interior of Free China he is laying the groundwork for a new chemical industry, despite the difficulties of transportation over the tortuous Burma Road.

It is against such a background that the author was requested by his publishers to prepare this Second Edition of "Manufacture of Soda." It is my privilege to say that he has not spared himself one bit in the

rewriting and revising of this treatise. When the first edition appeared, it was the first of its kind to appear in the English language. In bringing the book up to date and adding considerable new material, Dr. Hou has not only enhanced its usefulness but he has shown the public how an interesting and comprehensive treatise can be written on such a special subject as the Ammonia Soda industry.

K. C. LI

Woolworth Building  
New York, N. Y.

## Contents

	Page
FOREWORD .....	ix
PREFACE TO THE SECOND EDITION .....	xi
PREFACE TO THE FIRST EDITION .....	xiii
 CHAPTER	
I. INTRODUCTION. HISTORICAL SURVEY OF ALKALI INDUSTRY AND RELATION OF LeBLANC SODA INDUSTRY TO DEVELOPMENT OF OTHER CHEMICAL INDUSTRIES .....	1
II. NATURAL SODA .....	14
III. HISTORY OF AMMONIA SODA PROCESS: STATISTICS .....	31
IV. PREPARATION OF BRINE: ROCK SALT AND SEA SALT .....	46
V. PURIFICATION OF BRINE .....	63
VI. BURNING OF LIMESTONE .....	70
VII. AMMONIATION OF SATURATED BRINE .....	112
VIII. CARBONATION OF AMMONIATED BRINE .....	132
IX. WORKING OF CARBONATING TOWERS OR "COLUMNS".....	158
X. FILTRATION OF CRUDE SODIUM BICARBONATE (AMMONIA SODA): COMPOSITION OF THE BICARBONATE .....	167
XI. COMPOSITION OF MOTHER LIQUOR FROM CARBONATING TOWERS .....	185
XII. PHASE RULE IN TOWER REACTIONS: GRAPHICAL REPRESENTATION OF AMMONIA SODA PROCESS .....	194
XIII. DECOMPOSITION OF SODIUM BICARBONATE BY CALCINATION .....	206
XIV. RECOVERY OF AMMONIA—EFFICIENCY OF OPERATION IN AMMONIA STILL .....	225
XV. BY-PRODUCTS FROM DISTILLER WASTE .....	251
XVI. ALLIED PRODUCTS OF AMMONIA SODA INDUSTRY .....	257
XVII. POSITION OF AMMONIA SODA INDUSTRY .....	267
XVIII. MANUFACTURE OF REFINED SODIUM BICARBONATE .....	276
XIX. MANUFACTURE OF CAUSTIC SODA—CHEMICAL PROCESS..	284
XX. MANUFACTURE OF ELECTROLYTIC CAUSTIC, CHLORINE, AND CHLORINE PRODUCTS .....	312

## CONTENTS

CHAPTER	PAGE
XXI. WET CALCINATION OF SODIUM BICARBONATE .....	342
XXII. GENERATION OF POWER FOR AMMONIA SODA PLANTS ....	350
XXIII. BOILER OPERATION AND CONDITIONING OF BOILER FEED AND COOLING WATER IN AMMONIA SODA PLANT .....	371
XXIV. SPECIAL REQUIREMENTS OF AMMONIA SODA INDUSTRY ...	403
XXV. CONTROL IN AMMONIA SODA PROCESS .....	420
XXVI. LOSSES AND CONSUMPTION OF RAW MATERIALS IN AMMO- NIA SODA PROCESS .....	431
XXVII. MODIFICATIONS AND NEW DEVELOPMENTS OF AMMONIA SODA PROCESS .....	446
XXVIII. CHEMICAL ANALYSES AND TESTS IN ALKALI INDUSTRY	461
XXIX. BEHAVIOR OF SODA ASH IN STORAGE .....	509
XXX. LAYOUT, DESIGN AND LOCATION OF AMMONIA SODA PLANT	516
XXXI. CENTRIFUGAL PUMPS APPLIED TO AMMONIA SODA INDUS- TRY .....	531
APPENDIX .....	551
INDEX .....	573



## Chapter VII

### Ammoniation of Saturated Brine

The saturated brine for soda production is sent to the system generally treated according to one of the methods described in Chapter V. In the soda works the buildings are usually tall so that the brine can be pumped to a head tank, on top of one of the buildings, where it flows down by gravity to various units in the system. The fresh brine from this storage tank is employed first to scrub small quantities of ammonia from the filter gas in the filter washer, from the absorber outlet gas in the absorber weak washer, and from the tower outlet gases in the tower washers (Fig. 23). From this apparatus, the brine, having picked up a

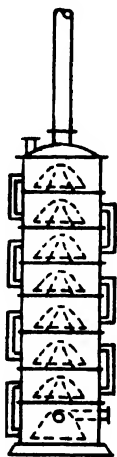


FIG. 23. Tower washer.

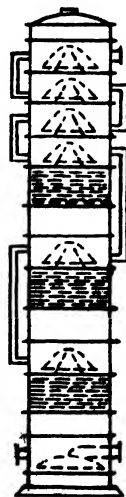


FIG. 24. Absorber

small amount of ammonia and absorbed as much carbon dioxide gas as can be retained by the alkalinity of the slightly ammoniacal solution, flows to the absorber washer and thence to the absorber itself (Fig. 24). From the outlet of one apparatus to the inlet of another a long "U" loop is usually provided in the brine line, to prevent escape of the gases, especially if one unit at one end is working under pressure while the other is under partial vacuum, or if two units are under different vacua.

Theoretically speaking, each leg of these "U" loops need be just so long that the static head of the column of brine will balance the differences of pressure above the brine in the two legs of the loop. Where the brine is flowing down with some velocity, this allowance is generally not sufficient and a longer loop must be allowed to take care of the velocity head.

In the process, the brine is allowed to absorb the desired amount of ammonia prior to its treatment with carbon dioxide in the carbonating towers. This order of treating the brine first with ammonia and then with carbon dioxide is a natural one, for it would be impossible to reverse the order, *i.e.*, to treat the brine first with carbon dioxide and then with ammonia successfully, as carbon dioxide is sparingly soluble in the neutral brine.

Formerly there was a process for distilling the filter liquor and condensing the ammonia vapors to form an ammonia solution of suitable strength in which solid salt was then dissolved to full saturation. Although this insured good saturation of sodium chloride in the resulting ammoniacal brine, the actual operation of the process was attended by considerable mechanical difficulties because of impurities in the salt and loss of ammonia. This procedure was therefore abandoned.

The ammoniation of the brine serves a two-fold purpose. First, it is a means of introducing the required amount of ammonia into the brine, and secondly, it is a means of eliminating the impurities of calcium and magnesium necessary for the production of a high quality soda ash. For, if calcium and magnesium are not eliminated at this stage, they will be precipitated with sodium bicarbonate in the carbonating towers later. The gases that carry ammonia also carry carbon dioxide, whether they come from the filters, from the absorber vacuum system, or from the carbonating towers. Consequently, ammonia dissolved in the brine exists partly also in the form of  $(\text{NH}_4)_2\text{CO}_3$ . Hence calcium and magnesium are precipitated in the brine as  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{MgCO}_3 \cdot \text{NaCl} \cdot \text{Na}_2\text{CO}_3$ , and to a small extent basic magnesium carbonate or  $\text{Mg}(\text{OH})_2$ .

1.  $\text{Ca}^{++} - \text{Salt} + (\text{NH}_4)_2\text{CO}_3 \rightarrow \text{CaCO}_3 + (\text{NH}_4)_2 - \text{Salt}$
2.  $\text{Mg}^{++} - \text{Salt} + (\text{NH}_4)_2\text{CO}_3 \rightarrow \text{MgCO}_3 + (\text{NH}_4)_2 - \text{Salt}$
3.  $\text{MgCO}_3 + (\text{NH}_4)_2\text{CO}_3 + \text{Aq} \rightarrow \text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$
4.  $\text{MgCO}_3 + \text{NaCl} + \text{Na}_2\text{CO}_3 \rightarrow \text{MgCO}_3 \cdot \text{NaCl} \cdot \text{Na}_2\text{CO}_3$
5.  $x\text{MgCO}_3 + y\text{Mg}(\text{OH})_2 \rightarrow (x+y)\text{MgO} \cdot x\text{CO}_2 \cdot y\text{H}_2\text{O}$
6.  $\text{Mg}^{++} - \text{Salt} + 2\text{NH}_4\text{OH} \rightarrow \text{Mg}(\text{OH})_2 + (\text{NH}_4)_2 - \text{Salt}$

However, in the tower washers and weak washers these precipitates of calcium and magnesium carbonates formed in the cold are in a milky suspension so that fortunately little is settled. Most of the precipitate flows with the brine stream to the absorber washer, thence to the absorber and the settling vats, where these impurities finally coagulate at a higher temperature.

Besides eliminating calcium and magnesium from the brine, the introduction of ammonia into brine, or the ammoniation with ammonia gas from the distiller has the following effects:

- (a) The decrease in solubility of sodium chloride in the resulting brine.
- (b) The increase in the volume of the resulting ammoniated brine.
- (c) The unavoidable dilution of the saturated brine by steam carried over with the ammonia gas.
- ✓ (d) The generation of a large quantity of heat of solution of ammonia in the resulting ammoniated brine, heat of partial neutralization of ammonia by  $\text{CO}_2$ , and heat of condensation from the steam carried over.

These individual factors will be treated more fully below.

(a) **The effect of the decrease in solubility of NaCl.** It is a general rule that a substance which does not react with the solute, or form any complex ion with the solute, commonly decreases the solubility of the solute when the substance is introduced into the same solution. The decrease in the solubility of salt upon the introduction of ammonia is one of the factors that reduced the quantity of sodium bicarbonate which could be formed in the towers due to the decrease in the concentration of sodium chloride in the resulting ammoniated brine.

TABLE 46. Specific Gravity and Concentration of Pure Sodium Chloride Solution at 15° C.

(Based on Gerlach's figures.)

NaCl in Brine Per Cent	Sp. Gr.	NaCl Grams per liter	Chlorin. Titer*
1	1.0073	10.073	3.447
2	1.0145	20.290	6.492
3	1.0217	30.652	10.488
4	1.0290	41.160	14.084
5	1.0362	51.812	17.729
6	1.0437	62.620	21.427
7	1.0511	73.576	25.174
8	1.0585	84.681	28.976
9	1.0659	95.934	32.826
10	1.0734	107.34	36.730
11	1.0810	118.91	40.688
12	1.0886	130.63	44.698
13	1.0962	142.51	48.763
14	1.1038	154.54	52.880
15	1.1115	166.72	57.048
16	1.1194	179.10	61.284
17	1.1273	191.64	65.575
18	1.1352	204.34	69.920
19	1.1432	217.20	74.320
20	1.1511	230.21	78.773
21	1.1593	243.45	83.302
22	1.1676	256.86	87.892
23	1.1758	270.43	92.536
24	1.1840	284.17	97.236
25	1.1923	298.07	101.99
26	1.2010	312.25	106.84
26.395	1.2043	317.88	108.77

\* One titer is one-twentieth of one normal.

Table 46 gives the specific gravity and concentration of sodium chloride in C. P. brine, based on Gerlach's figures. With the introduction of

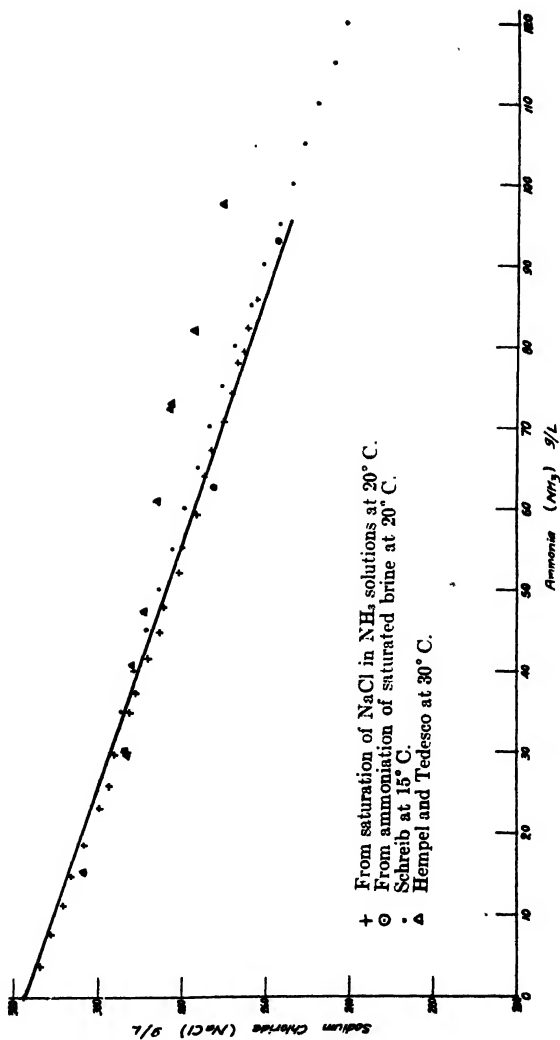


FIG. 25. Curve showing solubility of sodium chloride in aqueous ammonia solutions at  $20^\circ \text{C}$ .

ammonia into the brine, the solubility of sodium chloride in the resulting ammoniacal solution is decreased according to the concentration of ammonia in the brine.

Data on the solubility of sodium chloride in aqueous ammonia solutions seem to be still somewhat in doubt. The original published data were given by Schreib \* in "vol. %," i.e., in grams  $\text{NH}_3$  per 100 cc. of the solution. Schreib admitted that the results were only approximate. The same investigation was conducted by Hempel and Tedesco in 1911 at  $30^\circ \text{C}$ .† These results we desire to check. We have made the study at  $20^\circ \text{C}$ . approaching the equilibria from both directions, i.e., from the solution of sodium chloride in aqueous ammonia solutions and also (for four readings) from the ammoniation of the saturated brine, both at  $20^\circ \text{C}$ . The results are given in Tables 47 and 48. For comparison we have also plotted in Schreib's and Hempel and Tedesco's figures (Fig. 25).

Regarding the specific gravity of the resulting ammoniated brine, figures vary considerably. This is due principally to the varying carbon dioxide contents in the ammonia solutions: the higher the concentration of ammonium carbonate in the ammoniated brine, the higher the specific gravity for the same  $\text{NH}_3$  and  $\text{Cl}^-$  titers. High temperatures, of course, lower the specific gravity readings. In our investigation we have taken C. P. ammonia solutions; the specific gravity readings of the resulting solutions will therefore be lower than those of the strong liquors (containing carbon dioxide) in actual plant operation at the same temperature.

A word may be said about the ammonia component in the ammoniated brine. The solubility of ammonia in brine solutions is far greater than is required in operation. Given sufficient cooling, the ammonia titer could easily be brought beyond 110, but it would be quite out of proportion to the sodium chloride concentration, which tends to decrease as the ammonia concentration gets higher. When the ammonia concentration in the brine is made greater, the chlorine titer will necessarily be lowered because of the decrease in solubility of sodium chloride and of the increase in volume in the resulting ammoniated brine. This greatly decreases the concentration of sodium chloride in the liquor. Hence for optimum operating conditions we ammoniate the brine only up to or below 100 titer and do not attempt to push it to the limit of its solubility, because we wish at the same time to maintain the concentration of sodium chloride (i.e., chlorine titer) in the resulting ammoniated brine as high as possible. (See Tables 47 and 48.)

The presence of sodium chloride and of ammonium carbonate tends to raise the specific gravity of the ammonia solution, while ammonia tends to lower it.

If the process is started by introducing into the tower washer or filter washer a cold saturated brine, theoretically some sodium chloride should separate in the absorber during ammoniation. Yet in practice the ammoniated brine from the absorber is generally undersaturated in sodium

\* *Z. angew. Chem.*, 1888.

† *Ibid.*, 1911.

TABLE 47. Solubility of Sodium Chloride in Aqueous Ammonia.  
(From Saturation of Sodium Chloride in Ammonia Solutions at 20° C.)

Sample No.	Ammonia Solutions			Same Solutions Saturated with C. P. Sodium Chloride			NH <sub>3</sub>		NaCl Per Cent
	Sp. Gr. at 20° C.	Titer	NH <sub>3</sub> g./l.	Sp. Gr. at 20° C.	Titer	NH <sub>3</sub> g./l.	NaCl g./l.	Per Cent	
1	0.998	4.92	4.18	1.196	4.52	3.84	313.93	0.32	26.25
2	0.995	9.86	8.38	1.192	9.05	7.69	311.62	0.64	26.14
3	0.993	14.92	12.68	1.189	13.16	11.18	308.37	0.94	25.93
4	0.991	19.79	16.82	1.185	17.48	14.86	306.32	1.25	25.85
5	0.989	24.65	20.95	1.182	21.79	18.81	303.45	1.57	25.67
6	0.988	29.62	25.18	1.178	27.32	22.22	299.90	1.97	25.46
7	0.986	34.51	29.33	1.175	30.43	25.87	297.53	2.20	25.32
8	0.985	37.06	31.50	1.173	33.95	29.71	296.40	2.53	25.27
9	0.982	44.54	37.86	1.168	41.06	34.90	292.90	2.92	25.08
10	0.981	49.30	41.90	1.166	43.79	37.22	291.48	3.19	25.00
11	0.979	54.23	46.10	1.164	48.83	41.50	288.50	3.57	24.79
12	0.977	59.12	50.25	1.160	52.63	44.74	285.86	3.86	24.64
13	0.975	64.40	54.74	1.157	56.33	47.88	284.96	4.13	24.63
14	0.974	68.85	58.52	1.152	61.27	52.08	281.15	4.52	24.41
15	0.972	73.86	62.78	1.150	64.98	55.23	280.56	4.80	24.40
16	0.971	77.98	66.28	1.148	69.49	59.07	277.10	5.15	24.14
17	0.968	84.42	71.76	1.146	75.25	63.96	275.30	5.58	24.02
18	0.967	89.09	75.72	1.142	78.95	67.11	273.55	5.88	23.95
19	0.965	93.76	79.70	1.139	83.06	70.60	270.60	6.30	23.76
20	0.963	98.39	83.63	1.136	87.17	74.09	268.87	6.52	23.67
21	0.962	102.26	86.92	1.134	91.70	77.94	267.10	6.82	23.56
22	0.961	103.36	87.86	1.133	93.29	79.30	265.88	7.00	23.46
23	0.959	109.38	92.97	1.132	96.63	82.14	264.82	7.26	23.40
24	0.958	112.79	95.87	1.129	100.76	85.64	262.86	7.59	23.28

TABLE 48. Solubility of Sodium Chloride in Aqueous Ammonia.  
(From Ammoniation of Saturated Brine.)

Sp. Gr. at 20° C	NH <sub>3</sub> Titer	Cl- Titer	NH <sub>3</sub> Grams per liter	NaCl
1.186	18.09	103.82	15.38	303.46
1.175	35.36	100.60	30.08	294.05
1.147	73.60	93.40	62.56	273.01
1.124	109.38	88.13	92.97	257.60

chloride at the temperature in question due to the following reasons: (1) that the brine has picked up some moisture during the scrubbing of the gases saturated with water vapor at a higher temperature; (2) that in absorbing ammonia gases from the distiller considerable quantities of water are unavoidably introduced into the brine from the steam carried over; and (3) that, to start with, the brine, especially from brine wells, is seldom absolutely saturated. Consequently, the resulting ammoniated brine falls below full saturation with respect to sodium chloride, despite the decrease in solubility of sodium chloride by ammonia. Formerly, an effort was made to increase the concentration of sodium chloride by introducing solid salt into the ammoniated brine after it had left the absorber. As the operation was attended with mechanical difficulties, the practice has been generally discontinued. The increase of concentration of sodium chloride would undoubtedly increase the production of sodium bicarbonate in the towers by its mass action, although the gain may not warrant the trouble.

However, when ammonium chloride is to be recovered from the mother liquor from the columns, it is worth while to fortify the ammoniated brine with pure solid salt to bring the concentration of NaCl to theoretical saturation in the ammoniated brine at the top of the columns, or before the ammoniated brine is sent into the columns for precipitation of NaHCO<sub>3</sub>.

(b) **The increase in the volume of brine.** The ammonia gas dissolved in the brine increases its volume just as it increases the volume of water. In the case of pure water, the increase in volume of the aqueous solution of ammonia at 15° C. as shown by the decrease in the specific gravity is given by Lunge and Wiernik in Table 49.

TABLE 49. Specific Gravity of Ammonia Solutions.

Grams NH <sub>3</sub> in 1000 cc Solution at 15° C.	Sp. Gr. 15°/15° C.	Grams NH <sub>3</sub> in 1000 cc. Solution at 15° C	Sp. Gr. 15°/15° C
0	1.000	51.8	0.978
4.5	0.998	56.6	0.976
9.1	0.996	61.4	0.974
13.6	0.994	66.1	0.972
18.2	0.992	70.9	0.970
22.9	0.990	75.7	0.968
27.7	0.988	80.5	0.966
32.5	0.986	85.2	0.964
37.4	0.984	89.9	0.962
42.2	0.982	95.1	0.960
47.0	0.980	100.3	0.958

At a concentration of 80 grams of ammonia per liter, the increase of volume is a little less than 12 per cent. In the case of brine, at the same concentration of ammonia, the volume increase in the resulting ammoniated brine is slightly greater (about 13 per cent), as compared with plain brine of the same sodium chloride concentration. Fortunately, the presence of carbon dioxide in the ammonia gases forming some ammonium carbonate in the ammoniated brine tends to offset this increase in volume.

(c) **The dilution of the saturated brine by steam condensate.** Theoretically it is impossible to get perfectly dry  $\text{NH}_3$  gas from the distillers. Production of water vapor can be minimized only by operation at a low temperature, taking advantage of the fact that the aqueous tension of water is much less at a low than at a high temperature (at  $50^\circ \text{C}$ . it is only 12 per cent of what it would be at  $100^\circ \text{C}$ .). The question is: Can we work at as low a temperature as we desire? In practice, we cannot, because when we cool below about  $55^\circ \text{C}$ . the ammonia gases from the distiller containing carbon dioxide, there is a tendency for the solid ammonium carbonate, ammonium carbamate and ammonium bicarbonate crystals to deposit, blocking the gas passage. Equilibrium data from the  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$  system indicate the possibility of the existence of the following compounds:

Ammonium Carbonate,  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$   
 Ammonium Carbamate,  $\text{NH}_4\text{O} \cdot \text{CO} \cdot \text{NH}_2$   
 Ammonium Bicarbonate,  $\text{NH}_4\text{HCO}_3$   
 and the double salts,  $\text{NH}_4\text{HCO}_3 \cdot \text{NH}_4\text{O} \cdot \text{CO} \cdot \text{NH}_2$   
 and  $2\text{NH}_4\text{HCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$

This limitation is a practical one. Following are temperatures at which such substances exist in the solid state at atmospheric pressure.

Solid  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$  exists below  $58^\circ \text{C}$ .  
 Solid  $\text{NH}_4\text{HCO}_3$  exists below  $60^\circ \text{C}$ .  
 Solid  $\text{NH}_4\text{O} \cdot \text{NH}_2\text{CO}$  exists below  $60^\circ \text{C}$ .  
 Solid  $\text{NH}_4\text{HS}$  exists at low (unknown) temperature  
 Solid  $(\text{NH}_4)_2\text{S}$  exists at low (unknown) temperature

The crystallizing temperature of the ammonia gases varies according to the relative concentration of carbon dioxide the ammonia vapors carry.

Since the pipes are generally large, occasional periods of too low a temperature, if followed promptly by periods of higher temperatures, will clear up the passage by sublimation of the deposited crystals, or the blockade may be broken through by injecting exhaust steam. In such cases of fluctuation, generally considerable steam will be carried over to the absorber with the ammonia gas, diluting the ammoniated brine.

Theoretically at  $55^\circ \text{C}$ . and 754 mm. pressure ( $\frac{1}{4}$ " vacuum Hg) the partial vapor pressure of steam is 118 mm. Hg., and that of ammonia, hydrogen sulfide, carbon dioxide, and air, therefore, 636 mm. Hg. Of these gases, ammonia and carbon dioxide exist in predominating quantities, and hydrogen sulfide and air may be neglected in our calculations.



In the ammoniated brine obtained the ammonia "titer" (*i.e.*, number of cc. of  $N H_2SO_4$  per 20 cc. of solution) is about 95 (or 80.7 g./l. solution), and  $CO_2$ , 500 cc. per 20 cc. (or 49.1 g./l. solution). From this, the ratio of the partial vapor pressure of ammonia to that of carbon dioxide is as 80.7/17 is to 49.1/44 or as 4.75 is to 1.115. Therefore the partial vapor pressure of ammonia is 515 mm. The density of the ammonia vapor at 515 mm. Hg is 0.0395 lb. per cu. ft. and that of water vapor at 118 mm. Hg is 0.00650 lb. per cu. ft. This gives 164.5 grams of steam per 1000 grams of the ammonia distilled over. In this calculation we have assumed that all ammonia and carbon dioxide gases in the ammonia vapors coming over from the distiller have been completely taken up by brine in the absorption system and that the temperature of the ammonia vapors entering the absorber is held at 55° C. constantly. Actually some carbon dioxide gas is left unabsorbed in the spent gas and the temperature of the ammonia vapors from the distiller condensers does fluctuate and rise considerably above 55° C. So in practice from twice to three times the amount of water will go over to the absorber.

In practical absorption operations the 95 ammonia "titer" and 89 chlorine "titer" correspond to 80.7 grams of ammonia and 260 grams of sodium chloride per liter of the ammoniated brine. The Cl- titer of the cold saturated brine was 108, but the brine actually obtained has generally 104-105 Cl- titer. The combined increase in volume due to ammonia absorption and to dilution by the steam condensate in the absorber is therefore 17.6 per cent, of which 4.1 per cent has come from steam carried over by ammonia vapors from the distiller condensers and 13.5 per cent is due to the increase in volume from ammonia absorption, when the ammonia gas from the distiller condensers is maintained at 55° C.

(d) **The generation of heat by the solution of ammonia vapor in the brine and partial neutralization of ammonia by  $CO_2$ .** The heat of solution of ammonia gas is 8430 calories per g-mol—a very large quantity. Therefore, to make ammonia gas stay in the brine this quantity of heat must be extracted, *i.e.*, the brine must be cooled during absorption. Water in the brine absorbs ammonia gas with great avidity and there would be no difficulty in preparing an ammonia solution. The whole trouble lies in the ability to cool. Cooling on a large scale is attended with considerable difficulty because of incrustation of the cooling tubes. After ammonia absorption, the impurities in the brine begin to separate in the form of calcium and magnesium carbonates, ferrous sulfide, etc. On striking the cooling tubes these precipitates coagulate and settle on the tubes, in the apparatus, and in the piping system. This crust formation seriously reduces the cooling capacity. Occasionally the entire opening, both in the inlet and outlet of the apparatus and of the pipe, is filled with so much grayish sludge or black scale that no brine can flow through. This may result in the complete interruption of operations.

An approximate estimate of the quantities of heat liberated during absorption follows. This is based on the assumption of a 95 titer of ammonia and 500 cc. of carbon dioxide per 20 cc. of ammoniated brine

and 400 kg. of water vapor per 1000 kg. of ammonia. For every 1000 kg. of ammonia in the absorber, there are 12.4 cubic meters of ammoniated brine made. The specific heat of this ammoniated brine is 0.78 and the specific gravity is 1.175. (The specific gravity varies as the amount of carbon dioxide dissolved in the ammoniated brine.)

- (1) Heat of solution of  $\text{NH}_3$ :

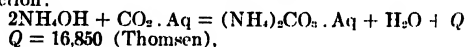
$$\frac{1000}{17} \times 8430 = 496,000 \text{ kg. Cal.}$$

- (2) Heat of solution of  $\text{CO}_2$ :

$$\frac{1000}{80.7} \times 49.1 \times \frac{5880}{44} \text{ (Thomsen)} = 81,500 \text{ kg. Cal.}$$

There is also a large quantity of heat generated from the neutralization of  $\text{NH}_3$  by  $\text{CO}_2$ .

- (3) Heat of neutralization of  $49.1 \times \frac{1000}{80.7}$  kg. of  $\text{CO}_2$  by  $\text{NH}_3$  by the following reaction:



$Q = 16,850$  (Thomsen),

$$\left( \frac{1000}{80.7} \times \frac{49.1}{44} \times 16,850 \right) = 233,000 \text{ kg. Cal.}$$

- (4) Heat from condensation of 400 kg. steam at  $55^\circ \text{C.} = 400 \times 564 = 226,000 \text{ kg. Cal.}$   
Total  $496,000 + 81,500 + 233,000 + 226,000 = 1,037,000 \text{ kg. Cal.}$

This quality of heat liberated is sufficient to raise the temperature of the ammoniated brine by

$$\frac{1,037,000}{12.4 \times 1000 \times 1.175 \times .78} = 91.2^\circ \text{C.}$$

Assuming that the temperature of the brine entering the absorber is  $25^\circ \text{C.}$ , the amount of heat liberated in it (if not conducted away by the cooling water and radiation) would raise the temperature of the resulting ammoniated brine above its boiling point ( $91 + 25 = 116^\circ \text{C.}$ ). This means that heat is being generated in the absorber at the rate of one-half of one million kilogram calories per ton of ash made, assuming the carbon dioxide titer in the ammoniated brine is 500 cc. per 20 cc. sample.

Consequently, inefficient cooling or an insufficient cooling surface may cause the whole absorber to become hot to the top—a phenomenon known as "hot top." In this condition ammonia gas cannot remain dissolved in the brine in the absorber but passes through to the absorber washer and even to the weak washer; and it may be sent with the exhaust gas to the air through the vacuum pump or "exhauster." This is a source of loss of ammonia which should be watched for. It is the temperature that makes the operation of the absorber the reverse of that of the distiller.

After a preliminary absorption of ammonia gas in the absorber washer and in the upper part of the absorber, the liquor is usually cooled in outside coils of the trombone type (called absorber coolers) made of 8-inch pipes, with return bends over the top tier of which cooling water is

allowed to play and flow down the outside surface of the pipes in thin films. The liquor from the upper part of the absorber enters the bottom tier of these coils and then returns to the bottom of the absorber from the top tier for final absorption. Here the liquor is finally ammoniated to the proper "titer" and flows to the settling vats at a temperature of 60 to 65° C. This temperature range is found suitable for the settling of the precipitate. These settling vats may be some 14 feet in diameter or larger by 25 feet overall height. They are provided with 45° conical bottoms. They may be made of  $\frac{3}{8}$ -inch steel plates, welded or riveted together. Three of such vats are connected in series so as to get the ammoniated brine from the last vat perfectly clear. Each vat is provided with an agitator to keep the precipitate of "mud" loose from the sides and bottoms. The agitators make from 1 r.p.m. in the first vat to 1 revolution per hour in the last vat (outlet vat). A set of three such vats in series has a capacity of from 100 to 250 tons of soda ash every 24 hours, depending upon the quality of brine used. The mud is drawn out regularly from the bottom of each vat by means of a small slow-moving plunger pump, and sent to the distiller to recover ammonia. But before doing this it is best to send the mud to an intermediate settler, called the mud settler, to concentrate the mud further so that as small a volume of mud as possible is sent to the distiller, and the clear ammoniated brine is returned to the system. This is to avoid pumping too large a volume of good brine to the distiller where all the salt it contains is lost. Besides, it would tax the capacity of the distiller unnecessarily. Since the mud so pumped is very thick, it is well to make a branch connection from the filter liquors to the mud pipe so that the mud pump may be flushed and the mud may be diluted by the filter liquor through the pump to the distiller.

The large settling capacity of the vats also helps maintain an ammoniated brine of constant strength for the column operation, making it less susceptible to changes in the concentration of the ammoniated brine made in the absorber.

Normally the heat transfer between a gas and a liquid is not so effective as between a liquid and a liquid. It would seem, therefore, to be more effective to cool the liquor rather than the gas in the absorber by means of cooling tubes. But as the scale formation of mud around the cooling tubes on the liquor side greatly lowers the coefficient of heat transfer, cooling of the liquor alone would not be adequate. In practice, the method of cooling both the liquor and the gases by cooling tubes is employed in the absorber. The liquor cooling surface should have roughly 25 sq. ft. per ton of soda ash, while the gas cooling surface should have 15 sq. ft. per ton of ash, making a total cooling area of 40 sq. ft. per ton of soda ash output. The estimate of cooling surface required, however, depends upon (1) the distribution of cooling area in the apparatus, (2) the temperature of the cooling water available, and (3) the scaling characteristics of the ammoniated brine (*i.e.*, the amount of impurities in the brine). High magnesium brine, such as sea brine, causes the forma-

tion of hard scale which may completely counteract the cooling effect of the liquor cooling system; whereas a high carbon dioxide content in the ammonia gases may cause ammonium carbonate (or bicarbonate) crystals to deposit on the cooling tubes in the gas-cooling system if the temperature drops excessively low. Inasmuch as so many factors are involved, the foregoing figures for cooling area per ton of ash merely afford a rough guide in the design of the absorber.

The absorber and vat house operation is chemically simple but mechanically very troublesome. The plugging of the piping system by the mud incrustation is a serious matter especially when sea salt is used. Duplicate piping systems and cooler sets are employed to facilitate cleaning without interrupting the operation. Tees and crosses are employed in pipe lines and overflow connections to facilitate opening up for cleaning. Tables 50 and 51 give typical analyses of the "mud" from the sea brine pipe main.

TABLE 50. Analysis of Ammoniated Brine Scale, Sample A.  
(Hard Scale from Brine Overflow Pipe Using Sea Brine.)

## I. Results of analysis

	Per Cent
1. Insoluble matter	0.350
2. $\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$	0.035
3. $\text{S}^-$	0.0012
4. $\text{Ca}^{++}$	2.752
5. $\text{Mg}^{++}$	8.840
6. $\text{Na}^+$	25.357
7. Total ammonia	0.055
8. $\text{Cl}^-$	12.979
9. $\text{SO}_4^{--}$	0.014
10. Total $\text{CO}_2$	36.050
11. Total alkalinity	16.222

## II. Calculated to conventional salts:

	Per Cent
1. Insoluble matter	0.350
2. $\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$	0.032
3. $\text{FeS}$	0.003
4. $\text{CaCO}_3$	6.88
5. $\text{MgCO}_3$	30.62
6. $(\text{NH}_4)_2\text{SO}_4$	0.019
7. $\text{NH}_4\text{HCO}_3$	0.232
8. $\text{NaCl}$	21.40
9. $\text{Na}_2\text{CO}_3$	37.33
10. $\text{NaHCO}_3$	2.63
11. $\text{H}_2\text{O}$ by diff.	0.504

Molecular ratios are:

$$\text{MgCO}_3 : \frac{30.62}{84.32} = 0.363 \quad \text{NaCl} : \frac{21.40}{58.45} = 0.366 \quad \text{Na}_2\text{CO}_3 : \frac{37.33}{106} = 0.352$$

The molecular ratios of  $\text{MgCO}_3$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3$  are approximately 1:1:1. Hence the triple salt in question should be:  $\text{MgCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot \text{NaCl}$ . This would correspond to Northupite crystal in natural deposits.

The reasons that tend to prove that the double salt of  $\text{CaCO}_3$  and  $\text{Na}_2\text{CO}_3$  (the Gaylussite  $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$  formation) does not exist here are given below:

- (1) That  $\text{CaCO}_3$  is present in different scale samples in widely varying ratios with respect to  $\text{Na}_2\text{CO}_3$ .
- (2) That  $\text{CaCO}_3$  percentage in each case here is too low to form Gaylussite ( $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$ ).
- (3) That water present is also far too low to form the hydrated crystals of Gaylussite.

TABLE 51. Analysis of Ammoniated Brine Scale, Sample B.  
(Hard Scale from Brine Overflow Pipe Using Sea Brine.)

## I. Results of analysis:

	Per Cent
1. Insoluble matter	0.165
2. $\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$	0.240
3. $\text{S}^{--}$	0.004
4. $\text{Ca}^{++}$	6.504
5. $\text{Mg}^{++}$	7.972
6. $\text{Na}^+$	22.838
7. Total ammonia	0.077
8. $\text{Cl}^-$	11.614
9. $\text{SO}_4^{--}$	0.288
10. Total $\text{CO}_2$	36.490

## II. Calculated to conventional salts:

	Per Cent
1. Insoluble matter	0.195
2. $\text{NaCl}$	19.152
3. $\text{Na}_2\text{CO}_3$	34.694
4. $\text{NaHCO}_3$	0.785
5. $\text{Na}_2\text{SO}_4$	0.105
6. $\text{MgCO}_3$	27.637
7. $\text{CaCO}_3$	16.480
8. $\text{FeS}$	0.010
9. $\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$	0.221
10. $(\text{NH}_4)_2\text{SO}_4$	0.299
	<hr/> 99.650
Moisture by difference	0.350
Total	<hr/> 100.00

Molecular ratios are again:

$$\text{MgCO}_3 : \frac{27.637}{84.32} = 0.328 \quad \text{NaCl} : \frac{19.152}{58.45} = 0.328 \quad \text{Na}_2\text{CO}_3 : \frac{34.694}{106} = 0.327$$

The molecular ratios of  $\text{MgCO}_3$ ,  $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3$  are as 1:1:1 and the triple salt in question is again  $\text{MgCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot \text{NaCl}$ .

These analyses show that the predominating constituents in the scale are  $\text{MgCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCl}$  and  $\text{CaCO}_3$ . Several points are noteworthy: (1) magnesium here is not precipitated from ammonia solutions as  $\text{Mg}(\text{OH})_2$  but in the form of  $\text{MgCO}_3$  which is normally more soluble than  $\text{Mg}(\text{OH})_2$ ; (2)  $\text{NaCl}$  is present in the mud in excessive quantities, which have been precipitated from an *unsaturated* ammoniated brine (unsaturated with respect to  $\text{NaCl}$ ); and (3)  $\text{Na}_2\text{CO}_3$  is formed at this stage instead of the far more insoluble  $\text{NaHCO}_3$ . Further study of the composition of the scale confirms the fact that there is a molecular relationship among the three main constituents and that they are in the following molecular ratio:

$$\text{MgCO}_3 : \text{NaCl} : \text{Na}_2\text{CO}_3 = 1 : 1 : 1$$

so that  $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3$  must have been formed from their respective ionic constituents with  $\text{MgCO}_3$  in the form of a triple salt  $\text{MgCO}_3 \cdot \text{NaCl} \cdot \text{Na}_2\text{CO}_3$  in the mud.

The foregoing description applies to brine that has not been treated before ammoniation. If the brine has been pre-treated, no such mud would be formed in large quantities. The loss of  $\text{NaCl}$  and  $\text{Na}_2\text{CO}_3$  present in the mud would be avoided and the troublesome operation in the absorber and vat system would be entirely eliminated.

Table 52 gives figures showing the concentrations of magnesium, chlorine, total ammonia, free ammonia, and fixed ammonia at different stages of ammoniation in the absorber system. Certain irregularities, however, are to be noted.

TABLE 52. Composition of Brine at Different Points in the Absorber System During a Certain Period.\*

Sample	Magnesium Content Mg./l.	Total Chlorine	Total Ammonia	Free Ammonia	Fixed Ammonia
			Titrals		
Fresh brine	1007.7	106.32	nil	nil	nil
Tower washer bottom	154.2	101.50	38.96	35.11	3.85
Absorber washer bottom	117.7	96.69	58.73	54.53	4.20
Pre-settler top	22.70	96.63	66.21	61.48	4.73
Absorber bottom section	19.44	92.10	88.33	84.12	4.21
First vat	13.32	92.28	92.83	87.77	5.06
Intermediate vat	10.50	92.68	91.55	86.50	5.05
Last vat	4.58	91.85	90.60	86.02	4.58
Ammoniated brine storage	4.15	92.48	90.46	87.34	3.12

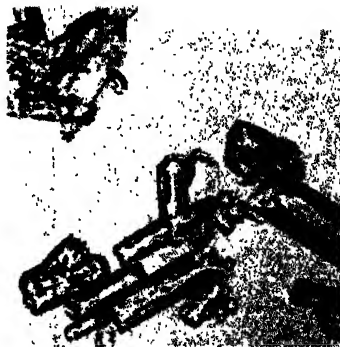
\* Thesis by Dr. W. C. Hsieh with the author.

The preceding analyses were made on the clear portion of each sample. There were 854 mg./l. calcium in the fresh brine sample but only traces in all other samples, showing that calcium is very readily precipitated as  $\text{CaCO}_3$ .

The question of impurities in the sea salt will center upon magnesium because there magnesium exists in larger proportions and also because the

FIG. 26.

Photomicrograph of artificial crystals of ammonium-magnesium carbonate tetrahydrate  $[(\text{NH}_4)_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot 4\text{H}_2\text{O}]$  found in ammoniated brine mud.



chemistry of magnesium is far more complicated than that of calcium. In the presence of  $\text{CO}_2$  in an ammoniacal solution, magnesium seems to have the tendency to precipitate as the carbonate ( $\text{MgCO}_3$ ) or at least as a basic carbonate, rather than as the hydroxide  $[\text{Mg}(\text{OH})_2]$ , as stated above. Seldom, however, does the magnesium precipitate exist as a simple salt: usually it comes down as a double or triple salt, except where the ammonia and  $\text{CO}_2$  gases are weak (such as at the tail end of a washer, where such a simple salt as the magnesium carbonate trihydrate ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ) may separate out instead). As the gases become stronger and the brine absorbs more ammonia and  $\text{CO}_2$ , the double salt of magnesium-ammonium carbonate tetrahydrate ( $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ )

$4\text{H}_2\text{O}$ ) and the triple salt of magnesium-sodium carbonate and sodium chloride ( $\text{MgCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot \text{NaCl}$ ) will occur in place of the simple salt. These salts appear under the microscope at high magnification as in Figs. 26 and 27.\* These double and triple salts of magnesium separate most readily at a temperature above  $50^\circ \text{C}$ .

