

THE COMMERCIAL DECOMPOSITION OF NITROSYL
" "
CHLORIDE FOR RECOVERY OF CHLORINE AND
OXIDES OF NITROGEN

by

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A Thesis Submitted for Partial
Fulfillment for the Degree of
MASTER OF SCIENCE
in
CHEMICAL ENGINEERING

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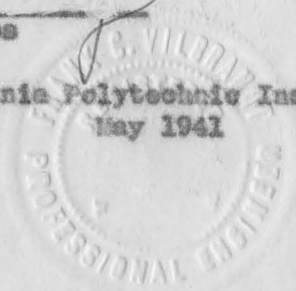


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THE COMMERCIAL DECOMPOSITION OF NITROSYL CHLORIDE FOR THE
RECOVERY OF CHLORINE AND OXIDES OF NITROGEN

I. INTRODUCTION

The Saltville plant of the Mathieson Alkali Works disposes of about 1,000,000 gallons of calcium chloride sludge from the ammonia distiller per day. This sludge contains about 11 per cent calcium chloride by weight based on total chlorides, approximately 85 per cent water, and smaller amounts of sodium chloride, sodium carbonate, calcium carbonate, calcium hydroxide, and insoluble material from the limestone. At the present time, this calcium chloride sludge is piped into a lake where the solid material settles out and the supernatant liquor drains into the river. This waste calcium chloride is not worth recovering and constitutes a stream pollution hazard.

It is believed that a process can be developed for the manufacture of commercial chlorine and a nitrate fertilizer from Solvay waste by reacting with oxides of nitrogen. In such a process, the products would be chlorine, calcium and sodium nitrate, and nitrosyl chloride. The chlorine and nitrate can be sold as such, but the nitrosyl chloride must be decomposed and the recovery of chlorine and oxides effected if the process is to be profitable.

In the commercial decomposition of nitrosyl chloride, since it is a very corrosive gas, provision must be made for handling the gas during the process of formation and decomposition.

The purpose of this investigation was to select, on the basis of the literature, a process for the decomposition of the nitrosyl chloride formed in the reaction between oxides of nitrogen and Solvay waste so as to recover the chlorine and oxides of nitrogen contained in the nitrosyl chloride. After a process was selected, it was the purpose of this investigation to determine the suitability of the process selected and to offer, insofar as possible, a solution to the problem of corrosion.

II. REVIEW OF LITERATURE

The Solvay Process

The Solvay Process for the production of soda ash is based on the fact that when ammonium bicarbonate is added to a saturated solution of common salt, the ammonium salt dissolves and sodium bicarbonate separates as a solid; if filtered, dried, and calcined, it is changed to soda ash, or sodium carbonate, Na_2CO_3 :



Commercially, a saturated solution of sodium chloride is treated with ammonia and carbon dioxide:



The ammonium bicarbonate then reacts with the sodium chloride to form sodium bicarbonate, which is in suspension and is filtered from the ammonium chloride and excess salt. The sodium bicarbonate is then calcined to produce soda ash.

The carbon dioxide for carbonating the brine is supplied from the calcining of the sodium bicarbonate and from the burning of limestone.

Calcium Chloride Production. The bulk of the ammonia is present, after the bicarbonate has been removed, in the form of ammonium chloride. Some ammonia is also present as carbonate, carbamate, and bicarbonate. The recovery is carried on in an ammonia still in which the ammonium chloride and milk of lime travel down the still and steam passes up. The free ammonia which is present in the form of carbonate is driven off first and

then milk of lime is added in order to liberate the fixed ammonia from the ammonium chloride. The following equation represents the reaction:



The waste liquor is drawn off at the bottom of the still and contains only a trace of ammonia but contains the calcium chloride, sodium chloride, and lime sludge. The liquor is piped to settling tanks or basins and the lime sludge settled out. The calcium chloride liquor is drawn off and except for a small portion which is used in refrigeration and on dirt roads, is wasted.

Production of Nitrosyl Chloride in the Manufacture of Chlorine

It has been proposed to manufacture commercial chlorine by the action of nitric acid on hydrochloric acid and by the action of nitric acid on sodium chloride. In each of these processes, nitrosyl chloride is formed along with the chlorine.

Chlorine from Hydrochloric Acid. The manufacture of chlorine from hydrochloric acid may be represented by the equation:



Such a process was proposed by Davis in 1890.⁽⁵⁾ Davis proposed to carry out such a process using five towers, feeding sulfuric acid into the fourth tower to remove any remaining nitric oxide and nitrosyl chloride. The process may be represented by the following equations:



There are a number of other reactions which take place:



"In the fifth tower, the hydrochloric acid from the nitric acid towers is mixed with nitrosyl sulfuric acid to release chlorine and regenerate nitric acid."⁽⁵⁾ It will be noted from the above reactions that the whole process is a cycle of reactions.

Chlorine from Sodium Chloride. When sodium chloride is acted on by nitric acid, chlorine, nitrosyl chloride, and sodium nitrate are formed according to the following equations:



It will be noticed that the second equation above is the starting point in the manufacture of chlorine from hydrochloric acid. Then, the same cycle of reactions which took place in the manufacture of chlorine from hydrochloric acid may be expected to take place in the manufacture of chlorine from sodium chloride. The above equations merely represent the net result

of treating sodium chloride with nitric acid.