Table 53 below reveals the crystal aggregate in the mud at various points starting from the saturated brine to strong liquor at the carbonating tower end.

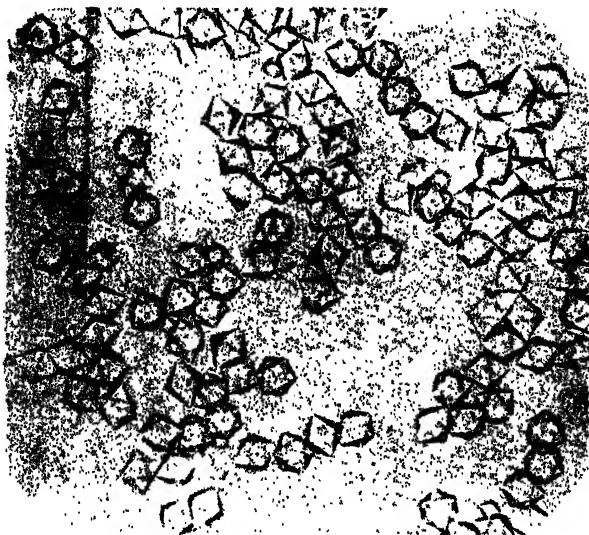


FIG. 27. Photomicrograph of artificial Northupite crystals ( $\text{Na}_2\text{CO}_3 \cdot \text{NaCl} \cdot \text{MgCO}_3$ ) found in ammoniated brine mud.

Most of the foregoing crystals are transparent with a wide range of sizes varying from what can be seen at 60-diameter magnification to what cannot be clearly discerned at 800-diameter magnification. They are generally difficult to see at high magnification because of their transparency, but can be seen best at 100-diameter magnification. From the above table it is apparent that at the bottom of absorber washer, absorber, brine cooler and ammoniated brine storage, the triple salt constitutes a large part of the mud formed.

The clear ammoniated brine is cooled to  $30^\circ \text{C}$ . in vat liquor coolers similar to the absorber coolers previously described, since hot ammoniated brine, if fed to the top of the columns, would cause excessive vaporization of ammonia by the carbon dioxide spent gases from the

\* Cf. Wilson, E. O., and Chiu, Y. C., "Brine Purification," *Ind. Eng. Chem.*, **26**, 1099 (1934).

TABLE 53. Microscopic Examination of Mud in Ammoniated Brine System.  
(From Brine Department to Carbonating Towers.)

No.	Points in System	Character of Crystals	Temp. (° C.)	Relative Proportions
1.	Saturated Brine	Cubic Cryst. (NaCl)	20	Isolated ones only
2.	Weak Washer Bottom Ring	Irr. Cluster Cryst. (Basic $MgCO_3$ ) Needle-shaped Cryst. ( $MgCO_3 \cdot 3H_2O$ ) Cubic Crystals (NaCl)	30	Predominating quantities Small amount Few isolated crystals
3.	Absorber Washer Bottom Ring	Octahedral Cryst. (Triple Salt, $MgCO_3 \cdot Na_2CO_3 \cdot NaCl$ ) Rhombohedral Double Salt ( $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$ ) Irr. Cluster Cryst. (Basic $MgCO_3$ )	45	Large quantities Small amount
4.	Absorber 5th Ring	Rhombohedral Double Salt ( $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$ ) Irr. Cluster Cryst. (Basic $MgCO_3$ ) Octahedral Cryst. (Triple Salt)	50	Predominating quantities Small amount Small amount
5.	Bottom of Intermediate Settler	Irr. Cluster Cryst. (Basic $MgCO_3$ ) Octahedral Cryst. (Triple Salt) Rhombohedral Cryst. (Double Salt)	35	Predominating quantities Small amount Very little (?)
6.	Absorber Bottom	Octahedral Cryst. (Triple Salt)	65	Predominating quantities, (very fine) Small amount
7.	Vat Bottom	Rhombohedral Cryst. (Double Salt) Irr. Cryst. (Basic $MgCO_3$ ) Octahedral Cryst. (Triple Salt) Black Irr. Cryst. (FeS)	60	Predominating quantities Small amount Small amount
8.	Brine Cooler Deposit	Octahedral Cryst. (Triple Salt) Black Irr. Cryst. (FeS)	35	Exclusively Isolated particles
9.	Mud at Bottom of Storage Tank	Octahedral Cryst. (Triple Salt) Irr. Black Cluster (FeS) Rhombohedral Cryst. (Double Salt)	30	Predominating quantities Small amount Very little
10.	Sediment in Ammoniated Brine Storage to Towers	Octahedral Cryst. (Triple Salt) Black Irr. Cryst. (FeS) Rhombohedral Cryst. (Double Salt)	30	Predominating quantities Small amount Very little

columns. On cooling the liquor, any magnesium mud, if not completely settled in the vats, would separate in the vat liquor coolers. This causes the formation of hard scale inside the cooling tubes, which obstructs the liquor passage and renders the coolers ineffective. This occurs especially when the temperature of the ammoniated brine is reduced below 30° C. Since the difference in temperature between the ammoniated brine and the cooling water in the vat liquor coolers is smaller than in the absorber coolers, much larger cooling area is required in these vat liquor coolers to get a cool liquor for the column operation. This can be shown mathematically as follows. Suppose in the absorber coolers the ammoniated brine enters the coolers at 60° C. and leaves at 40° C., and in the vat liquor coolers it enters the coolers at 50° C. and leaves at 30° C. Suppose also that the cooling water available has a temperature of 18° C. and its temperature is raised to 25° C. at the outlet in each case, the cooling system in each case being arranged counter-currently. Then the average temperature difference between the liquor and the cooling water in each case is represented by the logarithmic mean

$$\Delta t_{av} = \frac{\Delta t_1 - \Delta t_2}{2.303 \log \frac{\Delta t_1}{\Delta t_2}}$$

where  $\Delta t_{av}$  = average temperature difference between the liquor and the cooling water in the cooler.

$\Delta t_1$  = temperature difference between the liquor and the cooling water at the liquor entering end.

$\Delta t_2$  = temperature difference between the liquor and the cooling water at the liquor leaving end.



Therefore for absorber coolers

$$\Delta t_{av} = \frac{(60 - 25) - (40 - 18)}{2.3 \log \frac{60 - 25}{40 - 18}} = 28.0^\circ \text{C.}$$

For vat liquor coolers

$$\Delta t_{av} = \frac{(50 - 25) - (30 - 18)}{2.3 \log \frac{50 - 25}{30 - 18}} = 17.7^\circ \text{C}$$

so that, other conditions being equal, the cooling surface for the vat liquor coolers must be about 60 per cent larger than that for the absorber coolers. In practice 100 per cent larger area is recommended for the vat liquor coolers.

It is quite important that the ammoniated brine for the column operation should be well settled and free from mud. That good soda ash is made in the absorber and vat system should be kept in mind. For without perfectly clear ammoniated brine, mud would be carried over to the columns, be precipitated with the bicarbonate, and finally find its way to the soda ash, causing a turbid appearance or, in the worst case, a flocculent precipitate in the soda ash solution. This affects the quality of the product of the plant. Furthermore, if mud is accumulated in the columns, cleaning by the usual methods would not be effective and the columns might eventually have to be shut down for a boiling operation and mechanical removal of the scale. The scale would consist mostly of magnesium carbonate, which is difficultly soluble in hot water.

Magnesium mud is most difficult to settle out completely. If the brine used contains large amounts of magnesium with other impurities, magnesium is the last to be removed and small amounts of it will pass through with the brine stream. The amount of magnesium mud left in the ammoniated brine depends upon the settling capacity of the vat system and is determined by the rate of flow *vs.* the volume of the settling vats. With the usual proportion of the height to the diameter (or cross-section area) of the vat construction, it is the volume, rather than the area, of the vat that determines the settling capacity. Table 54 shows the relation of the

TABLE 54. Rate of Flow *vs.* Magnesium Carried in the Effluent.\*  
(Settling Vessel has  $23\frac{1}{2}$  cm.  $\times$   $23\frac{1}{2}$  cm.  $\times$  35 cm. Capacity.)

Rate of Flow (cc. per min.)	Mg. Carried in the Ammoniated Brine (gram per liter)	Rate of Flow (cc. per min.)	Mg. Carried in the Ammoniated Brine (gram per liter)
83.3	0.2293	25.0	0.0961
77.0	0.1878	20.0	0.0926
50.0	0.1214	14.3	0.0899
33.3	0.1057	11.1	0.0882

\* Thesis by Dr. W. C. Hsieh with the author.

rate of flow *vs.* the amount of magnesium left in the ammoniated brine (sea brine) coming from a settling vessel. These experiments were

carried out with a 5-gal. tin can ( $23\frac{1}{2} \times 23\frac{1}{2} \times 35$  cm. high), using normal ammoniated brine from the absorber. Brine enters at the bottom and flows out from the top. The rate of outflow is measured and the magnesium in the effluent determined by analysis. Samples in each case were collected after ten hours of constant flow.

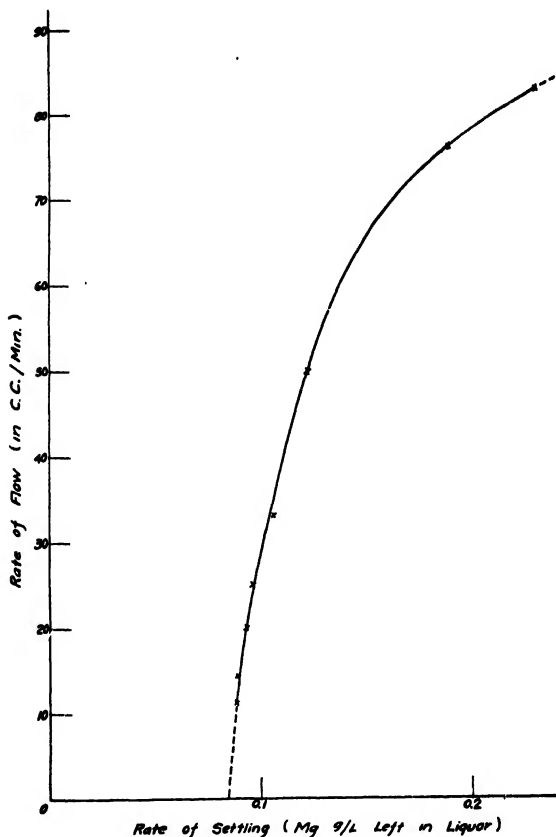


FIG. 28. Curve showing rate of settling vs. volume of flow.

These results are plotted in a curve (Fig. 28). From this curve it will be seen that for a settling volume of  $23.5 \times 23.5 \times 35$  cc., to reduce the magnesium content to within 0.1 milligram per liter in the ammoniated brine, the rate of flow must be below 30 cc. per minute. Granting that this is the highest limit in the green liquor for the column operation, with the usual proportion of the height to the diameter for each of the settling

vats, the minimum volume necessary for settling such brine per ton of soda ash made per 24 hrs. would be 95 cu. ft. for each settling vat.

$$\frac{23.5 \times 23.5 \times 35}{30 \times 60 \times 24} \times 6 \text{ cu. m.} \times 35.3 \text{ cu. ft.} = 95 \text{ cu. ft.}$$

Therefore for a 100-ton plant employing such brine, a minimum of 9500 cu. ft. of settling capacity is needed for the vats. Usually a capacity much in excess of 100 cu. ft. per ton of soda ash made per 24 hrs. must be provided, since allowance must be made for fluctuation of the flow. This indeed calls for a huge settling capacity, and applies to un-pretreated sea salt.

The matter of having a proper ratio of ammonia to sodium chloride in the ammoniated brine is important, for upon this depends the efficiency of the column operation. The Cl<sup>-</sup> titer (which represents sodium chloride) should be kept as high as possible; but because of dilatation of the volume of brine by ammonia and dilution by the steam condensate as described in the earlier part of the chapter, the sodium chloride concentration in the ammoniated brine is limited by the absorber operating conditions to below 90 Cl<sup>-</sup> titer. Should the ammoniation in the absorber be carried further, the concentration of sodium chloride (as shown by the Cl<sup>-</sup> titer) in the ammoniated brine would be greatly reduced. If the ammonia concentration in the brine is too high, excessive amounts of ammonium bicarbonate would also be precipitated together with sodium bicarbonate in the columns. If it is too low, the decomposition of sodium chloride in the columns would be low and too much salt wasted. This affects the rate of salt consumption and the utilization of ammonia and is vitally important to the financial success of the undertaking.

It is found best to have the ratio of 1.08 to 1.12 of NH<sub>3</sub> titer to 1.00 of Cl<sup>-</sup> titer in the ammoniated brine. Table 55 is based on Hempel and Tedesco's results. It will be noticed that a very high efficiency in the utilization of ammonia is necessarily accompanied by a low efficiency in the utilization of salt, and *vice versa*. The optimum point is reached

TABLE 55. Sodium Chloride and Ammonia Efficiencies for Different Concentrations of NH<sub>3</sub> and NaCl in Ammoniated Brine.\*

Grams NH <sub>3</sub> per 100 cc. of Solution	Grams NaCl per 100 cc. of Solution	NH <sub>3</sub> :Cl <sup>-</sup> Titers in Solution	Grams NaHCO <sub>3</sub> in Bicarbonate Obtained per 1000 cc. of Solution	NaCl in Bicarbonate Obtained	NH <sub>3</sub> HCO <sub>3</sub> in Bicar- bonate Obtained	NaCl Efficiency (decom- position)	NH <sub>3</sub> Efficiency
Per cent							
18.0	292	21.2: 99.8	74	0.681	0.40	17.7	83.4
57.9	275	68.1: 94.0	233	0.033	2.28	59.1	81.4
58.2	273	68.5: 93.3	234	0.016	2.33	59.8	81.4
63.7	271	75.0: 92.6	249	0.028	3.53	64.0	79.0
72.4	265	85.1: 90.6	258	0.037	3.84	67.9	72.3
76.5	260	90.0: 88.8	269	0.009	4.19	72.1	71.3
82.9	258	97.6: 88.1	282	0.005	3.91	76.2	68.9
133.3	223	157.0: 76.3	261	0.014	24.3	82.2	39.7
210.3	195	247.4: 66.7	249	0.001	69.5	89.6	24.5

\* Hempel and Tedesco, *Z. anorg. Chem.*, 24, 2459.

when the utilization of both of these principal raw materials reaches, or is slightly below, 75 per cent, *i.e.*, 99 to 97 for  $\text{NH}_3$  titer, and 89 to 90 for  $\text{Cl}^-$  titer with the ratio 1.10 of  $\text{NH}_3$  to 1.00 of  $\text{Cl}^-$ . These figures represent the best conditions obtainable in actual plant operation, although theoretically such ammoniated brine is still slightly undersaturated with respect to sodium chloride at this ammonia concentration.

Since in the ammoniating brine, there is a purification effect resulting in the precipitation of  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{Mg}(\text{OH})_2$ , etc., in the hot condition, a small amount of  $\text{NH}_3$  in the brine exists as  $\text{NH}_4\text{Cl}$  or  $(\text{NH}_4)_2\text{SO}_4$ , *i.e.*, as fixed ammonia as mentioned in Chapter V. The amount of the fixed ammonia in the ammoniated brine from the absorber depends upon the purity of the brine used. Generally, the fixed ammonia in the ammoniated brine is from 3 to 5 titer when rock salt brine is used, but it may be as high as 8 to 9 titer when sea salt is used. For the effect of this fixed ammonia on the column reaction, see Chapter V, on the purification of brine. Unless sea brine (which is obtained from sea water directly without crystallization) is used, this would not materially affect the decomposition of  $\text{NaCl}$  in the columns.

It should be remembered in designing the absorber that the absorption of ammonia requires depth of wash (barbotage). It is not unusual to provide a net depth of 18 to 20 inches in each passette from the serrated edge of the mushroom to the lower edge of the overflow opening.

As has been previously pointed out, if the brine was pre-treated to eliminate calcium and magnesium before it was sent to the system, ammoniation would be exceedingly simple. Most of the difficulties above described would then be avoided. The capacity of the absorber and the vat system would also be considerably increased, and the operating cost greatly lowered. The ammoniation then forms the final step of removing the last traces of impurities in the brine under the best settling conditions, making it possible to produce the highest grade of soda ash.

G. K. Ghose.  
2.1.45.

## Chapter VIII

### Carbonation of Ammoniated Brine

In early times solutions of salt and ammonium bicarbonate were used in the ammonia soda process. A great step, indeed, was made when ammonia was first employed in the form of a gas to be dissolved in brine and carbon dioxide gas was then introduced into the ammoniacal brine thus formed. This can be readily appreciated when one attempts to precipitate sodium bicarbonate in the laboratory, using brine and ammonium carbonate or bicarbonate solution, even though both these solutions are saturated to start with. From the saturated brine mixed with an equal volume of saturated ammonium bicarbonate in the cold, no immediate precipitate of sodium bicarbonate is obtained. Crystals separate out only after long standing. Sodium bicarbonate in the cold seems to have a great tendency to form supersaturated solutions. On the other hand, granting that both solutions were saturated before they were mixed, the resulting solution is only half saturated in respect to either NaCl or  $(\text{NH}_4)_2\text{CO}_3$  (or  $\text{NH}_4\text{HCO}_3$ ). A big advance was made when a method was discovered for introducing ammonia and carbon dioxide both in the form of a gas separately into brine without materially lowering the strength of the brine. The present method of ammoniation with tolerably dry ammonia gas followed by carbonation with carbon dioxide gas is indeed the key to the success of the ammonia soda process. Furthermore, ammoniation is incidentally an important process for the purification of crude brine when the brine has not been pre-treated, while the heat so developed is essential to the separation of calcium and magnesium precipitates from the resulting ammoniated brine. Then again, carbonation with  $\text{CO}_2$  gas gives the necessary carbonate and bicarbonate ions in the ammoniated brine, while the heat of neutralization of ammonium hydroxide in the brine by  $\text{CO}_2$  (though necessary to be extracted by cooling water towards the bottom of the column) is essential to the formation of good sodium bicarbonate crystals in the columns.

The ammoniated brine from the settling vats should be clear; otherwise the suspended solids would be precipitated with the bicarbonate in the carbonating towers, contaminating the soda ash made. It should be further cooled to about  $30^\circ \text{C}$ . in vat coolers, or brine coolers, before being sent to the towers for carbonation; otherwise, because of the increased vapor pressure of ammonia at an elevated temperature, an excessive quantity of ammonia gas that is otherwise available for reaction would be distilled over by the bubbling of  $\text{CO}_2$  gases out of the tower into the tower washer, where, on the other hand, more brine would be required to scrub the exit gases free of ammonia before letting them emerge into the

atmosphere. This can be done only within certain limits, because the quantity of fresh brine that can be so employed is limited by the output of soda ash in the plant, *i.e.*, by the quantity of the ammoniated brine made in the absorber at a fixed rate of ammonia distillation. For this

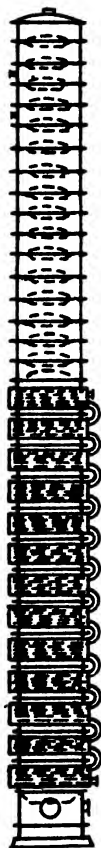


FIG. 29.

Carbonating tower.

reason, some of the older carbonating towers provided the admission of the fresh ammoniated brine, not at the top of the tower but near the middle. This was working on the theory that the free ammonia in the liquor would be converted to ammonium carbonate by  $\text{CO}_2$  gas before it could come to the top of the tower, and thus less ammonia would be distilled over by virtue of the lower ammonia vapor-pressure over ammonium carbonate than over free ammonia in the brine. In any case, there is some loss of ammonia in the towers due to gas distillation. This

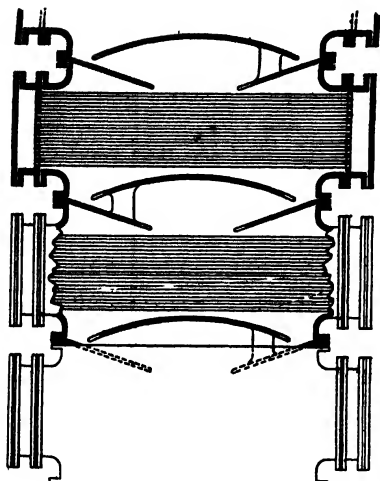


FIG. 30.

Carbonating tower cooling boxes.

is one reason why the ammonia titer in the ammoniated brine should be slightly higher than the chlorine titer.

The clear, cooled, ammoniated brine of proper concentration in sodium chloride and ammonia is treated with  $\text{CO}_2$  gas in a carbonating apparatus. There are several types of this apparatus, *e.g.*, Solvay's, Honigmann's,

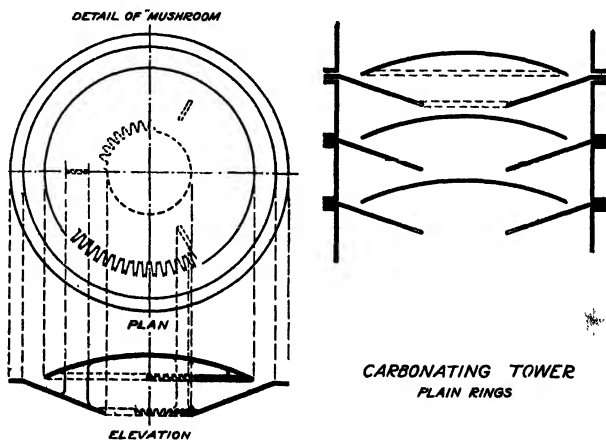


FIG. 31. Carbonating tower upper ring.

Boulouvard's, etc. Among these, Solvay's type is the most universally used (Fig. 29). A tall vertical structure consisting of a number of the mushrooms and division plates, or "passettes," one above the other, is

typical of Solvay's design. The carbonating tower is an example. It consists of cast iron cylindrical sections, or "rings" of about 6 feet or 2 meters inside diameter and 3 feet 4 inches high for each of the bottom cooling sections (Fig. 30) and 18 inches high for each of the upper plain rings (Fig. 31). The cooling system is of the Cogswell type, consisting

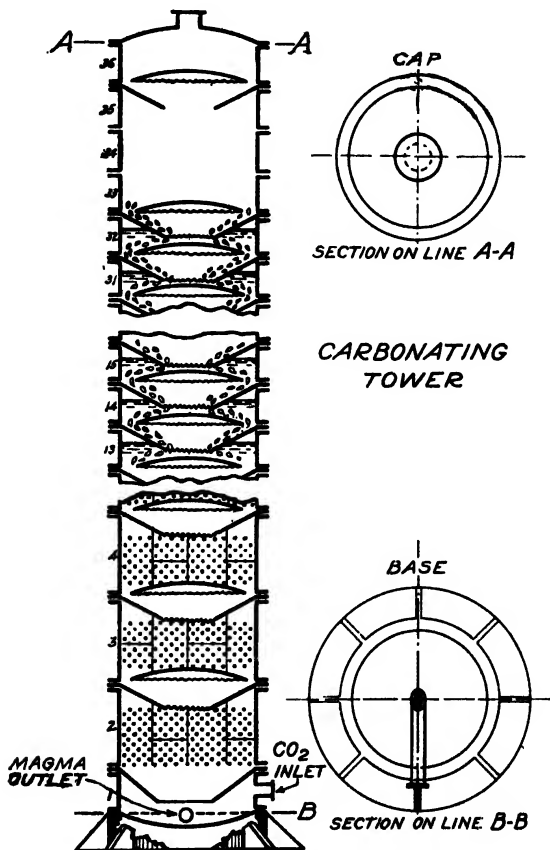


FIG. 32. Carbonating tower or "column."

of a large number of horizontal cast-iron tubes of 2 inches outside diameter,  $1\frac{1}{8}$  inches inside diameter, and about 7 feet 3 inches long, laid in rectangular, cast-iron tube sheets. The whole tower is about 75 feet high from the base to the top gas outlet. Carbon dioxide gas enters at the bottom, bubbling up around the edges of an inverted cone opening (Fig. 32). The draw opening through which the magma or bicarbonate sludge is drawn out is located at the bottom diametrically opposite the gas outlet.



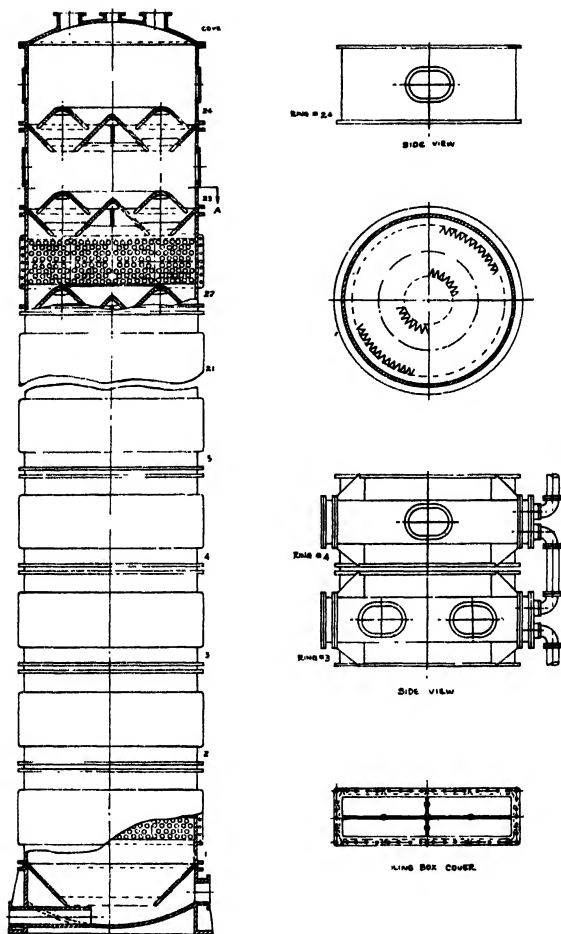


FIG. 33. Another type of carbonating tower.

Instead of working the bicarbonate on the bottom floor, however, the bicarbonate sludge is brought up through a 5-inch draw pipe to a height of 35 to 40 feet by the pressure in the tower itself. It then flows down to the bicarbonate filters located some 35 feet above the bottom floor. This elevation is necessary for vacuum filter working in order to provide a seal by means of a long leg of filter liquor to permit the rise of the liquor column under high vacuum above the level in the storage tanks which are located on the bottom floor, vented to atmosphere.

Within recent decades a departure in the size of the "standard" carbonating tower or "column" has been made. The diameter has been increased from six feet to seven feet six inches for substantially the same height with a large increase in capacity.

Another form of passette construction for the carbonating tower proposed by Mr. E. N. Trump is shown in Fig. 33. This type of passette has a clear passage and is especially good for the precipitating columns, in which fine crystals settle fast and have a tendency to block the passage. The passettes are particularly suitable for the manufacture of refined bicarbonate of soda.

The composition of the normal ammoniated brine to the towers is given in Table 56.

TABLE 56. Composition of Ammoniated Brine.

Sp. gr. (at 30° C.)	1.165-1.175
Free $\text{NH}_3$	97-99 titer
Fixed $\text{NH}_3$	3-5 titer
Chlorine	89-90 titer
Sulfide	0.02 titer
Carbon dioxide	450-500 cc. titer N.T.P.

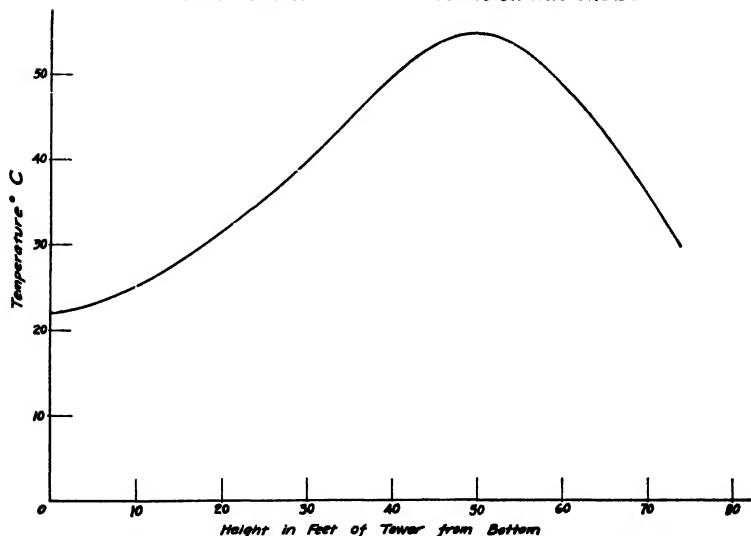


FIG. 34. Approximate temperature gradient in carbonating tower.

In tower operation temperature regulation is very essential. The temperature gradient in the towers should be so graduated by "bleeding" out of the cooling water that the bicarbonate crystals will grow larger and larger toward the bottom as the liquor descends and is cooled. The approximate temperature curve along the height of the tower is shown in Fig. 34.

The lowest temperature is of course to be found at the draw ring at the bottom as the cooling is arranged counter-currently. Various statements appear in textbooks for the best draw liquor temperature, such as 30° C., 32° C., 36° C., etc. Practice does not confirm these statements. With a well-constructed apparatus and good cooling facilities, as low a draw temperature as 22° C. or 20° C. has been found advantageous. It would seem indeed that the temperature for the draw liquor is primarily limited by the cooling capacity with the cooling water available, rather than by the desirability of working at a certain temperature for any chemical reasons. Low draw temperature does not necessarily mean poor crystals or pasty formation of sodium bicarbonate that is hard to filter. The formation of good crystals in the columns depends upon:

- (a) High concentrations of ammonia and sodium chloride in the cooled ammoniated brine with a proper ratio between the two titers.
- (b) Rich carbon dioxide gas properly cooled.
- (c) High reaction temperature at a point about two-thirds of the height of the column above the base.
- (d) Gradual cooling from this point down, ending with thorough cooling with as much cooling water as possible as the draw point is reached.

This is consistent with the theory of crystallization. In a solution containing high concentrations of the reacting constituents, sodium chloride, ammonia and carbon dioxide, the ionic concentrations are such that the solubility product of the desired compound is quickly exceeded and the sparingly soluble substance (in this case, sodium bicarbonate) is irreversibly precipitated in a solid form. Then when the reaction occurs at a high temperature, *i e*, when the precipitation, as of sodium bicarbonate, takes place in the hot condition, the crystals grow as the liquor is gradually cooled. Finally, cooling the mother liquor to a low temperature for drawing helps to throw as much of the substance out of solution as possible. Thus, a good conversion ratio, "per cent decomposition" and good crystals for filtration and washing operations are simultaneously effected. Furthermore, as the draw liquor is exposed to the air during filtration, the loss of ammonia by exposure is minimized. And further, no strong odor of ammonia gas will cause personal inconvenience to the workmen in the room. By following this procedure the draw temperature can be advantageously brought down as low as can be secured with the cooling water available with no undesirable results.

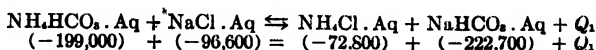
To get as low a draw temperature as 20° to 22° C. a very low cooling-water temperature is required. It would be impossible to get this draw temperature if surface water or river water were used for cooling during the summer. Underground water, or well water, is best suited for this purpose, as the temperature is always between 15° C. and 16½° C., summer and winter, at a depth of 400 to 450 feet below the surface. This uniform temperature of the cooling water all the year round is desirable,

as uniformity and regularity are required in the ammonia soda industry.

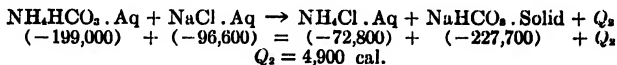
The main reaction in the tower is the double decomposition,



The heat effect is, however, very small as shown below, and the reaction is a typical one of equilibrium.



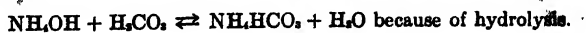
where  $Q_1 = -100$  cal. and is the heat of reaction at  $15^\circ \text{C}$ . Because of limited accuracy of the heat data available, these figures are evidently beyond the range of significant figures. It seems that the reaction is thermochemically neutral. But when the sparingly soluble sodium bicarbonate (which is still less soluble in the presence of an excess of sodium chloride and ammonium bicarbonate), separates out in a solid form, then there is a positive heat of reaction, which a moment's thought will tell us is nothing but the heat of solution of  $\text{NaHCO}_3$  crystals. The reaction is then exothermic.



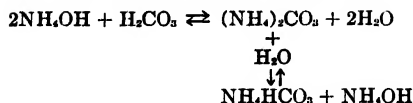
Or per ton of ash, at an average of 72 per cent decomposition, 260 grams per liter of sodium chloride and 6 cubic meters of ammoniated brine,

$$Q_2 = \frac{260 \times 0.72}{58.5} \times 4,900 \text{ cal.} \times 6,000 \text{ l.} = 94,000,000 \text{ cal.}$$

The main heat effect, however, comes from the formation in the liquor of ammonium carbonate from the neutralization of the dissolved ammonia by  $\text{CO}_2$  gas. It should be noted that not all this neutralization of the ammonia in the ammoniated brine is effected in the towers, as the ammoniated brine has picked up some carbon dioxide in the absorber system to the extent of about 500 cc. per 20 cc. Assuming 500 cc. of  $\text{CO}_2$  per 20 cc. of sample, this leaves  $80.7 - 37.9$  or  $42.8$  grams ammonia per liter yet to be neutralized to ammonium carbonate in the towers. Finally all this  $(\text{NH}_4)_2\text{CO}_3$  is converted to acid carbonate,  $\text{NH}_4\text{HCO}_3$ , by further treatment with  $\text{CO}_2$  gas in the making towers. The system is unfortunately complicated by the fact that before all the ammonia is neutralized to form normal carbonate, a part of the normal carbonate,  $(\text{NH}_4)_2\text{CO}_3$ , formed is immediately hydrolyzed to form  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_4\text{OH}$ , so that  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{NH}_4\text{HCO}_3$  are not formed in distinct stages as described above. Further, ammonia is never 100 per cent bicarbonated to  $\text{NH}_4\text{HCO}_3$ .



The reaction takes place in this way because it is a salt of a weak acid reacting with a weak base.



Hence the division of reaction between the cleaning and the making towers is not so distinct as described above.

J. Thomsen gives the heat of neutralization,



$Q_3 = 16,850$  cal. per mol and the heat of solution of  $\text{CO}_2$  gas to  $\text{CO}_2 \cdot \text{Aq}$  is  $5880$  cal. per mol., so that the neutralization of  $42.8$  grams  $\text{NH}_3$  per liter with  $\text{CO}_2$  gas to form  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{Aq}$  would cause the evolution of

$$\frac{42.8}{34} \times (16,850 + 5880) = \frac{42.8}{34} \times 22,730 = 28,600 \text{ cal.}$$

or per ton of ash,  $28,600 \text{ cal.} \times 6000 \text{ l.} = 171,600,000 \text{ cal.}$

The second stage



(if the reaction were so definitely marked) gives further heat of reaction

$$(-221,600) + (-168,000) = 2(-199,000) + Q_4$$

$$Q_4 = 8400 \text{ cal. per mol.}$$

The heat of reaction per mol of carbon dioxide due to this reaction then is

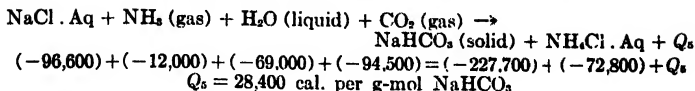
$$\frac{80.7}{17} \times \frac{1}{2} \times 8400 = 19,950 \text{ cal}$$

or per ton of ash,  $19,950 \text{ cal.} \times 6000 \text{ l.} = 119,700,000 \text{ cal.}$

To counteract the heat evolved due to the foregoing reaction it is sometimes argued that heat is absorbed because the carbon dioxide expands from  $3\frac{1}{2}$  atmospheres (34 to 36 lbs. gage pressure at the inlet) to  $1\frac{1}{2}$  atmospheres (3 to 4 lbs. gage pressure at the top of the tower). But this Joule-Thomson heat effect is in reality very small here and need not be taken into account. Hence per ton of ash, the total quantities of heat generated in the cleaning and making towers are:

(1) Heat from carbonation of $\text{NH}_3$ to $(\text{NH}_4)_2\text{CO}_3$ corresponding to the first stage on the tower side	171,600,000 cal.
(2) Heat from carbonation to $(\text{NH}_4)_2\text{HCO}_3$ by $\text{CO}_2$ corresponding to the second stage	119,700,000 cal.
(3) Heat from precipitation of $\text{NaHCO}_3$	94,000,000 cal.
<b>Total</b>	<b>385,300,000 cal.</b>
	per ton of ash
	or 385,300 kg. Cal.
	per ton of ash

The entire reaction starting from the saturated brine and gaseous ammonia and gaseous carbon dioxide is represented as follows:



This thermochemical equation represents the total heat effect in the absorbers and in the towers, apart from the heat of condensation of steam carried by the ammonia gases to the absorber. Of this all the heat of solution of ammonia and a part of the heat of neutralization ( $2\text{NH}_4\text{OH} + \text{CO}_2 \rightarrow (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}$ ), are liberated in the absorber, while the balance is liberated in the towers. The total per ton of ash is

$$\frac{28,400}{53} \times 1,000,000 = 536,000,000 \text{ cal. or } 536,000 \text{ kg. Cal. per ton of ash.}$$

With the heat of condensation of steam  $\frac{226,000}{12.4} \times 6 = 109,000$  (see p. 121), the total becomes  $536,000 + 109,000 = 645,000$  kg. Cal. per ton of ash. This is the theoretical minimum. Actually more ammonia and carbon dioxide are present in the liquor than the quantities called for by the above equation. Hence assuming 75 per cent ammonia efficiency, the minimum value may be put at

$$645,000 \times 1.33 = 860,000 \text{ kg. Cal. per ton of ash.}$$

In the cleaning tower, the heat of carbonation starting with green liquor containing 500 cc. of carbon dioxide per 20 cc. and ending in a pre-carbonated liquor containing 650 cc. carbon dioxide per 20 cc. is

$$\frac{64 - 49.1}{44} \times \frac{(16,850 + 5880)}{1000} \times \frac{6,000,000}{1000} = 46,100 \text{ kg. Cal. per ton of ash.}$$

In the making tower, the heat liberated by the reaction is:

- (a) Heat of carbonation  $(171,600 + 119,700 - 46,100) = 245,200$  } 339,200 kg. Cal.  
 (b) Heat of crystallization (or solution) of  $\text{NaHCO}_3 = 94,000$  } per ton of ash.

The heat generated in the cleaning tower is sufficient to raise its liquor temperature by

$$\frac{46,100}{\left(\frac{1.127 + 1.175}{2}\right) \times 0.78 \times 6,000} = 8.5^\circ \text{ C.}$$

(1.175 = av. specific gravity of the green liquor, 1.127 = av. specific gravity of the draw liquor, 0.78 = mean specific heat), so that if the green liquor fed to the cleaning tower is at  $30^\circ \text{ C.}$ , the temperature of the precarbonated liquor sent to the making towers will be about  $38.5^\circ \text{ C.}$  The making towers must then cool the liquor from  $38.5^\circ \text{ C.}$  to  $22^\circ \text{ C.}$  (the draw temperature) which requires

$$(38.5 - 22) \times \left(\frac{1.127 + 1.175}{2}\right) \times 0.78 \times 6,000 = 89,000 \text{ kg. Cal. per ton of ash.}$$

Therefore this heat of cooling must be added to the heat of reaction in the making towers above. The total heat which must be extracted by the cooling water in the making towers is then

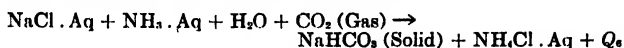
$$339,200 + 89,000 = 428,200 \text{ kg. Cal. per ton of ash.}$$

It is thus seen that the making towers need intensive cooling while the cleaning towers do not need any cooling at all. But in normal operation, the temperature of the liquor above the cooling section is about  $55^{\circ}\text{C.}$  and it is lowered by the cooling water to about  $22^{\circ}\text{C.}$  at the bottom of the tower.

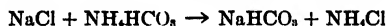
While the above quantity of heat does not represent any greater quantity of heat to be conducted away than that in the absorber, because of the low temperature to which the draw liquor is to be reduced, the mean temperature difference for the cooling water in the making towers is even less than in the vat coolers. The cooling tubes here are likely to be coated with crystals of  $\text{NaHCO}_3$  and  $\text{NH}_4\text{HCO}_3$  so that the coefficient of heat transfer is very small. Consequently, a much larger cooling surface is required in the towers than in the absorber coolers. More than 75 sq. ft. of cooling surface are required in the carbonating tower per ton of soda ash per day, but much depends upon the distribution of the cooling surface in the tower. As many of the cooling tubes as are consistent with the passage of gas and bicarbonate should be concentrated at the bottom sections of the tower. The number of these tubes per section gradually decreases with the height, leaving a very few only on the top sections which are located about half way up in the tower.

It should be remembered that many of the foregoing heat effects were merely calculated and have not been experimentally determined. The results are to be taken as a guide in the absence of experimentally determined data.

In tower operation we are more concerned with the reaction



or,



at equilibrium at any given temperature.

$$\frac{[\text{NaHCO}_3][\text{NH}_4\text{Cl}]}{[\text{NaCl}][\text{NH}_4\text{HCO}_3]} = \text{Constant} = K_c$$

where the brackets show molal concentrations of the substances per liter.

For most effective decomposition,  $K_c$  should be as high as possible. And for a given  $K_c$  at a given temperature the absolute value of the numerator is the larger, the larger the absolute value of the denominator. This means

- (1) high molal concentration of  $\text{NaCl}$  in the ammoniated liquor,
- (2) high molal concentration of  $\text{NH}_3$  in the ammoniated liquor,
- (3) high molal concentration of  $\text{CO}_2$  in the tower liquor.

For given concentrations of these substances in solution, the value of the equilibrium constant  $K_e$  with respect to the temperature is given by van't Hoff's equation,

$$\frac{d \ln K_e}{dt} = - \frac{Q}{RT^2}$$

where  $t$  is the temperature at which the reaction is carried out;  $T$  the absolute temperature  $= t + 273$ ;  $R$  the perfect gas molal constant  $= 1.985$  in cal.; and  $Q$  the heat of reaction, which is positive when the heat is evolved in the reaction and negative when absorbed. As  $Q$  is positive as shown above (*i.e.*, heat is evolved in the above exothermic reactions), this derivative is negative. That is,  $K_e$  is increased, as the temperature is lowered, and *vice versa*. This is in accordance with the LeChatelier principle. Hence,

(4) low draw temperature in the tower.

These four factors are discussed further.

(1) **High concentration of NaCl.** It is apparent from the absorber operation that owing to the increase in volume of brine as the result of ammonia absorption and the decrease in the concentration of sodium chloride as a result of ammoniation as well as the inevitable dilution by steam condensate, the concentration of sodium chloride in the resulting ammoniated brine cannot much exceed 260 grams per liter with an ammonia concentration of about 80 grams per liter. Usually the concentration is between 250 and 260 grams of sodium chloride per liter. The practice of strengthening the liquor by means of solid sodium chloride was attended with some difficulties and has been generally abandoned in modern soda works. For the time being, at least, we must rest contented with a concentration of about 260 grams per liter of sodium chloride in the ammoniated brine.

(2) **High concentration of  $\text{NH}_3$ .** With good cooling facilities, it is not difficult to get an ammonia concentration higher than 80 grams per liter, while in poorly constructed absorbers with poor cooling arrangements, a phenomenon of "hot top" may be the result. With a limited cooling capacity in the absorber, loss of ammonia through the vacuum pump exhaust is to be watched for, since the absorption of ammonia is simply a matter of cooling. But because of the tendency of the NaCl concentration to decrease in the ammoniated brine as ammoniation is carried further, it is inadvisable to employ an ammonia concentration very much greater than 80 grams per liter. Theoretically, an equivalent strength of ammonia with respect to sodium chloride is all that is required (see equation above). Based on the mass action principle, however, a higher concentration would of course be desirable, but it is found in practice that a very much higher concentration of ammonia greatly reduces the sodium chloride concentration in the resulting ammoniated brine and is not economical in the use of ammonia, because large amounts of free ammonia would be left in the draw liquor. The general practice now is



to employ not more than 12 per cent excess of ammonia over the equivalent amount of sodium chloride (*i.e.*, not over 1.12 equivalent of ammonia for every equivalent of sodium chloride, with about 260 grams of sodium chloride per liter in the ammoniated brine). When a much greater ammonia concentration, say 150 per cent as much as that of sodium chloride, is used, ammonium bicarbonate itself begins to separate in the towers causing cooling difficulties, and considerable ammonium bicarbonate will be formed with the sodium bicarbonate, especially at a low draw temperature. While this does not ultimately contaminate the soda ash, it represents just so much ammonia to be recovered from the dryers, and to be circulated between the towers and the dryers, so the loss of ammonia is proportionately greater. The plugging of the furnace condensers by the formation of ammonium carbonate crystals would also be more likely to occur.

(3) **High concentration of CO<sub>2</sub> gas.** The amount of carbon dioxide dissolved is proportional to the partial pressure of CO<sub>2</sub> gas in contact with the solution. This is Henry's law. It means a high concentration of CO<sub>2</sub> in the gaseous phase, *i.e.*, "rich gas." Theoretically, an equal quantity of CO<sub>2</sub> is recovered from calcination of the bicarbonate in the furnace. As there is always unused CO<sub>2</sub> in the tower waste gas, escaping in the exhaust into the atmosphere and, as is sometimes done, the exhaust gas from the absorber vacuum pump or "exhauster" is allowed to escape into the atmosphere instead of being returned to the carbonating tower, there is a constant loss of CO<sub>2</sub>. Consequently, more kiln gas, or "lean gas," must be drawn from the lime kiln. The ratio of the weight of CO<sub>2</sub> in the kiln gas taken to that furnished by the furnace gas is 1.0-1.2 to 1, depending on the rate of the dryer operation relative to the tower operation. Since 42 per cent CO<sub>2</sub> in the kiln gas and 95 per cent CO<sub>2</sub> in the returned gas represent a very good operating result, the percentage of CO<sub>2</sub> in the mixed gases from the carbonating towers cannot average more than 58.2 per cent without pushing the dryer operation beyond the rate of the column operation. When the furnace gas has only 90 per cent CO<sub>2</sub>, and the kiln gas 41 per cent, the theoretical percentage of CO<sub>2</sub> in the mixed gas into the column is only 56.3 per cent, when the rate of furnace operation is in step with column operation, *i.e.*, when the furnaces contribute the same amount of CO<sub>2</sub> by weight to the columns as the lime kilns. The volume of the kiln gas taken by the CO<sub>2</sub> compressors is then 2.2 times that of the furnace gas. There is a limit to the CO<sub>2</sub> concentration if the dryer gas is to be mixed with the kiln gas. When the dryer gas is introduced separately as in the double entry arrangement, then the percentage of CO<sub>2</sub> at the bottom gas inlet to the making towers could go up to as high as 90 per cent of CO<sub>2</sub> by volume, if desired.

Fortunately, in Solvay's carbonating towers the gas is forced up through a high column of liquor under a pressure of 34 to 36 lbs. The partial pressure of CO<sub>2</sub> is thus materially increased, giving higher absorption of CO<sub>2</sub> at the bottom of the tower and better utilization of the CO<sub>2</sub> gas. This is a distinct advantage in the Solvay type of carbonator and

the power spent in compressing the gas is well worth while. It is equivalent to introducing richer  $\text{CO}_2$  gas for reaction.

The exhaust gas from the absorber system should contain rich  $\text{CO}_2$  gas when the absorber system is reasonably air-tight. It should be as high as 60 to 70 per cent  $\text{CO}_2$  when there is not much air leakage. It pays to keep the distiller, absorber and vat systems reasonably air-tight to enable this gas to be returned to the towers, not only for the recovery of  $\text{CO}_2$  but also of some hydrogen sulfide which is also present in the absorber gas.

(4) **Low draw temperature.** Low temperature at the draw has been said to cause fine crystals of bicarbonate that cannot be filtered dry. This statement is not exactly true. With a high reaction temperature at about the two-thirds point and a proper temperature gradient from that point down, it is unquestionably better to draw the liquor at  $22^\circ\text{C}$ ., for example, than at  $30^\circ\text{C}$ . The decomposition is improved and the loss of ammonia gas by exposure is minimized. This demands a well-distributed and proportioned cooling surface, ample cooling area, a good cooling water, and close regulation of the cooling water course. The bicarbonate crystals will then give a good settling test and can be filtered, washed and calcined without difficulty.

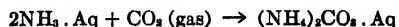
In the course of tower operation, the internal surface and the cooling tubes are gradually coated with bicarbonate crusts, with the result that it is difficult to cool the liquor to the desired draw temperature with a full stream of cooling water. Sometimes also the pressure necessary to force the gas from the  $\text{CO}_2$  compressor is materially increased because of the plugging tendency of the nest of cooling tubes by the crystals at the bottom section. But often the pressure *decreases* due to the gas lift effect through the restricted space in the towers. In this connection it may be remarked that never for any length of time should the gases be cut off from any tower while making bicarbonate, or the tower would be plugged solid and serious difficulties ensue. To overcome such difficulties, if the case does happen, steam is injected into the bottom of the tower and into the draw pipe to dissolve out the bicarbonate. When the bicarbonate has set solid at the bottom of the tower, thawing with steam in the draw opening may only open a channel through which the gas would blow through the draw opening and out through the draw pipe. In serious cases the gas comes out thus at the draw opening and the tower must be drawn empty, filled with water and cooked with steam. This always results in off-colored bicarbonate and is at best unsatisfactory. In the normal operation there should be no occasion to resort to such drastic measures. All that is needed would be to cut off the cooling water, change to the lean gas, draw the tower low and thin of bicarbonate, throttle down the  $\text{CO}_2$  gas from the compressor, and fill the tower with green liquor. All green liquor is then passed through this cleaning tower to feed making towers. The cooling water is completely cut off to permit the temperature of the liquor to rise to about  $39^\circ\text{C}$ . The green liquor tends to dissolve the

bicarbonate crust and the higher temperature drives the reaction backward, unmaking the bicarbonate:



This constitutes the cleaning tower operation and a schedule of about 4 days should be adopted for cleaning the making towers in rotation. The cleaning operation lasts from 18 to 24 hours, depending upon the effectiveness of cleaning (*i.e.*, the temperature of the ammoniated brine and the volume of the green liquor put through). If a tower is over-cleaned or "cleaned to the metal," the bicarbonate made may show a reddish tint and the ash obtained become slightly off-colored. The liquor from the cleaning tower is sent to the making towers by means of  $\text{CO}_2$  lift or booster pump. Generally, in cleaning, one tower can best supply carbonated liquor enough to feed 4 making towers.

In the cleaning tower, it is generally considered that the following reaction takes place,



This would mean that with 80.7 grams per liter of ammonia,  $\text{CO}_2$  can be present in the carbonated liquor up to  $\frac{80.7}{17} \times 22 = 104.4$  grams  $\text{CO}_2$  per liter. In practice such a concentration cannot be reached; and before we approach this figure, hydrolysis of ammonium carbonate has set in so far that the concentration of  $\text{HCO}_3^-$  has attained such a magnitude that  $[\text{HCO}_3^-] \times [\text{Na}^+]$  exceeds the solubility product of  $\text{NaHCO}_3$  and sodium bicarbonate separates out. Consequently, with the normal strength of ammonia in the ammoniated brine, at no time at any point either in the cleaning or making tower, is there ever in the liquor such a high concentration of  $\text{CO}_2$ . Generally, crystals begin to show in the carbonated liquor containing more than 80 grams of  $\text{CO}_2$  per liter. In actual cleaning operation the liquor is carbonated up to about 64 grams of  $\text{CO}_2$  per liter, a figure representing only 61 per cent of the above concentration. All green liquor is cut off from the making towers and it is sent through the cleaning tower as fast as possible to make the cleaning most effective. The precarbonated liquor from this cleaning tower is then fed to all making towers in the group.

In the tower liquor there are present in solution the ionic constituents,  $\text{Na}^+$ ,  $\text{HCO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{Cl}^-$ . There are thus four equilibrium equations, one for each of the four salts,  $\text{NaHCO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaCl}$ , and  $\text{NH}_4\text{HCO}_3$ , expressing the equilibria between the ions of these salts and their undissociated molecules. Two solubility products for the two least soluble salts,  $\text{NaHCO}_3$  and  $\text{NH}_4\text{HCO}_3$ , are important. Unfortunately, the exact data on the degree of dissociation (or the activity coefficient) for each of these four salts when present together at high concentrations in solution are not known at present. The solubility of each of these salts when present alone is given in Table 57.

TABLE 57. Solubility of Each Salt in Grams per 100 Cc. Water When Present Alone.\*

Temp. °C.	NaHCO <sub>3</sub>	NH <sub>4</sub> HCO <sub>3</sub> —Grams per 100 cc. of Water	NaCl	NH <sub>4</sub> Cl
0	6.90	11.9	35.63	29.4
10	8.15	15.8	35.69	33.3
15	9.03	18.3	35.75(?)	35.2
20	9.60	21.0	35.82	37.2
25	10.35	23.9	35.92	39.3
30	11.10	27.0	36.03	41.4
40	12.70	...	36.32	45.8
50	14.45	...	36.67	50.4
60	16.40	...	37.06	52.2

\* For this table and Tables 58 to 60 see A. Seidell's "Solubilities of Inorganic and Organic Substances," New York, D. Van Nostrand Co. These figures are given by Fedotieff, Dibbitts and Mulder.

These figures show that sodium bicarbonate is the least soluble of the four. Next comes ammonium bicarbonate and then sodium chloride and ammonium chloride at the temperature of the draw. When, however, the four salts are present together, the salting-out effect of any three salts in solution upon the fourth generally decreases the solubility of each. Then again the common-ion effect materially reduces the solubility of the salts concerned, *e.g.*, NaHCO<sub>3</sub> by NaCl and NH<sub>4</sub>HCO<sub>3</sub>, and NH<sub>4</sub>HCO<sub>3</sub> by NH<sub>4</sub>Cl. Consequently, NaHCO<sub>3</sub> and NH<sub>4</sub>HCO<sub>3</sub> are much less soluble in the liquor than when present alone in plain water at the same temperature. The solubilities of NaHCO<sub>3</sub> in NaCl solution and in NH<sub>4</sub>HCO<sub>3</sub> solution saturated with CO<sub>2</sub> is given by Fedotieff as follows:

TABLE 58. Solubility of NaHCO<sub>3</sub> in NaCl Solution Saturated with CO<sub>2</sub>.

At 15° C.			At 30° C.		
Sp. Gr.	NaCl Grams/100 cc. Water	Solubility NaHCO <sub>3</sub>	Sp. Gr.	NaCl Grams/100 cc. Water	Solubility NaHCO <sub>3</sub>
1.056	0.00	8.80	....	....	....
1.063	3.02	6.86	1.066	0.00	11.02
1.073	6.01	5.36	1.079	5.99	7.28
1.096	12.31	3.48	1.100	12.19	4.73
1.127	18.72	2.30	1.127	18.63	3.20
1.158	25.69	1.61	1.156	25.60	2.23
1.203	35.46	1.00	1.199	35.81	1.39

TABLE 59. Solubility of NaHCO<sub>3</sub> in NH<sub>4</sub>HCO<sub>3</sub> Solution Saturated with CO<sub>2</sub>.

At 15° C.		Solubility of NaHCO <sub>3</sub>
Sp. Gr.	NH <sub>4</sub> HCO <sub>3</sub> in Solution — Grams/100 cc. Water	
1.056	0.00	8.80
1.061	2.30	8.00
1.065	4.40	7.46
1.073	8.57	6.67
1.090	17.06	5.92

Table 59 shows that the molal decrease by NH<sub>4</sub>HCO<sub>3</sub> on the solubility of NaHCO<sub>3</sub> is not so much as the molal decrease by NaCl.

Fedotieff also gives the solubility of NH<sub>4</sub>HCO<sub>3</sub> in NH<sub>4</sub>Cl solutions saturated with CO<sub>2</sub>.

TABLE 60. Solubility of  $\text{NH}_4\text{HCO}_3$  in  $\text{NH}_4\text{Cl}$  Solutions Saturated with  $\text{CO}_2$ .

Sp. Gr.	At 15° C.	Solubility of
	$\text{NH}_4\text{Cl}$	$\text{NH}_4\text{HCO}_3$
	Grams/100 cc. Water	
1.064	0.0	18.64
1.063	2.99	16.29
1.062	6.06	14.22
1.062	8.51	12.60
1.065	11.68	11.68
1.069	18.30	9.33
1.076	26.93	7.73
1.085	32.25	6.64
1.085	34.35	6.42

The solubilities of sodium bicarbonate and ammonium bicarbonate in water in the range of the tower operating temperatures (between 22° and 32° C.) have been redetermined by the author. The solubility in each case was determined by taking an excess of C. P. sodium bicarbonate or C. P. ammonium carbonate in 600 cc. water in a tall glass beaker of about one liter capacity, provided with a glass stirrer. The beaker was immersed in an oil bath containing a refined petroleum oil which was circulated by a

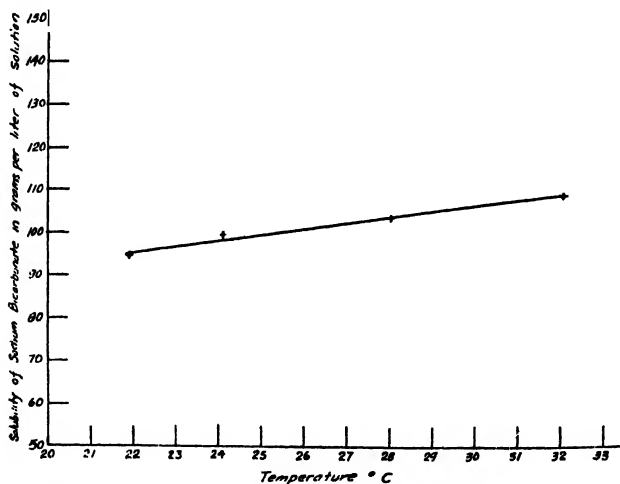


FIG. 35. Curve showing solubility of sodium bicarbonate in water.

pump between the bath and an outside reservoir provided with both electric heating elements and copper cooling water coils for the purposes of heating and cooling respectively. Carbon dioxide gas was bubbled continuously through the suspension in the beaker through a small tubing introduced through a hole in the cover which loosely fitted the mouth of the tall beaker, so that the solution of  $\text{NaHCO}_3$  or of  $\text{NH}_4\text{HCO}_3$  was in constant contact with, and kept under the atmosphere of, the  $\text{CO}_2$  gas. After the temperature in the beaker had been maintained constant for about

30 minutes with constant stirring, the suspension was allowed to settle for 15 minutes, after which a 20 cc. sample of the clear supernatant liquid was drawn into a 250-cc. volumetric flask and the volume made up to the mark. Ten cc. of the diluted sample was then taken for titration against

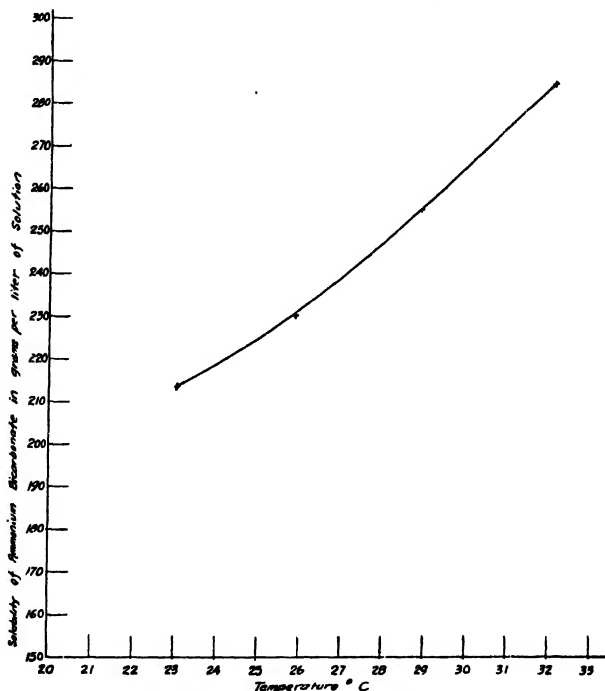


FIG. 36. Curve showing solubility of ammonium bicarbonate in water.

a standard *N*/10 hydrochloric acid solution using methyl orange as the indicator. The results, expressed in grams per liter of the solution, are given in Table 61 (see also Figs. 35 and 36). In the case of ammonium

TABLE 61. Solubilities of Sodium Bicarbonate and Ammonium Bicarbonate in Aqueous Solutions.

Temp. °C.	NaHCO <sub>3</sub> Grams/1000 cc. Sol.	Temp. °C.	NH <sub>4</sub> HCO <sub>3</sub> Grams/1000 cc. Sol.
21.90	94.4	23.05	213.4
24.10	99.1	25.90	230.5
28.00	103.0	28.90	255.8
32.05	108.2	32.10	286.0

bicarbonate the salt in solution was constantly decomposing, especially at the higher temperatures, so that fine bubbles were evolving from the solution.

In the normal tower liquor after the reaction, there are dissolved in the liquor the quantities of the four salts shown in Table 62.

TABLE 62. Composition of Mother Liquor.  
(Sp. gr. 1.126-1.127 at 29.5° C.)

	Grams per Liter of Liquor
NH <sub>4</sub> Cl	180-200
NH <sub>4</sub> HCO <sub>3</sub>	90-100 { (all free NH <sub>3</sub> calculated to NH <sub>4</sub> HCO <sub>3</sub> )
NaCl	70-80
NaHCO <sub>3</sub>	6-8
CO <sub>2</sub>	40-50
Sulfide	.010-.020 titer.

Just how much sodium bicarbonate remains dissolved depends upon the concentrations of the other three salts in the liquor and upon the temperature of the draw. Calculations on the basis of dissociation constants, solubility products, and general mass action laws do not give accurate results in these strong electrolytes at such high concentrations. Bradburn (*Z. angew. Chem.*, p. 82, 1898) gave valuable experimental results for the conditions of operation and the strength of ammoniated brine used in his time. They are given in Table 63.

TABLE 63. Conditions of Carbonating Tower in Operation.

Liquor from Tower Ring No.	Temp. ° C.	NH <sub>3</sub>		NH <sub>4</sub> Cl	NaCl	CO <sub>2</sub>
		Free Titer	Total Titer		Grams/liter	
Green liquor	34	85.0	89.0	10.7	248.8	67.0
18th ring	40	81.2	89.2	21.4	242.4	77.2
17th "	44	77.4	89.0	31.03	231.0	76.0
16th "	47	71.4	88.3	45.20	221.0	73.3
15th "	48.5	66.0	88.6	60.45	210.0	69.1
14th "	50.5	62.5	89.0	70.88	191.0	65.5
13th "	50.5	58.2	89.0	82.39	188.2	63.0
12th "	49	53.0	89.3	96.83	170.0	59.3
11th "	48	50.0	89.2	104.86	162.2	57.0
10th "	47	46.8	89.0	112.88	150.6	54.0
9th "	46	44.0	89.0	120.37	139.4	52.0
8th "	44.5	40.0	89.0	131.07	131.0	49.0
7th "	42	36.5	89.2	140.97	123.0	47.1
6th "	40	33.3	89.6	150.59	115.0	45.0
5th "	37	30.0	89.6	159.42	105.8	43.3
4th "	33.5	27.0	89.3	167.85	99.7	41.8
3rd "	31	24.7	89.8	174.14	94.0	40.6
2nd "	28.5	23.0	90.0	179.22	88.0	40.0
1st "	29	23.0	89.8	178.69	88.3	40.0
(Draw)						

The free NH<sub>3</sub> titer is lowered if the temperature of the draw liquor is lowered, i.e., if there is sufficient cooling capacity in the tower, and if good regulation is maintained. At a draw temperature of 22° C. the free titer in the draw liquor normally is about 20. The free titer in the draw liquor and its temperature run parallel but will be dependent upon the initial ammonia concentration in the green liquor employed. Low ammonia

liquor may give only 12 to 16 free titers in the draw liquor. Yet the per cent decomposition is low. The amount of  $\text{CO}_2$  dissolved in the draw liquor depends upon its free ammonia titer.

As has been remarked above and from a table giving the results obtained by Hempel and Tedesco, page 130, it may be shown that a very high  $\text{NH}_3$  titer as compared to  $\text{Cl}^-$  titer, say 157  $\text{NH}_3$  titer : 76  $\text{Cl}^-$  titer, causes considerable ammonium bicarbonate to precipitate in the tower with the sodium bicarbonate. The utilization of the available ammonia in the ammoniated brine then is low, *i.e.*, the ratio:

$$\frac{\text{NH}_3 \text{ converted to NH}_4\text{Cl in the tower}}{\text{Total available free NH}_3 \text{ in the NH}_3\text{-brine}}$$

is low, and the handling of ammonia is greater per ton of soda ash made. Consequently, the loss of ammonia is necessarily greater. On the other hand, if the  $\text{NH}_3$  titer is low as compared to the  $\text{Cl}^-$  titer, say the ratio of  $\text{NH}_3$  to  $\text{Cl}^-$  is less than 1, the utilization of available sodium chloride in the brine is low, *i.e.*, the percentage decomposition is poor. Table 64, based on that given by P. P. Fedotieff (*see* Chapter XII), illustrates this point.

TABLE 64. Efficiencies of Na and  $\text{NH}_3$  in Varying Ratios of  $\text{Cl}^-$  to  $\text{NH}_3$  Titrers.

Sample No.	Ammoniated Brine		Ratio $\text{Cl}^-/\text{NH}_3$ Titrers	Solutions Obtained				Utilization of Na	Utilization of $\text{NH}_3$
	Grams/1000 Cc. of Water	Free $\text{NH}_3$		$\text{HCO}_3^-$ Equiv. per 1000 cc. Water	$\text{Cl}^-$	Na	$\text{NH}_3$		
1	479	63.4	1: 0.456	0.18	8.17	4.62	3.73	43.3	95.1
2	448	77.5	1: 0.595	0.31	7.65	3.39	4.56	55.7	93.4
3	417	92.7	1: 0.764	0.51	7.13	2.19	5.45	69.2	90.5
4	397	106.8	1: 0.925	0.93	6.79	1.44	6.28	78.8	85.1
5	351	96.1	1: 0.942	0.99	6.00	1.34	5.65	77.7	82.5
6	316	88.6	1: 0.965	1.07	5.41	1.27	5.21	76.4	79.5
7	294	83.6	1: 0.978	1.12	5.03	1.23	4.92	75.5	75.1
8	234	70.4	1: 1.03	1.30	4.00	1.16	4.14	71.0	68.6

It will be seen from Table 64 that there should have been solid sodium chloride in the ammoniated brine in the first five samples. The percentage utilization of sodium chloride is thus decreased when that of ammonia is increased, and *vice versa*. Only Samples Nos. 6 and 7 will give results of any value to actual plant operation.

Table 65 gives average values of the different substances in the normal draw liquor (clear portion).

TABLE 65. Titrers in Draw Liquor.

Sp. gr.	1.126-1.127 at 30° C.
Total $\text{Cl}^-$	98-100 titer
Fixed $\text{NH}_3$	72-74 titer
Free $\text{NH}_3$	22-26 titer
$\text{CO}_2$	400-500 cc. per 20 cc. N.T.P.
$\text{S}^{=}$	0.010-0.020 titer



TABLE 66. Results from Operation of a Highly Ammoniated Brine in an Experimental Column.

Time Min.	Temp. Reaction Ring ° C.	Temp. Draw ° C.	Draw Titer (Free NH <sub>3</sub> )	CO <sub>2</sub> Inlet Per Cent	CO <sub>2</sub> Exit Per Cent	Total NH <sub>3</sub>	Fixed NH <sub>3</sub>	Total Cl	Sp. Gr. Draw Liquor	CO <sub>2</sub> Diss. Grams per Liter	Conver- sion Per Cent	NH <sub>3</sub> Efficiency Per Cent
0	22.0	20.0	107.7 *	59.5	0.0	108.4	0.7	87.0	1.1207	1.2	...	...
15	24.5	25.0	104.8	60.5	0.2	105.5	0.7	86.9	1.1563	37.8	...	...
30	25.2	22.9	104.8	60.0	0.0	105.3	0.5	87.0	1.1632	44.5	...	...
45	25.7	24.0	103.9	56.8	0.4	104.4	0.5	87.0	1.1771	59.5	...	...
60	25.0	15.0	105.1	55.6	0.5	105.7	0.6	87.6	1.1864	70.4	...	...
75	26.5	19.5	103.0	59.5	1.8	104.2	1.2	89.0	1.1985	82.2	1.4	1.2
90	29.4	24.0	103.3	59.0	3.5	104.2	0.9	87.2	1.2020	95.0	1.0	0.9
106	30.0	21.0	97.8	58.4	4.2	105.0	7.2	88.0	1.1970	91.3	8.18	6.86
120	30.2	21.4	91.3	56.0	5.4	105.8	14.5	88.2	1.1875	82.8	16.44	13.70
135	30.0	20.0	88.0	54.2	25.8	106.1	18.1	89.1	1.1828	81.6	20.3	17.0
150	31.1	22.0	83.1†	70.0	44.5	106.9	23.8	90.1	1.1765	77.0	26.4	22.3
165	31.1	19.0	75.1	62.9	25.2	106.2	31.1	92.0	1.1694	74.6	33.8	29.3
180	31.8	20.6	69.6‡	61.0	35.9	106.6	37.0	92.3	1.1630	72.1	40.1	34.7
195	30.0	18.2	63.2	63.6	42.5	107.0	43.8	92.4	1.1531	68.5	47.5	41.0
210	29.3	22.8	53.6	61.0	48.7	107.0	53.4	92.4	1.1465	65.7	57.8	49.9
225	27.6	18.6	49.6	60.0	51.6	108.5	58.9	93.5	1.1391	63.3	63.0	54.2
240	25.0	21.0	45.4	59.0	55.8	109.0	63.6	93.8	1.1349	59.2	67.8	58.4
255	24.5	20.8	43.3	60.0	55.9	109.0	65.7	93.9	1.1328	58.0	70.0	60.2
285	...	20.0	35.2	56.0	55.3	105.5	70.3	96.0	1.1287	52.1	73.3	66.6
360	...	21.0	33.1	59.4	58.8	106.0	72.9	96.0	1.1275	50.6	76.0	68.7

\* This is green liquor sample.

† First ppt. separated from milky suspension.

‡ No new green liquor fed in.

Note.—It is to be observed that in such a small tower operating for such a short duration, the reaction temperature at the two-thirds' point could not possibly rise to such figures as obtain in the plant operation, and the crystals obtained were necessarily poor. Also, it was difficult to effect any temperature regulation in the body of the tower.

It is evident from the Cl<sup>-</sup> titer in the draw liquor that the liquor volume is here reduced by about 10 per cent, as compared to the ammoniated brine used.

This draw titer (NH<sub>3</sub> titer) depends largely upon the ratio of NH<sub>3</sub> titer to Cl<sup>-</sup> titer in the green liquor (*i.e.*, the composition of ammoniated brine). When the NH<sub>3</sub> titer is low relative to the Cl<sup>-</sup> titer, a very low draw titer will be obtained. For example, when the NH<sub>3</sub> titer is only 82 and the Cl<sup>-</sup> titer 91, a draw of 16 may be obtained. When the NH<sub>3</sub> titer in the green liquor is high, a correspondingly high draw titer will result. For example, when the NH<sub>3</sub> titer is 102 and the Cl<sup>-</sup> titer 89, a draw titer of 30 will show good decomposition. On the other hand, when the Cl<sup>-</sup> titer in the green liquor is low (*i.e.*, when brine is too dilute), a high draw titer always ensues. For example, when the Cl<sup>-</sup> titer is 80 or 78 and the NH<sub>3</sub> titer 90, a draw titer of 40 may be obtained, and the loss of salt will be great.

Table 66 shows an experimental run in a miniature carbonating tower holding a gallon of ammoniated brine, employing as high an ammonia concentration as is practically feasible in actual plant operation. The ammoniated brine (green liquor) had a 107.7 NH<sub>3</sub> titer but the Cl<sup>-</sup> titer obtained was necessarily lowered to 87.0. As refined salt was used in this experiment, only a negligible amount of fixed ammonia was present in the resulting ammoniated brine. It will be seen also that the saturated brine was ammoniated with practically pure ammonia gas and little CO<sub>2</sub> was present in the ammoniated brine. Hence it should be observed that the specific gravity of this ammoniated brine is lower than what it would be under actual plant operating conditions. In the course of carbonation in the experimental tower, the specific gravity increases, reaching a maximum of 1.202, and then decreases as the precipitation of sodium bicarbonate sets in. The specific gravity readings were determined by a pycnometer and so are more accurate than are actually needed. The CO<sub>2</sub> content in the tower liquor also increases in the course of carbonation, reaching a maximum of 95 grams per liter in the highly ammoniated green liquor, representing correspondingly higher values than would obtain in plant operation with normal ammoniated brine. This is also indicated by the high free titer in the draw.

Unless otherwise specified, the figures in Table 66 represent "titers," *i.e.*, the number of cc. of normal solutions per 20-cc. sample.

After 6 hours of carbonation, equilibrium was reached and the "free titer" in the draw reached a constant value. The draw temperature was regulated by the amount of cooling water sent through the cooling sections in this experimental tower. Hence it fluctuated considerably. The average of CO<sub>2</sub> gases used in the carbonation was 59.6 per cent by volume, representing good plant practice, where mixed gases are used.

From the results in Table 66 it will be seen that with an ammonia titer as high as 1.24 times as much as the chlorine titer, keeping the latter at its highest value (87.0 titer), the sodium efficiency obtained (*i.e.*, percentage conversion) was increased only to 76.0 per cent, while the ammo-

nia efficiency was lowered to 68.7 per cent, and this with the mixed gas at about 60 per cent concentration and a low draw temperature of 20° to 21° C.

These results are plotted in Fig. 37, and the curves show that these items are straight-line functions of the fixed ammonia titers in the liquor.

The S<sup>-</sup> content in the draw liquor shows that there is an excess of sulfide in the system. It is necessary to keep this small excess of sulfide in the tower to ensure the production of white soda ash. The soluble

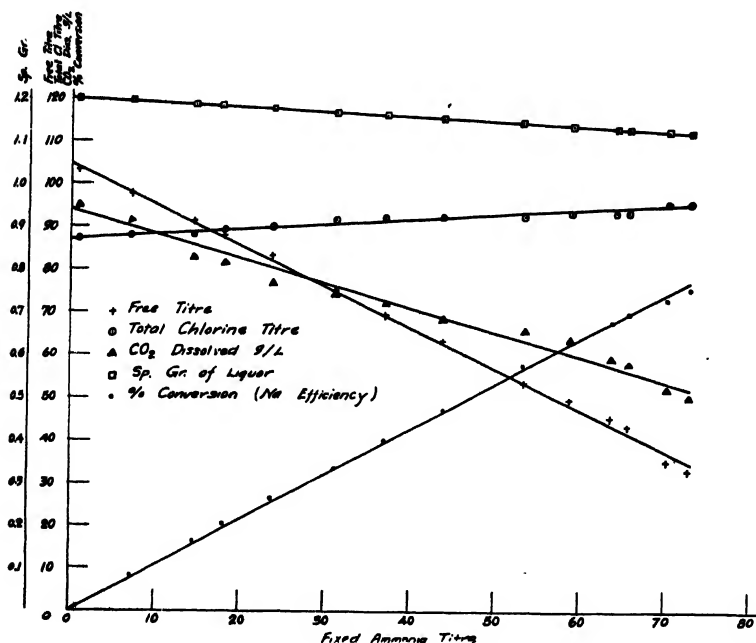


FIG. 37. Curves showing condition in making tower using a highly ammoniated brine.

sulfide in the liquor reacts with the exposed surface of the apparatus and pipes forming a black coating of ferrous sulfide which is not soluble in alkaline solution and so is not attacked by either sodium chloride or CO<sub>2</sub>. The sulfide is present naturally in the crude ammonia liquor from the gas works which is the usual source of ammonia supply for alkali plants. In the case of a deficiency of sulfide, sodium sulfide, preferably in a fused form (60%), can be purchased and a solution made from it fed to the still with the filter liquor to compensate for the loss of sulfide from the system. In the towers, some sulfide is oxidized by the air in the CO<sub>2</sub> gases, and some is blown out with the waste gases through the tower

washer into the atmosphere. Hence the necessity of replenishing sulfide in the system to maintain a small excess.

In the cleaning tower,  $\text{CO}_2$  in the waste gases should be very small (a fraction of 1 per cent); whereas in the making towers, it runs between 3 and 5 per cent. Sometimes a double gas inlet to the tower, as mentioned above, is provided so that the rich gas from the furnace can be admitted to the bottom of the tower and the best effect of mass action can be obtained. The lean gas is then admitted to the upper gas inlet a few rings above, where the partial pressure of  $\text{CO}_2$  in the gas falls to the same value as in the lean gas which is to be admitted there.

The rate of production in the towers and the success of tower operation depend largely upon the richness of  $\text{CO}_2$  gases introduced into the towers. This in turn depends upon the percentage of  $\text{CO}_2$  in the kiln gas and in the dryer gas. Efforts to secure as rich a  $\text{CO}_2$  gas from the lime kilns as possible are well repaid. For every ton of ash there should be delivered to the tower a volume of 800 to 900 cubic meters of the average gas under standard conditions of temperature and pressure. The  $\text{CO}_2$  compressors must provide for a piston displacement of 1000 to 1200 cubic meters per ton of ash.

Between the top of the carbonating towers and the tower washer, there is inserted in the gas line a cyclone separator which separates the entrained liquor in the outlet gases and lets it drain back to the top of the towers.

The capacity of a tower depends largely upon the cooling surface. A 6-foot standard tower, about 75 feet high, has a capacity of 50 to 60 metric tons of ash per 24 hours. For a 7½-foot I.D. tower, the capacity is increased to 100-120 tons of soda ash for 24 hours.

The  $\text{CO}_2$  compressor in the ammonia soda industry requires some special provisions in its design. In principle it is nothing more or less than a gas pump. But the corrosive character of  $\text{CO}_2$  and the dust and ammonia, the gases are likely to carry, make the duty severe. It should meet the following specifications:

- (1) The inside of the gas cylinder should have a lining which can be re-bored or renewed when worn.
- (2) It should have simple gas valves to insure action because of the corrosive property of  $\text{CO}_2$  gas and the presence of some dust in the kiln.
- (3) The part in contact with the gas should be all iron owing to the possible presence of some ammonia in the furnace gas.
- (4) Ordinary steel cup valves used in the air compressors for gas outlet are rapidly corroded by  $\text{CO}_2$  and simple Stainless steel plate valves or heavy rubber disc valves may be used instead. Mechanically operated, plunger-seated steel cup valves of special design, however, have been found very satisfactory. But Stainless steel construction is preferable and resists corrosion much better.
- (5) Ordinary lubricating oil in the gas cylinders is affected by  $\text{CO}_2$  and becomes sticky. Soda water of about 10 titer strength

injected into the gas cylinders gives clean surfaces and good lubrication.

- (6) Besides jacket cooling, water may be injected into the gas outlet pipe. Soda water in large volumes with provisions for circulating and cooling will serve for both lubrication and cooling in the gas cylinders.

Because of low piston speeds (less than 500 f.p.m.) the gas cylinders can tolerate considerable quantities of soda water without knocking; but it is best to locate the discharge valves at the bottom of the gas cylinder, *i.e.*, with top gas intake and bottom discharge.

Between the CO<sub>2</sub> compressors and the tower inlet, the gases pass through a separator so that soda water may not be carried over to the towers. The gas passing from the CO<sub>2</sub> compressors to the columns should be cooled to about 30° C. The column inlet pipe is provided with a tall loop somewhat higher than the tower itself so that liquor from the column cannot run back through the gas pipe, if for any reason the CO<sub>2</sub> compressor is stopped or when the gas delivery fails. The CO<sub>2</sub> compressor for the Solvay tower is the biggest power consumer in the soda plant outside of the main power-generating units.

Lately, some ammonia soda works have installed turbo-compressors for compressing CO<sub>2</sub> gases for carbonation. These compact machines have a very large capacity compared to their size, 15,000 to 25,000 cu. ft. of free gas per min. at a speed of 10,000 to 12,000 r.p.m. It is clearly seen that one such machine can do the work of 5 or 6 piston-type low-speed compressor units (each unit of which may be in itself a duplex machine, having two gas cylinders each delivering gas to a tower). The use of these turbo-compressors results in a great saving in floor space, and also a saving in the first cost. But if the gas volume is small, as in a small alkali plant, the first cost is not low, and the power consumption is even higher. Its drawback is that the gas delivery is not positive, so that if one column is partially plugged and offers greater resistance, little gas is delivered to that column. Also, because of its huge capacity, a large number of columns must be grouped together and run in parallel. This makes the regulation of gases to each individual column rather difficult. As for smaller units with a capacity comparable to that of one unit of the piston-type CO<sub>2</sub> compressor, these turbo-type compressors would be economical neither in first cost nor in maintenance. For large-scale operation, however, these turbo-units offer great possibilities of application.

In one instance, a four-stage turbo-compressor running at 12,500 r.p.m. at 40 lbs. pressure gage and delivering CO<sub>2</sub> gas to a single making tower (1300 cu. ft. per min. piston displacement) requires more than twice as much steam per I.H.P. as would a piston-type compressor for the same service, but the first cost is about the same. At twice this capacity (2600 cu. ft. per min. piston displacement for two making towers), the steam consumption per I.H.P. is still about 80 per cent higher, while the first

cost is cut to a half. At a still higher capacity, however, where one turbo-compressor serves eight making towers, the steam consumption begins to compare favorably with that of the piston-type low-speed compressors, and the first cost is then reduced to a small fraction. This applies to turbo-compressors driven by either single-stage non-condensing turbines or multi-stage bleeder turbines.

At present, the Elliott Company, Ridgway, Pa., the Ingersoll-Rand Company, New York, N. Y., and Allis-Chalmers Mfg. Co., Milwaukee, Wis., are leading in the manufacture of turbo-type compressors in the United States.

The speed of the piston type CO<sub>2</sub> compressors is taken at about 60 to 80 r.p.m., because it is believed that, at this speed, the pulsation effect of the gas delivered to the towers will help keep them open, *i.e.*, the bicarbonate in the towers is not so likely to form incrustations tending to plug them up. But this is just a belief which has grown up in this industry, and lacks scientific background.