In 1847, Dunlop patented a process for making chlorine from nitric acid and salt. The process operated for some time but eventually failed because of the enormous quantities of sulfuric acid used for decomposing the nitrosyl chloride. By 1887, two processes had been patented for making chlorine from hydrochloric acid and nitric acid but none were ever commercially feasible.

Treating the Nitrosyl Chloride with Sulfuric Acid. In both the process for chlorine from salt and for chlorine from hydrochloric acid, the nitrosyl chloride was finally absorbed in concentrated sulfuric acid. In the latter process, the hydrochloric acid from the nitric acid towers was added to the nitrosyl sulfuric acid to remove chlorine and recover nitric acid. In the former process, however, the nitrosyl chloride was finally absorbed in sulfuric acid and the resulting nitrosyl sulfuric acid denitrated with steam and air. The following equations represent this action:



It can be seen from the above equations that the sulfuric acid is recovered but it absorbs large quantities of water which makes it necessary to concentrate the acid before it can be used again. About 2,000 tons of sulfuric acid were required per 35 tons of chlorine produced.

Properties of Nitrosyl Chloride

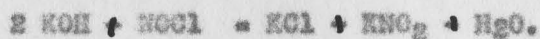
Physical Properties. The following table gives the physical properties of nitrosyl chloride which have been determined at the present time.

TABLE I

Physical Properties of Nitrosyl Chloride

State at atmospheric conditions	Gas
Molecular Weight	65.46
Color of gas	Brownish-orange
Color of liquid	Orange-red
Boiling point	-6 to -8°C
Specific gravity (Rel. to air)	2.51
Specific gravity (Rel. to water)	1.417 at -18°C

Chemical Properties. Nitrosyl chloride reacts with water readily giving nitrous and hydrochloric acids. It reacts with most metallic oxides and hydroxides forming the nitrite and chloride of the metal:



Nitrosyl chloride will attack silver, manganese, and nickel only slightly at 100°C but will attack gold, copper, cadmium, lead, platinum, and thallium at 100°C while tin, mercury, arsenic, antimony, bismuth, and iron are attacked in the cold. The gas decomposes with silver or aluminum at 500°C. The gas cannot be decomposed without a catalyst below 700°C.

Nitrosyl chloride forms double compounds with many metallic chlorides,

such as antimony chloride, aluminum chloride, and copper chloride. The compounds formed are of the nature $\text{CuCl} \cdot \text{NOCl}$. Some of these double compounds decompose on heating while others may be sublimed.

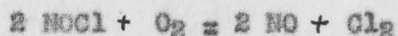
Nitrosyl chloride reacts with unsaturated organic compounds forming additional products. With amines, nitrogen is evolved and the chloride formed. The gas reacts with sulfur trioxide forming $\text{NO}_2 \cdot \text{SO}_2 \cdot \text{Cl}$.

Decomposition. With the addition of hydrogen, nitrosyl chloride may be decomposed at 400°C .



The mixture of nitrosyl chloride and hydrogen may be either heated directly or passed over a catalyst such as aluminum oxide, manganese dioxide, manganese chloride, chromium oxide, silicon dioxide, or activated carbon.

Nitrosyl chloride may also be decomposed by the addition of oxygen:



The only method which seems to have been used commercially in connection with the production of chlorine is that of reacting the gas with sulfuric acid followed by the addition of air and steam or hydrochloric acid.

Separation. Nitrosyl chloride, oxides of nitrogen, and chlorine can be separated by fractional condensation and subsequent distillation. By cooling slightly below -34.6°C , which is the boiling point of chlorine, the nitric oxide can be separated from the remaining gases as it will not liquify above -151°C . The nitrogen dioxide, nitrogen tetroxide, chlorine, and nitrosyl chloride can then be separated by fractional distillation. Nitrogen dioxide and nitrogen tetroxide boil at 21.3°C .

III. EXPERIMENTAL

Purpose of Investigation

The purpose of this investigation was:

1. To select, on the basis of the literature and properties of nitrosyl chloride, a method for the decomposition of the nitrosyl chloride produced in the reaction between oxides of nitrogen and Solvay waste so as to recover the chlorine and oxides of nitrogen.
2. To determine the suitability of the method of decomposing the nitrosyl chloride by causing a reaction between the nitrosyl chloride and the Solvay waste itself.
3. To determine the effect of reacting temperature on the amount of chlorine recoverable from nitrosyl chloride by causing a reaction with Solvay waste.
4. To determine the effect of reacting varying amounts of nitrosyl chloride with a given amount of waste at a constant gas rate.
5. To determine the effect of relative concentration of nitrosyl chloride and Solvay waste on amount of recoverable chlorine.
6. To offer at least a partial solution to the problem of corrosion caused by the nitrosyl chloride.

Plan of Investigation

The plan of this investigation was as follows:

1. The literature was searched for reactions of nitrosyl chloride on the substances contained in Solvay waste so as to determine a suitable method of decomposing the nitrosyl chloride.
2. Having decided upon a method of recovery based on causing a reaction between nitrosyl chloride and Solvay waste by bubbling nitrosyl chloride through the waste, the effect of reacting the waste with varying amounts of nitrosyl chloride at constant rate by passing nitrosyl chloride through a given amount of waste for different lengths of time was studied.
3. The effect of reacting temperature on the amount of chlorine recoverable from the nitrosyl chloride was studied by reacting nitrosyl chloride with the Solvay waste at varying temperatures.
4. The effect of relative concentration of nitrosyl chloride and Solvay waste was studied by reacting for one hour a constant amount of nitrosyl chloride with varying amounts of waste.

Materials

Solvay Waste. The Solvay waste used in this investigation was obtained from the base of the ammonia recovery tower at the Saltville plant of the Mathieson Alkali Works. The waste was transported and stored in a steel drum.

Nitrosyl Chloride. The nitrosyl chloride used was prepared in the laboratory.

Standard Solutions:

Sodium Carbonate. Exactly 6.6250 grams of C.P. sodium carbonate were dissolved in enough distilled water to make 500 cc of solution. This solution was considered to be 0.25 normal.

Sulfuric Acid. Eleven cubic centimeters of 95 per cent sulfuric acid (Sp. g. 1.8) were added to enough water to make two liters of solution. To standardize, 10 cc of the sodium carbonate solution were titrated with the sulfuric acid using methyl orange as an indicator. The acid used was 0.086 normal.

Sodium Hydroxide. Eight grams of C.P. sodium hydroxide were dissolved in enough water to make two liters of solution. To standardize, 10 cc portions of the solution were titrated with the standard sulfuric acid using phenol as an indicator. The sodium hydroxide used was 0.112 normal.

Silver Nitrate. About 50 grams of C.P. silver nitrate were dissolved in distilled water and the solution diluted to three liters. To standardize, 10 cc portions of a standard hydrochloric acid were neutralized with ammonium hydroxide and titrated with the silver nitrate solution. The silver nitrate solution used was 0.0859 normal with respect to chlorine.

Potassium Permanganate. Approximately 3.16 grams of potassium permanganate were dissolved in enough water to make 500 cc of solution. To standardize, about 0.1 to 0.2 gram of sodium oxalate was weighed and dissolved in hot distilled water to which had been added about five cubic centimeters of dilute sulfuric acid. This sodium oxalate solution was titrated with the potassium permanganate. The potassium permanganate used was 0.2 normal with respect to sodium oxalate.

Potassium Chromate Indicator. Approximately 0.7 gram of potassium chromate were dissolved in enough water to make 500 cc of solution. This is approximately 0.1 molar.

Ammonium Chloride. The ammonium chloride solution was made by dissolving 25 grams of ammonium chloride in enough water to make 250 cc of solution. This is approximately a ten per cent solution. Ten cubic centimeters of this solution were added to each calcium sample.

Ammonium Oxalate. Twenty grams of ammonium oxalate were dissolved in enough water to make 200 cc of solution. This is about a ten per cent solution. Twenty cubic centimeters of this solution were used to precipitate the calcium.

Concentrated Sulfuric Acid. Sulfuric acid of specific gravity 1.8 and 95 per cent sulfuric acid was used for absorbing the nitrosyl chloride.

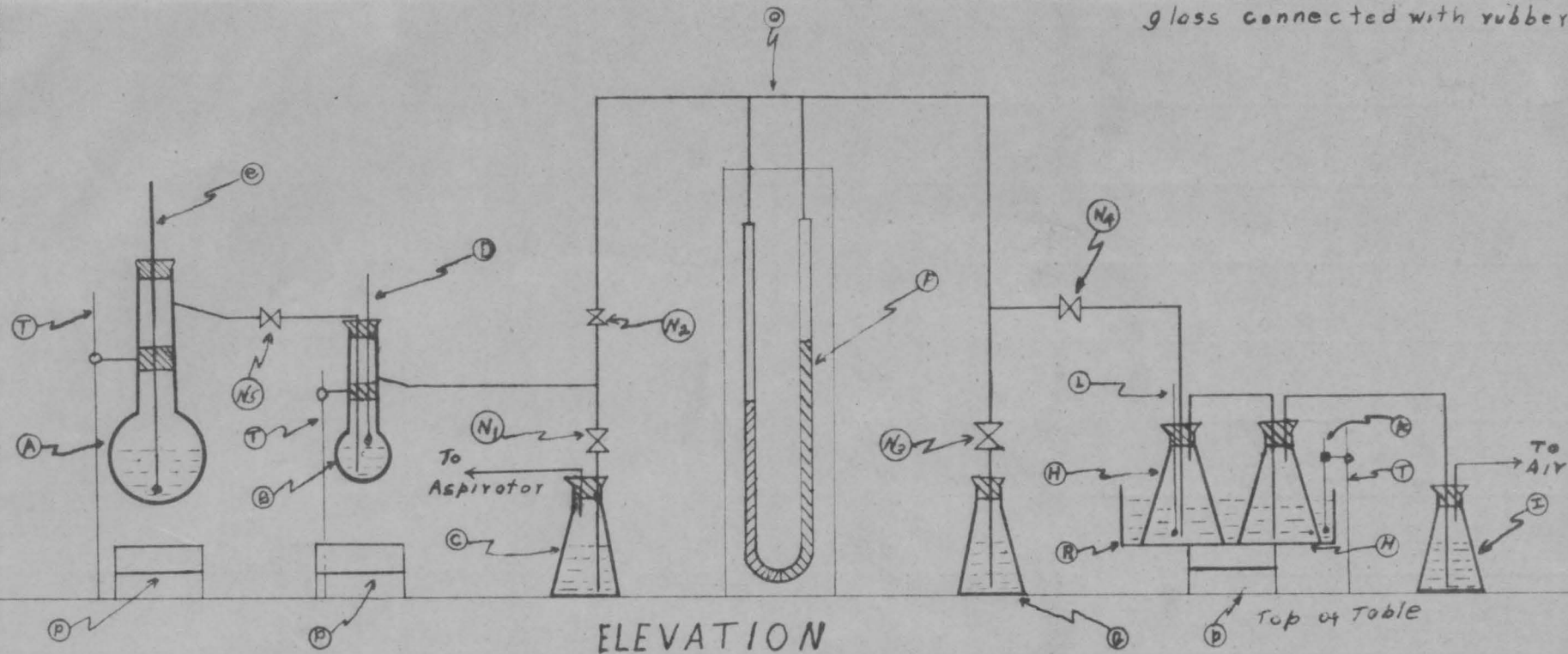
Concentrated Nitric Acid. Chemically pure concentrated nitric acid was used for making the nitrosyl chloride. The dilute acid was prepared by adding 50 cc of concentrated nitric acid to 200 cc of distilled water.