## Chapter IX

### Working of Carbonating Towers or "Columns"

The carbonating towers or "columns" of Solvay design which have about 35 gas-distributing mushrooms, stacked one above the other, separated by plain rings or cooling tube sections, as the case may be, are efficient in gas absorption, but they are very delicate pieces of apparatus when a slurry is involved. In the first place, under no circumstances must the flow of gas entering the tower be interrupted while the tower is full of sodium bicarbonate so as to permit the suspended bicarbonate to settle in the tower. The surging (or pulsation) effect of the carbon dioxide gas delivered from the carbon dioxide compressors is believed to be beneficial in keeping the bicarbonate in the columns in suspension. The flow of gas to the towers will be interrupted either by the failure of the carbon dioxide compressor or, what is more likely to happen and what constitutes a treacherous affair for even an experienced operator, by the failure of one or more of the gas delivery valves to seat properly, so that little or no gas is being delivered to the tower, even though the compressor may be running at its normal speed. Such a case may be diagnosed by the surging up and down of the water levels in the U-shaped manometer located on the suction main. If this condition is allowed to go on undetected for any length of time, the effect will soon begin to show on the tower. Large quantities of sodium bicarbonate crystals will settle in the tower, of which little can be drawn out through the draw line. The only remedy is to introduce steam into the tower bottom. The steam can be introduced best through the steam connections at the sides and through the draw opening in the bottom section. The steam dissolves the bicarbonate, reversing the process according to the following reaction:



and opens its way through the blockade. The introduction of steam must be carefully carried out, or the bicarbonate will show a reddish tint. No more steam should be passed in than is necessary to open up the tower, and the duration of steaming should be as short as possible.

In the second place, even when a tower has been operating smoothly, it needs frequent cleaning. The cooling tubes become coated with precipitated bicarbonate after three or four days' running ("making") and the tower is then said to be getting "dirty." This "dirty" condition is shown by the increase in the percentage of carbon dioxide in the exit gas and in the rise of the draw temperature, since the cooling water is unable to absorb the heat generated in the tower by the chemical reaction because of insulation of the cooling tubes by the bicarbonate scale. The resistance

to gas passage in the tower may have been increased, but in point of fact it is more often attended by a fall, rather than a rise, in the gas pressure through the column. This can be understood when we realize that the space in the tower is decreased by the deposition of large amounts of solid bicarbonate in each section and that the net height of the static column of the liquor is reduced. When the liquor is saturated with carbon dioxide gas, forming a foamy liquid or emulsion, the static head of this emulsified liquor in the tower is also reduced. Such has actually been found to be the case. Only in case of obstruction of the tower bottom by the settling of sodium bicarbonate does the gas pressure increase in the course of operation. The rise in draw temperature is, however, always an infallible indication that the tower needs to be cleaned. In the worst case, the magma at the draw comes out, not in a smooth, continuous stream, but in broken jets, and considerable carbon dioxide gas foam appears in the draw liquor. This shows that the tower is badly plugged and that a channel has been cut in the obstruction in the bottom ring where the draw opening is located, through which the gas finds its way out with the magma. Such a case requires immediate attention.

In a carbonating tower possessing a large number of cooling tubes (hence a large cooling capacity but a limited liquor space), if the exit gas rises excessively on account of a serious shortage of green liquor (or ammoniated brine) or because of the decrease in the rate of draw due to partial plugging of the pipe or of the draw opening, large amounts of bicarbonate accumulate in the tower not only at the bottom but also in the upper cooling sections. If these conditions are allowed to continue, bicarbonate may completely plug the column and the draw stops by itself. When such conditions occur, the best remedy is to shoot in steam momentarily through the draw pipe into the tower bottom. If after repeated application of steam, the tower refuses to be opened up, the only safe way is to turn it to cleaning immediately. This is done by closing off all cooling water, changing over to "lean gas" with gradual bleeding out of the gas, and drawing out the bicarbonate with or without the help of steam at the bottom of the column. In one actual case, because of shortage of green liquor, the exit gas in one making tower rose as high as 45 per cent carbon dioxide, the inlet gas pressure fell from 38 to 30 lbs. per sq. in., the upper tower temperature rose from 55° to 67° C., and the draw became so sluggish that it stopped by itself. The draw liquor became foamy; and after each application of steam, the draw came out in a discontinuous stream and gradually stopped of itself. The ultimate salvation was to turn the tower to cleaning at once. Hence the simultaneous occurrence of an excessive rise in the percentage of carbon dioxide in the exit gas, of a drop in the inlet gas pressure, of a rise of temperature in the upper portion of the tower, and of the appearance of foamy and ever-decreasing volumes of draw liquor indicates that the tower is being badly plugged and that the condition demands immediate attention.

The process of cleaning consists in putting the tower on the lean gas, cutting out the cooling water entirely, bleeding out a portion of the lean



gas, and at the same time drawing the tower hard, until the bicarbonate in the magma is about 8 per cent or less by volume. The normal percentage of bicarbonate by volume after 3 minutes' settling is about 40 to 45 per cent. All the green liquor then is fed to the tower, from the bottom of which this cleaning (precarbonated) liquor is sent to feed the other ("making") towers by means of a booster pump, or better, by means of a carbon dioxide gas lift. The cleaning tower is kept warm (approximately 40° C.) by shutting off the cooling water to help dissolve the deposited bicarbonate therein. By bleeding out the desired portion of the lean gas, the liquor in the cleaning tower is carbonated to just below the precipitating point (65 grams of carbon dioxide per liter). The process of cleaning lasts from 18 to 24 hours. At the end of the cleaning period, the normal process of "making" is resumed, rich gas being turned in and the cooling water admitted about 15 to 20 minutes later. About 5 minutes after the cooling water has been admitted, the tower can be drawn, at first lightly, then in gradually increasing amounts until a normal stream is obtained. The following is an actual sequence of operation when a tower was changed from cleaning to making:

TABLE 67. Interim Conditions of a Column from Cleaning to Making.

10:45 A.M.	Tower changed to making	11:55 A.M.	Draw temp. at 37.0° C
11:00 "	Put on cooling water	12:00 noon	" " " 36.5° C
11:05 "	Draw commences (in a very small stream)	12:05 P.M.	" " " 36.0° C
		12:10 "	" " " 35.5° C
11:10 "	Draw temp. at 46.0° C.	12:20 "	" " " 34.8° C
11:15 "	" " " 44.0° C.	12:30 "	" " " 34.1° C
11:20 "	" " " 42.0° C.	12:40 "	" " " 33.5° C
11:25 "	" " " 41.0° C.	12:50 "	" " " 32.9° C
11:30 "	" " " 40.0° C.	1:00 "	" " " 31.9° C
11:35 "	" " " 39.5° C.	1:20 "	" " " 29.0° C
11:40 "	" " " 39.2° C.	2:10 "	" " " 27.2° C
11:45 "	" " " 38.8° C.	2:40 "	" " " 27.0° C
11:50 "	" " " 38.1° C.		

At 2:40 the draw had been increased to the normal stream. Thus, it takes two to three hours after cooling water has been admitted for the draw to reach its normal temperature. At the start the temperature above the cooling section in the upper portions of the column is 33 to 34° C. and the exit gas contains only 0.8 to 1.0 per cent carbon dioxide. The tower being cold at the start, the grain of the bicarbonate crystals from the tower is necessarily irregular, and the bicarbonate from the filter is wet and difficult to dry. Such bicarbonate needs greater amounts of returned ash for drying. But this does not affect dryer operation, when normal crystals from the other (making) towers are mixed with such bicarbonate in drying. The crystals improve when the tower reaction temperature increases to above 50° C. at about the two-thirds point. When the operation is finally normal, this temperature will be about 60° C.

Experience has shown that a column must be put on cleaning after it has been making for four days (96 hours). This means that with a group of five towers, one tower must be "cleaning" every day, and the

cleaning is done by rotation. With less than four towers, as in very small plants, an equivalent length of time must be adopted for the cleaning period, but the cleaning is less effective because of the small volume of green liquor that can be put through the cleaning tower to feed the making towers. Under these circumstances, it may be necessary to boil the contents of the tower with water and steam once every four to six months. The tower then is first emptied of the bicarbonate and the liquor. It is then filled with water about  $\frac{3}{4}$  full, and steam is introduced at the middle rings as well as the bottom ring of the tower at several points. A small quantity of lean gas is admitted to help agitation, and the circulating pump or gas lift is used to circulate the water in the tower. The temperature of the water in the tower should not be increased above  $80^{\circ}\text{C.}$ , as a higher temperature is neither desirable nor necessary. With two or three changes of water in the course of steaming, which lasts for 36 to 48 hours altogether, the entire content will have been practically all dissolved out. All bicarbonates ( $\text{NaHCO}_3$  and  $\text{NH}_4\text{HCO}_3$ ) are dissolved, what is left being small pieces of iron scale (black) and the incrustation of magnesium carbonate (white). Scale in the lower (bottom) portions of the tower normally consists exclusively of sodium bicarbonate, completely soluble in hot water; but the small quantity occurring in the upper portion of the column consists of magnesium carbonate with layers of dark iron scale which is insoluble in hot water, but which may be loosened from the surface by steaming. Such loose pieces must be raked out through manholes or flushed down to the bottom of the tower. It is essential that such pieces be all taken out, for, if they are left in the column, they will form nuclei for scale formation in the column, blocking the draw pipe. For this purpose, as well as for inspection, manholes should be provided diametrically opposite on each side of each ring and of each cooling section of the tower. Because of these cleaning difficulties the minimum number of columns in a plant must be *three*. A maximum number for a group is *five*, one out of five running "on cleaning" every day. This defines the smallest economic unit possible for an ammonia soda plant, and consequently determines the smallest number of units in the plant. This is why the smallest ammonia soda plant that will work efficiently must have a minimum daily output of 100 to 150 tons.

With a group of five columns as a working unit and with the green liquor (ammoniated brine) reasonably free from magnesium, the drastic method described above for cleaning the column by cooking should not be necessary and the usual method of cleaning by running through warm ammoniated brine will suffice. Five columns of standard size should then produce on the average 200 tons of soda ash a day. Larger plants have more than one group of five columns each.

Historically, in the Solvay Process plant, Syracuse, N. Y., the first carbonating towers were 2 meters in diameter and had flat plates with 9-inch holes in the center. These towers were showered with water outside but had no internal cooling. They had a capacity of ten tons of soda ash each per day. Mr. W. B. Cogswell suggested internal cooling, and

nozzles were bolted on several of the rings, through which passed 4-inch tubes carrying cooling water. The capacity was then increased to 20 tons each.

When the second set of towers was built, the lower 8 rings in each tower were provided with 2-inch cast-iron tubes held in the tube sheets with 2-inch lead caulking rings. The division plates, instead of being flat, were made conical and the center holes were increased from 9 inches to 20 inches in diameter. Those center holes were also provided with teeth to subdivide and distribute the gas bubbles in the column.

No steaming or heating of the towers to dissolve the scale from the tubes was found necessary when the columns were properly "cleaned" by running green liquor through them, as mentioned above. These columns were always five in a group, one "cleaning" and four "making." Each day one of the five was put on "cleaning" in rotation. It was reported that in this way each "making" column of 2-meter diameter averaged 60 short tons of soda ash a day.

TABLE 68. Composition of Scale in the Lower Portion of Column.

Analytical Results		Calculated Results	
	Per Cent		Per Cent
NH <sub>3</sub> (free)	1.20	NaHCO <sub>3</sub>	83.13
CO <sub>3</sub> <sup>2-</sup>	3.48	NH <sub>4</sub> HCO <sub>3</sub>	5.58
HCO <sub>3</sub> <sup>-</sup>	64.75	Na <sub>2</sub> CO <sub>3</sub>	5.36
Cl <sup>-</sup>	0.34	NaCl	0.56
SO <sub>4</sub> <sup>2-</sup>	Trace	CaCO <sub>3</sub>	0.22
Fe <sub>2</sub> O <sub>3</sub>	Trace	MgCO <sub>3</sub>	0.42
Ca <sup>++</sup>	0.09	Water by diff.	4.73
Mg <sup>++</sup>	0.12		
Na <sup>+</sup>	25.30		

The tower draw pipes are also subject to scale formation. Crusts of sodium bicarbonate are formed around the internal walls of the pipes. By a gradual building up of these scales to a thickness of 1 to 2 inches, the pipe opening is gradually reduced, restricting the passage of the draw magma. Frequently these pipes have to be taken down and replaced by new sections of C. I. pipes. Scale is best cleaned out by heating the pipes externally over a small fire or blowing steam through them. Analyses of the scales in the upper and lower portions of a column, respectively, are given in Tables 68 and 69.

Thus it will be seen that the scale in the lower portions of the column, on the internal walls, and around the cooling tubes is practically all sodium bicarbonate, but that that of the upper portion consists also of magnesium carbonate and iron scale.

Magnesium in the tower comes from the mud in the ammoniated brine which has not been completely settled. It is deposited in the upper portions of the tower where the green liquor first strikes the carbon dioxide gas. This is a serious matter. It may be the result of not having sufficient capacity in the settling vats for the quantity of the brine flow, or else it may be due to excessive amounts of magnesium in the brine. As

boiling-out is the most drastic means of cleaning a column, magnesium scale, being difficultly soluble in water, must be removed by hand after the boiling-out operation. As not all rings are provided with ample man-hole area, and not all manholes are so located as to reach every cooling tube or every corner of the column sections, blocking caused by magnesium scale in the upper cooling sections is detrimental to successful operation of the column. Magnesium mud ( $\text{MgCO}_3$ ) in the ammoniated brine is very much more difficult to settle out than calcium mud ( $\text{CaCO}_3$ ) as has been mentioned many times elsewhere. The fact that considerable magnesium and no calcium is found in the column scale bears out the

TABLE 69. Composition of Scale in the Upper Portion of Column.

Analytical Results		Calculated Results	
	Per Cent		Per Cent
$\text{SiO}_2$	0.10	$\text{NaHCO}_3$	41.30
$\text{Fe}_2\text{O}_3$	0.71	$\text{Na}_2\text{CO}_3$	21.00
$\text{SO}_4^{=}$	0.12	$\text{MgCO}_3$	19.39
$\text{Cl}^-$	7.37	$\text{NaCl}$	12.15
$\text{S}^{=}$	0.12	$\text{NH}_4\text{HCO}_3$	3.90
$\text{CO}_3^{=}$	26.01	$\text{CaCO}_3$	0.53
$\text{HCO}_3^-$	33.00	$\text{FeS}$	0.33
$\text{NH}_3$ (free)	0.84	$\text{CaSO}_4$	0.61
$\text{Ca}^{++}$	0.39	$\text{Fe}_2\text{O}_3$	0.30
$\text{Mg}^{++}$	5.59	$\text{SiO}_2$	0.10
$\text{Na}^+$	25.19	Water by diff.	0.39

truth of this statement. With an effective depth of not less than 15 feet in the vats it is found that a minimum of 6 sq. ft. of settling area is necessary per gallon (U. S.) of liquor flow per minute for an untreated sea brine in order to bring the total mud content in the clarified ammoniated brine to below 0.1 gram per liter.

Following each boiling, an off-color ash is certain to be produced, or an ash yielding a cloudy solution containing considerable insoluble matter. Hence boiling-out or steaming of a column is not to be recommended unless absolutely necessary.

For a good temperature gradient in the tower, the cooling water coming out of the uppermost cooling section of the tower should be quite warm and have a temperature of about  $45^\circ\text{C}$ . There should not be a sudden chilling of the liquor upon striking the first bank of cooling tubes as it descends from the top. Cooling water entering the bottom section should be as cold as possible but it must be able to take up heat gradually and become warmed to about  $45^\circ\text{C}$ . at the top outlet (*i.e.*, from the uppermost cooling section of the tower). The maximum temperature in the tower occurs at about two-thirds of the height from the bottom and is in the neighborhood of  $60^\circ\text{C}$ ., as stated above.

Table 70 gives the temperature observations in a carbonating tower in operation.

In order that the outlet water leaving the tower may be warm ( $45^\circ\text{C}$ .), if we start with a very low temperature of the cooling water (16 to  $16\frac{1}{2}^\circ\text{C}$ .) at the bottom, it is evident that there must be a large cooling

TABLE 70. Temperature Gradations in a Tower.

(Unless otherwise mentioned, all temperatures are taken at the outer surface of tower walls.)

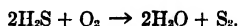
	° C.
Green liquor entering Ring 33 (inside wall).....	43.0
Tower exit gas at Ring 36 (inside wall).....	47.0
Surface of Ring 34 .....	48.2
"    "    "    33 .....	46.6
"    "    "    32 .....	47.8
"    "    "    31 .....	47.2
"    "    "    30 .....	49.2
"    "    "    29 .....	47.2
"    "    "    28 .....	51.5
"    "    "    27 .....	52.3
"    "    "    26 .....	52.3
"    "    "    25 .....	52.7
"    "    "    24 .....	51.8
"    "    "    23 .....	51.8
"    "    "    22 .....	53.0
Inside wall of Ring 22 .....	57.0
Surface of Ring 21 .....	52.0
"    "    "    20 .....	....
"    "    "    19 .....	49.6
"    "    "    18 .....	49.6
"    "    "    17 .....	49.0
"    "    "    16 .....	49.6
"    "    "    15 .....	45.6
"    "    "    14 .....	44.5
"    "    "    13 .....	44.4
"    "    "    12 .....	42.0
"    "    "    11 .....	38.9
"    "    "    10 (Uppermost cooling section)....	35.8
"    "    "    9 .....	34.8
"    "    "    8 .....	34.5
"    "    "    7 .....	31.6
"    "    "    6 .....	30.5
"    "    "    5 (Portion cooling water bled out here) .....	29.8
"    "    "    4 .....	28.0
"    "    "    3 .....	26.9
"    "    "    2 .....	24.8
"    "    "    1 .....	22.5
Cooling water entering tower bottom .....	16.5
"    "    bled out from mid-cooling section ....	24.0
"    "    at exit, topmost cooling section .....	21.0

surface and a long course of water flow. This is secured by having multiple cooling-water passages in the tower cooling sections and by having a number of these sections, one on top of the other, with a gradually decreasing number of cooling tubes toward the top, the total height of the cooling sections aggregating about one-half of the tower's overall height. Under these conditions, the lower the temperature of the cooling water, the lower will be the draw temperature, and the lower the free ammonia titer in the draw. Consequently, the higher will be the decomposition, with excellent bicarbonate crystals, provided the gas and liquor concentrations are up to normal.

Good bicarbonate crystals should feel gritty or granular between the thumb and the finger, and the layer of bicarbonate on the vacuum drum

filter should be about  $\frac{1}{2}$  inch thick at a vacuum of 8 to 10 inches Hg. The free ammonia titer in the draw runs parallel to the draw temperature in the normal rate of draw. For instance, with normal ammoniated brine, when the draw temperature varies from 22 to 40° C. (a very wide range of temperature change) the free titer in the draw follows closely or may be one or two points behind the temperature. This shows how important the draw temperature is and how essential it is to have an ample cooling surface and a cold underground water supply for the cooling medium. With the above cooling arrangement maintaining a high reaction temperature at the two-thirds point in the column, there can be no lower point for the draw temperature, the limit of the draw temperature being the ability of the cooling water to cool and the heat conductivity of the cooling tubes. Using well water having an average temperature of 16 to 16.5° C., it is impossible to cool the draw liquor below 20° C. This at present is the draw temperature limit, unless the cooling water is refrigerated.

The author has actually known of a case where, in the course of years of operation, free sulfur was deposited in the top rings of a column, obstructing the gas passage. This deposit was undoubtedly formed from the oxidation of hydrogen sulfide by the oxygen in the carbon dioxide gas. Thus,



Such an excess of oxygen comes from the leakage of air into the furnace gas, which is to a certain extent unavoidable. It has been occasionally observed in the gage glass at the top of the column that the liquor contains suspended free sulfur in the form of a yellowish-white, fine emulsion. The analysis of the free sulfur deposited at the top ring of the column is given in Table 71.

TABLE 71. Analysis of Air-Dried Sample of Deposited Sulfur at the Top of the Column.

	Per Cent
Free sulfur	59.50
NaCl	13.51
NaHCO <sub>3</sub>	24.11
Na <sub>2</sub> CO <sub>3</sub>	1.14
NH <sub>3</sub>	Trace
Moisture by diff.	1.74

Evidently considerable ammonia had disappeared here and the small amount of sodium carbonate present came from the loss of carbon dioxide in the sodium bicarbonate on exposure to the air.

The capacity of a carbonating tower, like the boiler rating, depends much upon how it is operated. With a given amount of cooling surface (which determines the capacity to a large extent) the quantity of production from a tower depends upon the richness of the CO<sub>2</sub> gases pumped to the tower (also its volume-rate) and the concentration of salt and ammonia in the ammoniated brine fed to the tower, *i.e.*, the Cl<sup>-</sup> and

free  $\text{NH}_3$  titers. A large tower may have very low production when working on a dilute mixed gas or on an ammoniated brine too dilute in chlorine or ammonia. Furthermore, the crystals obtained from columns under such conditions, *i.e.*, with low chlorine titer (weak brine) or with weak mixed gases, or both, are very fine and the soda ash obtained has an abnormally low density (lighter than normal light ash). The one most important factor that determines the capacity of a column is the temperature of the cooling water available.

## Chapter X

### Filtration of Crude Sodium Bicarbonate (Ammonia Soda): Composition of the Bicarbonate

The crude sodium bicarbonate drawn from the columns is filtered off from the mother liquor. The older type of filter consisted of an open wooden tank with a false bottom, over which was laid a filtering fabric. Mother liquor was sucked from the compartment below the false bottom by means of a piston pump. This inefficient batch filter is now obsolete.

At present, the rotary open-drum filter and the centrifugal filter are the two standard machines. The drum filter has a pipe through the journal at one end, where suction is applied, and a smaller pipe through the journal at the same end or at the other end, where compressed air or waste carbon dioxide gas under pressure from the column exit is introduced. The filtering medium is a woolen felt or blanket wrapped on the drum.

The vacuum helps dry the bicarbonate on the filter and sucks the ammonia gas inward so that ammonia loss to the atmosphere is reduced.

The woolen fabric has a tendency to become plugged by crystals of the bicarbonate, and frequent blowing out with compressed air or carbon dioxide gas is necessary to open the pores. A self-blowing drum filter has one compartment that revolves just past the scraping knife or "doctor"; this compartment is about to enter the liquor, blowing under pressure, while all other compartments are under vacuum. An internal sliding pressure valve connects the opening leading to this compartment with the pressure pipe, so that each compartment is blown once during each revolution. In this way the drum can pick out bicarbonate continuously without stopping for blowing or cleaning. Water in a thin film from a weir is allowed to play on the surface of the bicarbonate to wash the salt (NaCl) from it. The weir box is provided with a standpipe, at the bottom of which is an orifice plate. The standpipe is provided with a gage glass to show the level of water above the orifice plate, feeding the weir box below. Generally, a cold, weak ammonia water from the cooling tower is used for this purpose. Between the weir box and the scraper, or doctor, is provided a number of press rolls made of heavy cast iron (each having about 300 lbs. pressure per foot of length) resting on the surface of the bicarbonate layer, the pressure on the bicarbonate being adjustable. Each press roll serves to level the surface of, and fill any channels in, the bicarbonate layer, and to squeeze out water by its pressure so as to give a drier bicarbonate for furnacing. Because of this crushing action, too, the bicarbonate leaves the scraper in a looser form, free from solid cakes. Each press roll revolves at exactly the same peripheral speed as the



peripheral speed of the bicarbonate on the drum (making allowance for the thickness of the bicarbonate layer). It is independently driven from the same drive of the filter—not merely caused to revolve by the rolling contact with the face of the drum. These pressure rolls, however, have the disadvantage of causing more rapid wearing out of the felt, especially when the edges of the slots on the cylindrical segments of the cage below are not properly rounded off and smoothed. When the bicarbonate crystals are good, the yield (*i.e.*, the weight of sodium carbonate plus sodium chloride obtained per 100 grams of the filtered and washed sodium bicarbonate) should be about 54 grams (*i.e.*, with free moisture about 14 per cent).

The filter drum is a squirrel-cage affair, having slotted segments or cross bars with slots between them. The ends of the drum are closed with covers. It should be all cast iron. Sometimes the cage is covered with cylindrical segments of cast iron or steel plates having a large number of oblique slots. On the face of the slotted drum is wrapped a layer of coarse backing nickel wire cloth or screen which supports a fabric wrapped over it for the filtering medium. This fabric is in the form of a woolen felt or blanket, about  $\frac{1}{8}$  inch thick, and is of a loose but uniform texture. Neither the nickel wire cloth nor the woolen blanket stands the corrosion of the mother liquor very well. The life of a woolen blanket for this purpose is about three weeks of continuous service. Ammonia seems to have considerable action on the animal fibers. Yet vegetable fibers like cotton or hemp, which stand the alkaline action of ammonia much better, do not serve the purpose well, because they do not possess the even porosity of woolen felt, and they swell up unevenly and become tight when soaked in the liquor. Consequently, instead of a uniform layer of bicarbonate, there would be uneven spots over the larger pores in the cotton or hemp fabric. Through these pores considerable bicarbonate may pass into the filter liquor and be lost. In place of the nickel wire cloth, a finely fabricated bamboo matting made of small bamboo sticks serves the purpose very well. It lasts longer, and the costly nickel wire cloth can be successfully replaced by the inexpensive, inert bamboo material.

It may not be out of place to dwell somewhat on the early history of the filters introduced into the ammonia soda industry. In the early days of the Solvay Process plant at Syracuse, N. Y., long rectangular filter tanks were used; some of these were 60 feet long by 30 inches wide, and were provided with woven flannel cloths supported on grates at the bottom. In the false bottom below, mother liquor was drawn off by vacuum and the bicarbonate was shovelled out by hand into bottom-dump cars standing alongside. The crystals were washed by means of a swinging perforated pipe. This involved a great deal of labor.

Mr. Ernest Solvay, who was visiting the Syracuse works, suggested to the engineer, Mr. Edward N. Trump, that he devise "a sort of a revolving perforated cylinder with vacuum inside," and the result was the first rotary vacuum filter built by Mr. Trump for the Syracuse plant. Six of

these rotary units replaced all the long, rectangular filter tanks. At first, the scraper knife tended to "glaze" the surface of the blanket so that vacuum had to be taken off every 15 minutes and the blanket washed. The machine was anything but continuous. To avoid "glazing" of the crystals on the blanket, the scraper knife was then attached to the agitator shaft which gave it an oscillating motion, so that the knife would not bear on the same spot during each revolution and form a corrugated surface on the bicarbonate. Later, compressed air was used for blowing back and back-washing. This was a decided improvement, but the filter still had to be stopped for back-washing. A big stride was made when it was found possible to do away with this intermittent operation in back-washing and introduce an automatic self-blowing device. A continuous rotary vacuum filter was developed. The inside of the filter drum was divided into compartments around the circumference, and compressed air was introduced by a valve closing the commutator leading to that particular compartment having just passed over the scraper knife and blowing it when that compartment just entered the liquor again, thus enabling it to pick up a fresh layer of bicarbonate. Then it emerged from the liquor at the back where the cake was washed by a film of water over a weir. The next development was the addition of heavy press-rolls, driven independently at a speed somewhat faster than the peripheral speed of the filter drum itself, to level the bicarbonate layer and squeeze the moisture out of it after it had been washed and before it was scraped off.

The filter thus developed was soon adopted by European Solvay plants as one of the standard pieces of equipment. From a filter one meter wide and two meters in diameter, it was found possible to obtain enough ammonia soda (crude bicarbonate) to make 120 tons of soda ash a day, using a 10-inch mercury vacuum. Filters were then used also for other service. For ammonia soda service, flannel cloth or felt was used; but for filtering caustic mud, a close-woven rectangular-mesh nickel wire cloth (20 × 120 mesh or finer) was used in place of the woolen blanket. Narrow grooves supported by internal flanges, or circumferential grooves supported by cross ribs, were milled in the cylinder, and the flannel cloth or nickel wire cloth, as the case might be, was held on the drum by winding it with nickel wire.

These continuous rotary vacuum filters could give a bicarbonate cake containing 12 per cent moisture when good crystals were obtained from the columns. Vertical-suspended, bottom-discharge batch-type centrifugals had been tried in place of these filters, but it was found that the capacity was low, the labor required high, and, above all, the loss of ammonia excessive. A combination of the continuous filter and the centrifuge had been successfully employed. While it did not cause much ammonia loss and did yield a drier bicarbonate, the labor involved was considerable, and the somewhat better yield in the ammonia soda obtained offered no particular advantage in the rotary dryer operation as conducted in present practice.

Continuous rotary vacuum filters are now made in units as large as three meters in diameter and two or more meters long.

The salt content can be reduced but it cannot be entirely eliminated. The "yield" of the bicarbonate (which measures the dryness of the bicarbonate from the filters) is very essential to the successful operation of the soda dryers. Table 72 shows a control analysis of the normal crude bicarbonate from the filter.

TABLE 72. Result of Control Analysis of Filter Bicarbonate.

	Per Cent
(a) Yield	53.52
(b) NaCl	0.36
(c) $\text{NH}_3$ (total)	0.92

A complete laboratory analysis on a typical sample is given in Table 73.

TABLE 73. Analysis of Crude Bicarbonate from the Filters.

	Per Cent
$\text{NaHCO}_3$	75.60
$\text{Na}_2\text{CO}_3$	6.94
$\text{NH}_4\text{HCO}_3$	3.42
NaCl	0.39
$\text{CaCO}_3$	Nil
$\text{MgCO}_3$	Trace
Water by diff.	13.65

With the introduction of wash water, the mother liquor is diluted by about 8-10 per cent, *i.e.*, from 6 cubic meters of the liquor per ton of ash the total volume becomes 6.5-6.7 cubic meters. This is found by the

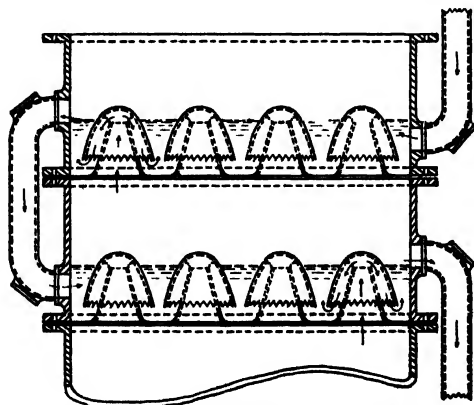


FIG. 38. Multiple passette filter washer.

determination of the chlorine concentrations, Cl<sup>-</sup> titers, in the liquors entering and leaving the filters. When bicarbonate crystals are poor, more water is consumed in washing out the sodium chloride to the allow-

able limit, and then higher vacuum is required. The loss of bicarbonate through solution by the wash water is estimated normally at 2-4 per cent.

The filter wash water should be a good, soft water. Any hardness in the water will be thrown down as calcium and magnesium carbonates or magnesium hydroxide, plugging the filter blanket. This is a serious matter because it would soon throw the filter out of commission. Generally, one reserve filter is standing by, running empty in water to clean the blanket. Each filter in the battery can be cleaned in this way by rotation. The bicarbonate should not appear dead white but should have a slightly bluish tone, showing a slight excess of sulfide. It should be light and loose, feel like sand between the fingers, and should not produce slimy juice when continually squeezed by forced kneading in the palm of the hand. The bulk specific gravity of the bicarbonate varies with the moisture content and with the crystalline character, *i.e.*, whether it is grainy or pasty. Normally, it should weigh 38 to 42 (average 40) pounds per cubic foot when loosely packed. The vacuum for the drum filter is 8 to 10 inches Hg at the filter. Coarser crystals of bicarbonate require less vacuum than the pasty kind, and the filter takes on a heavier layer of bicarbonate on the blanket—as thick as  $\frac{1}{2}$  inch. The coarse crystals also wash better, yielding lower sodium chloride content and drier sodium bicarbonate.

The gases from the filter are drawn through a small washer called the filter washer (Fig. 38) which is similar to the tower washer, but smaller in size and with fewer passettes. The ammonia present in the gases is scrubbed in this filter washer with fresh brine and the brine sent to the tower washer, thence to the absorber washer, and finally to the absorber for making ammoniated brine. The gases are sucked through by means of a vacuum pump, or exhauster, and the exhaust goes to the atmosphere. The volume displacement of the filter exhauster is 120-200 cubic meters per ton of soda ash produced, depending on the crystalline character of the bicarbonate and the size of the filter unit.

The drum filter should have a peripheral speed of 20 to 40 feet per minute. If it runs much faster, the bicarbonate may not filter dry. Too slow a speed, of course, gives a slightly drier product but cuts down the capacity. A self-blowing filter, one meter wide and two meters in diameter, today has a capacity of 150-200 tons of ash per 24 hours working on a good bicarbonate. A small filter, 30 inches wide and 4 feet in diameter, has a capacity of 80-100 tons of ash per 24 hours. The capacity of the filter is largely dependent upon the crystalline character of the bicarbonate. A filter turning out 80 tons of ash on coarse-grained bicarbonate may work with great difficulty on a pasty bicarbonate at the rate of only 45 tons per 24 hours.

The filter operation is important because a difference of a few per cent in the moisture content, measured as the "yield" of the bicarbonate, makes a great difference in the behavior of the bicarbonate in the drying operation.

The composition of crude sodium bicarbonate has been carefully studied and the results of analyses are given in Table 74.

TABLE 74. Complete Analysis of Bicarbonate from Filter.

(Sample granular to the feel. Setting test 3 minutes to a clear solution with sharp solid sludge boundary.)

	Per Cent
1. Analytical Results:	
NH <sub>3</sub> (total)	0.74
CO <sub>3</sub> <sup>=</sup>	4.52
HCO <sub>3</sub> <sup>-</sup>	53.02
Cl <sup>-</sup>	0.16
SO <sub>4</sub> <sup>=</sup>	0.07
Fe <sub>2</sub> O <sub>3</sub>	Trace
Ca <sup>++</sup>	Trace
Mg <sup>++</sup>	0.05
Na <sup>+</sup>	22.18
2. Calculated Results:	
NaHCO <sub>3</sub>	69.28
Na <sub>2</sub> CO <sub>3</sub>	7.76
NH <sub>4</sub> HCO <sub>3</sub>	3.45
NaCl	0.26
MgCO <sub>3</sub>	0.17
Na <sub>2</sub> SO <sub>4</sub>	0.10
H <sub>2</sub> O by diff.	18.98
The small amount of NH <sub>4</sub> Cl has been neglected.	
3. Confirmatory Checks on Results:	
A. Yield by weighing residue on ignition:	
a. Residue on ignition	52.00
b. Residue from NaHCO <sub>3</sub> , $69.28 \times \frac{53}{84}$	43.72
" Na <sub>2</sub> CO <sub>3</sub>	7.76
" NaCl	0.26
" Na <sub>2</sub> SO <sub>4</sub>	0.10
" MgCO <sub>3</sub>	0.17
Total	52.01
B. Total losses on ignition:	
a. Total loss on ignition (expt.)	48.00
b. Total loss on ignition (calc.)	
From H <sub>2</sub> O	18.98
" NaHCO <sub>3</sub> , $69.28 \times 0.369$	25.56
" NH <sub>4</sub> HCO <sub>3</sub>	3.45
Total	47.99
C. Yield by titration using methyl orange:	
a. Na <sub>2</sub> CO <sub>3</sub> yield (expt.)	51.74
b. Na <sub>2</sub> CO <sub>3</sub> yield (calc.) from Na <sub>2</sub> CO <sub>3</sub>	7.76
From NaHCO <sub>3</sub> , $69.28 \times 0.631$	43.72
" MgCO <sub>3</sub> as Na <sub>2</sub> CO <sub>3</sub> $0.17 \times \frac{106}{84}$	0.21
Total	51.69

From the foregoing results it is proved beyond doubt that the bicarbonate actually contains normal sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) which is present to the extent of  $7 \pm$  per cent. When the acidic and basic constituents from the analysis are combined to form various salts, it is found that there is a surplus of  $\text{Na}^+$  unaccounted for and at the same time also a corresponding surplus of  $\text{CO}_3^{--}$ , after all possible acidic radicals have been combined with  $\text{Na}^+$  and the small amounts of  $\text{NH}_4^+$  and  $\text{Mg}^{++}$  present. Independent checks from the "yields" of the bicarbonate and from the losses on ignition both give concordant results. So it can be concluded that the normal carbonate is present in the sample of the crude bicarbonate from the filters. Study of the mother liquor from the towers shows that this sodium carbonate is largely formed by the rapid loss of carbon dioxide on exposure to the air (see Chapter XI). Further, if the fresh solution of the crude bicarbonate is immediately taken from the filter without exposure to the air, it gives no coloration to phenolphthalein at first. However, the red color develops gradually but increases rapidly on standing *i.e.*, on exposure to the air.

Some ammonium bicarbonate is also found to be present to the extent of about 5 per cent  $\text{NH}_4\text{HCO}_3$  on the weight of dry  $\text{NaHCO}_3$  in the crude bicarbonate from the filters. The presence of  $\text{NH}_4\text{HCO}_3$  is due to an entirely different source, however. No matter how thoroughly the crude bicarbonate on the filter has been washed, some  $\text{NH}_4\text{HCO}_3$  is always found—in fact in a definite percentage of ammonium bicarbonate on the weight of dry sodium bicarbonate obtained. It would thus be seen that  $\text{NH}_4\text{HCO}_3$  and  $\text{NaHCO}_3$  have separated in the columns in the form of a solid solution with a definite ratio between them. This molar ratio is 1 mol  $\text{NH}_4\text{HCO}_3$  per 19 mols  $\text{NaHCO}_3$ , which gives approximately 5.0 per cent  $\text{NH}_4\text{HCO}_3$ .

The size of the crystals of the bicarbonate formed in the towers has an important bearing on the drying properties of the bicarbonate in the dryers. When the bicarbonate crystals are coarser, they filter better, wash better, and come drier, *i.e.*, the moisture content is lower and the "yield" in  $\text{Na}_2\text{CO}_3$  higher. Drier bicarbonate always means less tendency to scale formation in the dryer, less returned ash required, larger drying capacity for the dryer, and less coal consumption in the furnace per ton of soda ash calcined. When the bicarbonate crystals are coarser, a thicker layer of bicarbonate (as much as  $\frac{5}{8}$  inch thick) can be picked up on the filter, even though a smaller vacuum is required. Poor crystals, formed from cold towers, for instance, require a high vacuum for filtering (as much as 12 to 18 inches Hg); yet only a thin layer can be picked up, yielding a wet bicarbonate which is difficult to dry and which contains high sodium chloride. This cuts down the capacity of the filter as well as that of the dryer. Bicarbonate that will not produce any slimy juice on long squeezing and forced kneading in the palm of the hand will dry without difficulty. This is a rough and ready test for the quality of the bicarbonate. Bicarbonate having a "yield" of more than 47.5 per cent will not produce any slimy juice in this way, nor stick together to form

a ball in the hand. Good bicarbonate crystals should feel granular, like fine sand between fingers, while poor crystals will feel sticky, like a starch paste. Good, coarse crystals will settle to a compact sludge in a 100-cc. cylinder in less than three minutes, while poor ones will require a much longer time (7 to 10 minutes), and they will not settle to a compact sludge but to a voluminous, mobile, slimy paste. Too high a draw temperature may also produce this condition because of partial re-solution of the bicarbonate crystals in the liquor. Under normal conditions, the volume of the completely settled bicarbonate at the bottom of the glass cylinder should be 40 to 45 per cent of the total volume of the tower draw sample. But when the crystals are poor, the precipitate is less compact and may occupy a volume of 50-55 per cent. The percentage of suspended solids ( $\text{NaHCO}_3$  crystals, etc.) in the slurry from the columns generally runs 20.5-21.0 per cent by weight.

As mentioned above, filtration of crude bicarbonate by means of continuous, rotary vacuum filters has been most generally employed in ammonia soda plants. This is essentially a constant-pressure filtration, in which the pressure differential between the atmospheric pressure outside the drum and the partial vacuum inside furnishes the driving force. In ammonia soda plants, the rate of draw from the columns to the filters is maintained constant, and so is the output from each filter. Due to the care exercised to maintain the crystal size, the thickness of the cake on the filter and the vacuum required are practically constant day in and day out. To understand better the principles underlying filtration, we may pause for a few moments to dwell briefly on some theoretical discussion. Not unlike a filter press, the cake on the filter has to be built up under a pressure differential to a desired thickness from solids caught on the surface of the filtering medium when the liquid is forced through. It is thus seen that the resistance through the cake increases proportionally as the thickness of the cake that is being built up, other conditions being equal, and so also increases proportionally as the volume of the filtrate that is being collected. At the same time it is also easily seen that this resistance varies inversely as the filter area. The filtering medium in the form of a woolen felt possesses numerous pores through which liquor passes, closely approximating the condition of flow called for in Poiseuille's law, i.e., the pressure drop across the filtering medium is directly proportional to the viscosity of the liquid, the velocity of the flow, and the length of the path; and it is inversely proportional to the cross-sectional area. From the slowness of infiltration of the liquor through the pores of the cake and of the blanket, it is safe to assume that the flow within these pores would be "viscous" or "streamline," and we may expect Poiseuille's law to hold. Under these conditions, we may expect the rate of filtration to be:

$$\frac{dV}{d\theta} \propto \frac{AP}{\mu R}$$

where  $V$  = volume of the filtrate in cu. ft. passing through the filter;  
 $\theta$  = time of filtration in sec.;  
 $A$  = area of filter in sq. ft.;  
 $P$  = pressure differential in lb. per sq. ft.;  
 $\mu$  = viscosity of the liquor in poises;  
 $R$  = characteristic constant depending on resistance of the cake, etc.