Concentrated Hydrochloric Acid. Chemically pure concentrated hydrochloric acid was used for making the nitrosyl chloride.

Apparatus

Figure 1 shows the apparatus used in this investigation. Flask (A) is a 500 cc distilling flask in which is placed 200 cc of concentrated hydrochloric acid and 50 cc of concentrated nitric acid. Flask (B) is a 250 cc distilling flask in which is placed 50 cc of concentrated sulfuric acid for absorbing the nitrosyl chloride gas produced in (A). Flasks (A) and (B) are provided with a thermometer for controlling the temperature

glass connected with rubber



LEGEND

- | | |
|---|--|
| Ⓐ 500cc Reaction Flask (HCl + HNO ₃) | Ⓒ Capillary Tube |
| Ⓑ 250cc H ₂ SO ₄ Flask for Absorbing NOCl | Ⓓ Hot plates |
| Ⓒ 350cc Flask for Absorbing Cl ₂ | Ⓔ Pinch Cocks |
| Ⓓ 220°F Therm for NOCl Temp | Ⓕ 14" x 10" x 4" Heating Water Container |
| Ⓔ 110°C Therm for Aqua Regia Temp | Ⓖ Ring Stands With Clamp |
| Ⓕ Manometer filled With Conc HCl | Ⓖ 350cc Flask for Absorbing Gases in Water |
| Ⓖ 350cc Flask to Regulate Gas Flow | Ⓗ 360°C Therm for Heating Water Temp |
| Ⓗ 500cc Flasks for Reacting Waste | |
| Ⓖ 110°C Therm for Waste Temp | |

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NOCl DECOMPOSITION
 APPARATUS

Drawn by H.C.S. Scale: No Scale
 Approved by Fig. 1

in each. The heat is supplied by two hot plates, one under each flask. Flask (C) contains water and is connected to an aspirator to remove the chlorine and hydrochloric acid produced in flasks (A) and (B). The flow of nitrosyl chloride gas was controlled by the amount of heat supplied to flask (B). The quantity of nitrosyl chloride reacting with the waste was measured by means of manometer (F), which is an elongated U made of medium glass tubing and filled with concentrated hydrochloric acid. The two arms were connected by a small capillary tube, (G), about two inches in length. Flask (C) contains water which is used to absorb the nitrosyl chloride gas until the flow is regulated. The two flasks, (H), in which the Solvay waste is placed are kept at constant temperature by the water in container (H) which is heated by means of a hot plate. Flask (I) contains water which is used to absorb the gases given off in the reaction and is open to the atmosphere.

Theory of the Process Selected

The process selected for recovering the chlorine and oxides of nitrogen in the nitrosyl chloride was that of reacting the nitrosyl chloride with the waste itself, it was decided to carry on this reaction by bubbling the nitrosyl chloride gas through a given quantity of Solvay waste. In such a method, the amount of recoverable chlorine can be measured directly by analysis. The amount of recoverable chlorine is dependent upon the amount of oxides of nitrogen produced by the decomposition of the nitrosyl chloride since no chlorine can be released until the nitrous acid produced by the decomposition of the nitrosyl chloride has been converted into nitric acid. The following equations represent the major reactions involved:



It can be seen from the above equations that for any chlorine to be released the oxides of nitrogen in the nitrosyl chloride must at least be partially utilized. Therefore, the amount of chlorine recoverable from the nitrosyl chloride is also an indication of the amount of oxides of nitrogen recovered.

Method of Procedure

Preparation of Nitrosyl Chloride. With reference to figure 1, 50 cc of cold concentrated sulfuric acid was placed in the 250 cc distilling flask (B). Approximately 200 cc of cold concentrated hydrochloric acid was then put in the 500 cc distilling flask (A). Approximately 50 cc of cold concentrated nitric acid was then added to flask (A) and the connections made as shown. The pinch cock between the sulfuric acid flask and the manometer was closed and the pinch cock between the two flasks (A) and (B) and between (B) and (C) opened. The hydrochloric and nitric acids were then gently heated and the gases absorbed in the sulfuric acid until the temperature in flask (A) reached about 105°C. This usually required from three to four hours. Approximately 50 cc of sulfuric acid saturated with nitrosyl chloride produced enough nitrosyl chloride, after the addition of salt, to react with the waste for about two hours.

Reacting the Nitrosyl Chloride with the Waste. Enough water was placed in the heating bath (R) to come about half way upon flasks (H) and brought to the desired reacting temperature by means of the hot plate (P). Approximately 500 cc of waste was at first divided equally and put in flasks (H). This was later found to be too large a volume of waste and reduced to 250 cc. Pinch cock (N_5) was closed after the nitrosyl sulfuric acid had cooled to room temperature. About ten grams of dry sodium chloride were now added to the nitrosyl sulfuric acid and as soon as the first sudden flow of gas from flask (B) has almost stopped, pinch cocks (N_2) and (N_3) were closed. The nitrosyl sulfuric acid was then heated very gently until the manometer read one inch of hydrochloric acid. At this point, pinch cock (N_4) was opened, (N_3) closed and the time recorded. Readings were taken on thermometer (D), the nitrosyl chloride temperature, manometer, thermometer (L), the waste temperature, and thermometer (K), the heating water temperature. Readings were taken on all fifteen minute runs every two minutes considering the time that the pinch cock N_4 was opened as zero time. Readings were taken on all thirty minute runs every three minutes and on all other runs every five minutes.

Runs were made for 15, 30, 60, 90, and 120 minutes at approximately 22°C, 40°C, 60°C, 80°C, and 88°C. At the end of each run, the reacted waste was analyzed for chlorides, bicarbonates, insoluble material, calcium and nitrates.

Five one-hour runs were also made at room temperature using 100, 200, 300, 600, and 1000 cc of waste and analyses run as above.

Analyses of Waste

The waste was analyzed for; (1) chlorides, (2) bicarbonates, (3) carbonates, (4) calcium, (5) insoluble material, and (6) nitrites after each run. The unreacted waste was also analyzed for the same components. The method of analyzing was as follows:

Insoluble Material. About 20 grams of waste were weighed in a ground glass weighing bottle. The waste was then filtered through a weighed filter paper and the filter containing the insoluble material dried overnight in an oven at 100°C. The dried material was then placed in a weighing bottle and weighed. The dry weight divided by the original of the sample gives the percentage insoluble material.

About 20 grams of waste were weighed in the weighing bottle and washed into a 500 cc volumetric flask and the flask diluted to the mark. The calcium, chlorides, carbonates and bicarbonates were determined as follows:

Calcium Determination. Ten cubic centimeters of the dilute waste were withdrawn by means of a pipette and put into a 400 cc beaker and a few drops of concentrated hydrochloric acid added to insure complete solution. Then five cc of dilute nitric acid were added and solution boiled for two or three minutes. Ten cubic centimeters of the ammonium chloride solution were then added and the solution made alkaline with concentrated ammonium hydroxide. The solution was then boiled for five minutes, diluted to about 200 cc, and filtered. To the filtrate, a little additional ammonium hydroxide was added and then 20 cc of the ammonium oxalate solution. The solution was kept warm and allowed to stand until clear and filtered. The precipitate was washed with hot dilute sulfuric acid and enough distilled water was added to make about 50 cc of solution. The solution was brought to a boil

and titrated with the standard potassium permanganate solution. The percentage calcium was calculated by the following equation:

$$\% \text{ Ca} = \frac{\text{cc KMnO}_4 \times 0.2 \times 50}{\text{Wt. of sample}}$$

Chloride Determination. Mohr's method for the determination of chlorides in a neutral solution was used. Ten cubic centimeters of the diluted waste were put in a 300 cc evaporating dish and a small amount of distilled water added. Two drops of phenolphthalein indicator were added and concentrated ammonium hydroxide added drop by drop with a stirring rod until the solution just turned pink. Then, drop by drop with a stirring rod, dilute nitric acid was added until the pink color just disappeared. About one cubic centimeter of potassium chromate indicator solution was added and the solution titrated with the standard silver nitrate solution until the first red tinge appears. The per cent chlorides was calculated by the following equation:

$$\% \text{ chlorides} = \frac{\text{cc AgNO}_3 \times 0.0859 \times 50}{\text{Wt. of sample}}$$

Bicarbonates and Carbonates. Fifty cubic centimeters of the diluted waste solution were put in a 400 cc beaker and a little distilled water added. Two drops of phenol indicator were added and the solution titrated with the standard sulfuric acid until the first permanent pink color appears. Two drops of methyl orange indicator were then added and ten cubic centimeters of sulfuric acid solution. The solution was then back titrated with the standard sodium hydroxide solution. It was found that only in the unreacted waste were any carbonates present and no carbonate determination was run on the reacted waste. The carbonates were calculated as calcium carbonate by the following equation:

$$\% \text{CaCO}_3 = \frac{\text{cc H}_2\text{SO}_4 \times 0.036 \times 0.5 \times 10}{\text{Wt. of sample}}$$

The bicarbonates were calculated as calcium bicarbonate as follows:

$$\% \text{Calcium bicarbonate} = 10 - \frac{\text{cc NaOH} \times 0.036 \times 0.081 \times 10}{1.3 \text{ Wt. of sample}}$$

Determination of Density of Waste. About 50 cc of distilled water and 50 cc of waste were each put in a separate flask and allowed to come to room temperature. Then a 10 cc pipette was filled with distilled water and weighed in a weighing bottle. This weight was divided by the density of water at the temperature of the distilled water and the volume calculated. The same pipette was then filled with the waste and weighed as was the water. This weight divided by the volume was taken as the density of the unreacted waste.

Qualitative Determination of Nitrites. About ten cubic centimeters of the waste were put in a graduated cylinder and a few drops of ferrous sulphate solution added. This usually gave a brown ring test for nitrites. However, on the addition of a few drops of dilute sulfuric acid, the brown ring was easily discernable.

Data and Results

The analysis of the unreacted Solvay waste used in this investigation is given in Table II. This analysis only included chlorides, carbonates, bicarbonates, insoluble material, calcium, and a qualitative determination of nitrites.