For a given filter operating on a given liquor at a substantially constant-pressure differential,  $\frac{AP}{\mu}$  is a constant ( $=K'$ ), i.e.,

$$\frac{dV}{d\theta} = \frac{K'}{R}$$

But, as mentioned above, the resistance of the cake depends upon the thickness of the cake being built up, which in turn varies as the volume of the filtrate passing through the filtering medium.

Therefore  $\frac{dV}{d\theta} = \frac{K}{V}$ , where  $K$  is now a combined constant  
 or  $VdV = Kd\theta$

Integrating we get

$$(V + V_0)^2 = K(\theta + \theta_0),$$

where  $V_0$  is an integration constant having the significance of an initial volume of filtrate building up an imaginary thickness of a cake having the same resistance as the filtering medium itself, and  $\theta_0$  a constant establishing the starting time from which this imaginary cake may be said to have been formed.\* The curve showing the relationship between the volume of the filtrate passing through ( $V$ ) and the time of building up the cake ( $\theta$ ) is thus a parabola, and is true of a constant-pressure filtration operation, such as in the filtration of the crude bicarbonate from the columns, where the solids are highly crystalline and the cake is substantially non-compressible under the pressure differential employed.

As mentioned above, a centrifugal filter is sometimes used as a final filter, which brings the moisture content in the bicarbonate down still further to about 58 per cent of the yield, with the moisture content less than 7 per cent. Sometimes the moisture content in the bicarbonate from the centrifuge is claimed to be as low as 4 per cent, i.e., the yield as high as 60 per cent. Under such conditions little returned ash would be required in drying the bicarbonate in the rotary dryers. The centrifugal filter is, however, an intermittent machine operating in batches with a bottom discharge for the vertical type, and side discharge for the horizontal type. It revolves at from 1000 to 1800 r.p.m. A batch-type machine with a 48-inch basket will produce 30-35 tons of bicarbonate per 24 hours. The intermittency of the batch and the difficulty of keeping down the loss of ammonia caused a serious problem in the adaptation of the

\* Ruth, B. F., *Studies in Filtration. III. Derivation of General Filtration Equations, Ind. Eng. Chem.*, 27, 708 (1935); *Studies in Filtration. IV. Nature of Flow through Filter Septa and Its Importance in the Filtration Equation, Ibid.*, 27, 806 (1935).



centrifugal to soda-ash manufacture. However, the use of centrifugals for filtering is more general in connection with the manufacture of refined sodium bicarbonate (see Chapter XVIII). A continuous centrifuge is now offered in the market. It greatly cuts down the labor of handling and increases the output per unit with a saving in floor space.

Continuous centrifuges may be classified into two types. One is the automatic type which is continuous as regards the different operations in the cycle, but intermittent in feeding and unloading. It is really an automatic intermittent machine. The other type is a strictly continuous one, both taking the feed and discharging the cake continuously. To avoid confusion we shall refer to the former as the "automatic" type and the



*Courtesy Bird Machine Co.*

FIG. 39. Continuous centrifuge (screen type).

latter as the "continuous" type. The automatic machines are generally horizontal and have a speed of from 500 r.p.m. in the large machines to 1800 r.p.m. in the small ones (with a basket of small diameter). They may be single or double (*i.e.*, single basket, or double baskets placed back to back).

The continuous type, *i.e.*, one having the slurry fed continuously at one end of the basket and the dried crystals unloaded at the other end, is, generally speaking, still in the process of development as far as the filtration of crude bicarbonate (ammonia soda) is concerned, and has so far been confronted with several mechanical difficulties. Some of these may be mentioned here. For very fine crystals (such as  $\text{NaHCO}_3$ ), this continuous type requires a very large number of extremely fine slits in the basket (such as 0.004 to 0.006 inch wide by  $\frac{3}{4}$  to 1 inch long) which is

rather difficult and expensive to make. The screen is either cut from a solid plate or made up of a large number of special-shaped bars of uniform cross-section. Even then, the smaller crystals (the fines) are apt to pass through the screen and find their way to the filtrate. This is sometimes a very serious matter if the filtrate is to be processed subsequently. Furthermore, the mechanism of transferring (or conveying, or pushing) the crystals on the screen from the feed end to the discharge end, is generally a difficult problem because of the high speed. This mechanism is now either in the shape of a ribbon screw conveyor, running at a differential speed to the basket, usually at a differential of from 1/60 to 1/80 of the basket speed, as in the Bird continuous machine.\*



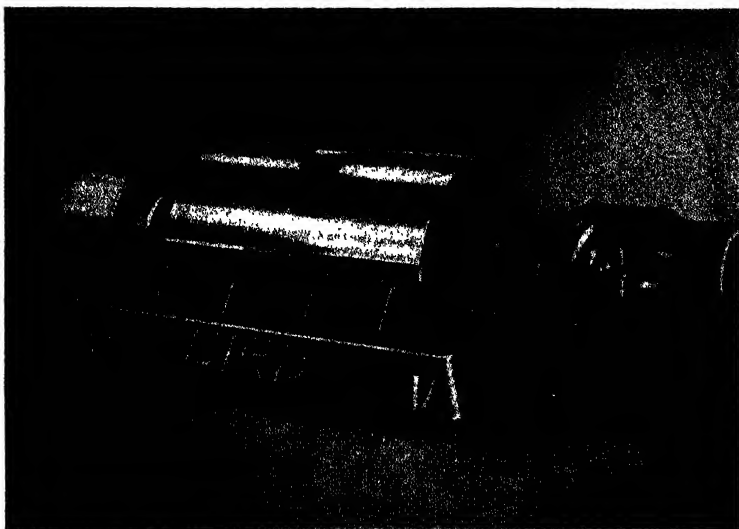
*Courtesy Escher Wyss Engineering Works Ltd*

FIG 40 Continuous centrifuge (pusher type)

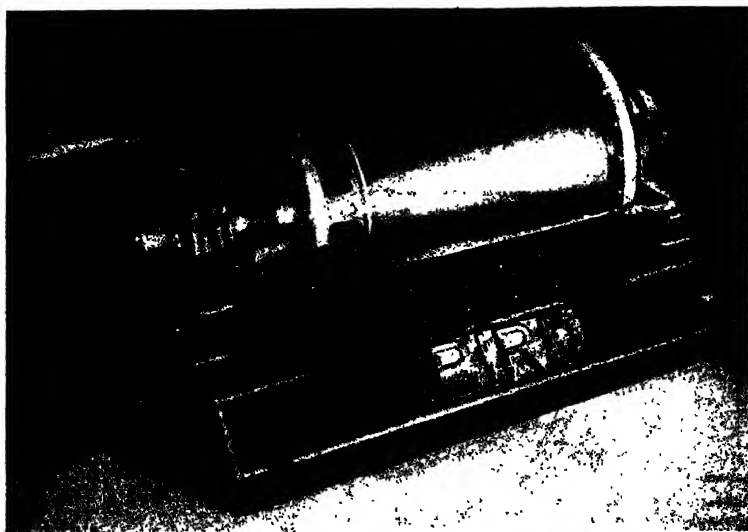
(Fig 39), or in the form of a piston pusher making 8 to 18 strokes per minute with the length of stroke about 40 mm, as in the Escher Wyss continuous machine† (Fig 40). The push-type mechanism runs very smoothly and has no tendency to crush the crystals in the basket. The differential speed conveyor as developed by the Bird Machine Co. is now operating steadily and stably, but the ribbon conveyor edge has a scraping action, grinding the crystals forward over the surface layer of the cake in the basket. Both types at the present stage require the crystal size to be no finer than 0.20 mm, or 65 mesh, and are not adaptable to crystals finer than 0.10 mm, or 150 mesh, otherwise too much of the fines would

\* The Bird Machine Co, South Walpole, Mass.

† Escher Wyss Engineering Works, Ltd, Zurich, Switzerland, and Escher Wyss Maschinenfabrik, G m b H, Ravensburg, Germany.



(a) *Casing on.*

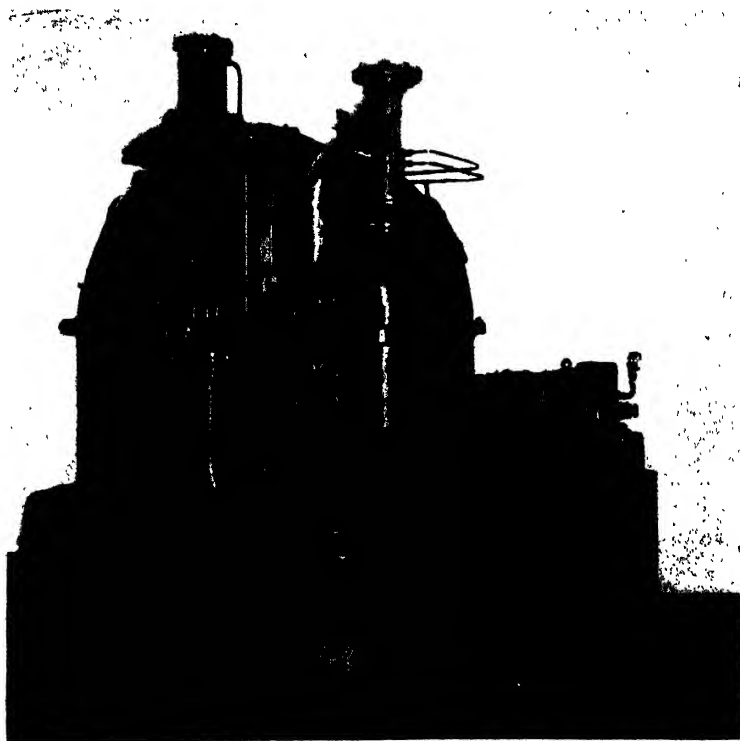


(b) *Casing removed.*

*Courtesy Bird Machine Co.*

FIG. 41. Bird solid bowl centrifugal filter.

pass through the screen. To meet this difficulty, the Bird Machine Co. put out a solid bowl machine having solid walls in the "basket" (*i.e.*, doing away with the slots and depending solely upon the centrifugal action to separate the solids from the liquid in the bowl (Fig. 41). The machine is otherwise no different from the continuous basket type. This solid bowl machine is particularly suitable for handling fine slimes, such as cement, clay, sewage sludge, lithopone pigment, etc. But for bicarbonate of soda crystals, it is not so satisfactory, because it has a tendency to break up



*Courtesy Escher Wyss Engineering Works, Ltd.*

FIG. 42. Escher Wyss (ter Meer) automatic centrifuge.

the crystals and knead them into a dough-like mass, so that the dryness or "yield" of the bicarbonate obtained is not much better than the "yield" obtainable from a well-designed modern rotary vacuum filter. Strange to say, however, bicarbonate of soda crystals could be handled in the ordinary batch-type, vertical, suspended centrifuges, without such difficulties, and these centrifuges are used extensively for refined bicarbonate of soda, as mentioned above.

At present, only certain of the automatic type centrifuges—notably the Escher Wyss (ter Meer) automatic machine (Fig. 42)—have been used for the crude bicarbonate of soda service in place of rotary filters. This ter Meer automatic will handle the fine crystals of bicarbonate of soda because of the special feature in its basket construction, but more particularly because it also uses a woolen felt as the filtering medium (Fig. 43). The dryness obtained is 8-10 per cent moisture, depending upon the size of the bicarbonate of soda crystals from the columns.

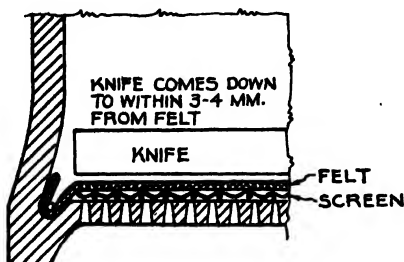


FIG. 43.

Escher Wyss automatic centrifuge using felt as filtering medium.

On the other hand, these automatic centrifuges are very well suited to the drying of coarse crystals, *e.g.*,  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{CuSO}_4$ , or other substances that habitually crystallize in large crystals. The better known ones are the ter Meer automatic of from 1700 to 2100 mm. diameter, and the Sharples 63" automatic and 20" Super-D-Hydrator.\*

As regards the cycle or the period of intermittency, these automatic machines vary widely. For example, the Sharples Super-D-Hydrator with 20" basket has a cycle of only 45 seconds, while a large ter Meer machine has a cycle of 18-20 minutes. Other automatic machines such as the Haubold machine† have a cycle of from 4 to 7 minutes. These cycles

TABLE 75. Timing of Events in a Cycle of Automatic Centrifuge.

Events	Sharples Super-D-Hydrator	Sharples 63" Automatic	Escher Wyss "ter Meer" Automatic 1700 mm.	Escher Wyss "ter Meer" Single Automatic 2100 mm.
Feeding	8 sec.	1 min.	4 min.	5 min.
First drying	4 "	$\frac{1}{4}$ "	1 "	1 "
Rinsing	6 "	$\frac{1}{4}$ "	4 "	3 "
Drying (spinning)	21 "	2 $\frac{1}{2}$ "	7 "	8 "
Unloading	6 "	$\frac{1}{2}$ "	2 "	3 "
Total	45 sec.	4 $\frac{1}{2}$ min.	18 min.	20 min.
Vol. in basket	1 cu. ft.	7.8 cu. ft.	0.56 M*	1.05 M*
Speed	1800 r.p.m.	480 r.p.m.	700 r.p.m.	550 r.p.m.
Horsepower	20 H.P.	30 H.P.	30 KW	45 KW
Centrifugal force	920 × gravity	206 × gravity	440 × gravity	338 × gravity

\* The Sharples Specialty Company, Philadelphia, Pa.

† Haubold Maschinenfabrik, Chemnitz, Germany.

are, however, adjustable within a certain range. Table 75 illustrates the distribution of time among the several events in the cycle in some typical makes.

The present tendency is to go to smaller diameters, but higher speeds (Sharples Super-D-Hydrator, 20" diameter, and the Bird continuous, 18" diameter) with smaller amounts of material in the baskets. According to the simple laws of physics,

$$\begin{aligned}
 \text{If} \quad & \alpha = \text{acceleration in feet per sec. per sec.} \\
 & v = \text{peripheral velocity in feet per sec.} \\
 & r = \text{radius of basket in feet} \\
 \text{Then} \quad & \alpha = \frac{v^2}{r} \\
 \text{Let} \quad & W = \text{weight of crystals in the basket in lbs.} \\
 & \frac{W}{g} = \text{mass of crystals in the basket} = m \\
 & F = \text{centrifugal force developed in lbs.} \\
 & N = \text{r.p.m. of the basket} \\
 & \omega = \text{its angular velocity} = \frac{2\pi N}{60} = \frac{v}{r} \text{ radians}
 \end{aligned}$$

$$\begin{aligned}
 \text{Therefore} \quad F &= m\alpha = \frac{W}{g} \cdot \frac{v^2}{r} = \frac{W}{g} \omega^2 r \text{ lbs.} \\
 &= \frac{W}{32.2} \cdot \left( \frac{2\pi N}{60} \right)^2 \cdot r \text{ lbs.}
 \end{aligned}$$

$$\text{Therefore} \quad F = 0.000341 W N^2 r \text{ lbs.}$$

One often speaks of the centrifugal force developed as being so many times gravity. This means so many times the weight of its mass. Thus,

$$\frac{F}{W} = 0.000341 N^2 r \text{ (times gravity)}$$

This centrifugal force as developed commercially varies within a wide range of from 200 to 1800 times gravity, the higher figure being for speeds as high as 1800 r.p.m., using a 40-inch basket in a batch type machine. Normally, a high-speed commercial centrifuge develops about a thousand times gravity.

It is apparent that the greater the centrifugal force, the greater the drying power, or for the same dryness, the shorter the time required for spinning. Now, to accomplish this, either the speed,  $N$ , or the radius of the basket,  $r$ , must be increased. But since the centrifugal force is increased as the square of the speed, but only linearly as the diameter, it is advantageous to increase the speed rather than the diameter. Also, from the consideration of mechanical strength, it is also desirable to keep the diameter small. Hence the tendency of the design for a good factor of safety is rather to have a smaller basket with a correspondingly smaller mass in it, working at a higher speed, than to have a larger diameter, larger volume and consequently greater mass.

The following screen analyses on some of the typical crystals, such as  $\text{NaCl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HCO}_3$  and  $\text{NaHCO}_3$ , are given to illus-

## MANUFACTURE OF SODA

TABLE 76. Screen Analyses of Some Typical Crystals.

Crystals — Mesh Opening mm	Evaporator — Salt (NaCl) Retained Cumula- tive % on %	By-Product Ammonium Sulphate ((NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ) Retained Cumula- tive % on %	Crude Ammonium Chloride (NH <sub>4</sub> Cl) Retained Cumula- tive % on %	Refined Ammonium Chloride (NH <sub>4</sub> Cl) Retained Cumula- tive % on %	Ammonium Bicarbonate (NH <sub>4</sub> HCO <sub>3</sub> ) Retained Cumula- tive % on %	Crude Sodium Bicarbonate (NaHCO <sub>3</sub> ) (Ammonia Soda) Retained Cumula- tive % on %	Refined Sodium Bicarbonate (NaHCO <sub>3</sub> ) Retained Cumula- tive % on %
20 0.833	0.000	0.000	0.000	1.180	0.280	0.000	0.000
28 0.589	0.000	3.107	5.116	3.650	2.040	0.000	0.000
35 0.417	5.893	29.405	30.796	18.784	3.320	0.050	0.149
48 0.295	54.869	37.534	69.120	33.564	8.580	1.502	0.826
65 0.208	32.541	21.580	85.556	27.180	15.450	4.896	3.523
100 0.147	6.264	5.762	93.910	12.730	19.180	14.369	7.126
150 0.104	0.434	1.819	99.507	2.452	16.380	25.883	17.765
Through							
150 0.104	0.000	0.493	0.746	0.450	34.500	53.305	70.611

trate the range of crystal size ordinarily met with in industrial plants (see Table 76). It can be seen that the refined bicarbonate of soda has the smallest crystals among them; next comes the crude bicarbonate of soda (ammonia soda). Crystals such as  $\text{NaCl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$  and the like, which have over 80 per cent larger than 0.20 mm. or coarser than (retained on) 65 mesh, are all suitable for use in the continuous centrifuges developed at the present time. Crystals such as refined  $\text{NaHCO}_3$ , over 50 per cent of which will pass through 150 mesh, cannot be used on the continuous machine, using metal screens. The Bird Machine Company's solid bowl machine, which has no screen at all, is unique among all types of continuous machines in that it can handle any fine, slimy solids down to even the cement size. This solid bowl machine will handle sodium bicarbonate crystals (crude or refined), but the moisture content in the cake is not less than that obtainable from a high-yield rotary vacuum filter. Further, the bicarbonate cake obtained from the solid bowl machine becomes denser and glazed because of the kneading action of the screw conveyor on the crystals.

From the above, it can be safely said, as regards continuous type centrifuges in general, that they have so far not found satisfactory application in the ammonia-soda service. But because of their strictly continuous character and because of the higher "yield" possible, there always exists a temptation to try to adapt them to the ammonia-soda industry; indeed extensive efforts are being made in this direction. There are, however, certain drawbacks to their use, among which are (1) that the cost of the machine is far too great as compared to the capacity obtainable, and (2) that the power required to drive such a machine is also greater. Compare this with a moderate sized, continuous, rotary, vacuum filter of the latest high-yield type, which has a capacity of 200-300 tons of soda ash per day (i.e., 300-500 tons in terms of sodium bicarbonate per day), requiring only a 5 H.P. motor to drive it, taking into consideration the fact that the difference in the "yield" obtained from the filter vs. the continuous centrifugal may be only a trifle.

Also, with the advent of the continuous and automatic horizontal machines, it does not necessarily follow that the batch-type, vertical, suspended centrifuges will be entirely superseded. Nowadays, these batch-type centrifuges (which, since they are most generally used in the sugar industry, have become known as "sugar centrifugals") have also been brought to a high degree of perfection. A 48-inch vertical-suspended machine is now capable of operating at 1200 r.p.m., while a 40-inch machine may now run at as high as 1800 r.p.m. Being suspended and free to seek its balance, this batch-type vertical machine may be operated safely at a higher speed than a two-bearing or overhung horizontal continuous machine of the same basket diameter. Further, certain automatic mechanisms, such as the charging and unloading devices, may now also be fitted to these batch-type machines, so that one person also can look after a number of them at the same time.

As regards the crystalline forms of the four main salts in equilib-



rium in the liquor, the crystals of sodium chloride are of course cubic (isometric); those of sodium bicarbonate monoclinic; those of ammonium bicarbonate are also monoclinic; and those of ammonium chloride isometric or tetragonal. Under normal operating conditions, the ammoniated brine is undersaturated with respect to sodium chloride, and so no crystals of sodium chloride should deposit out. Because of the mode of formation in the towers, the crystals of sodium bicarbonate are necessarily small. Under a microscope even at a magnification of 400 diameters, these bicarbonate crystals appear merely as long rods, the individual shape of the rod being still difficult to examine. This is because of the violent stirring effect due to the bubbling of the carbon dioxide gases in the tower, with the result that the crystals formed are very small, especially when the tower temperature has not been properly regulated or when the carbon dioxide gas delivered to the tower is greatly weakened. These bicarbonate crystals have a "twinning" habit and often form "daisies." These are seldom seen as perfect, well-developed, crystal individuals. As seen under a microscope, a few of these crystals are very large, but these are rather agglomerations of many individuals. Under good operating conditions, the size of the average crystals as seen under a microscope and estimated on a "counting chamber" is between 100 and 200 microns (0.10-0.20 mm), while under poor operating conditions yielding a pasty sludge, the size may be between 50 and 100 microns (0.05-0.10 mm.) or smaller.

Under certain conditions the crystals of ammonium bicarbonate may be deposited with the sodium bicarbonate. If this happens, it will be seen that they are coarser and are more plate-like in formation, quite different from the rod formation of the sodium bicarbonate, though belonging to the same system (monoclinic). The crystals of ammonium chloride are not formed under these conditions because it is extremely soluble and exists in the solution far below saturation point. Consequently, there are only the crystals of sodium bicarbonate and, to a much smaller extent, of ammonium bicarbonate, to be considered in this reaction, since the other salts, sodium and ammonium chlorides, are merely carried by the mother liquor which has not been completely washed from the crystal cake.

Good tower control should include a daily photomicrographic study of the bicarbonate crystals from the towers. Not only must these crystals be maintained coarse and filterable but they should be of uniform size, free as far as possible from the secondary smaller crystals.

Attempts have also been made to study the composition of the mother liquor from the towers. It is of a much more complex character than the precipitated sodium bicarbonate with which it is in equilibrium. The result of this investigation will be given in the following chapter.

## Chapter XII

### Phase Rule in Tower Reactions: Graphical Representation of Ammonia Soda Process

The reaction between sodium chloride in the ammoniated brine and ammonium bicarbonate formed in the brine represents a system of four components. Unlike the four-component system consisting of three salts with a common ion in an aqueous solution, such as sodium, potassium and ammonium chlorides, which can be conveniently represented by the three sides of a regular tetrahedron, placing the fourth component (water) at the vertex (Fig. 44), the system, which consists of two salts in an aqueous

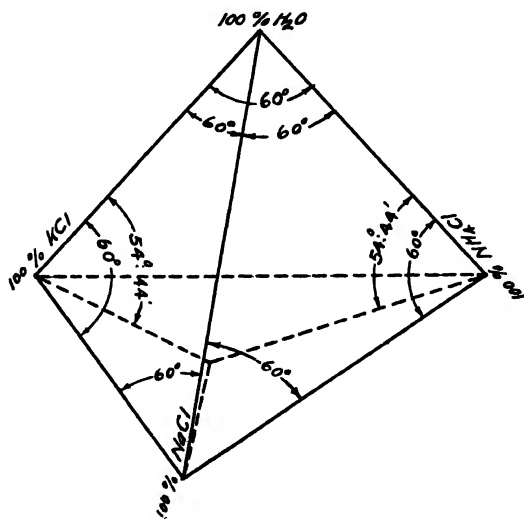


FIG. 44. For space figure.

solution with no common ions, forming together with water also a four-component system, is best represented by the four sides of one-half of a regular octahedron (Fig. 45). In this case, salts having a common ion are represented on the adjacent sides of a solid angle of the octahedron. The isothermal diagram in each case will be a plane orthogonal projection of the space figure onto the triangular base in the case of the tetrahedron (Fig. 46), or onto the square mid-section in the case of the octahedron

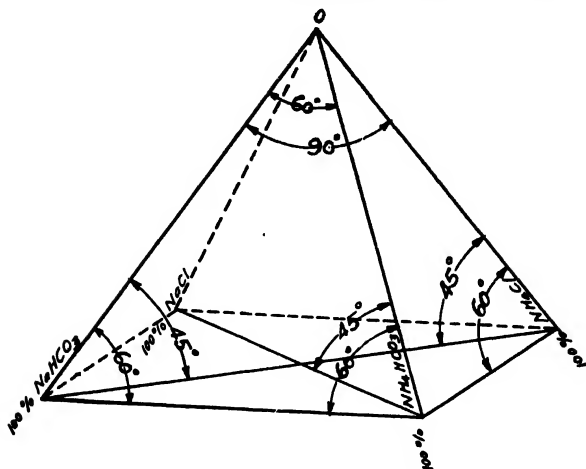


FIG. 45. For space figure (Cf. Fig. 44).

(Fig. 47). In the last case, with which we are here concerned, the isothermal diagram is represented by four rectangular coordinate axes, each axis being separate and meeting at the origin at right angles to the

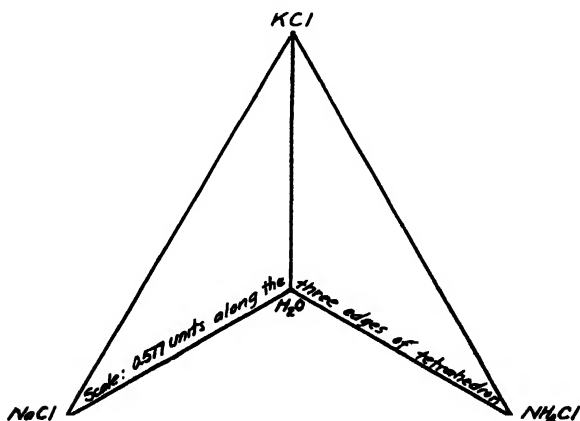


FIG. 46. For plane isothermal projection.

adjacent ones, so that they do not form two continuous axes intersecting at the origin. This isothermal diagram is nothing more or less than a plane projection from the space figure onto the square base with the units measured along the four axes equal to  $\frac{1}{\sqrt{2}}$  of the units measured along

the four sides of the upper half of the octahedron starting from the vertex and making an angle of  $45^\circ$  with the base. In this way the plane coördinate curves can be taken as representing the space figure of the octahedron at a constant temperature.

By double decomposition the two salts with no common ions can be supposed to rearrange themselves, forming another pair of salts in solution in the following fashion:

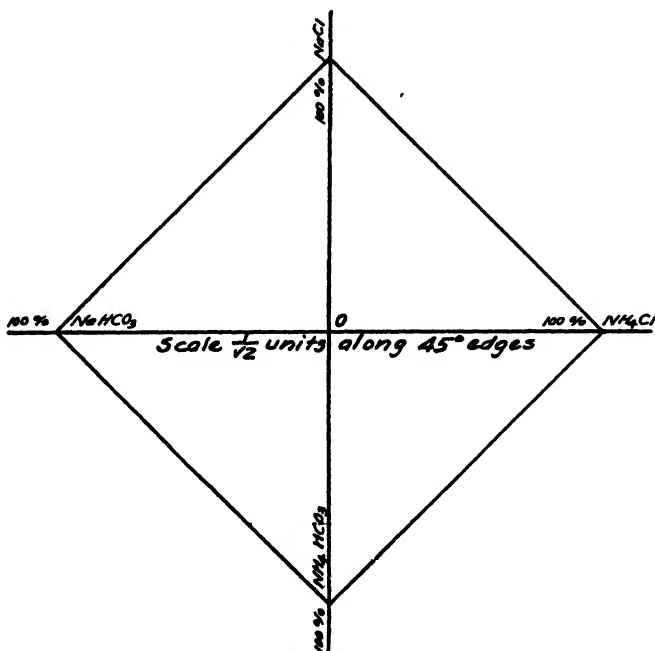
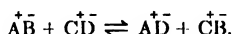
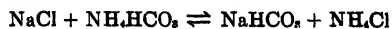


FIG. 47. For plane isothermal projection (Cf. Fig. 46)

It was from this consideration that the name "the reciprocal pairs of salts" originated. In this way there would be formed four individual salts which might be thought to constitute, together with water, a five-component system. But the four salts are so related that any three of them could determine the fourth. In other words, only three of them are independent, and the three salts, with water, form the four-component system. Thus, the tower reaction



constitutes a four-component system. In practice, however, an ammoniacal brine is taken and carbonated with carbon dioxide gas. Precipitation

of sodium bicarbonate progresses as the carbonation proceeds, so that ammonium bicarbonate may be said to be formed *in situ*. It is evident then that the ammoniacal brine is always saturated with carbon dioxide gas at the temperature in question. It may be thought that this carbon dioxide gas should be considered as another component, but this is taken care of by the restriction imposed that the partial pressure of carbon dioxide, together with the partial pressures of ammonia and water, must add up to a given total pressure above the solution. Since in this heterogeneous system we must have a vapor phase and a solution, the maximum possible number of solid phases at the invariant point would be four.

Degrees of Freedom + No. of Phases = No. of Components + 2 = 6.

At a given temperature we have used up one degree of freedom, and the number of solid phases possible is then only three. The number of combinations of three out of a total of four salts is  $\frac{4 \times 3 \times 2}{3!} = 4$ . These

four possible cases are enumerated below:

- (1) Solid NaCl + solid  $\text{NH}_4\text{HCO}_3$  + solid  $\text{NH}_4\text{Cl}$  in co-existence with solution;
- (2) Solid NaCl + solid  $\text{NH}_4\text{HCO}_3$  + solid  $\text{NaHCO}_3$  in co-existence with solution;
- (3) Solid NaCl + solid  $\text{NH}_4\text{Cl}$  + solid  $\text{NaHCO}_3$  in co-existence with solution;
- (4) Solid  $\text{NaHCO}_3$  + solid  $\text{NH}_4\text{HCO}_3$  + solid  $\text{NH}_4\text{Cl}$  in co-existence with solution.

Returning to the general expression above,  $\bar{A}\bar{B} + \bar{C}\bar{D} = \bar{A}\bar{D} + \bar{C}\bar{B}$ , when the four solid salts are in equilibrium with the solution we have the product of molal concentrations of the salts  $\bar{A}\bar{B}$  and  $\bar{C}\bar{D}$  equal to that of the molal concentrations of  $\bar{A}\bar{D}$  and  $\bar{C}\bar{B}$ . This is a necessary condition for the two pairs of solid salts  $\bar{A}\bar{B} - \bar{C}\bar{D}$  and  $\bar{A}\bar{D} - \bar{C}\bar{B}$  to be in stable equilibrium with each other and with the solution. If the product of solubilities of one pair of the solid salts  $\bar{A}\bar{B}$  and  $\bar{C}\bar{D}$  is greater than the corresponding product of the solid salts  $\bar{A}\bar{D}$  and  $\bar{C}\bar{B}$  at the same temperature, the first pair are said to be in a metastable equilibrium with the second pair and will disappear, yielding the second pair as the solid phase in contact with the solution. Conversely, if the product of solubilities of the second pair of salts,  $\bar{A}\bar{D}$  and  $\bar{C}\bar{B}$ , is greater than the corresponding product of the first pair,  $\bar{A}\bar{B}$  and  $\bar{C}\bar{D}$ , the second pair will disappear, leaving the first pair in a stable equilibrium with the solution. In this reaction we have the solubility relationship at different temperatures as given in Table 79, page 198.

Thus, we see that the product of solubilities of NaCl and  $\text{NH}_4\text{HCO}_3$  at each temperature is greater than the corresponding product of  $\text{NaHCO}_3$

TABLE 79. Solubility Relationship of NaCl,  $\text{NH}_4\text{HCO}_3$ ,  $\text{NaHCO}_3$  and  $\text{NH}_4\text{Cl}$  in Water.

Temp. (° C.)	Solubilities in Mols per Liter of Water						Ratio of Their Products
	NaCl	$\text{NH}_4\text{HCO}_3$	Product	$\text{NaHCO}_3$	$\text{NH}_4\text{Cl}$	Product	
0	6.09	1.51	9.20	0.82	5.50	4.52	2.03
10	6.10	2.00	12.2	0.97	6.23	6.05	2.02
15	6.11	2.32	14.2	1.07	6.58	7.07	2.01
20	6.13	2.66	16.3	1.14	6.95	7.94	2.05
25	6.14	3.03	18.6	1.23	7.36	9.06	2.05
30	6.16	3.42	21.1	1.32	7.75	10.23	2.06

and  $\text{NH}_4\text{Cl}$ , and the ratio is roughly 2 to 1 in each case. This means that at all these temperatures the coexistence of solid NaCl and solid  $\text{NH}_4\text{HCO}_3$  in contact with the solution is in a metastable equilibrium and these two solid phases cannot exist side by side. Consequently, of the four possible combinations of the three solid salts in equilibrium with the solution enumerated above, only combinations (3) and (4) need be discussed, because both combinations (1) and (2) would involve the coexistence of solid NaCl and solid  $\text{NH}_4\text{HCO}_3$  in contact with the solution. In the actual study at a fixed temperature there exist only two invariant points such as *J* and *K* illustrated by the isothermal diagram for 15° C. (Fig. 48).\*

From the phase rule we know that each area in this plane projection represents a region where one particular salt will separate out as a solid phase from the solution of the composition given by a point within the area, and that each internal line such as *EJ*, *FJ*, *JK*, *KG*, or *KH* represents the locus where two salts represented by the two areas adjoining each other by such a line will separate out as the coexisting solid phases in contact with a solution of the composition shown by a point on this line. These are known as univariant lines. The intersections of these univariant curves give the invariant points such as *J* and *K* shown in Fig. 48. These invariant points are located by plotting the compositions of the solutions in the following manner: Set off the molal concentration of NaCl in the solution from the common point *O* along the NaCl-axis and the difference between the molal concentrations of  $\text{NH}_4\text{Cl}$  and  $\text{NaHCO}_3$  from *O* along that axis which has the greater concentration. The two coordinates will determine a point. Notice that at either *J* or *K* the composition of the solution is determined by the molal concentrations of the three salts, namely NaCl,  $\text{NH}_4\text{Cl}$  and  $\text{NaHCO}_3$ , the difference between the last two being taken as one of the coordinates. But *J* and *K* represent the two invariant points at the temperature in question where three solid phases can coexist with one another and the solution. At *J*, the three solid phases are NaCl,  $\text{NaHCO}_3$ , and  $\text{NH}_4\text{Cl}$ , and at *K* they are  $\text{NaHCO}_3$ ,  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_4\text{Cl}$ . It is thus seen that at *K* the three salts separating out from the solution do not correspond exactly to those present in the solution. Hence *K* is called the "incongruent" point, while *J*, which marks the same three salts in the solid phases as in the solution

\* Cf. P. P. Fedotieff, "Der Ammoniaksodaprocess vom Standpunkte der Phasenlehre," *Z. physik. Chem.*, 1904.

from which these salts separate out, is designated as the "congruent" point. It might be added here that by adding solid sodium chloride to the incongruent system, solid ammonium bicarbonate can be gradually used up until, when solid sodium chloride has been added in excess, solid sodium chloride remains in place of the solid ammonium bicarbonate and the system is again congruent.

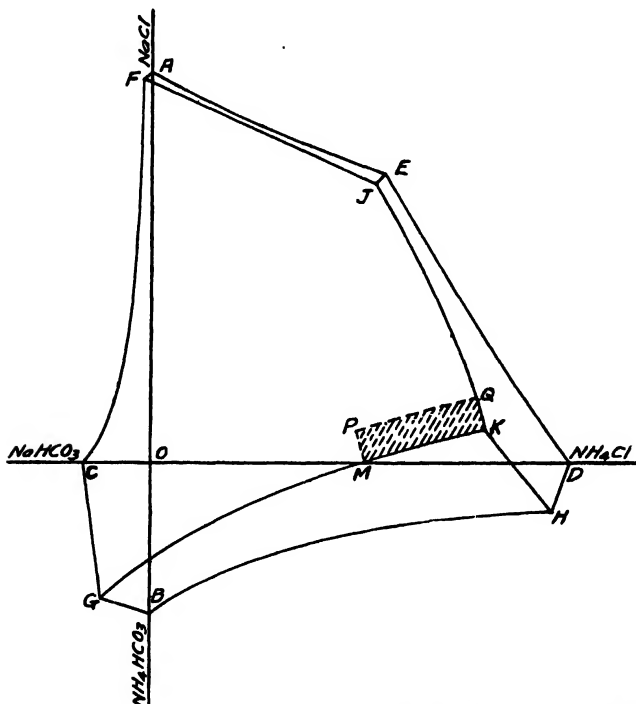


FIG. 48. Plane isothermal projection from octahedral space figure for system consisting of reciprocal pairs  $\text{NaCl} + \text{NH}_4\text{HCO}_3$  and  $\text{NaHCO}_3 + \text{NH}_4\text{Cl}$ .

From the diagram (Fig. 48) it is seen that at  $15^\circ \text{C}$ . the  $\text{NaCl}$ -area does not come in contact at any point with the  $\text{NH}_4\text{HCO}_3$ -area, and as the temperature is raised the two areas do not approach each other. In other words, at all these temperatures solid sodium chloride cannot coexist with solid  $\text{NH}_4\text{HCO}_3$  in contact with the solution. This just corroborates the above statement that the two combinations (1) and (2) are non-existent and need not be considered.

As our aim is to precipitate sodium bicarbonate from the ammoniated brine we need only consider those three border lines of the  $\text{NaHCO}_3$ -area, namely  $GK$ ,  $KJ$  and  $JF$ . A moment's thought will tell us that in the dia-

gram (Fig. 48) points lying higher up above *O* represent higher concentrations of NaCl in solution, and that points lying farther to the right of *O* represent greater concentrations of fixed ammonia in the form of  $\text{NH}_4\text{Cl}$  in solution. To secure a high decomposition of NaCl to  $\text{NaHCO}_3$  in the towers, therefore, we must get as close to the  $\text{NH}_4\text{Cl}$ -axis from above this axis as possible, and as far to the right of *O* along the  $\text{NH}_4\text{Cl}$ -axis as possible. But for a high conversion of  $\text{NH}_4\text{HCO}_3$  to  $\text{NH}_4\text{Cl}$  we must operate as far up from *B* and above the  $\text{NH}_4\text{Cl}$ -axis as possible. Therefore it is to be expected generally that a high percentage conversion of NaCl to  $\text{NaHCO}_3$  is likely to be accompanied by a low percentage conversion of  $\text{NH}_4\text{HCO}_3$  to  $\text{NH}_4\text{Cl}$ . As a matter of fact, percentage conversion of  $\text{NH}_4\text{HCO}_3$  to  $\text{NH}_4\text{Cl}$  increases as we move from *G* to *K* along *GK*, from *K* to *J* along *KJ*, and from *J* to *F* along *JF*, until at *F* it reaches a maximum of 100 per cent. On the other hand, percentage conversion of NaCl to  $\text{NaHCO}_3$  increases as we move down from *F* to *J* along *FJ* and from *J* to *K* along *JK*; but at *K* it reaches a maximum (not 100 per cent) and starts to fall off again as we move from *K* across the  $\text{NH}_4\text{Cl}$ -axis in the direction *KG*. Along *FJ*, NaCl can exist in the solid phase as well as  $\text{NaHCO}_3$ . This does not represent the actual fact, because under plant-operating conditions the NaCl concentration in the ammoniated brine employed practically never even reaches its saturation point. Therefore the curve *JF* need not be considered. Again, since the reaction between NaCl and  $\text{NH}_4\text{HCO}_3$  is a reversible one, there will always be some NaCl left in the solution. That is to say, the concentration of NaCl in solution can only approach zero and is never equal to zero, and such points will lie above the  $\text{NH}_4\text{Cl}$ -axis. *KG* intersects the  $\text{NH}_4\text{Cl}$ -axis at *M*. That section of *KG* lying below the  $\text{NH}_4\text{Cl}$ -axis therefore has no meaning. By this elimination there are left only the curve *KJ* and a section *KM*. *KJ* is the curve along which  $\text{NH}_4\text{Cl}$  reaches its saturation point and tends to separate out with  $\text{NaHCO}_3$  in the solid phases. Further, it is the curve along which the percentage decomposition of NaCl from the reaction decreases, the concentration of NaCl left in solution increasing as we move up from *K* to *J*. In the plant operation any possibility for solid  $\text{NH}_4\text{Cl}$  to separate out with  $\text{NaHCO}_3$  is to be carefully avoided. For it would lead to a high salt content in the soda ash after calcination.