TABLE II
Analysis of Unreacted Solvay Waste

Chlorides	7.73 %
Chlorides as CaCl_2	11.98 %
Carbonates as CaCO_3	0.53 %
Bicarbonates as $\text{Ca}(\text{HCO}_3)_2$	0.88 %
Calcium	4.97 %
Insoluble material	1.56 %
Nitrites	None
Water and undetermined material (Approx.)	85.00 %
Density	1.12 g/cc

The analysis given in Table II was used as the composition of the unreacted waste in calculating a chlorine material balance and also in all other material balance calculations.

Effect of Time and Temperature on Chlorine Recoverable from Nitrosyl Chloride. Tables III to XXII inclusive give the actual laboratory data on the time of reaction, nitrosyl chloride flow rate and temperature, and the temperature of the waste.

The volume and weight of waste used for absorbing the nitrosyl chloride are shown at the top of each table. Tables III to XXII give the weight of nitrosyl chloride reacting, the time of absorption, and the approximate reacting temperature. By the reacting temperature is meant the approximate temperature of the surroundings of the reaction flasks containing the waste during the time of absorption of the nitrosyl chloride. The nitrosyl chloride temperature is the reading of the thermometer in the nitrosyl sulfuric acid-sodium chloride reacting flask. The thermometer bulb was placed just above the surface of the liquid in the flask. The waste temperature in each case is the temperature of the waste in the first reaction flask at the time of the reading.

TABLE III

Data Sheet on Absorption on Nitrosyl Chloride in Solvay
Waste at Approximately 26.5°C.

Vol. of Waste - 500 cc
Wt. of Waste - 560 gm
Wt. of NOCl - 1.81 gm
Absorbing time - 15 min.
Approx. React. Temp. 26.5°C.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)
0	0.90	34	26.5
2	1.25	38	26.5
4	1.35	39	27.0
6	0.75	39	27.5
8	0.75	40	27.5
10	0.90	41	27.5
12	0.90	42	28.0
14	1.00	43	27.5
Av.	0.96	40	

TABLE IV

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 26.5°C

Vol. of Waste - 500 cc
Wt. of Waste - 560 gm
Wt. of NOCl - 3.23 gm
Absorbing time - 30 min.
Approx. React. Temp. 26.5°C

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)
0	0.80	45	27.5
3	0.75	48	28.0
6	1.00	49	28.0
9	0.90	50	28.5
12	0.95	52	28.5
15	0.95	53	28.5
18	0.80	54	28.5
21	0.75	55	28.5
24	0.90	57	28.5
27	1.00	57	28.0
30	1.00	57	28.0
Av.	0.89	55	

TABLE V

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 29°C

Vol. of Waste - 500 cc
Wt. of Waste - 560 gm
Wt. of NOCl - 7.15 gm
Absorbing time - 60 min.
Approx. React. Temp. - 29°C.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)
0	1.0	50	28
5	1.1	50	30
10	0.9	50	30
15	1.0	53	30
20	1.1	54	31
25	0.9	56	32
30	1.0	57	35
35	1.0	59	33
40	1.0	64	35
45	1.0	66	34
50	1.0	66	34
55	1.0	67	34
60	1.0	68	34
Av.	1.0	59	

TABLE VI

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 27°C

Vol. of Waste - 500 cc
Wt. of Waste - 560 gm
Wt. of NOCl - 10.19 gm
Absorbing Time - 90 min.
Approx. React. Temp. 27°C

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)
0	0.59	57	28
5	0.75	60	28
10	1.00	63	28
15	1.00	63	29
20	1.00	64	29
25	1.15	65	29
30	1.15	69	29
35	1.15	70	29
40	1.15	72	29
45	0.75	72	29
50	1.00	74	29
55	1.25	74	29
60	0.95	74	29
65	1.00	75	29
70	1.25	77	29
75	0.90	80	29
80	1.00	78	29
85	1.10	80	29
90	0.90	80	29
Av.	0.99	72	

TABLE VII

Data Sheet on Absorption of Nitrosyl Chloride in Solvay Waste at Approximately 29° C

Vol. of Waste - 250 cc
 Wt. of Waste - 280 gm
 Wt. of NOCl - 12.90 gm
 Absorbing Time - 120 min.
 Approx. React. Temp. - 29°C.

Time (min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)
0	1.00	37	28
5	0.95	40	28
10	1.00	43	28
15	0.95	48	28
20	0.85	52	29
25	1.05	55	29
30	1.05	57	29
35	1.05	59	29
40	1.05	61	29
45	1.25	62	29
50	1.15	65	29
55	0.90	65	29
60	1.15	65	29
65	0.75	69	29
70	1.05	67	29
75	1.05	65	29
80	1.10	69	29
85	1.20	72	29
90	1.20	72	29
95	0.75	71	29
100	0.60	65	29
105	0.65	72	29
110	0.60	72	29
115	0.75	73	29
120	1.05	74	29
Av.	0.93	62	

TABLE VIII

Data Sheet on Absorption of Nitroayl Chloride in Solvay
Waste at Approximately 40°C

Vol. of Waste - 500 cc
Wt. of Waste - 560 gm
Wt. of NOCl - 1.83 gm
Absorption Time - 15 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	0.75	56	37.5	39.0
2	1.10	61	38.5	40.0
4	0.85	61	39.5	40.0
6	1.20	62	39.5	40.5
8	1.45	66	40.5	40.5
10	1.40	66	41.5	40.5
12	0.80	65	41.75	40.5
14	1.00	72	42.0	40.5
Av.	1.06	64		

TABLE IX

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 40°C

Vol. of Waste - 500 cc
Wt. of Waste - 560 gm
Wt. of NOCl - 3.54 gm
Absorbing Time - 30 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	0.95	70	38.0	40.0
3	1.20	71	39.0	40.0
6	1.10	72	40.5	40.5
9	0.85	71	41.0	40.5
12	0.90	77	42.0	40.5
15	0.75	74	42.0	40.5
18	0.80	74	42.0	40.5
21	1.05	74	42.0	40.5
24	1.35	76	42.0	40.0
27	0.95	77	41.5	40.0
30	1.10	79	41.5	40.0
Av.	1.00	74		

TABLE X

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 40°C

Vol. of Waste - 500 cc
Wt. of Waste - 560 gm
Wt. of NOCl - 6.98 gm
Absorbing Time - 60 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	1.40	39	40.0	42.0
5	1.00	44	42.0	41.5
10	0.95	48	42.5	41.5
15	0.85	52	42.5	41.5
20	0.95	52	42.0	40.5
25	0.80	53	41.5	40.0
30	1.05	56	41.0	39.5
35	0.90	57	41.0	39.5
40	0.80	58	41.0	40.5
45	1.00	60	41.5	40.5
50	0.80	61	41.5	40.5
55	1.15	64	41.0	40.0
60	1.00	65	41.0	39.5
Av.	0.97	56		

TABLE XI

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 40°C

Vol. of Waste - 500 cc
Wt. of Waste - 560 gm
Wt. of NOCl - 9.96 gm
Absorbing time - 90 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	1.25	66	39.5	41.0
5	0.90	67	41.0	40.5
10	0.75	70	41.5	40 ()
15	0.85	70	41.5	40.0
20	1.15	72	41.0	40.0
25	0.85	71	41.0	39.0
30	0.85	73	40.5	39.0
35	0.90	76	41.0	40.0
40	0.70	75	42.0	42.0
45	1.00	79	42.5	42.0
50	0.85	75	43.0	42.0
55	1.00	79	43.0	42.0
60	1.15	77	42.5	41.5
65	0.85	80	42.0	41.5
70	0.75	79	41.5	41.0
75	0.75	81	41.0	41.0
80	1.45	84	41.0	40.0
85	1.15	84	40.5	39.5
90	1.25	86	39.5	38.0
Av.	0.97	76		

TABLE XII

Data Sheet on Absorption of Nitrosyl Chloride in Solvay Waste
At Approximately 40°C

Vol. of Waste - 250 cc
Wt. of Waste - 280 gm
Wt. of NOCl - 13.50 gm.
Absorbing time - 120 mins.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Waste Temp. (°C)
0	1.00	34	42.5	42.0
5	1.00	38	43.0	42.0
10	0.75	42	43.5	41.5
15	1.00	46	43.0	41.0
20	1.10	48	42.0	40.0
25	1.00	52	41.5	40.0
30	1.00	53	40.5	39.0
35	0.85	55	40.5	39.5
40	1.05	59	41.0	40.5
45	0.80	61	42.0	41.0
50	1.00	64	42.5	41.0
55	1.05	67	42.5	41.0
60	1.25	76	42.0	41.0
65	1.25	67	41.5	40.5
70	1.45	67	41.0	40.0
75	1.20	67	40.0	29.5
80	1.25	67	41.0	40.0
85	0.75	66	41.0	40.5
90	1.00	74	42.0	41.0
95	1.05	70	42.5	41.0
100	0.70	73	42.5	41.0
105	0.50	71	42.0	41.0
110	0.50	72	41.5	40.5
115	0.75	73	41.0	40.0
120	0.55	73	41.0	40.0
Av.	0.95	62		

TABLE XIII

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 60°C

Vol. of Waste - 250 cc
Wt. of Waste - 280 cc
Wt. of NOCl - 1.78 gm
Absorbing Time - 15 min.

Time (Min)	Manometer Reading (in-H ₂ O)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	1.10	31	58.0	58.0
2	0.75	31	58.5	58.5
4	1.15	35	59.0	59.0
6	1.00	39	59.5	59.0
8	0.95	40	60.0	59.0
10	0.85	41	60.0	59.0
12	0.95	43	60.0	59.5
14	0.95	45	60.0	60.0
Av.	0.94	38		

TABLE XIV

Data Sheet on Absorption of Nitrosyl Chloride in Solvay Waste
at Approximately 60°C

Vol. of Waste - 250 cc
Wt. of Waste - 280 gm
Wt. of NOCl - 3.59 gm
Absorbing time - 30 min.