This consideration, together with the facts that, because of mechanical perfection, the loss of ammonia in the cycle in the present-day ammonia soda plants has been reduced to a very low figure, and that the cost of ammonia is now a small item in the cost of manufacture, has dictated a condition of operation whereby a high percentage conversion of NaCl alone is aimed at. The present tendency in ammonia soda plants is to go to a higher ammonia concentration in the ammoniation operation (in the neighborhood of 100 titers of free  $\text{NH}_3$ ), while making every effort to maintain as high a NaCl concentration in the ammoniated brine as pos-



sible—at best considerably below saturation with respect to  $\text{NaCl}$ . The ratio of free  $\text{NH}_3$  to  $\text{Cl}^-$  in the resulting ammoniated brine now employed (expressed in molal concentrations) is 1.08 or even 1.12 to 1. This means that modern plants operate approximately within the narrow strip of area bordering on the short section of the curve  $KM$ , as shown by the shaded area in the diagram ( $PQKM$ ), where there is a tendency for a small amount of solid  $\text{NH}_4\text{HCO}_3$  rather than solid  $\text{NH}_4\text{Cl}$  to separate out with the precipitate of  $\text{NaHCO}_3$ . The presence of  $\text{NH}_4\text{HCO}_3$  in the crude  $\text{NaHCO}_3$  from the towers is less objectionable and all of it will be decomposed and recovered in the dryers.

Another revision of the conclusion reached by P. P. Fedotieff in his classical research on the ammonia soda process in 1904 is that it has not been found desirable to operate at high temperatures such as  $32^\circ\text{C}$ ., at which point he said that both the ammonia efficiency and the sodium efficiency were 84 per cent and that there was “a greater yield of sodium bicarbonate” from the reaction. If solid ammonium bicarbonate were used in the reaction instead of the ammonium bicarbonate formed in solution by carbonating the ammonia in the brine with carbon dioxide gas, this temperature might be desirable. But as we have to bubble rather dilute carbon dioxide gases through ammoniated brine in the towers, and as the draw liquor has to be exposed to the air before and during filtration, high temperatures of the liquor at the draw have been found to be undesirable. For the sake of keeping down ammonia losses as well as getting a high percentage sodium chloride decomposition in the brine, a draw temperature below  $25^\circ\text{C}$ . and even as low as  $20^\circ\text{C}$ . has been found beneficial. The point  $K$ , where the decomposition of  $\text{NaCl}$  reaches its maximum, is unique, furnishing a good guide for plant operation. This point moves toward the  $\text{NH}_4\text{Cl}$ -axis as the temperature rises above  $15^\circ\text{C}$ ., according to the results of P. P. Fedotieff, and lies on the  $\text{NH}_4\text{Cl}$ -axis at about  $32^\circ\text{C}$ . Consequently, as the temperature rises above  $15^\circ\text{C}$ ., the section of the curve  $KM$  dwindles in length. Therefore it might be correct to say that we are then operating around the point  $K$  on the  $\text{NaHCO}_3$  side.

#### GRAPHICAL REPRESENTATION OF AMMONIA SODA PROCESS

We shall make use of triangular coördinates to represent the composition and solubility relationship in a more complex system such as the liquor and slurry in the ammonia soda process. This graphical representation has the advantage that it enables the reader to visualize the steps in the process more clearly. But before we present these diagrams it may be well to review briefly the properties of the triangular graphs. It is evident that triangular coördinates present to us plain curves. By adding a vertical coördinate—a fourth variable—a space curve is readily obtained in the body of a prism.

Let the triangle be an equilateral triangle  $ABC$ ; each of the vertices represents a variable. In our present case, each of the three vertices may

represent a component in a solution or slurry. Thus, we may let  $A$  be  $\text{Cl}^-$ ,  $B$  be  $\text{OH}^-$  and  $C$  be  $\text{HCO}_3^-$  as in Fig. 49 (b). Each side of the equilateral triangle represents molar percentage or fractions of a two-component system and its total length adds up to 100 per cent (from 0 to 100 per cent of one component and conversely from 100 to 0 per cent of the second component). Thus, point  $R$  in (b) represents 15 per cent  $\text{OH}^-$  and 85 per cent  $\text{Cl}^-$  on one side ( $AB$ ), and point  $P$  represents 15 per cent  $\text{OH}^-$ , 55 per cent  $\text{HCO}_3^-$  and 30 per cent  $\text{Cl}^-$ . The three coördinates drawn parallel to

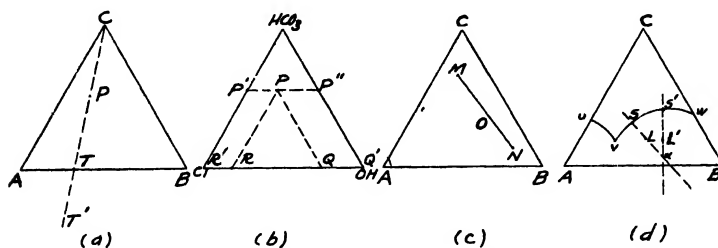


FIG. 49. Triangular graphs.

the respective sides of the equilateral triangle in successive order are  $R'R$ ,  $Q'Q$  and  $R'P'$ , or  $R'R$ ,  $QQ'$  and  $RP$  ( $=RQ$ ). Therefore the following propositions may be readily proved:

- (1) The sum of the three coördinates of a point in a triangular graph is a constant and is equal to the length of one side of the equilateral triangle, and each side may thus be graduated to read from 0 to 100 per cent of each of the two components.
- (2) If  $M$  and  $N$ , Fig. 49 (c), represent the composition of two different solutions, the composition of a mixture of these two solutions mixed in any proportion is represented by a point on a straight line connecting  $M$  and  $N$ , such as  $O$ , and by no other point. Further, if  $O$  is the composition of the resulting mixture of the two solutions whose compositions are represented by  $M$  and  $N$ ,  $MO$  then represents quantitatively (to scale) the quantity of the solution  $N$  and  $NO$  the quantity of the solution  $M$  present in the mixture.
- (3) If  $P$  represents the composition of a system of three components, Fig. 49 (a), the removal or addition of one of three components is represented by points on the straight line connecting  $P$  and the vertex representing that component. Thus, in Fig. 49 (a), connect  $P$  and the vertex  $C$ , and produce  $CP$  to intersect the opposite side  $AB$  at  $T$ . Addition of component  $C$  to the system is represented by a point moving from  $P$  toward  $C$ ; while removal of component  $C$  is represented by a point moving away from  $P$  along the line  $CP$  produced, and at  $T$ , component  $C$  is entirely eliminated, and the system then becomes a two-component one.  $AT$  then represents

the percentage of B, and  $BT$  the percentage of A in the resulting two-component system. Further, by taking points beyond  $T$ , such as  $T'$ , we can conceive that  $T'$  represents algebraically a negative coördinate  $C$  in the three-component system. Suppose now  $C$  represents water in a solution, in which  $A$  and  $B$  are two solutes, addition of water (dilution of solution) is represented by a point moving from  $P$  toward the vertex  $C$ ; while removal of water (concentration of solution) is represented by a point moving away from  $P$  toward  $T$  on the line  $CP$  produced.

- (4) If in Fig. 49 (d)  $\alpha$  represents the composition of a double salt in a system where  $C$  represents  $H_2O$  and  $uvw$  represents the solubility curve of the double salt at a certain temperature  $t$ , a straight line connecting any point,  $S$ , on this solubility (saturation) curve with  $\alpha$  represents a mixture of the solid double salt and its mother liquor. If  $L$  represents such a mixture, the ratio of the weight of the double salt to that of the mother liquor present in the slurry is as  $SL:\alpha L$ . Further, if  $S'L'$  represents the compositions of another slurry at different temperatures yielding a series of saturated solutions with the same double salt in the solid phase, the intersection point  $\alpha$  between the two straight lines  $SL$  and  $S'L'$  then determines the composition of the double salt  $\alpha$  itself and thus locates it on the graph.

In general, as can be seen above, if a point  $P$ , representing the composition of a system, is to vary with respect to one component only, join  $P$  with the vertex of the triangle representing that particular component. Then any point on the line or on this line produced, represents the composition resulting from the variation of this one component alone, and consequently is a locus of constant ratio between the two components represented by the two remaining vertices.

Graphical representation of the ammonia soda process by means of a triangular prism is shown in Fig. 50. This process diagram is based on a system of triangular coördinates for  $OH^-$ ,  $HCO_3^-$  and  $Cl^-$  with a fourth (vertical) ordinate for  $Na^+—NH_4^+$  in the space relationship. Each edge of the prism is graduated to read from 0 to 100 per cent of one component or from 100 to 0 per cent of the other, and the six corners (or apices) represent respectively  $NaCl$ ,  $NaHCO_3$ ,  $NaOH$ ,  $NH_4Cl$ ,  $NH_4HCO_3$  and  $NH_4OH$ . We have not considered  $H_2O$ , but represent these six components on the dry basis.

Let us start with brine at the  $NaCl$  apex. Because of the presence in the salt of certain calcium and magnesium salts which upon ammoniation yield equivalent amounts of fixed ammonia (3-5 per cent as  $NH_4Cl$ ), this point is represented not by the  $NaCl$  apex but by  $A$ , along the edge  $NaCl—NH_4Cl$ . We ammoniate this brine in the absorber with ammonia gas from the distiller, cooled through the distiller condenser, containing about 0.2 mol  $CO_2$  per mol of  $NH_3$ . In other words, this distiller ammonia gas is already about 20 per cent bicarbonated and is therefore repre-

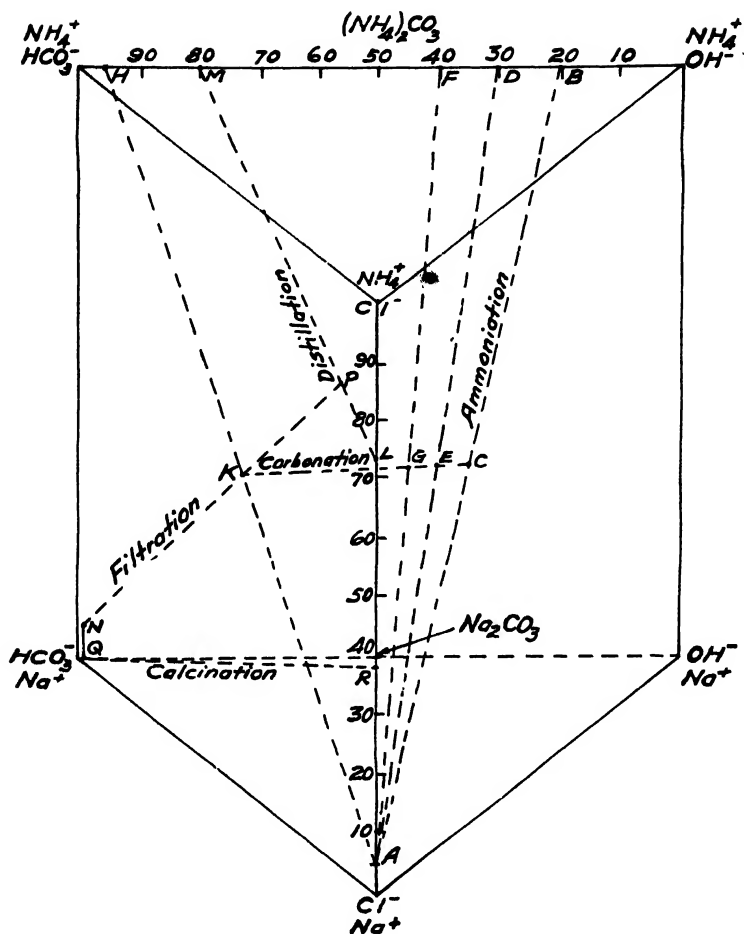


FIG. 50. Ammonia Soda Process Diagram.

- (A) Crude brine (Ca and Mg impurities converted to fixed ammonia).
- (B) Distiller gas to absorber (ammonia gas 20% bicarbonated).
- (C) Ammoniated brine from absorber (about 99  $\text{NH}_3$  titer and 89 Cl titer).
- (D) Pre-carbonated liquor from cleaning tower (below 32% bicarbonation).
- (E) Draw slurry from making tower (about 85% bicarbonated).
- (F) Ammonia gas liberated from top of heater (about 80% bicarbonated).
- (G) Heater liquor to prefilter containing only fixed ammonia.
- (H) Crude bicarbonate from filter containing  $\text{NH}_4\text{HCO}_3$  and  $\text{NaCl}$ .
- (I) Light ash from Rotary Dryer containing small amount of  $\text{NaCl}$ .

sented by B. Join A and B. As ammoniation proceeds, we arrive at C where the titer of Cl is about 89 and that of ammonia 99, or when the ratio of ammonia to sodium chloride in the ammoniated brine is as 1.11

to 1. This ammoniated brine, after settling and cooling, is pumped first to the cleaning tower where a small amount of lean  $\text{CO}_2$  gas is passed in. The liquor is allowed to be carbonated in the cleaning tower to less than 30 per cent bicarbonation, or until it contains about 65 g  $\text{CO}_2$  per l. This is represented by point  $E$  at the intersection of the carbonation line  $KC$  and the line  $AD$  connecting  $A$  with the 30 per cent bicarbonation point  $D$ . This precarbonated liquor is then sent into the making towers where it is finally carbonated to the highest degree possible. The carbonation line,  $KC$ , is not exactly parallel to the ammonia plane or  $\text{NH}_4\text{HCO}_3\text{--NH}_4\text{OH}$  edge, but is slightly inclined away from it on account of loss of ammonia gas from the ammoniated brine due to the stripping effect of the  $\text{CO}_2$  gas in the towers.

Precipitation of  $\text{NaHCO}_3$  gradually occurs in the making towers; for above about 32 per cent bicarbonation, the solubility product of sodium bicarbonate ( $\text{Na}^+ \times \text{HCO}_3^-$ ) begins to be exceeded, and the precipitation commences long before the ammoniated brine reaches its maximum bicarbonation. Because of hydrolysis, it is not possible to get 100 per cent bicarbonation. In fact, precipitation of  $\text{NaHCO}_3$  in the making tower takes place considerably at the 40 per cent bicarbonation point  $G$ , and continues as carbonation progresses until the maximum point  $K$  is reached at about 95 per cent bicarbonation, which occurs at the bottom of the making tower, where the richest  $\text{CO}_2$  gas comes into contact with the liquor, and the magma is about to be drawn out. But, strange to say, the mother liquor in the magma in equilibrium with the bicarbonate crystals is still only about 82 per cent bicarbonated. The highest degree of bicarbonation,  $K$ , is at the point of intersection of the carbonation line  $KC$  and the line from  $A$  to  $H$ , the 95 per cent bicarbonation point.

The slurry at  $K$  is filtered, giving the filter liquor  $P$  and the crude bicarbonate (ammonia soda)  $N$ . Because of the presence of  $\text{NH}_4\text{HCO}_3$  to the extent of 5 molal per cent in the crude bicarbonate, the line  $KN$  does not pass through the  $\text{NaHCO}_3$  apex but some point  $N$  near it. Upon calcination,  $\text{NH}_4\text{HCO}_3$  is driven off so that  $Q$  is reached.  $\text{NaHCO}_3$   $Q$  is then decomposed to light ash,  $R$ , which does not quite coincide with the middle point  $\text{Na}\left(\frac{\text{CO}_3}{2}\right)$  or  $\text{Na}_2\text{CO}_3$  of the  $\text{NaHCO}_3\text{--NaOH}$  edge, as it should. Here again the calcination line  $QR$  does not exactly follow the  $\text{NaHCO}_3\text{--NaOH}$  edge on account of the presence of some  $\text{NaCl}$  as one of the impurities in the soda ash.

The filter liquor at  $P$  is first sent to the distiller heater and the "free ammonia" is decomposed, yielding about 80 per cent bicarbonated ammonia gas  $M$ , and a heater liquor  $L$ , containing about 72 per cent fixed ammonia (as  $\text{NH}_4\text{Cl}$ ). This heater liquor flows into the preliher and finally passes through the lime still giving rise to  $\text{CaCl}_2$  in the distiller waste. The 80% bicarbonated heater gas is mixed with the ammonia gas from the lime still, coming over as 20% bicarbonated distiller gas to the absorber.

## Chapter XIV

### Recovery of Ammonia—Efficiency of Operation in Ammonia Still

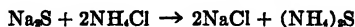
The price of soda ash is normally about \$30 per ton but that of ammonium sulfate \$30 to \$40.\* Based on a 25 per cent ammonia content, the price of ammonia is \$120 to \$160 per ton, or about 4 to 5 times that of soda ash. Evidently we cannot afford to lose much ammonia in the manufacture of soda ash. Ammonia is a comparatively expensive commodity. One of the reasons for the failure of the ammonia soda process earlier in the history was the lack of an efficient method of recovering ammonia from the mother liquor and the inability to minimize ammonia losses during operation. The heavy losses of ammonia in the cycle made it impossible for the process to compete with the LeBlanc process. It is now a systematic practice in ammonia soda plants to save all ammonia-bearing liquors and send them to the distiller for recovering  $\text{NH}_3$ . So much attention is now devoted to saving ammonia that it has become almost a matter of habit on the part of plant operators to consider the loss of sodium chloride as a very minor matter in comparison with that of ammonia.

Naturally in the early history of the ammonia soda process the loss of ammonia was great. Toward 1880, the loss of ammonia was still in the neighborhood of 4 to 8 per cent as  $(\text{NH}_4)_2\text{SO}_4$  on the weight of soda ash made. Now the conservation of ammonia in the soda ash plants has received so much attention that the loss is only from 0.20 to 0.40 per cent as  $(\text{NH}_4)_2\text{SO}_4$  on the soda ash produced.

The draw liquor contains from 65 to 74 titer of fixed ammonia and 22-26 titer of free ammonia. In other words, there are approximately a little less than 3 parts of fixed ammonia to 1 part of free ammonia. But the proportion of free ammonia to fixed ammonia in the feed liquor is increased by (1) the addition of the furnace condenser condensate which contains high ammonia and ammonium carbonate; (2) the absorption of free ammonia when a portion of the filter liquor is employed in scrubbing furnace gases (in the furnace gas scrubber); (3) the addition of crude liquor which contains only the free ammonia (but little fixed ammonia) to replace the ammonia lost in the system; and (4) the addition of sodium sulfide solution to make up for the deficiency of sulfide in

\* At present, the price of ammonia because of the production by the direct synthesis is rather low, but the demand and supply will adjust themselves as times get normal.

the ammoniated brine system. The sodium sulfide converts an equivalent quantity of fixed ammonia to "free ammonia."



On the other hand, if crude liquor is not available, ammonium sulfate solution is generally made from ammonium sulfate crystals and added to the filter liquor for distillation. This then would increase the ratio of fixed ammonia to free ammonia in the feed liquor to the distiller. On the whole, however, the proportion of free ammonia to fixed ammonia is considerably increased as the filter liquor arrives at the distiller, and the distiller feed may have the ratio of free ammonia to fixed ammonia as high as 3 to 7. At the same time, the liquor on its way to the distiller is diluted, as far as  $\text{Cl}^-$  is concerned, by:

- (1) wash water on the filters;
- (2) steam condensate from the furnace condenser drain line;
- (3) steam condensate from gases in the furnace gas scrubber;
- (4) water contained in the crude liquor, or in the ammonium sulfate solution, added to replace the ammonia lost.
- (5) water contained in the sodium sulfide solution added when the sulfide in the crude liquor is insufficient.

The filter liquor is pumped up to feed the distiller through an orifice regulation.

The composition of one sample of crude ammonia liquor is given in Table 92.

TABLE 92. Composition of Crude Ammonia Liquor.

Sp. gr. at 23° C.	1.025
Total ammonia (as $\text{NH}_3$ )	20.14%
$(\text{NH}_4)_2\text{CO}_3$	31.60%
Sulfide as $(\text{NH}_4)_2\text{S}$	10.98%
$\text{NH}_3$ (free)	3.46%

There are two types of modern ammonia column stills or distillers, one of the internal overflow type and the other of the external overflow type, both consisting of a number of compartments or rings with mushroom, division plates, and overflow pipes. These rings are placed one above another like a sort of column or tower (Fig. 58). The internal overflow type has a pipe inside each division plate, and the upper end of the pipe controls the depth of liquor or barbotage on the division plate, while the lower end dips well below the surface of the liquor in the next compartment below to give the necessary seal. These overflow pipes alternate from one division plate to another in a diametrically opposite position, so that the liquor is obliged to travel across each plate and down in a zigzag manner (Fig. 59).

The external overflow type has these overflow connections outside of the distiller from one ring to the next below, alternating in diametrically opposite positions as above. The edge of the overflow opening in this case controls the height of the liquor in each section and the inlet opening

into the section below is located well below the level of the liquor line. These overflow pipes are usually rectangular in cross-section, long horizontally and narrow vertically; and in order to provide the most direct flow for the lime sludge which has a great tendency to plug the passage, the horizontal part of the shoulder connecting the overflow pipe with the side of the distiller is made as short as possible. In fact, one construction has the overflow trough directly attached to the side of the distiller, making the outside wall of the distiller the bottom side of the rectangular overflow trough.



FIG. 58. Distiller.

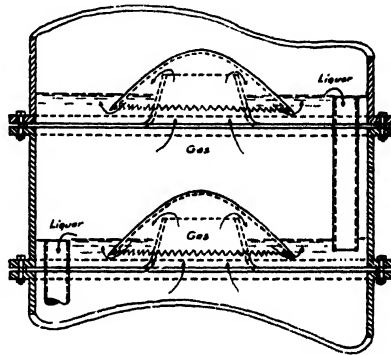


FIG. 59. Distiller sections of internal overflow type.

The advantages of the internal overflow type are a more direct passage for the thick lime sludge to travel from one section to another below, and no heat losses by radiation from these overflow conduits. The advantages of the external overflow type, on the other hand, are that a clear space inside the distiller is available for ammonia distillation and that the overflow passages are more accessible. At present the external overflow type is common in soda plants (Fig. 60).

The size of the mushroom in each compartment is dependent on the shape of its sides or wings. The diameter of the mushroom at the base of its serrated edge is generally from 55 to 70 per cent of the inside diameter of the compartment. For example, for a 2500-mm inside diameter, the diameter of the mushroom may be from 1400 to 1700 mm. For a mushroom with a steep slope at the sides, of the type shown in Fig. 59, the diameter should be smaller; while for a mushroom with widespread sides of the type shown in Fig. 61, this diameter takes a somewhat higher ratio. Often the bottom of the compartment (the division plate) is



curved in the manner shown in Fig. 60, the idea being so to direct the flow of steam that it may come into intimate contact with the whole volume of the liquor and may spread itself in fine bubbles in the liquor, encountering least resistance in its radial sweep. With a large number of mush-

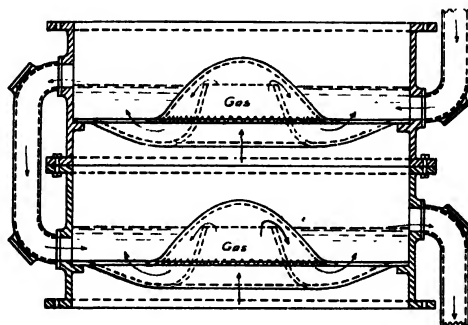


FIG. 60. Distiller sections of external overflow type.

rooms placed one on top of another throughout the height of the distiller, the resistance may be considerable, especially if the depth of the liquor in each compartment (the depth of wash or barbotage) is considerable. For ammonia absorption, such as in an absorber where the gas is to be dissolved by the brine, the depth of the wash should be greater; but for a distilling operation as in the distiller discussed here, the quantity of the liquor carried in each compartment should be small.

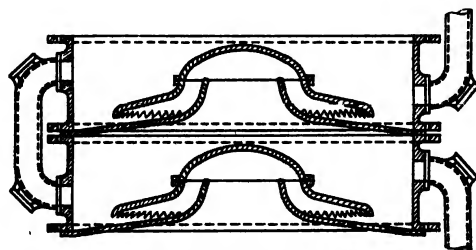


FIG. 61. "Bubble-Cap" type of heater sections.

If the diameter of the compartment is large, a multiple system of mushrooms is provided to distribute the steam evenly over the entire area of the compartment; in this case, either several long, narrow mushrooms or several small, circular mushrooms are placed at equidistant points on the division plate.

One important point that should be observed in the design of the distiller is so to proportion the mushroom dimensions and so to locate the overflow points that the liquor shall have no tendency to be blocked up by the upward flow of steam. A condition in which the upper compart-

ments tend to run full and the liquor refuses to descend readily is known as the "suspension" of the liquor (similar to the "gas-locking" or "gas-binding" in the absorber). Normally, this is caused by the deposit of scale or sludge at the overflow points; but with faulty design of the bubble-caps and division plates, this tendency is greatly increased, with the result that steam enters the liquor passage and blocks its downward flow.

A column distiller for soda manufacture consists of three main parts: the upper part above the lime inlet, called the "heater"; the lower part below the lime inlet, the lime still, or the distiller proper; and the partial condenser located on the top of the heater. The heater is to vaporize "free ammonia" from the filter liquor by steam, and the lime still is to decompose the fixed ammonia by milk of lime and vaporize the free ammonia so liberated by steam. The partial condenser is to provide the overflow to the top of the heater and to secure richer (drier) ammonia gases distilled over. Under "free ammonia" are included (besides free  $\text{NH}_3$ ),  $\text{NH}_4\text{HCO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{S}$ , etc., *i.e.*, all the ammonium compounds that are readily decomposable and volatilized by steam. The fixed ammonia which requires lime is mostly in the form of  $\text{NH}_4\text{Cl}$ , and in small quantities also in the form of  $(\text{NH}_4)_2\text{SO}_4$ . This column type of distiller was the invention of Dr. Ludwig Mond, who designed and built it in 1883.

The older forms of lime still consisted of four large tanks in series. Steam entered the one containing the weakest ammonia liquor, and the outlet from this went to the next, and so forth. When all the ammonia in one unit had been boiled out, it was cut out and the content emptied. Steam entered the next one in the series as a head tank. The empty kettle was filled with filter liquor and the requisite quantity of milk of lime, and became the last one in the series. This is a batch process. The handling required considerable labor. Although there might be a saving in lime by being able to control the quantity of lime in each batch, the time and labor involved made it unsuitable for any large-scale production.

The reactions in the heater are as follows:

- (1)  $\text{NH}_3 \cdot \text{Aq} \rightarrow \text{NH}_3 \text{ gas}$
- (2)  $\text{NH}_4\text{HCO}_3 \rightarrow \text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$
- (3)  $(\text{NH}_4)_2\text{CO}_3 \rightarrow 2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$
- (4)  $\text{NaHCO}_3 + \text{NH}_4\text{Cl} \rightarrow \text{NaCl} + \text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$
- (5)  $\text{Na}_2\text{CO}_3 + 2\text{NH}_4\text{Cl} \rightarrow 2\text{NaCl} + 2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$
- (6)  $(\text{NH}_4)_2\text{S} \rightarrow 2\text{NH}_3 + \text{H}_2\text{S}$
- (7)  $\text{NH}_4\text{HS} \rightarrow \text{NH}_3 + \text{H}_2\text{S}$
- (8)  $\text{Na}_2\text{S} + 2\text{NH}_4\text{Cl} \rightarrow 2\text{NaCl} + 2\text{NH}_3 + \text{H}_2\text{S}$
- (9)  $\text{Na}_2\text{S} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{S}$

The reactions in the lime still or distiller proper are:

- (10)  $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{NaOH} + \text{CaCO}_3$
- (11)  $\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
- (12)  $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCl}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O}$
- (13)  $(\text{NH}_4)_2\text{SO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_4 + 2\text{NH}_3 + 2\text{H}_2\text{O}$

The following reaction:



requires prolonged cooking over a long period to get satisfactory completion. It takes place only when finely divided calcium carbonate, such as the precipitated carbonate from the causticization tanks, is used in excess and also when the ammonium chloride concentration is high. Under the prevailing conditions of distiller operation, however, such a reaction does not occur to any extent. For the same reasons, with the insoluble magnesium oxide in milk of lime, the reaction



can hardly take place in the lime still under ordinary conditions.

The heater is either packed with coke, about 6 inches in size, or with earthenware tiles, the so-called chemical tiles. The spiral tiles made of stoneware are best of 5 inches inside diameter by 6 inches outside diam-

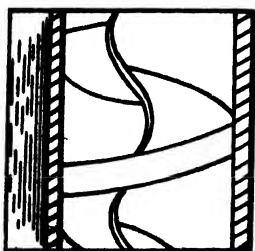


Fig. 62. Spiral chemical tile.

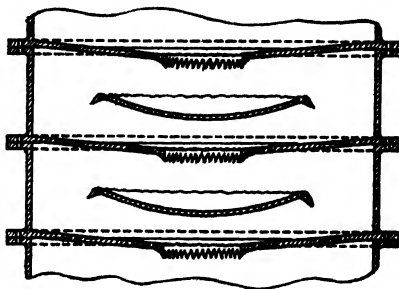


Fig. 63. "Spray dish" type of heater sections.

eter and 6 inches high, with a spiral ribbon inside (Fig. 62). Some heaters also have mushrooms and division plates (the "bubble-cap" type) as in the distiller proper (Fig. 61), while others have, instead of these, inverted spray dishes having serrated edges with serrated overflow openings in the center of the division plates underneath (Fig. 63). Still others have sections consisting of long, narrow mushrooms on each division plate (as in Fig. 38, p. 170). A good distribution method is to use a large number of long and narrow distributing troughs or trays, packed one on top of the other and staggered over each other, in the manner of the packing in some of the deaerating heaters for the liberation of oxygen from boiler feed-water (see Fig. 64). But in a large majority of cases a combination of these "bubble" or "spray" devices and the tile or coke packing is used. Coke packing offers more resistance to the gas passage than tile packing and may build up excessive pressure. The coke-packed heaters while working properly when properly packed, are likely to become partially plugged by dirt. When this happens, steam blows to one side and chan-

nelling occurs, when a portion of the coke may be blown up forming a pit on the top of the packing. The distiller proper (the lime still), on the other hand, always has the simple mushrooms and the division plates (or bubble-caps and plates).

On top of the heater are sections of the coolers and condensers, usually consisting of a large number of horizontal 2-inch cast iron tubes (Fig. 65). These are divided into two main divisions, the upper division of which uses water as the cooling medium, while the lower division uses the filter liquor as the cooling medium so that the feed liquor is preheated on its way to the heater. These are partial condensers for the ammonia gases,

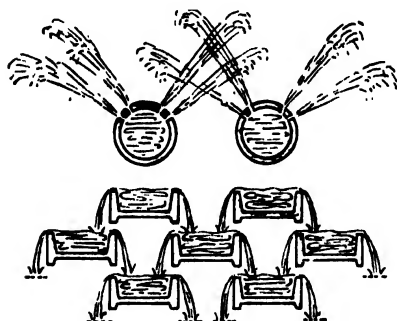


FIG. 64. Distributing trays.

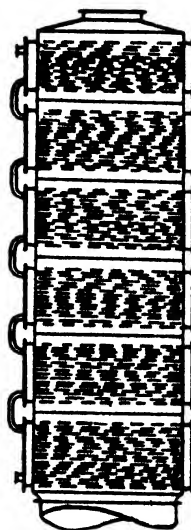


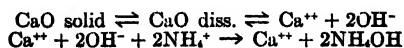
FIG. 65.  
Distiller condenser.

and the condensate is allowed to drain back to the heater. The feed liquor is thus heated to about  $70^{\circ}\text{C}$ . before entering the heater. The gases from the distiller consist of ammonia, carbon dioxide, steam, and some hydrogen sulfide and air. The steam, of course, should be condensed out as far as possible, but with it also a portion of the ammonia vapor. Hence the condensate returned to the distiller is necessarily a strong ammonia solution carrying some  $\text{CO}_2$ . The purpose of the distiller coolers and condensers is to condense out most of the steam, thereby obtaining a sufficiently dry ammonia gas for the absorber operation. Hence the top portion of the distiller, including the coolers and condensers and a part of the heater, may be called a rectifier or dephlegmator. As was explained in detail in Chapter VII, excessive steam carried over by the ammonia gas from the distiller would unnecessarily dilute the brine and generate too

much heat in the absorber. Sometimes the distiller coolers and condensers are installed separately and located below the distiller top, but their proper place is on the top of the distiller so that the condensate may be drained back directly to the heater where the strong ammonia liquor properly belongs. When they are installed separately, they are placed high enough so that the condensate may flow into the heater through a U-loop seal. This is done to avoid pumping the hot, corrosive ammonia-carbon dioxide condensate back to the top of the distiller. The distiller coolers and condensers are subject to very severe chemical corrosion because of the presence of ammonia,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , etc., carried by the ammonia gases at an elevated temperature. The cooling tubes must be made of a good grade of cast iron (not steel) to withstand the corrosion.

Liquor from the bottom of the heater, which should be free from  $\text{CO}_2$ , flows to the top of the lime still or the preliher, where milk of lime is introduced to decompose the fixed ammonia; and the free ammonia so liberated is distilled off by steam just as in the heater above, as the liquor flows down from one passette to another in the lime still. In actual operation, in the arrangement in which the heater is placed on top of the lime still, not all the free ammonia can be driven from the heater liquor. On arriving at the bottom of the lime still, however, all ammonia should have been distilled out, leaving the waste liquor with a small excess of lime to be run off to waste. Open steam enters at the bottom compartment in the lime still diametrically opposite the blow-off opening. In actual practice, exhaust steam from the engines, or better from the bleeder turbines, is employed for this purpose. The engine cylinders are so designed as to give 8 to 10 pounds back pressure in the exhaust. Generally, there is a tendency toward shortage, rather than surplus, of the exhaust steam for distillation, and at times some live steam may have to be introduced into the distiller. Live steam is not so suitable as the exhaust steam which, by virtue of its low pressure, has a large volume, giving a large contact surface and more even bubbling action in the distiller. The exhaust steam, however, must be dry and the condensate trapped out in order to avoid unnecessary dilution in the distiller.

The rate of decomposition of the fixed ammonia by lime is wholly dependent upon the rate of hydration and solution of  $\text{CaO}$  in the lime still. While the ionic reaction is instantaneous, the solution of  $\text{CaO}$  is slow; which, therefore, controls the speed of its reaction with fixed ammonia.



Lime has the peculiar property of becoming less readily soluble when burned at a high temperature, i.e., when it is overburned or dead-burned it dissolves with great difficulty. In order to make more lime available for ammonia liberation, the time of contact in the liquor should be lengthened. This is accomplished by having a large reservoir outside where the heater liquor is intimately mixed with the milk of lime and

allowed much longer time of contact before entering the lime still. This reservoir, called the prelimer or preliming tank, is provided with a stirrer to keep the milk of lime in suspension, and the heater liquor in intimate contact. By gradual displacement, the top portion of the liquor overflows to the lime still. Thus, a major part of the reaction is caused to take place in the prelimer outside, returning virtually free ammonia liquor to the lime still for distillation. There are several advantages in having the prelimer. First, it gives a more thorough mixing of milk of lime and heater liquor; secondly, it allows more time for lime to dissolve and react with the fixed ammonia; and thirdly, it affords easier control of the excess of lime in the distiller, avoiding sharp fluctuation in the lime used for distillation.

The volume of filter liquor by the time it reaches the distiller is about 7 cubic meters per ton of ash. Table 93 gives its approximate composition after the liquor has received various ammonia condensates and liquors.

TABLE 93. Composition of Distiller Feed Liquor.

Fixed NH <sub>3</sub>	55 titer
Free NH <sub>3</sub>	25 titer
NaCl	75 grams per liter
CO <sub>2</sub>	35 grams per liter

The heater liquor contains all the fixed ammonia and sodium chloride, and should contain no CO<sub>2</sub> or free ammonia. But in practice, as mentioned above, there still remains about 4 titer of free NH<sub>3</sub>. The freedom from CO<sub>2</sub> in the heater liquor is a test for the efficiency of the heater, and is generally dependent upon (1) the temperature in the heater, (2) the intimate and thorough contact between the liquor and the steam in the heater, and (3) the time that the liquor is exposed to the action of steam, assuming a uniform gradient of the partial vapor pressure of ammonia throughout the heater. The heater liquor should be practically free from CO<sub>2</sub> before entering the prelimer, or the calcium hydroxide would be converted to calcium carbonate, which is unavailable for ammonia liberation in the lime still. For the following reaction, as mentioned above,



does not take place under normal operating conditions in the lime still.

The pressure at the bottom of the distiller should be from 8 to 10 lbs. gage (sometimes as high as 12 lbs.); and there should be a slight vacuum at the top of the distiller, about  $\frac{1}{4}$  inch Hg, so that the pressure in the distiller decreases from 8 to 10 lbs. per sq. in. at the bottom to a slight vacuum at the gas outlet at the top. The use of a slight vacuum at the top decidedly helps the vaporization of ammonia in the liquor. The whole distiller and absorber system must be air-tight; or air will leak in and render the exhaust gas from the absorber system too weak in CO<sub>2</sub> to be returned to the carbonating towers. In any case a slight vacuum is to be preferred both from the viewpoint of avoiding loss of ammonia gas to the

atmosphere and of the more rapid removal of ammonia vapors from the distiller. The top temperature is 82 to 86° C.

Roughly speaking, as described above, the heater and the condenser may be said to correspond to a rectifier and the lime still to the distiller proper. However, as it is actually conducted in ammonia soda plants, the function of each portion of the distiller is not so simple. When the heater is set on top of the lime still integrally, the rich ammonia gas from the lime still below is not (and cannot be) in equilibrium with the liquor in the heater. The heater then cannot be purely a rectifier or dephlegmator, because while receiving the overflow at the top from the partial condenser, it also receives dilute feed liquor. Its function is primarily to distill "free ammonia" from the feed liquor, and consequently cannot be simply one of rectifying or dephlegmation. Again, the heater liquor containing fixed ammonia is limed in an outside tank (preliming tank or preliher) and then returned to the top of the lime still, containing some excess lime. This is really another feed to the distiller introduced at another point of the distiller body. Hence the whole distiller is in reality a two-feed column (filter liquor at the top of the heater and a limed liquor at the top of the lime still coming from the preliher), entailing complexities inherent to a two-feed system—nevertheless a simple two-component (ammonia-water) system where the composition in the vapor phase from the top of the lime still is not in equilibrium with that in the liquid phase from the bottom of the heater, and where the rich ammonia gas from the top of the heater is not in equilibrium with the rather cold, dilute filter liquor introduced there.

As the bottom of the distiller is under a pressure of 8-10 lbs. gage, the liquor is therefore at a temperature above the boiling point under atmospheric pressure. When, therefore, the liquor is blown out and is released to the atmospheric pressure, it partially flashes into steam, which can be utilized for distillation at a lower pressure. Indeed, in practice, the blow-off is first blown into a flash tank near the bottom of the distiller and the steam from the uptake of the flash tank is utilized to operate a weak liquor distiller which is merely a small still about 1 m. in diameter and 8 m. high, distilling floor liquor and other weak ammonia liquors. Such a weak liquor distiller has been installed in most ammonia soda plants, utilizing the blow-off steam.

TABLE 94. Composition of Distiller Scale.

	Per Cent		Per Cent
$\text{CaSO}_4$	62.41	$\text{NaCl}$	1.65
$\text{CaO}$	30.32	$\text{Fe}_2\text{O}_3$	0.20
$\text{MgSO}_4$	2.35	$\text{Al}_2\text{O}_3$	0.08
$\text{MgCO}_3$	1.62	$\text{SiO}_2$	0.32
$\text{Na}_2\text{SO}_4$	1.17	Moisture	0.60

In the lime still or the distiller proper, hard scale is likely to form and the distiller needs to be shut down and cleaned every so often. This happens once in 1 or 2 months, depending upon the rate of operation and

the quality of lime used. Frequent interruption in the distiller operation would cause solids to settle in the lime still, necessitating more frequent cleaning. The scale formed in the upper portion of the lime still contains much calcium carbonate; while calcium sulfate predominates below, although lime is also present in considerable quantities.

Table 94 gives the results of analysis of a scale taken near the bottom of the distiller.

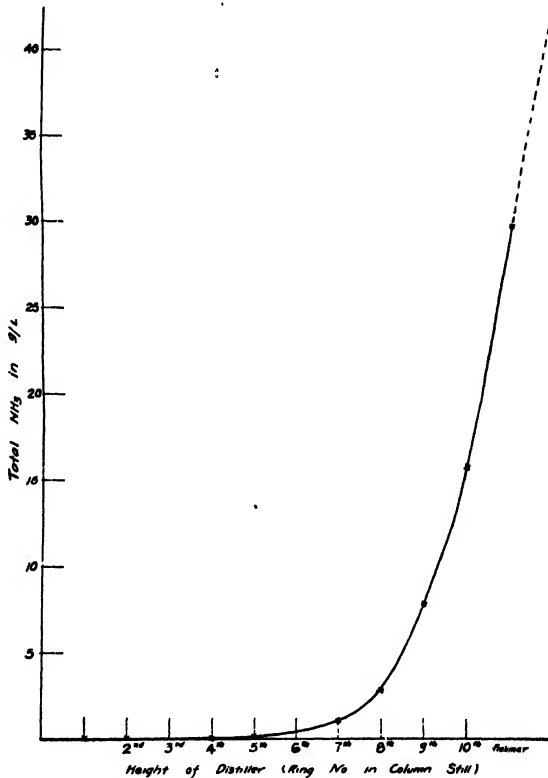


FIG. 66. Analyses of distiller liquor showing condition of operation.

This scale is very hard and attains a thickness of 1 to 2 inches. It has to be chiselled off by hand or by a pneumatic scaling hammer. Before shutting down a distiller, it should be cooked for several hours with steam to drive out all ammonia. The distiller is then cut out and allowed to cool. The manhole covers are opened and the cleaning work is started.

Table 95 gives some idea about the ammonia concentrations in the different samples at different points in a distiller in operation. Figure 66



shows the ammonia gradient in the liquor phase in the lime still and the preliher.

TABLE 95. Analyses of Distiller Liquors Showing Condition of Operation.

	Sample	Sp. Gr. and Temp.	Total NH <sub>3</sub> (Grams per Liter)	Total Chlorine (as Cl-)
	Filter liquor	1.122 at 27° C.	61.20	140.82
	Heater liquor	1.093 at 27° C.	43.03	125.55
Heater and preliher	Prelimer liquor	1.120 at 26° C.	29.89	99.26
	Ring No.			
	10	1.121 at 23° C.	15.78	90.56
	9		7.93	
	8		2.83	
	7		1.04	
Lime still	6		....	
	5		0.108	
	4		0.025	
	3		....	
	2		0.018	
	1		0.012	

As to the composition of the liquors in different rings of the distiller, Bradburn's \* data in Table 96 illustrate the conditions of operation in the distiller at his time.

TABLE 96. Composition of Liquors at Different Points in Distiller.

		Total NH <sub>3</sub>	Free NH <sub>3</sub>	Fixed NH <sub>3</sub>	CO <sub>2</sub>
	Feed liquor	67.2	15.0	52.2	39.3
	Ring No.				
Heater	21	83.4	39.0	44.4	26.2
	20	74.0	30.7	43.3	9.0
	19	66.0	23.1	42.9	3.8
	18	62.8	20.4	42.4	2.0
	17	60.5	18.5	42.0	1.2
	16	57.7	16.2	41.5	0.71
	15	55.0	13.8	41.2	0.38
	14	53.0	12.1	40.9	0.20
	13	52.6	12.1	40.5	nil
	12	39.0	39.0	nil	nil
Lime still	11	9.7	9.7	nil	nil
	10	4.0	4.0	nil	nil
	9	1.9	1.9	nil	nil
	8	1.0	1.0	nil	nil
	7	0.6	0.6	nil	nil
	6	0.33	0.33	nil	nil
	5	0.20	0.20	nil	nil
	4	0.13	0.13	nil	nil
	3	0.05	0.05	nil	nil
	2	0.03	0.03	nil	nil
	1	0.017	0.017	nil	nil

The distiller waste, or run-off liquor, contains all the undecomposed salt in the filter liquor, calcium chloride in a quantity equivalent to the

\* Ullmann, "Enzyklopädie der technischen Chemie," Vol. 8, p. 31, Berlin, Urban & Schwarzenberg, 1931.

amount of sodium chloride decomposed, a small quantity of calcium hydroxide (2 to 4 grams per liter) from the slight excess of lime used to insure the complete decomposition of fixed ammonia in the lime still, and all the impurities of sand, unburned and overburned stone, etc. present in the lime. The composition of the waste liquor varies greatly according to the quality of brine and limestone used, the volume of the feed liquor to be distilled per ton of ash, the percentage of decomposition in the towers, and the strength of the milk of lime employed. Normally, there are about 10 to 12 cubic meters of the waste liquor per ton of ash made. (See Table 97.)

TABLE 97. Calculation of Volume of Distiller Waste.

	For Small Works Where Dilution is Comparatively Great	For Average Conditions
	Cubic Meters	
Draw liquor .....	6	5.4
Wash water on the filters, steam condensate, condenser drain, etc. ....	1	0.6
Milk of lime .....	2½	2.0
Dilution by exhaust steam .....	2½	2.0
Total .....	12	10.0

The composition of the distiller waste also varies greatly. Its approximate composition is shown in Table 98.

TABLE 98. Composition of Distiller Waste.

Sp. gr. of waste liquor	1.10-1.13
CaCl <sub>2</sub>	85-95 grams per liter
NaCl	45-50 grams per liter
CaCO <sub>3</sub>	6-15 grams per liter
CaSO <sub>4</sub>	3-5 grams per liter
Mg(OH) <sub>2</sub>	3-10 grams per liter
CaO	2-4 grams per liter
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub>	1-3 grams per liter
SiO <sub>2</sub>	1-4 grams per liter
NH <sub>3</sub>	0.006-0.012 gram per liter

The composition of the distiller waste liquor and the relative concentrations of various substances therein is a barometer indicating the efficiency of the whole ammonia soda process. For, from the analysis of this liquor, it is possible to obtain many data bearing on the consumption of raw materials employed and consequently the efficiency of the operation. For instance,

- (1) Low specific gravity of the liquor and the proportionately low concentrations of various substances present indicate a large volume of feed liquor to be distilled and consequently a high consumption of steam and coal, and a greater ammonia loss per ton of ash.
- (2) Low ratio of calcium chloride to sodium chloride indicates low decomposition in the carbonating towers (or columns) and high wastage of sodium chloride.

- (3) Presence of much ammonia indicates a heavy loss of ammonia through the distiller.
- (4) High percentage of lime indicates a large excess of milk of lime and high consumption of limestone.
- (5) High percentage of calcium carbonate indicates inefficient operation in the heater (from  $\text{CO}_2$  in the heater liquor) and high consumption of lime and coke.
- (6) Large amounts of insoluble solids in the waste liquor relative to calcium chloride, such as magnesium oxide, silicon dioxide, ferric oxide, and aluminum oxide (all of which must have come from the milk of lime), indicates poor quality of limestone being used.

The distiller waste liquor carries considerable solids in suspension. The disposal of this waste is a matter of no little concern to ammonia soda manufacturers. The solids accumulate very fast, and the liquid portion containing free lime and calcium chloride, if allowed to run into a stream, may kill the fish and contaminate the water. Towns where the industry is located will pass laws forbidding the discharge of this waste to the river in the community. The general practice is to employ a large tract of land, 100 acres or larger, adjoining the factory site and pipe the waste in 8- to 12-inch steel pipes first to one-half of this field and then to the other. Settling takes place and the solids are left behind. Only the liquid portion is allowed to flow out. How fast these solids accumulate can be appreciated from the fact that one plant producing 100 to 150 tons of ash daily filled a piece of land 10 acres in area to a height of 20 feet in about 9 years. As the solids build up in one half of the land, they are dug out and thrown on the sides, making an embankment surrounding it. Meanwhile, the discharge goes to the other half. As the land is being filled up, the elevation becomes too much for the gravity flow of the liquor from the bottom of the distiller. A centrifugal booster pump is then employed to give the head necessary to discharge to these fields. If limestone quarries lie near at hand, the waste is best sent to fill the old quarry pits.

The waste as shown above contains chiefly calcium chloride, sodium chloride, calcium carbonate, silicious matter, and lime. Attempts have been made to work up this waste liquor for anhydrous calcium chloride, refined salt, etc. In fact, several ammonia soda plants are doing this. But the limited demands for calcium chloride in comparison with the quantity produced can utilize hardly a fourth or a fifth of the total output. The balance has to be disposed of.

The blow-off liquor from the bottom of the distiller is at a temperature slightly above the boiling point of plain water. Its sensible heat is therefore enormous because of the very large volume involved. This will flater be shown by the fact that it takes about 64 per cent of the total heat required just to heat up the liquor. The heat in the blow-off liquor should therefore be utilized for preheating, but unfortunately the liquor contains considerable suspended solids which may settle and form scale

in a preheater or heat exchanger, making the scheme impracticable. Some heat, however, is utilized in evaporation when the clarified blow-off liquor is evaporated for the recovery of calcium chloride and salt.

The distiller operation is rather delicate in its control, and good judgment must be exercised at all times. The rate of feed, the varying composition and concentrations of the feed liquor, the adjustment of the quantity of milk of lime to give the proper excess, the varying strength in the milk of lime—all demand close attention on the part of the operators. If there is a deficiency of steam, ammonia may not be completely driven out before the liquor reaches the bottom. This is a phenomenon called the "Sour Bottom," in which case the sour liquor at the distiller bottom must be temporarily emptied out to a pit to be pumped back to the distiller later; otherwise much ammonia would be lost in the waste. Also in such cases  $\text{CO}_2$  may not be completely driven out from the heater liquor, and the sulfide from sodium sulfide added may not be completely decomposed; some may remain in the distiller waste and be lost. If, on the other hand, too much steam is used, it may be beyond the capacity of the condensers and coolers to cool, the gas outlet temperature would be too high, and the gas would carry over too much steam to the absorber. Normally the gas enters the absorber at a temperature of 55 to 60° C. A temperature much lower than 55° C. may, if allowed to remain for any length of time, cause crystallization of "ammonium carbonates" both in the distiller cooler passage and in the gas mains leading to the bottom of the absorber, thereby plugging up the system. On the other hand, a temperature above 60° C. would bring too much steam condensate to the absorber, unnecessarily diluting the brine, with the result that the Cl-titer in the ammoniated brine falls low. This, of course, causes low decomposition in the columns because of low concentration of  $\text{Na}^+$  in the green liquor. A serious case that sometimes ensues is the "hot-top" condition in the absorber created by the heat thus carried to the absorber from the condensation of much steam.

Further, if there is a deficiency in lime, there will be some undecomposed fixed ammonia at the distiller bottom. The liquor, of course, would then smell "sweet," but ammonia may have been sent to waste unnoticed. As ammonia is an expensive material and normally the still is the largest single source of ammonia loss, the liquor at the still bottom should be continually titrated for an excess of lime and tested for "sweetness" by its odor as often as every few minutes.

Regarding the corrosion of the apparatus by ammonia, Pennock and Morton\* found that if the iron surface was clean and free from rust, ammonia not only would not corrode the iron but would protect it. If, on the other hand, corrosion of iron had started, ammonia would accelerate it. It is therefore necessary to have a ferrous sulfide coating on the exposed surface of the iron to prevent corrosive action.

\* *J. Am. Chem. Soc.*, p. 377 (1902).

## EFFICIENCY OF AMMONIA STILL OPERATION

The distillation of ammonia from the filter liquor is an example of separating a more volatile constituent from a less volatile one, when the two are soluble in each other in practically all proportions, to form one liquid phase. It is a binary solution with one liquid and one gaseous phase. The system is therefore divariant. The fixing of any two factors, or independent variables, out of the three—temperature, pressure, and composition in the liquor—will thus determine the whole system. These are generally the temperature in the still and the composition in the liquor, the two being as far as possible maintained constant or uniform in the distiller operation.

Aqueous ammonia solutions behave quite normally. The ammonia concentration in the vapor phase in equilibrium with the solution is consistently greater than its concentration in the solution at all temperatures and in all concentrations, there being no maximum or minimum constant boiling point for the solution. In a dilute solution its vapor pressure may be said to follow Henry's law.

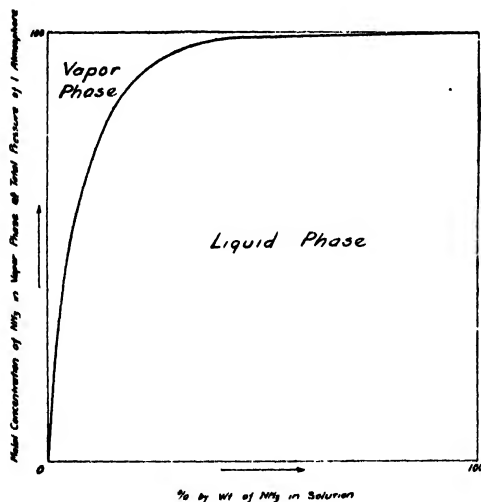


FIG. 67.

Composition of ammonia in vapor and liquid phases.

That is, if  $c$  is the concentration of ammonia in solution, and  $C$  that in the vapor,  $C > c$  at all concentrations in the solution (Fig. 67). The partial vapor pressure of ammonia in equilibrium with dilute solutions at 30° C., within the range of from 0 to 40 grams  $\text{NH}_3$  per liter, may be expressed as follows:

$$p = 0.99 C$$

where

$p$  = partial vapor pressure of  $\text{NH}_3$  in mm Hg  
 $C$  = conc. of  $\text{NH}_3$  grams per 1000 grams of  $\text{H}_2\text{O}$

As described above, the modern ammonia distiller consists of a lime still and a heater set on top of the lime still, receiving ammonia vapors and all the heat from the lime still below. Although this gives a simple arrangement, it is not done without some sacrifice. For, while a counter-current arrangement in the heat transfer is thus maintained, this is not true of the ammonia vapor flow, and also frequently is not true of the introduction of the feed liquor.

In order that a distiller may operate efficiently the following conditions must be satisfied:

- (1) There shall be a countercurrent heat supply to the distiller.
- (2) The distiller body shall be insulated against radiation losses.
- (3) The partial pressure of ammonia in the vapor rising from bottom to top shall not at any point be greater than the ammonia vapor tension in the liquor with which the vapor comes in contact.
- (4) The feed liquor shall be preheated and introduced at a point where its ammonia vapor tension is greater than the partial pressure of ammonia at that point.
- (5) The volume of filter liquor to be distilled and of the milk of lime employed per ton of soda ash shall be as small as possible, *i.e.*, both of these shall be as concentrated and hot as possible.

(1) **Countercurrent heat supply.** Although ammonia gas is readily expelled from the solution, the last trace of it is driven out with considerable difficulty. Hence, as ammonia in the liquor gets dilute, more steam and a higher temperature are required to complete the work with a given excess of lime. The supply of steam is so arranged that the weakest ammonia liquor meets the fresh steam, and is subject to the highest temperature available, before the waste liquor is run out. The supply of exhaust steam in the form of open steam is introduced at the bottom of the lime still and the countercurrent feature is closely adhered to in practice.

(2) **Lagging of distiller body against radiation.** The vapors of ammonia and steam in the distiller rise and gradually meet the stronger overflow liquors from the upper division plates. In equilibrium with the increasing ammonia concentrations in the overflows above, the vapor in contact with the liquors is gradually enriched in ammonia. When the vapor strikes the condensers at the top of the distiller, a large portion of steam with a comparatively small portion of ammonia is condensed and flows back to the still. The distiller condensers on top of the heater form what is known as a partial condenser as mentioned before. In the ideal condition, the vapor from one compartment below should be condensed on the division plates above, giving all its heat of condensation for the vaporization of a richer liquor on that plate, and so on, so that a poorer ammonia vapor disappears and in its place appears a richer one. This process is repeated until the partial condenser on the top is reached. Furthermore, it can be shown that in order to obtain a maximum separation between ammonia and water, the amount of overflow from each divi-

sion plate throughout the body of the distiller should be the largest possible. That means that all condensation by cooling should be done in the partial condenser at the top of the heater, and the overflow should start from this partial condenser down. If there is a loss of heat by radiation from the body of the distiller, the vapor will be condensed in the lower part of the distiller before it reaches the partial condenser at the top, and this condensate gives rise to overflows arising from the lower division plates only. Hence, to utilize all the heat coming in the form of vapor below for vaporizing a richer liquor above, and to secure the maximum overflow possible from the division plates throughout the height of the distiller, it is necessary to insulate the body of the distiller and to minimize the heat loss by radiation, so that all the cooling shall be done in the partial condenser and cooler at the top of the heater, and not in any part of the body of the distiller.

(3) **Larger ammonia tension in liquor phase than partial ammonia pressure in gas phase.** In order to cause ammonia to vaporize from the liquor, its vapor tension in the liquor must be greater than the partial pressure in the vapor. If the partial pressure is greater than that which corresponds to the equilibrium value of the tension in the liquor, ammonia from the vapor will be dissolved in the liquor. At equilibrium, the rate of vaporization of ammonia from the liquor equals that of solution in the liquor. While this countercurrent principle is followed on the whole in actual practice, there are departures at certain points in the distiller, notably at the junction between the heater and the lime still and at the feed inlet at the top of the heater. In the distiller construction prevalent in ammonia soda plants, the heater takes all the heat from the lime still, and all the rich ammonia gas from the lime still below is allowed to come in contact with the heater liquor at the bottom of the heater; which liquor contains practically all the ammonia as fixed ammonia. The ammonia vapor tension from the fixed ammonia liquor is practically nil, and consequently at this point some ammonia from the vapor phase will be redissolved in the liquor until equilibrium takes place. This is why the heater liquor leaving the bottom of the heater cannot be completely free from free ammonia in this type of arrangement. This decreases the efficiency of ammonia separation in the distiller and increases the burden on the lime still. The old arrangement of having a separate heater and lime still taking their heat supply (steam) independently and delivering the ammonia gases to a common condenser, also independently, did not have this objectionable feature.

(4) **Feed liquor introduced at a point where its ammonia tension is not smaller than partial pressure of ammonia in gas at that point.** Another point is the feed inlet at the top of the heater. In order not to break the gradient of ammonia concentrations in the overflow liquors, the feed should be introduced at a point where its ammonia vapor tension is just larger than that of the overflow liquor at that point. At the top of the heater where the filter liquor is customarily introduced, the hot condensate from the partial condenser is usually at a much higher ammonia

vapor tension than that in the feed liquor introduced there, especially when the latter is dilute and comparatively cold; and so the gas is richer in ammonia than that which corresponds to the equilibrium value in the feed liquor. As a result, ammonia vapor is actually redissolved by the feed liquor under such conditions. In the present-day ammonia soda plants effort has been made to preheat the feed liquor by using it as a wash liquor in the furnace gas scrubber and further as a cooling medium in one section of the partial condenser at the top of the heater. This not only conserves the heat by treating the partial condenser as a heat inter-changer, but also improves the ammonia tension gradient in the heater. The condition is illustrated qualitatively in Figs. 68, 69, and 70.

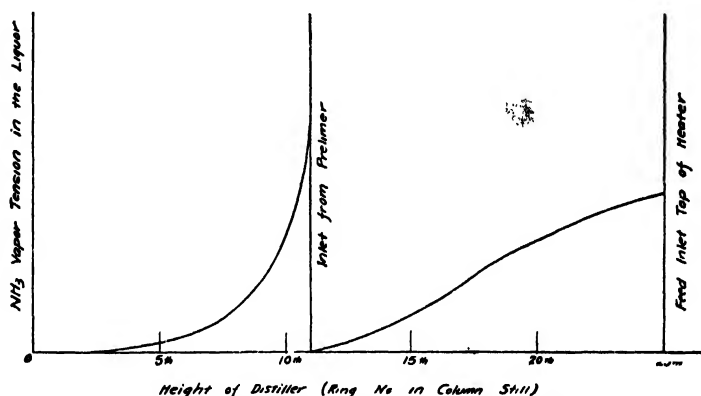


Fig. 68. Curve showing vapor tension of ammonia in liquor phase.

At  $x_1$ , Fig. 69, re-solution of ammonia from the vapor always occurs, and at  $x_2$  re-solution of ammonia may occur if the feed liquor is dilute and not properly preheated. Fig. 70 shows the resultant condition from the combination of the conditions in Figs. 69 and 68. The same is particularly true of the mud inlet. The mud from the settling vats, which contains rich free ammonia and  $\text{CO}_2$ , should enter at the top of the heater.

(5) **Minimum volume of filter liquor to be distilled and of milk of lime used.** From the above it is seen that one objection in the distiller operation is the weak feed liquor, *i.e.*, a large volume of filter liquor to be distilled. In the matter of heat consumption in the distiller, a large volume of filter liquor requires a correspondingly large amount of steam for distillation. This means a wastage of steam and consequently of coal. In the matter of ammonia loss, a large volume of filter liquor means a correspondingly large volume of the waste liquor to be disposed of. As there is always a small amount of ammonia left in the distiller waste liquor, a large volume of this waste liquor would result in a higher ammonia loss through the distiller. Indeed, in normal operation, the distiller is a source of the largest single item of ammonia loss. For the same reason the milk



of lime must be made as strong as can be handled, i.e., containing about 250 grams per liter, or 180 titer lime. For high efficiency it is therefore imperative to keep the volume of filter liquor as small as possible and to employ as strong a milk of lime as can be handled through the pumps

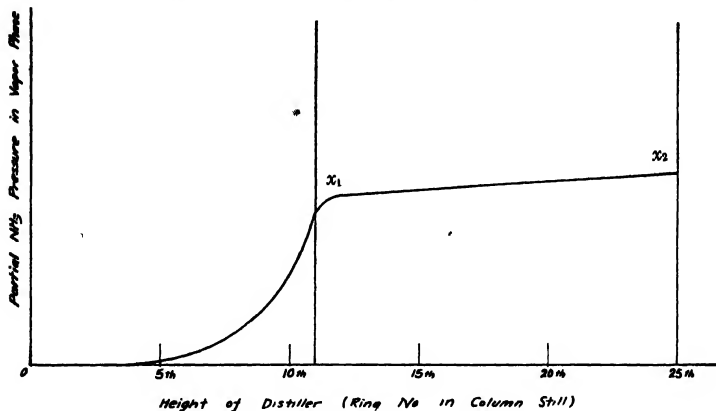


FIG. 69. Curve showing theoretical partial pressure of ammonia in gas phase.

and piping lines, and also a hot milk of lime. The effect is cumulative: weak filter liquor and milk of lime require more exhaust steam per ton of soda ash made, which would cause a still larger volume in the distiller waste. When calcium chloride and sodium chloride are to be recovered

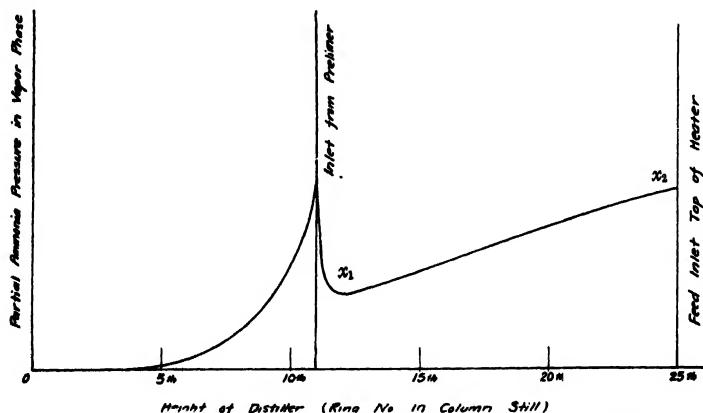


FIG. 70. Curve showing resultant partial pressure of ammonia in gaseous phase.

from the distiller waste, it becomes a *sine qua non* that the distiller waste (and therefore the filter liquor and the milk of lime entering the distiller) should be as concentrated as possible.

To aid in the understanding of the distiller operation, we give a boiling-point table for various concentrations of ammonia in aqueous solutions (Table 99). The values are plotted in Fig. 71.

TABLE 99. Boiling Points of Aqueous Ammonia Solutions of Various Concentrations of Ammonia under Atmospheric Pressure.

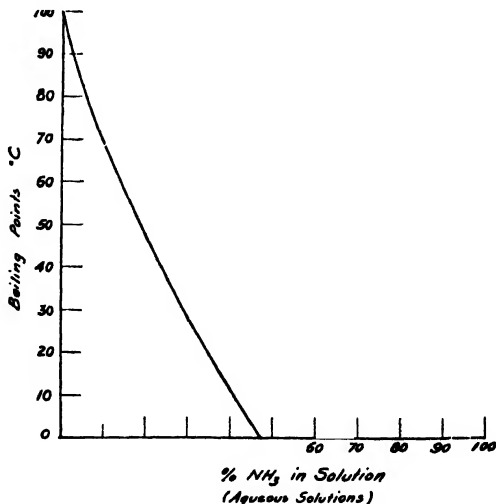
NH <sub>3</sub> Per Cent	Boiling Points °C.	NH <sub>3</sub> Per Cent	Boiling Points °C.
1	95.6	14	60.3
2	90.0	15	58.3
3	88.3	16	55.9
4	85.0	17	53.9
5	82.2	18	51.7
6	79.4	19	49.7
7	76.6	20	47.5
8	74.2	25	37.2
9	71.6	30	28.0
10	69.2	35	19.75
11	67.0	40	11.67
12	65.0	45	3.33
13	62.5	47.4	0.0

Other design features concerning the efficiency of an ammonia distiller are:

- (a) The velocity of the vapor passage through the distiller and the diameter of the distiller.

FIG. 71.

Boiling points vs. per cent by weight of ammonia in solution under 1 atmosphere total pressure.



- (b) The surface contact between the vapor and the liquor and the agitation of the liquor by steam.  
 (c) The depth of the liquor on the division plate and the number of passettes.

(a) **Velocity of vapor passage through distiller and diameter of distiller.** Efficiency in the separation of ammonia gas from the liquor is decreased if the liquor on one passette (bubble-cap assembly) is carried up and mixed with the liquor in the other passette above. Such entrainment disturbs the equilibrium relationship between the vapor and the liquid phases. It is generally caused by spattering and splashing of the liquor by steam, and in the worst case the liquor may be "suspended" due to the gas-lock effect of the vapor. Such phenomena are generally caused by excessive velocity of the vapor passing up through the distiller, when the diameter of the distiller is inadequate for the volume of vapor handled. Normally the average vapor velocity from one passette to the other is about 3-6 feet per second, and so the spacing between two adjacent passettes is 2 feet 3 inches on the top to 3 feet 4 inches toward the bottom, with one deepest ring of about 5 feet at the bottom of the lime still where low-pressure steam enters. This is approximately the proportion for an 8-foot distiller. Thus, an 8-foot diameter distiller with standard proportions will under normal conditions have a production capacity of 200-250 tons of soda ash per unit per day, without having too high vapor velocities.

(b) **Surface of contact between vapor and liquor and agitation of liquor by steam.** The lower edge of each mushroom is serrated, so that steam in passing around the edge and bubbling up through the liquor on the division plate may be subdivided and broken up into numerous small bubbles, thus getting more intimate contact with the liquor. Also, the bottom of the division plate, instead of being flat, is best curved to conform to the shape of the path of the flowing steam under the mushroom, so that there may not be any dead spot on the division plate where liquor does not have a chance to come into direct contact with the steam. This helps break up the steam bubbles and stir up liquor body so as to present fresh surfaces of contact between the vapor and the liquid, and to destroy the inactive film layer existing at the liquid-vapor boundary. As the result, the molal fraction of ammonia in the vapor phase approaches more closely the theoretical value in equilibrium with that in the liquid phase on each plate. Further, the overflow outlet is located diametrically opposite the inlet, and the liquor is compelled to travel across the full area of the division plate before leaving the plate. All this results in high efficiency in the performance of each passette.

(c) **Depth of liquor on division plate and number of plates (passettes).** To obtain good contact and effective stirring action, it is necessary that not too large a volume of the liquor, nor too deep a liquor body, is allowed to remain on each division plate. The depth of the liquor on each plate is generally no more than 6 to 7 inches. Contrary to ammonia absorption in the absorber, the depth of wash in the distiller is thus less than that in the corresponding passettes in the absorber. Also the number of passettes in the distiller is larger. The depth of liquor on the plate is controlled by the overflow outlet above the bottom of the plate, while the depth of wash is determined by the submergence of the serrated edge

below the liquor surface. The number of plates (passettes) required may be determined by McCabe and Thiele's graphical method.\* Take, for example, the lime still. If we determine the molal fraction of  $\text{NH}_3$  (1) in the limed liquor fed from the preliher, (2) in the blow-off, and (3) in the overhead condensate overflowing back to the heater, we can estimate graphically the number of plates required in the lime still, knowing the volume of overflow. However, since the relationship between the lime still and the heater is complicated and the function of the heater is not purely one of rectification, the results so obtained are misleading, and so generally considerably more plates over and above what is theoretically required according to the graphical solution will be needed.

To estimate the quantity of heat to be extracted by the distiller condenser and cooler per ton of soda ash made and the cooling surface necessary, take for example

Distiller top temperature .....	82° C.
Condenser outlet temperature .....	56° C.
Total pressure at condenser outlet .....	754 mm. Hg abs.
Partial pressure steam at 82° C. ....	385 mm. Hg abs.
Partial pressure $\text{NH}_3$ vapor + $\text{CO}_2$ at 82° C. ....	369 mm. Hg abs.
Partial pressure steam at 56° C. ....	123 mm. Hg abs.
Partial pressure $\text{NH}_3$ vapor + $\text{CO}_2$ at 56° C. ....	631 mm. Hg abs.
Condensate from condenser at 56° C. ....	16% $\text{NH}_3$
$\text{NH}_3$ in ammoniated brine at 95 titer .....	80.7 grams per liter
$\text{CO}_2$ in ammoniated brine at 450 cc. per 20 cc. ....	44.2 grams per liter

Therefore partial pressure of ammonia alone at 82° C. is

$$\frac{\frac{80.7}{17}}{\frac{80.7}{17} + \frac{44.2}{44}} \times 369 = \frac{4.75}{5.75} \times 369 = 305 \text{ mm.}$$

and partial pressure of ammonia alone at 56° C. is (assuming same ratio of  $\text{NH}_3$  to  $\text{CO}_2$ )

$$\frac{4.75}{5.75} \times 631 = 521 \text{ mm.}$$

Therefore the ratio of ammonia to steam in the vapor coming over from the distiller top at 82° C. is as the density of ammonia at 305 mm. is to that of steam at 385 mm. or as 0.0235 lb./ft.<sup>3</sup>:0.0198 lb./ft.<sup>3</sup> = 1.186:1. Similarly the ratio of ammonia to steam in the vapor at 56° C. is as the density of ammonia at 521 mm. to that of steam at 123 mm. as 0.0387 lb./ft.<sup>3</sup>:0.00683 lb./ft.<sup>3</sup> = 5.67:1. And the composition of the condensate is 16 per cent ammonia and 84 per cent water, neglecting the carbon dioxide dissolved. At 56° C. per ton of ash there will be:

$$6.1 \text{ cu. m.} \times 80.7 \text{ kg. NH}_3/\text{cu. m.} = 492 \text{ kg. NH}_3 \text{ going into the absorber}$$

\* McCabe, W. L., and Thiele, E. W., Graphical Design of Fractionating Columns, *Ind. Eng. Chem.*, 17, 605 (1925); and Badger, W. L., and McCabe, W. L., "Elements of Chemical Engineering," pp. 340-372, McGraw-Hill Book Co., Inc., New York, Second Edition, 1936.

or

$$492 \times \frac{6.67}{5.67} = 578 \text{ kg. NH}_3 \text{ + steam into the absorber.}$$

Let  $W$  = Wt. of condensate in the condenser at  $56^\circ \text{C.}$  per ton of ash.

Then

$$0.16W + 578 \times \frac{5.67}{6.67} = (W + 578) \times \frac{1.186}{2.186}$$

$$W = 466 \text{ kg. of condensate}$$

Of this, there are 70 kg.  $\text{NH}_3$  and 396 kg. steam.

The quantity of heat to be extracted per ton of ash is:

- (1) Heat of condensation of steam at  $56^\circ \text{C.}$  at 565 kg. Cal./kg. .... 224,000 kg. Cal.  
 $565 \times 396$
  - (2) Heat of solution of  $\text{NH}_3$  in steam condensate at 8430 cal./mol  
 $8430 \times \frac{70}{17}$  ..... 34,700 kg. Cal.
  - (3) Heat from cooling of steam from  $82^\circ$  to  $56^\circ \text{C.}$  at 0.435  
 $396 \times 0.435 \times 26$  ..... 4,480 kg. Cal.
  - (4) Heat of cooling  $\text{NH}_3$  from  $82^\circ$  to  $56^\circ \text{C.}$  at sp. ht. = 0.52  $(70 + 492) \times 0.52 \times 26$  ..... 7,600 kg. Cal.
- Assuming the same proportion of  $\text{CO}_2$  in the condensate and ammonia gas from the distiller as being 20% bicarbonated.
- (5) Heat of cooling  $\text{CO}_2$  gas from 82 to  $56^\circ \text{C.}$  at sp. ht. = 0.20  $\frac{(70 + 492)}{17} \times 44 \times 20\% \times 0.20 \times 26^\circ \text{C.} =$  ..... 1,510 kg. Cal.
  - (6) Heat of solution of  $\text{CO}_2$   $(70/80.7) \times (44.2/44) \times 5880$  ..... 5,120 kg. Cal.
  - (7) Heat of neutralization of  $\text{CO}_2$  by  $\text{NH}_4\text{OH}$  to  $(\text{NH}_4)_2\text{CO}_3$   
 $= (70/80.7) \left( \frac{44.2}{44} \right) \times 16,850$  ..... 14,650 kg. Cal.
- Total heat to be extracted ..... 292,000 kg. Cal. per ton of ash

Among the various cooling duties to be performed in the soda ash plants, such as in the absorber coolers, vat coolers, carbonating tower cooling boxes, furnace condensers, etc., the cooling duty of the distiller condensers is one of the most important and should require provision for one of the largest cooling surfaces in the whole equipment. Fortunately, the mean temperature difference for the flow of heat from the condensing vapor to the cooling water is generally great. Thus, suppose the temperature of the ammonia gases is  $82^\circ \text{C.}$  and it is desired to cool the gases to  $56^\circ \text{C.}$  Suppose the cooling water has a temperature of  $20^\circ \text{C.}$  and is warmed to  $40^\circ \text{C.}$  at the exit. The mean temperature difference then is

$$\frac{(82 - 40) - (56 - 20)}{2.3 \log \left\{ \frac{42}{36} \right\}} = \frac{6}{2.3 \log 1.167} = \frac{6}{2.3 \times .0671} = 38.9^\circ \text{C.}$$

The heat transfer from condensing steam to water should also be favorable. It is, however, very difficult to calculate exactly the cooling surface required because the coefficient of heat transfer depends largely upon the tube conditions both inside and outside. An insulating layer of ammonium carbonate crystals, iron scale, etc., on the vapor side of the cooling tubes, and a hard scale formed from the hardness or mud in the cooling water on the water side are liable to be formed. These would greatly reduce the rate of heat flow from the condensing steam to the cooling water.

The specific gravity readings (at room temperature) of different liquors are given in Table 100.

TABLE 100. Specific Gravity of Different Liquors.

Crude saturated sea brine .....	1.205-1.210
Saturated rock salt brine .....	1.195-1.200
Ammoniated brine .....	1.165-1.175 (depending upon CO <sub>2</sub> content)
Precarbonated liquor .....	1.220-1.230 (depending upon CO <sub>2</sub> content)
Draw liquor .....	1.126-1.127 (depending upon tower decomposition)
Distiller waste liquor .....	1.100-1.130 (depending upon filter liquor volume, etc.)

Between the distiller top outlet and absorber bottom inlet, the temperature of the ammonia gases should drop from about 86 to 56° C. In other words, the distiller condensers and coolers should have sufficient capacity to cool the hot ammonia gases coming from the heater by about 30° C. As a rough guide there should be 70 square feet of total cooling surface in the distiller coolers and condensers combined per ton of soda ash made per day.

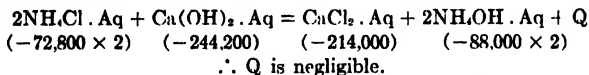
Following is an estimation of the exhaust steam required in the distillers. For the estimation of steam required in the distiller per ton of soda ash made, not all the necessary data are available; some assumptions must be based on practical observations. We shall assume, in the absence of the specific figures available, that the heat effect of the neutralization of the first hydrogen of the carbonic acid by ammonia is 11,000 cal. per mol. Next, we shall place the figure for heat loss by radiation from the well-lagged distiller at 10 per cent of the total heat required per ton of ash. We shall take the following set of data:

Vol. of feed liquor per ton of ash .....	7,000 liters
Vol. of milk of lime required per ton of ash .....	2,500 liters
Free ammonia (NH <sub>3</sub> HCO <sub>3</sub> ) per ton of ash .....	150 kg. NH <sub>3</sub>
Fixed NH <sub>3</sub> (NH <sub>4</sub> Cl) per ton of ash .....	350 kg. NH <sub>3</sub>
CO <sub>2</sub> dissolved in the liquor .....	39 grams per liter
Heat of neutralization	
$\text{NH}_3 \cdot \text{Aq} + \text{H}_2\text{O} + \text{CO}_2 \cdot \text{Aq} \rightarrow \text{NH}_4\text{HCO}_3 \cdot \text{Aq} + \text{Q}$	
Q = 11,000 cal./mol NH <sub>3</sub> .....	647 cal./gram
Heat of solution of NH <sub>3</sub> .....	8,430 cal./mol
Heat of solution of CO <sub>2</sub> .....	5,880 cal./mol
Exhaust steam at 10 lbs. gage (115° C.) from steam at 10 lbs. to water at 10 lbs. ....	529 cal./gram
Temperature of feed liquor to distiller .....	45° C.
Temperature of milk of lime .....	55° C.

Then,

7000 l. $\times$ (115° - 45° C.) = 7000 $\times$ 70 .....	490,000 kg. Cal.
2500 l. $\times$ (115° - 55° C.) = 2500 $\times$ 60 .....	150,000 kg. Cal.
Heat of decomposition of 150 kg. $\text{NH}_3$ from $\text{NH}_4\text{HCO}_3$ = 150 $\times$ 647 .....	97,050 kg. Cal.
Heat to drive 150 kg. $\text{NH}_3$ from solution = 150 $\times$ $\frac{8430}{17}$ ....	74,400 kg. Cal.
Heat to drive 39 kg. $\text{CO}_2$ from solution = 39 $\times$ $\frac{5880}{44}$ $\times$ 7000	36,500 kg. Cal.
Heat to drive 350 kg. $\text{NH}_3$ from fixed $\text{NH}_3$ and $\text{CaO}$ = 350 $\times$ $\frac{8430}{17}$ .....	173,560 kg. Cal.
Total .....	1,021,500 kg. Cal.
Heat loss by radiation at 10% .....	102,150 kg. Cal.
Total heat required .....	1,123,650 kg. Cal.
Exhaust steam required $\frac{1,123,650}{529}$ .....	2.12 cu. m. (as condensate water)

Note that the heat of reaction for the 350 kg.  $\text{NH}_3$  in the following reaction is negligible, because it is an equilibrium reaction with all components in solution:



That is, the heat effect in the above equilibrium reaction may be neglected.

From the above it will be seen that the greatest item of heat required is that required to heat up the liquors. This takes 64 per cent of the total heat required. Therefore, for good efficiency, the feed liquor and the milk of lime must be preheated and kept hot and be as concentrated as possible. The exhaust steam to the distiller must be dry, i.e., the condensate in it must be previously completely separated out. In practice, the smaller the volume of the filtered liquor and of the milk of lime, the smaller will be the amount of exhaust steam required for distillation, and consequently the smaller the volume of the distiller waste, and the smaller the losses of both ammonia and lime in the distiller waste sent out.

## Chapter XV

### By-products from Distiller Waste

The distiller run-off liquor consists of some 85 grams per liter of calcium chloride, 50 grams per liter of sodium chloride, and some excess of lime, together with other solid matter such as silicious matter, calcium carbonate, magnesia, calcium sulfate, etc. The concentration of these constituents varies widely in individual plants depending upon the operating conditions and upon the efficiency of the plant. The liquor contains all the chlorine from the salt used; for, unlike the LeBlanc process, the ammonia process makes no use of the chlorine. Because of the high cost of the fuel required to concentrate such a weak liquor, and because of the limited demand for calcium chloride and the cheapness of this product, and salt, comparatively little of this distiller waste has been worked up, considering the very large volume of the waste turned out daily by the ammonium soda industry.

The solid matter from the waste accumulates so fast that the disposal of this waste is a matter of no small concern to ammonia soda manufacturers. Calcium chloride in solution permeates the soil bed and contaminates sources of water supply. Municipal authorities permit only a very limited portion of the waste (except the clear portion of the liquid) to be sent to a river or any public waterway, and that only after complete settling to eliminate the solids. Cases are on record where fish in the river were killed by the harmful constituents, especially the free lime carried in the liquor, so that ammonia soda manufacturers are obliged to do something to this waste. Proposals have been made to utilize it in many different ways, and various products have been claimed to have been prepared therefrom. Many of these proposals have no practical value. The preparation of chlorine gas (from which bleaching powder is made) or the production of hydrochloric acid from the calcium chloride in the waste by electrolysis can no longer be considered practicable in view of the present much more economical methods for preparing these products.

There is a considerable excess of unconverted salt in the waste. It must be said that the ammonia soda process is very wasteful in the use of salt, the average efficiency in conversion of salt to sodium bicarbonate in the carbonating towers in actual operation being not more than 75 per cent; considering some additional losses in the form of "mud" pumped to the distiller, more than 25 per cent of the total salt is wasted. As a consequence, the very existence of an ammonia soda works presupposes a cheap and abundant supply of salt. Because of this fact it generally does not pay to recover this salt from distiller waste. The salt so recovered,



however, possesses a high degree of purity and is comparable to the product obtained from brine purified by the soda-lime treatment. This salt is recovered in conjunction with the manufacture of calcium chloride.

We shall enumerate a few of the principal products that have been prepared from distiller waste on a commercial scale; namely, refined salt, calcium chloride, calcium sulfate, and ammonium chloride.

**Refined salt and calcium chloride.** It is the aim of ammonia soda operators to keep the volume of distiller waste as small as possible, especially when any of it is to be worked up. This is done by keeping the volume of the filter liquor as small as possible, by securing the highest decomposition possible in the columns, by using as little wash water on the filters as is necessary to reduce the sodium chloride content in the ash within allowable limits, and by employing a strong milk of lime containing not less than 250 grams of lime per liter (sp. gr. 1.21). In certain cases even solid lime has been tried in the preliming tanks for distiller operation. This waste liquor, which contains a small excess of free lime as mentioned above, is carbonated by passing some waste  $\text{CO}_2$  gases through it. On settling, the precipitated calcium carbonate and all the solid matter, such as magnesia, silica, calcium sulfate, etc., carried in the liquor separate out. The clear solution containing calcium chloride, sodium chloride, and a very small proportion of dissolved calcium sulfate, is concentrated in a double-effect evaporator, when sodium chloride together with the small amount of calcium sulfate commences to crystallize out. The salt crystals are dried in centrifuges, a little water being sprayed on them to wash any calcium chloride from the salt. From the centrifuges the salt can be packed directly in bags of 200 pounds or in barrels of 400 pounds, frequently without further drying. If drying is necessary, the salt from the centrifuges or drum filters is charged to steam-heated, hot-air rotary dryers using exhaust steam.

The liquor entering the evaporator with a specific gravity of 1.11 is concentrated to 1.22 in the first effect, and evaporation is carried on until the specific gravity of the liquor in the last effect is 1.42. At this point practically all the salt can be settled out.

If necessary, some "chloride of lime" may be added to oxidize the iron and the liquor is then allowed to settle. The liquor should not be allowed to cool too much, or hexahydrate calcium chloride crystals ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) would separate out. This clarified calcium chloride liquor containing 42 to 45 per cent calcium chloride is known in commerce as "liquid calcium chloride." It is shipped in tank cars like liquid caustic. It is used in refrigerating plants, for road sprinkling, and for making liquid concrete accelerators.

If solid or flake calcium chloride is desired, the clarified liquor may be further concentrated in cast-iron open pots until the molten mass, solidifying on cooling, gives what is known as 75-per cent calcium chloride, corresponding to the formula  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . A more recent method is to use a high-pressure, single-effect evaporator to concentrate this 1.42 sp. gr. liquor directly to 75-per cent calcium chloride, using a higher pres-

sure steam instead of the exhaust. The heat economy in the evaporators is far greater than in the cast-iron open pots. This product in the molten state is pumped to steel drums, each holding about 650 lbs., and the drums are sealed. The composition of 75-per cent solid calcium chloride is given in Table 101.

TABLE 101. Composition of 75-per cent Calcium Chloride.

	Per Cent
$\text{CaCl}_2$	73.6
$\text{NaCl}$	1.4
Alkalinity as $\text{Ca}(\text{OH})_2$	0.14
Insoluble matter	0.08
Water by difference	24.78

Flaked calcium chloride is made by sending the 75-per cent molten calcium chloride to flaking machines provided with revolving water-cooled drums, as in flake caustic manufacture.

Anhydrous calcium chloride can be made by heating 75-per cent calcium chloride in a reverberatory or puddling furnace, fired by producer gas or oil. The molten mass is frequently raked, when some calcium chloride is decomposed, giving lime and hydrogen chloride. The escape of this hydrogen chloride gas leaves a porous mass of fused calcium chloride, which is known as 95-per cent  $\text{CaCl}_2$ . The cooled anhydrous mass, somewhat fluorescent, is packed in steel drums or paper-lined wooden barrels, hermetically sealed, each holding from 350 to 400 pounds.

Fused calcium chloride, like fused caustic soda, has a density of about 2 (sp. gr. of anhydrous  $\text{CaCl}_2$ , 2.22); but unlike caustic soda the melting point is much higher ( $775^\circ \text{C}.$ ). Hence molten anhydrous calcium chloride could not be readily obtained in fusion pots, as is the case with fused caustic soda.

There is a process for making powdered calcium chloride by drying the granular calcium chloride in a rotary furnace by means of furnace gases entering at  $400$  to  $475^\circ \text{C}.$  and leaving at  $100^\circ \text{C}.$  The coarse particles drop out of the lower end of the rotary, while the fine dust suspended in the current passes out of the upper end and is recovered in a collector containing about 73 per cent anhydrous calcium chloride, which is non-caking.

Calcium chloride is used as a refrigerant in the manufacture of ice, as a dust palliative in flake or granular form to minimize dusts on gravel roads, and as an anti-freezing solution (freezing point  $-50^\circ \text{F}.$ ) In the anhydrous form small quantities are used as a catalyst to promote the reaction between calcium carbide and nitrogen gas in the manufacture of calcium cyanamide, permitting a lower temperature to be employed.

**Calcium sulfate.** The crystalline  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is known as "Crown Filler" among the Solvay products. It is a much purer product than natural gypsum. The process of manufacture consists in settling the distiller waste and treating the settled liquor while still hot with salt cake. The excess of free lime carried in the liquor will be neutralized by the slight excess of sulfuric acid in the salt cake. If the resulting solution is acid, some milk of lime may be added. The precipitated  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

in finely divided form is filtered on a vacuum drum filter and further dried in a centrifuge, water being sprinkled on the crystals to wash away salt. The crystals of gypsum are dried at a reduced temperature in much the same way as sodium bicarbonate (see Chapter XVIII). It is packed in wooden barrels of about 350 to 400 pounds and used as a paper filler. A small quantity is used as a water hardener in the fermentation industries.

When dried at or below 190° C., this gives plaster of Paris ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) which is used for making molds. When calcined at a temperature above 204° C. it loses all its water, care being taken that none of the sulfate is reduced to sulfide. When traces of iron are present, the calcined mass is discolored and gives a yellow tint.

Calcined calcium sulfate is used in the manufacture of certain tooth pastes and in the manufacture of wall and flooring plasters which give a smooth and hard finish.

The filtered liquor, after removal of the precipitated calcium sulfate, is a very pure brine which is sent to the soda works for making saturated brine for soda manufacture.

**Ammonium chloride.** In this connection may be mentioned sal ammoniac (ammonium chloride), which can be obtained by concentrating the carbonated and settled waste liquor to remove most of the salt ( $\text{NaCl}$ ) and treating it with ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$ , whereby the following reaction takes place:

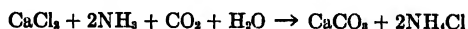


The mother liquor is further concentrated, allowed to settle, and cooled. Crystals of ammonium chloride then separate out. This process was originally patented by Richardson.

Another process proposed for the manufacture of sal ammoniac that may involve important changes in the ammonia soda industry is as follows: From the mother liquor (or filter liquor) before distillation, it is proposed to separate ammonium chloride by cooling. This was done in Germany during the World War by the Badische Anilin- und Soda-Fabrik using synthetic ammonia. In Japan it was claimed that by freezing out ammonium chloride from the mother liquor and by adding a fresh supply of salt, the resulting liquor can be sent back to the carbonating towers for making sodium bicarbonate, thus doing away with distillation. It is claimed that in this way the distiller can be dispensed with and the operation in the ammonia soda works simplified.

The detailed procedure consists of introducing more ammonia and salt to the mother liquor after filtration and carbonating the resulting liquor again to throw out more sodium bicarbonate, using a rather low temperature. The bicarbonate is filtered off as usual, and the mother liquor, which is now very rich in ammonium chloride, is strongly cooled so that ammonium chloride crystals separate out. The crystals are then centrifuged and washed in the usual manner.

Solvay makes a large amount of ammonium chloride—more than 50 or 60 tons a day. It is made from distiller waste liquor by first settling off the solids from the liquor and concentrating the solution in evaporators. The small percentage of lime remaining dissolved in the solution up to about 2 grams per liter makes calcium chloride liquor less corrosive on evaporators. The solution is concentrated to 40° Bé., containing about 40 per cent  $\text{CaCl}_2$ , when most of the salt separates out. The slurry containing salt crystals is filtered off and the filter liquor ammoniated. The ammoniacal calcium chloride solution is then carbonated in tanks at a temperature of 60° C. with stirrers; at this point very coarse calcium carbonate crystals are formed, which filter very readily, and the filtrate containing high concentration of ammonium chloride is cooled when the ammonium chloride crystals begin to separate.



The liquor is then concentrated so that further crops of ammonium chloride crystals are obtained. Solvay at first used wooden tank filters with false bottoms for such purpose, although ordinary filters work very successfully. Ammonium chloride crystals made in this way contain only 0.3 to 0.4 per cent sodium chloride.

The ammonium chloride crystals are dried with hot air at a low temperature. The same equipment as is used for drying refined sodium bicarbonate is suitable for this purpose. (See Chapter XVIII, Manufacture of Refined Sodium Bicarbonate.)

This process of making ammonium chloride runs exactly parallel to the gypsum process of making ammonium sulfate used by I. G. Farbenindustrie in Ludwigshaven-Oppau, Germany, the differences being that calcium chloride is used in place of calcium sulfate, and that ammonium chloride is obtained instead of ammonium sulfate.

Ammonium chloride is used in the manufacture of dry cell batteries and in metal working for soldering and galvanizing. For this purpose, a minimum purity of 99.2-99.4 per cent  $\text{NH}_4\text{Cl}$  is required; whereas for fertilizer, anything above 97 per cent  $\text{NH}_4\text{Cl}$  is acceptable, the impurities being mostly  $\text{NaCl}$ .

**Soil Lime.** Solids carried in the waste liquor, consisting of waste sand, finely divided calcium carbonate, excess lime, calcium sulfate, magnesia, etc., are allowed to separate by settling, and the sludge is sometimes used as "fertilizer" for correcting acidic soil. However, the calcium chloride content of the waste lime should be allowed to weather and be washed off by rain before it is applied to farms. What fertilizing value it has is difficult to determine, but some farmers do use this waste sludge on their farms with favorable results.

An ammonia soda plant is considered to be happily situated if it can send its distiller waste to the neighboring lands freely. If a plant is situated among quarry hills where the distiller waste can be sent to fill the quarry pits or the adjoining valleys, or if a plant can be situated near

the sea or on a large lake to which distiller waste can be discharged freely, the situation approaches an ideal one. For the time is still far distant when such waste, which is produced daily in enormous quantities, can all be worked up into by-products. The great bulk of waste must be disposed of and the space for its disposal must receive attention from ammonia soda manufacturers at the outset.

Distiller waste accumulated in the neighborhood of an ammonia soda plant leaves a rather unsightly feature in our landscape. In the course of years, after weathering has set in, green vegetation will grow on it. The muck may then become a good farm land again.

## Chapter XXX

### Layout, Design and Location of Ammonia Soda Plant

Ammonia soda plants require as raw materials the following commodities arranged in the order of quantities required:

- (1) Salt (rock salt brine or sea brine)
- (2) Limestone
- (3) Coal
- (4) Coke
- (5) Ammonia [crude liquor or  $(\text{NH}_4)_2\text{SO}_4$ ]
- (6) Sulfide of soda, or 60 per cent  $\text{Na}_2\text{S}$  [when  $(\text{NH}_4)_2\text{SO}_4$  alone is used]

Arranged in the order of the expenses involved per ton of soda ash made (quantity and cost) these raw materials stand as follows:

- |               |                     |
|---------------|---------------------|
| (1) Coal      | (4) Coke            |
| (2) Limestone | (5) Ammonia         |
| (3) Salt      | (6) Sulfide of soda |

The latter arrangement may vary somewhat for different plants because the comparative costs of coal, salt, and limestone entering the manufacture depend upon the relative location of the plants in regard to the sources of supply of these materials, their quality, and their prevailing prices in a particular locality.

The prices of the first three raw materials when they are plentiful and their source is in close proximity to the works may be as low as:

Salt in the form of brine	\$0.50 per ton, delivered at plant
Limestone	\$0.60-\$0.75 per ton, delivered at plant
Coal	\$2.00-\$3.00 per ton, delivered at plant

But it is seldom that a site for an ammonia soda plant can be so fortunately located as to have all three raw materials in close proximity, at the minimum prices, and in large quantities. With soda ash at its normal price, plants obtaining these raw materials at prices varying from 100 to 300 per cent higher than the above figures operate at a good profit, especially when they have a moderately large output.

The foregoing is a direct cost dealing with cost of raw materials only. In the following we shall include also the indirect costs, thus approaching more nearly the cost statistics of a plant operation. These may be arranged as follows:

- |               |                         |
|---------------|-------------------------|
| (1) Fuel      | (5) Ammonia             |
| (2) Labor     | (6) Some form of sulfur |
| (3) Limestone | (7) Factory supplies    |
| (4) Salt      |                         |

The positions of the first two items might be reversed in locations where fuel is exceptionally cheap and where the proper arrangement of equipment for reasonably low attendance labor does not exist.

In only the most exceptional circumstances could limestone be more expensive than either of the first two items, although occasionally salt may cost more than limestone. The last three items are frequently in other relationships to one another since they depend on many factors. They have been included because they have some bearing on the selection of the plant site, and their effect will be discussed briefly in this chapter. "Depreciation and obsolescence" at the customary rate of 10 per cent on, say, a \$15,000 investment per ton of daily capacity in soda ash and a 70 per cent annual load factor introduce a cost per ton which leads the above list by an appreciable margin. It is thus obvious that the lowest possible initial cost of plant is important to low-cost production. A layout which results in low initial cost and yet permits the above seven items to have a low total is obtained only from capable, highly experienced design engineers. This chapter does not attempt to describe all the factors and variables entering into the problem of obtaining the best layout and design of an ammonia soda plant; it merely calls attention to the effects of some of the more important variables.

Favorable unit prices for the four large items given in the foregoing list follow. These are delivered prices and represent a fairly plentiful supply close to the sites under consideration. Occasionally some one of the materials may be even higher. Well designed plants can be operated at a profit where raw material prices are considerably higher, since then the soda price is generally also higher.

- (1) Fuel
  - (a) Coal, \$3 per ton, or 11 cents per million Btu.
  - (b) Coke, \$6.50 per ton, or 23 cents per million Btu.
  - (c) Bunker "C" fuel oil, \$0.85 per barrel or 13.5 cents per million Btu.
  - (d) Natural gas, 15 cents per thousand cubic feet or 15 cents per million Btu.
- (2) Attendance and Maintenance Labor (weighted mean of all classes needed)  
\$0.65 per man-hour
- (3) Limestone  
\$0.60-\$0.75 per ton stone, as already given
- (4) Salt, as saturated raw brine  
\$0.50 per ton NaCl, as already given

There is almost nowhere a peculiarly favorable site where all the raw materials and intelligent labor required at the lowest unit prices can be found. Furthermore, it is the alkali manufacturer's problem to deliver his product to his customer's doorstep at the least possible cost. In selecting a site he must therefore consider not only the purchase and transportation of raw materials to his plant, but also the transportation of his soda products to the plants of his customers (or potential customers).

The layout of an ammonia soda plant is a matter largely of local conditions and individual preference. However, there are some general rules on which those qualified to make a design will agree. For instance, the boiler room should be located adjacent to the engine room furnishing steam to the carbon dioxide compressors, electric generators, exhausters, cooling water pumps, air compressors and other steam-driven machinery; and the lime department should be adjacent to the distiller house so that the concentrated milk of lime can be sent to the distillers in short pipe lines. Next to the distiller house should come the ammonia absorber house, with an adjoining space for the location of settling vats. Next comes the tower house taking the ammoniated brine from the vats in the absorber system. The furnace room is located reasonably near the tower house so that crude bicarbonate can be taken from under the filters in belt conveyors to the furnaces and the returned gas from the furnaces sent back to the columns through a set of condensers. The engine room, where all the steam-driven machinery, the carbon dioxide compressors, etc., are located, should be sufficiently close to both the furnace room and the tower house to bring the gas from the furnaces through scrubbers and coolers to the columns and at the same time take the kiln gas from the lime kilns through a kiln gas scrubber. The carbon dioxide compressors, the generators, the exhausters, the cooling water pumps and the air compressors may be advantageously steam driven, and the exhaust steam utilized for the distillation of ammonia in the distiller house. Outside of the engine room in the various houses, the machinery is individually driven by electric motors.

The buildings in an ammonia soda works are usually high. The distiller house must be high enough to accommodate the tall distillers together with the condensers. It is general practice to put the heater on top of the lime still, and the condensers on top of the heater, making the overall height of the whole apparatus over 100 feet. The distiller house is then at least 125 feet high and frequently much higher.

In the absorber house, the elevation of the bottom of the absorber must be above the top of the settling vats, so that the ammoniated brine can flow to the vats by gravity. The vats are located on the main floor on pedestals high enough to provide a working height to pump "mud" from the bottom. On the top of the absorber can be located an ammonia gas cooler, and on top of this the absorber washer, necessitating a height about 80 feet for the absorber house. In between the bottom compartments of the absorber and the middle passette, the partially ammoniated



brine is cooled in outside surface coolers (absorber coolers) before final ammoniation at the absorber bottom.

In the tower house are located the columns, or carbonating towers, from 75 to 80 feet high. The exit gas containing ammonia passes through a cyclone separator located near the top of the tower and is scrubbed in washers called tower washers, whose bottoms are below the top of the towers, but must be above the inlet point in the inlet compartment of the absorber washer to avoid the use of a centrifugal pump. The brine from the bottom of the tower washers, containing some ammonia, flows to the middle compartment of the absorber washer through a long U-loop seal. The brine from the bottom of the filter washer enters the tower washer at a few sections below the top compartment. The filter gas washer must be located on a higher level (not less than 10 feet above the top of the tower washer) so that the brine from the bottom of the filter washer can flow by gravity with a U-loop seal to the inlet compartment in the absorber washer from a higher vacuum on the filter washer side, or to the inlet compartment at the tower washers against pressure on the tower washer side. This arrangement avoids the necessity of having centrifugal booster pumps to send brine from the bottom of the filter washer to the inlet compartment of the absorber washer or of the tower washer. The total height of the tower house including the washer house portion is over 120 feet. On top of the roof may be situated a large brine storage tank feeding fresh brine by gravity to the top of the tower washers, the filter washers and the absorber washers. The draw liquor being cold, very little brine is required to scrub ammonia from the gas in the filter washer. The absorber washer and the tower washer are the two places where fresh brine is required in proper quantities. The bicarbonate filters are generally located on a floor at least 30 feet above ground so that the filter liquor can flow down to the filter liquor main under high vacuum with sufficient liquor leg for a seal. From the filter trap, or separator, the gas is piped up to the bottom of the filter washer, located on an approximately 100-foot level.

In the lime department, the lime drawn from the bottom of the kiln may be elevated to a bin in bucket elevators. From the bin the lime is fed to a rotary slaker by means of a conveyor feeder. The discharge end of this horizontal slaker must be high enough to allow the rejected "sand" to be hauled out in cars from the main floor and the milk of lime to flow by gravity to a lime well (or storage tank) situated on the main floor, where the lime pump sends the milk of lime to the distiller. With the lime kiln standing above the building, the total height of the house should be about 50 feet. On top of the lime kiln, there should be a working platform to which access may be gained conveniently by means of a stairway or elevator.

The furnace room contains the rotary furnaces and the conveyor system, with a clear floor space on the top for storing and feeding bicarbonate to the furnaces below. The building need not be over 45 feet high. It is one of the lowest buildings in the whole plant. The soda conveyors

can go outside of the building or between buildings. A good overhead space, however, must be provided so that the place may not be too hot or oppressive to the workmen. Ventilation points should be freely provided in the roof construction; otherwise the hot atmosphere in a low room coupled with the soda dust and ammonia gases (to a certain extent unavoidable) may make the place quite uncomfortable to the workmen. This applies to the space required over the conveyors as well as over the dryers.

The boiler room is normally just high enough to accommodate the boilers and their accessories and its height depends upon the type of boilers installed, but a full-height basement must be provided for hauling out the ash. The engine room is a low building, generally one story high, to house various machinery; but it must be high enough to allow an overhead space under the trusses for installing a travelling crane. It must also have a full-height basement to house various steam lines, exhaust lines, etc.

The packing room and the rest of the buildings are low and generally not more than two stories high, but high enough to house various soda ash elevators and conveyors. But the main or ground floor of all the houses in the works should be located 10-12 feet from the normal ground level with a full-height basement on the ground level. This basement space may be utilized for ash hauling (in the boiler room), for locating steam mains and exhaust mains (in the engine room), and for locating various gas liquor and water pipes and also waste liquor sumps (in the tower and distiller houses). This arrangement sets the working floor at 10-12 feet above ground level with various pipes introduced below the floor and yet allowing a clear space overhead for working in the basement. It is both a neat and convenient arrangement.

The packing and loading facilities for the dry products should be immediately adjacent to loading tracks and docks. There should also be proper approaches for motor trucks. The docks for handling products onto both trucks and railroad cars should be designed for minimum labor. The raw material storage yard and the finished product storage should be located near the shipping points, in order to facilitate moving the raw materials in and sending the finished products out.

The packing and shipping buildings should be reasonably close to the rotary furnace building so that conveyors for the dry products may be as short as possible. This minimizes power consumption, maintenance cost and breakdown hazards. Prior to the filter operation, substantially all the materials are in the liquid state so that the arrangement of buildings need sacrifice relatively little of the requirements of short pipe lines. Pipe lines are very cheap compared to dry product conveyors. From the filters on, the handling of the solids by conveyors starts. The furnace room needs to be within good conveying distance of the crude bicarbonate filters.

There must be a storage reservoir for cooling water and another for brines. If these reservoirs can be placed as high as needed to feed into

all apparatus by gravity, an advantage is gained in that no pump is required and the hazard of pump breakdown is thereby eliminated.

The buildings are of either steel or reinforced concrete structure (preferably the former), and must be heavy to take care of the heavy, tall, cast-iron apparatus. The foundation must be made of heavy reinforced concrete (made waterproof) with concrete or timber piles driven under each piece of heavy apparatus, such as the ammonia distillers, the carbonating towers, etc., where the whole load is concentrated on a small base. Overhead inter-building pipes should be supported from the trusses or beams, while those underground pipes between buildings should be located in a tunnel or trench, but not buried in the soil, so that settling of the buildings at either end will not throw strain on the pipes, and also so that repairs may be made conveniently. Where a pipe passes through a brick wall, clearance above the pipe in the wall should be allowed so that settling of the wall will not bear on the pipe. This applies especially to cast-iron pipes, which are used extensively in the works. Sewers and fire hydrant lines should be located below ground around the buildings. Cooling water from the exit of different units of the apparatus is run off to the sewers, but the distiller waste liquor must be sent out with or without a booster pump to an open field for settling or to a large body of water through pipes or in a specially constructed channel or canal.

The materials used in the construction of buildings and equipment depend to some extent upon local supplies. As pointed out in earlier chapters, the apparatus for handling ammoniated brine and filter liquor must be of cast iron; high-copper alloys are entirely unsuitable. Building frames constructed of mild steel will suffer from corrosion, and factors of safety in the original design must take this into account. Timber buildings are reasonably resistant, but are exposed to fire hazards. Concrete made of ordinary silica sand and a coarse aggregate of good rock does reasonably well for floors if they are amply pitched to minimize the effect of puddles of corrosive liquor.

In the caustic plant, concrete floors should be very steeply pitched and the design must be carefully prepared to avoid seepage of caustic liquor under important weightbearing footings. Although concrete is not very resistant to caustic there is no other suitable material having an economical advantage over the usual local concrete. The dust in the air near the caustic operations is corrosive enough to deserve careful consideration in the design.

The tallest buildings in an alkali plant afford protection to portions of apparatus which rarely have men near them. It is sometimes advisable to consider the climate and the cost of a simpler type of protection, such as heat insulation, painting, weatherproofing, etc. of the apparatus and piping rather than a housing over them.

The following summary gives a broad consideration regarding general requirements in the layout and the design of an ammonia soda plant:

- (1) It must fit the contours of the land and take best advantages of high and low points.
- (2) It must bear a proper relationship to existing or potential railroads, motor highways, docks and waterfront.
- (3) It must be arranged for lowest handling costs.
- (4) It must be arranged to permit extension of the plant and leave room for additional units or for possible by-product operations.
- (5) Interconnecting piping and material conveyors should be as short as possible.
- (6) Apparatus should be arranged so that direct attendance labor can control a maximum of the operations.
- (7) It should leave room for adequate storage of raw materials and finished products.
- (8) It should bring about minimum maintenance cost.

Since the contours of the actual site and the variations in the elevation of the ground affect the building arrangement more than any other factor, no hard and fast rule can be laid down for the best arrangement. A number of expedients are possible for reducing installation costs by compact, and yet not cramped, layout. Further improvement can be attained by ingenious interrelation of equipment so that a single operator can adequately attend a maximum of it. Not only does this save money in direct operating labor cost, but a more adequate control is possible where a single individual depends least on the cooperation of others. Unfortunately, no direct statement as to how this is achieved can be made because, depending on the best location for railroad and docks, the various products to be manufactured, etc., certain operations will be adjacent to each other in one plant and not in another.

#### SELECTION OF PLANT SITE

For the location of an ammonia soda plant the site must fulfill the following main requirements:

- |                             |   |   |
|-----------------------------|---|---|
| (1) General Requirements    | { | a) Good transportation facilities preferably both by boat and by rail.<br>(b) Sufficient nearness to the market or to the center of distribution.   |
| (2) Particular Requirements | { | (c) Close proximity to the sources of salt, limestone, and coal (and consequently also coke and crude liquor).<br>(d) Plenty of underground cold water available for cooling.<br>(e) Ample land or waterway available for waste disposal. |

If all these requirements cannot be met, expert judgment is necessary to decide, by a detailed study of the conditions, which of the above items are most essential. For example, if both salt and limestone are not

available close together, it may be better to locate the plant near the source of supply of limestone and transport the salt, than vice versa, since salt can be transported in the form of brine at little cost.

Items (a) and (b) above apply to most industries and are therefore the general requirements for any given industry. They will not be discussed in detail here, as this is quite evident.

As salt (in the form of rock salt brine or sea brine), limestone, and coal are the three main raw materials in soda ash manufacture, it is necessary that these materials be plentiful and cheap, and their continuous supply assured. The first two, salt and limestone, furthermore, must be produced by the manufacturers of soda ash. The soda works must own and operate salt wells (in the case of rock salt brine) or salt fields (in the case of sea brine), and quarry their own stone. As these are the two raw materials used in the largest quantities, the economical development of the works depends upon a cheap and inexhaustible supply of both. They must also be of good quality, especially the limestone. A poorer grade of limestone is very uneconomical to use. Coal can be purchased on the open market but it must be sufficiently cheap. Where bituminous coal is abundant, and coal mines are not far away, crude ammonia liquor and coke will be available from the gas works. Coke is a standard commodity that can be bought in the market, but the crude liquor must be secured from the gas works by special arrangement. Ammonia and coke, though used in comparatively small quantities, constitute important materials in the ammonia soda process because of their comparatively high cost, so much so that the manufacturers frequently operate their own by-product coke ovens. The crude liquor is desirable not only because it is a cheap source of ammonia but also it contains the sulfide required for the system. At present some synthetic ammonia is being used, and sodium sulfide is all the more necessary in the process. All these enter into the consideration of a plant site.

The question of water supply is important. Not only is water used in large quantities in the boilers for power generation, but a much larger quantity is needed for various cooling purposes. The requirements for the two purposes may not be the same. The surface water, *e.g.*, river water, while it may be very good for the boilers, is not suitable for cooling, as the temperature may be too high in summer. On the other hand, well water may be too hard for boilers but it is excellent for cooling purposes. A good source of supply of cooling water is from artesian wells, as it is practically at a constant temperature (16 to 18.5° C. in summer and winter at 400 to 500 feet below the surface level). Good water is comparatively difficult to obtain for plants which are located near the sea-coast, where sea brine may be used as the source of the salt supply and where probably only well water will be available for the boilers. For small works, the quantity of cooling water required is in the neighborhood of 2,000 to 2,500 cubic feet per ton of ash. For large works it is less per ton of the output; but much depends upon the cooling

surface available, the design of the apparatus, and the arrangement of different cooling units. Therefore cooling water is a factor in the choice of the site.

The distiller waste is always a source of trouble. The quantity is large (about 350 cubic feet of liquor per ton of ash) and its disposal in public waterways has been in most cases prohibited by law. Calcium chloride in solution permeates the ground and finds its way to the underground water. It causes excessive chlorine in the soil. Solids separating out from the waste do not readily become hard and firm. If the waste liquor is sent directly into a river, its lime and calcium chloride content may be objectionable. Besides, the solids carried in it may silt up the river. Its satisfactory disposal has become a problem unless the works is fortunate enough to be located near the sea, near a big lake, or among the hills (in this last place, the waste may be sent to fill old quarry pits or a nearby valley). Not all the waste produced can be converted into by-products; a large quantity must still be disposed of. If the works is located near the sea, on a lake, or near a very large body of water it is a comparatively simple matter, but inland this waste can only be sent to a pond to settle, from which only the clear portion is allowed to run out to the river. The lime content in the waste liquor is particularly harmful to the fish in the river. This waste disposal must receive consideration in the selection of the site.

The foremost problem is to find an area where potential market and the present delivery costs of alkali are attractive and at the same time reasonably near sources of the necessary raw materials and fuels. Facilities for adequate and rapid service to customers eventually must be provided. This requires that a number of good transportation facilities be available (actually or potentially) in the area, for ocean, rail and motor highway movements of products. Within such an area, the few specific locations where the foregoing are favorable must be rated quantitatively on the basis of many factors. The following detailed consideration may govern the choice of the site and are given here as a resume:

- (1) Delivered cost, quality and potential continuity of main fuel supply.
- (2) Delivered cost, quality and assurance of an alternative or emergency fuel supply.
- (3) Delivered cost, quality and reserves of limestones available.
- (4) Delivered cost, quality and reserves of salt supply.
- (5) Total freight cost of all products to present and potential consumers.
- (6) Temperature, quantity, and chemical properties of cooling water supply.
- (7) Treatment cost and treatment results of best and second best boiler feedwater supplies.
- (8) Cost of solid waste disposal in near and distant future.
- (9) Cost of liquid waste disposal procedure.

- (10) Soil-bearing capacity and character and cost of land.
- (11) Availability, intelligence and character of labor.
- (12) Adequacy of housing, schools and other living facilities for personnel and workmen.
- (13) Cost, adequacy and assurance of ammonia supply.
- (14) Cost of coke and availability of crude ammonia liquor supply.
- (15) Flood, hurricane, earthquake, etc. hazards.
- (16) Cost of space for expansion or growth.
- (17) Potentialities or incentive for location and growth of alkali-consuming industries.
- (18) Attitude of adjacent communities toward large-scale industry.
- (19) Adequacy of mill-supply and mechanical services.

In what follows we shall elaborate these points in greater detail. It is necessary that expert engineering judgment be exercised in weighting factors such as listed above relative to one another, and in computing or estimating the rating of each of the prospective sites. Since fuel, limestone and salt are the three main requirements, the selection of a site will be governed by the quality and mining cost of those which are available within the territory considered. Some of the factors which require consideration are further elaborated in the following:

The quantity and kind of fuel required have been discussed in Chapters XXII and XXVI. In this chapter it need be pointed out that ammonia soda plants can burn any kind of fuel so long as it is cheap. Fuel equivalent to half a ton of high-grade coal per ton of soda is near the minimum consumption for all purposes in the direct manufacture of soda by the ammonia process. A small amount of the fuel will be burned in preparing the lime. Almost invariably this must be metallurgical coke, which is a standard commodity with a standardized market, but can conceivably be very expensive. Such is quite unlikely to be the case in any territory having a high alkali market, but is true with certain alkali plants on the Gulf Coast. A somewhat larger amount of the fuel will be required in soda dryers, and this may be bituminous coal. Since most of the fuel is used in the generation of steam, the fuel problems in selecting a site are much the same as for any other industry. These were discussed in Chapter XXII, and hence will not be dealt with here.

Continuity of operations, important as it is to economical production and high quality product, requires either very large stocks of fuel and raw materials, or assured emergency or "second-string" supplies. A combination of the two is usual. This is more important with fuel than with limestone or salt, for the latter are usually under the control of local management. The second-string fuel supply can be more costly if it is dependable.

It is decidedly advantageous that the production of salt and limestone be under the control of the soda ash manufacturer, as is generally done. That is, one department of the works should be in charge of the brine field operation and another in charge of the quarrying and prepara-

tion of the stone. Not only must sources of these raw materials give assurance of long-time inexpensive supply, but their quality must also fulfill certain requirements. This is particularly important with limestone, as is discussed in Chapter VI. Likewise an impure brine or high-magnesium sea-salt introduces added costs, as discussed in Chapters IV and V. The adequacy of each on the basis of the principles mentioned must be exhaustively considered in selecting an ideal site.

More than eight tons of brine, stone and fuel are handled into the works per ton of soda ash shipped out; and more than 12 tons, per ton of chemical caustic shipped out. On a strict ton-mile basis, therefore, the plant should occupy a position considerably nearer to its raw materials than to its market. However, about 60 per cent of the raw materials are very cheaply transported by pipe line, and freight rates on stone and coal are cheaper than on finished products like soda ash and caustic soda. Furthermore, there are local discontinuities in freight rates which prevent setting up a "formula" for finding the site of minimum transportation costs. A finite (and small) number of potentially good sites can be determined by a rapid qualitative consideration of the most important factors. For these and the few suitable raw material and fuel sources, an experienced engineer should compute actual annual transportation costs based on previously prepared market estimates.

The question of cooling water supply is of considerable importance. If during the months of warm weather, no reasonably cool (ten to fifteen degrees below wet-bulb temperature) water is available, the production of the plant will suffer. Furthermore, the power required for circulating excessively large volumes of water is considerable. If a site affords a large volume of water which gets quite warm (approaches wet-bulb temperature) in the summer time, it is necessary to investigate the possibility of a supply of artesian well water for summer operation. Equipment for refrigeration of water will, under certain conditions, compete with deep-well water if the latter is scarce. Exhaust steam is suitable as the source of power for such refrigeration and is thus a sort of summer complement to the winter space-heating load. Only a small portion of each unit of cooling apparatus needs to be supplied with refrigerated water. Besides the temperature of the cooling water, it is necessary to investigate its behavior in cooling equipment. Certain waters contain temporary hardness or other solids which deposit difficultly removable crusts on cooling surfaces. Many sources of water are conducive to algae-growth in warm weather when the plant can least afford any impeded heat transfer. Others have properties of causing corrosion of metals of construction in the cooling apparatus. So it may be necessary to give the cooling water a suitable chemical treatment. This has been dealt with at great length in Chapter XXIII.

An additional supply of water may be desirable for steam generation. As mentioned before, frequently a source of excellent cooling water is a poor source for boiler feedwater. Organic contamination in this course of water is not so harmful as in the cooling water, but scale-forming solids



in solution would bring about high operating expense. Since the supply of boiler feedwater should (for best fuel economy) be given as much preheating as possible from sources of low-pressure waste heat, it must also be considered as a cooling medium. The quality of the contemplated source of feedwater, both from the standpoint of behavior in cooling equipment and from the standpoint of adequate treatment to inhibit scale forming and boiler corrosion, must be given very careful consideration. Alkali engineers generally employ water specialists on this problem.

The difference between the quantities of raw materials and finished products mentioned above must be disposed of as solid, liquid and gaseous wastes. There should be a large area adjacent to the plant for the disposal of the solid wastes, as mentioned above. These come from the distiller blow-off, the lime caustic mud, the boiler ashes, the slaker rejects, etc. This is one of the most serious problems connected with an alkali plant. The physical character of most of these solids is such that they are very poor material for land fills. The caustic mud contains excess lime. The distiller waste does not dry or harden over long periods of time. There is sufficient free lime and chloride in it so that vegetation will not grow on it for many years. Consequently the deposits are considered unsightly by most people. It cannot be disposed of in the usual rivers or public waterways. A proper site for an alkali plant should have available a large area of swamp or marsh land or valleys, which can be cheaply diked or dammed to make room for the waste disposal for a number of years. The boiler ashes and the slaker rejects may be utilized in road making for a country community.

All alkali plants have to dispose of large quantities of calcium chloride. For plants located on the seacoast, once the distiller blow-off has had the solids settled from it, this presents no problem. Inland plants, however, are faced with a difficulty caused by the introduction of the chlorine into the irrigation waters of the district. An alkali plant must therefore be located within reach of a reasonably large stream so that the chloride to be disposed of does not add appreciably to the salinity of the river water.

As explained above, most of the buildings in an alkali plant are unusually tall. Consequently unusually heavy foundation loads are encountered under the buildings as well as under the taller equipment. If an alkali plant is not located on good ground, the foundation costs may be exorbitant. Furthermore, large foundation masses inhibit pipe tunnel, elevator pit, and similar features of design, which add to the cost of the entire plant. There should be an adequate, reasonably level area and sufficiently high land for quick drainage of rainfall. The site should avoid regions of congestion and high land values.

Modern ammonia soda plants use relatively little labor, compared to most other industries, measured either per dollar of investment or per ton of the output. The usual complement of skilled maintenance artisans employed on apparatus and building repairs is required, as in most other plants. The labor for handling and loading the finished product is like-

wise the same in quantity and quality as in other industries, having a comparable division between bulk and package shipments. In direct production, however, one painstakingly trained and intelligent operator can, because of the continuity and automatic control in the operation, attend an exceptionally large amount of apparatus. Abnormalities of operation occur so seldom that it takes a long time to gain direct experience. Consequently "steady" workers are demanded. Pay rates must be such as to avoid high turn-over of labor. The incentive of a clear and substantial route of promotion for operating personnel must be "built" into the plant organization. Certain communities afford a larger market for the steady type of workers, and these must be kept in view in the selection of the site, as labor problems should not be allowed to interfere with the continuity of operations.

If housing, school and living facilities are not available in the vicinity of a favored plant site, such site must be penalized to the extent of adding the cost of such facilities to the first cost of the venture. In America, the operation of such facilities introduces additional management burdens. However, it behooves the management to provide housing facilities on a cooperative basis.

Ammonia in the form of crude coke-oven liquor must generally be contracted for, since it is hardly a commodity with a standardized market availability. Since synthetic ammonia, as anhydrous liquefied gas in tank-car lots, has become cheaper, the availability of ammonia from coke-ovens is no longer so important to a prospective alkali plant as it was 15 years ago. It was a widespread practice before the first World War (1914-1918) for alkali manufacturers either to operate their own by-product coke ovens or to locate near a by-product coke plant. Today, as a matter of fact, the combination of the alkali industry with the synthetic ammonia industry has been worked out very advantageously to the ammonia soda industry.

When anhydrous ammonia is being used, the consumption of sulfur will be much higher. Although the quantity of sulfur in any case is small, the unit cost can be quite high, as was pointed out in Chapter XXVI. Since the quality of the product is quite seriously dependent on the sulfur control, this item should receive due consideration. However, where good coking bituminous coal is available in abundance, the problem of fuel, of coke, of ammonia, and of sulfur required will be once and for all solved together, when a suitable site has been selected.

Flood, hurricane, and such *force majeure* characteristics of sites should be compared on the basis of insurance rates and probability of lost production based on known history. The elevation of the ground and the design of the buildings should take into consideration the highest flood level and the maximum wind pressure likely to be encountered. Such special provisions are noticeable in the construction of certain alkali plants on the Gulf Coast.

The alkali plant site should leave room for growth. Not only can the main products be expected to increase at a reasonable rate, but also

it is reasonable to expect that by-products or end-products will be developed to the point of finding profitable production immediately adjacent to the main works. That land is preferred which permits a layout of the original plant for a methodical growth without introducing undue expense in the piping and handling of materials. Ultimate plant layout should be visualized also from the operating and maintenance standpoint.

An alkali plant serves a number of major industries. The consumer products, for which alkali is a large-scale raw material, are glass, soap, rayon, paper, petroleum oil, etc. The choice of a site for a new alkali plant must consider the proximity of the other raw materials required for the alkali-consuming industries. For example, if two sites are very nearly equal in all other respects, but one of them is reasonably close to sources of glass sand and the other is not, the former would certainly be the favored location, since it would double the incentive for the location of a glass plant adjacent to it.

An alkali plant causes no severe industrial hazards such as the fire hazard connected with a petroleum refinery or the explosion hazard of a powder works. It is not particularly malodorous, dusty or smoky. Nevertheless, it has chimneys and machinery noises to which some communities object. It has accumulation of wastes. Inordinate local taxation or other forms of burdensome legislation may be found in a community unsympathetic to this large-scale activity.

The most carefully planned and operated plant supply stores occasionally run out or fail to stock sufficient maintenance materials of great importance. The store stock also represents a large share of working capital. Some sites, therefore, have considerable monetary advantage in being close to a favorable market for factory and mill supplies. Likewise ready availability of services of specialists like gas compressor experts or large foundry and machine shop facilities is a decided asset in the assurance of lower operating costs.

As was explained in the preface and has been repeatedly emphasized in the text, this book is not intended to replace the services of a consulting engineer or an expert alkali plant designer. Before the consideration of a new alkali project has advanced beyond the preliminary market and raw material studies, capable engineering talent should be engaged to criticize such studies and later to secure the best possible plant site, plant layout and design.

In the foregoing discussion one factor has not received consideration. This may have a momentous bearing and may exert a great influence on the decision to be made, as far as plant location and the method of construction are concerned. It may be that this single factor will outweigh all others. This single factor is that of air-raid protection. When air-raid precaution is to be considered, a great many of the orthodox provisions for an ammonia soda plant layout may have to be discarded. As long as aerial warfare remains one of the vital means of military attack, no country can afford to ignore its potential menace. The principle

involved in the grouping of the various divisions of the works, in the sequence of operation, in the interrelation among the various steps in the process, in the convenience of having close proximity of one product to the next step where it is to be further processed, in the relationship between the raw materials and finished products—all these may, in part, have to be re-examined and modified. For instance, instead of locating the buildings close to one another or in rows parallel to one another in a regular formation, they may have to be scattered far apart and placed irregularly. The buildings themselves may have to be arranged and constructed just in a certain way. This will be appreciated when we bear in mind that an ammonia soda plant has many a tall building which might readily become a target from the air, and that the ammonia soda industry is strictly one of the defense industries of a nation. However, it has not been considered wise to include this in the above discussion except to mention that air-raid protection will and must receive due consideration in the location, design and construction of the ammonia soda plants of tomorrow.