Time (Min)	Manometer Reading (in-H ₂ O)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	0.80	43	59.5	60.0
3	0.75	47	60.0	59.5
6	1.00	49	61.0	59.5
9	1.00	51	61.0	59.5
12	1.15	52	61.0	59.5
15	0.85	52	61.5	60.0
18	0.95	54	61.0	60.0
21	1.05	55	61.5	60.0
24	0.80	56	61.5	60.0
27	1.00	58	61.5	60.0
30	1.15	60	61.0	60.5
Av.	0.95	52		

TABLE XV

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 60°C

Vol. of Waste - 250 cc
Wt. of Waste - 280 gm
Wt. of NOCl - 7.00 gm
Absorbing Time - 60 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	0.85	57	58.0	59.5
5	0.85	60	58.0	58.0
10	1.50	65	60.0	58.0
15	1.25	66	59.5	58.5
20	1.00	67	60.0	59.0
25	1.10	67	60.0	59.0
30	1.05	69	60.0	59.5
35	0.90	70	60.5	60.0
40	1.00	72	60.5	60.0
45	0.80	71	60.5	60.0
50	0.75	71	61.0	60.0
55	1.25	76	61.5	60.5
60	1.15	74	61.0	60.5
Av.	1.03	68		

TABLE XVI

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 60°C

Vol. of Waste - 250 cc
Wt. of Waste - 280 gm
Wt. of NOCl - 10.78 gm
Absorbing Time - 90 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	1.31	53	59.0	59.0
5	1.25	58	60.0	59.0
10	1.00	48	61.0	59.0
15	0.85	45	60.5	59.0
20	1.50	52	61.0	59.0
25	0.95	50	61.0	59.0
30	0.95	52	61.0	59.0
35	0.95	54	61.0	59.0
40	0.75	54	61.0	59.0
45	1.00	57	58.0	56.5
50	1.00	58	58.0	57.0
55	1.05	60	58.5	57.0
60	0.95	62	59.0	59.0
65	1.00	63	59.5	59.0
70	1.05	65	60.0	59.0
75	1.25	66	60.0	59.0
80	0.60	65	60.5	59.5
85	0.75	66	60.0	59.5
90	0.75	68	60.5	59.5
Av.	1.00	57		

TABLE XVII

Data Sheet on Absorption of Nitrosyl Chloride in Solvay Waste
at Approximately 60°C

Vol. of Waste - 250 cc
Wt. of Waste - 280 gm
Wt. of NOCl - 13.10 gm
Absorbing time - 120 min.

Time (Min)	Manometer Reading (in)HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	1.25	39	58.5	61.0
5	0.55	46	60.0	60.5
10	1.05	49	60.0	60.0
15	1.05	51	59.0	58.5
20	1.00	52	58.0	58.0
25	0.90	54	58.5	59.0
30	0.80	57	59.0	60.0
35	1.00	57	59.5	61.0
40	1.00	60	60.0	59.0
45	1.00	60	59.0	58.5
50	0.85	60	59.5	59.0
55	1.00	62	59.0	59.0
60	1.00	63	59.5	59.0
65	0.90	63	59.0	59.5
70	0.90	66	60.0	61.0
75	1.10	68	60.5	59.5
80	0.90	68	59.5	59.0
85	1.00	71	59.5	59.5
90	0.90	70	60.5	61.0
95	0.90	72	60.5	60.0
100	0.80	73	60.0	59.0
105	1.00	74	58.0	58.5
110	1.00	75	58.5	59.0
115	0.75	75	58.5	60.0
120	0.75	82	59.5	60.0
AV.	0.93	65		

TABLE XVIII

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 80°C

Vol. of Waste - 250 cc
Wt. of Waste - 280 gm
Wt. of NOCl - 2.04 gm
Absorbing Time - 15 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	1.25	34	78.5	82
2	0.95	32	79.0	82
4	1.15	33	80.0	81
6	1.05	33	80.0	80
8	1.05	33	79.5	80
10	0.95	34	79.5	80
12	1.00	36	79.0	80
14	1.00	38	79.5	80
Av.	1.05	34		

TABLE XIX

Data Sheet on Absorption of Nitrosyl Chloride in Solvay Waste at Approximately 80°C

Vol. of Waste - 250 cc
Wt. of Waste - 280 gm
Wt. of NOCl - 3.62 gm
Absorbing time - 30 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	1.00	58	78.0	81.0
3	1.15	43	79.0	81.0
6	1.00	45	79.5	81.0
9	1.15	47	79.0	80.0
12	0.85	48	78.0	79.0
15	0.95	49	77.0	79.0
18	0.85	49	77.0	79.0
21	0.95	52	77.0	79.0
24	1.00	53	77.5	79.5
27	0.90	57	78.0	80.0
30	1.10	57	79.0	80.0
Av.	0.99	49		

TABLE IX

Data Sheet on Absorption of Nitrosyl Chloride in Solvay

Waste at Approximately 80°C

Vol. of Waste - 250 cc
 Wt. of Waste - 280 gm
 Wt. of NOCl - 6.68 gm
 Absorbing time - 60 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	0.95	48	80.0	83.0
5	1.00	48	81.0	83.0
10	1.00	50	82.0	83.0
15	0.85	52	81.5	83.0
20	1.00	52	81.0	81.0
25	0.75	54	78.5	78.0
30	0.90	57	77.0	78.0
35	1.20	58	76.5	78.5
40	1.00	62	76.5	79.0
45	0.90	64	78.0	80.0
50	1.00	65	79.0	80.5
55	0.95	66	80.0	82.5
60	1.05	66	80.5	82.0
Av.	0.95	57		

TABLE XXI

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 80°C

Vol. of Waste - 250 cc
Wt. of Waste - 280 gm
Wt. of NOCl - 10.53 gm
Absorbing time - 90 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	1.25	59	81.3	82.0
5	0.75	63	82.0	81.0
10	0.95	65	82.0	82.0
15	1.00	66	82.0	82.0
20	1.50	67	81.0	82.0
25	1.10	68	80.0	82.0
30	0.90	68	79.0	80.0
35	0.90	68	79.5	81.0
40	0.95	69	80.5	82.0
45	1.00	70	79.5	81.0
50	1.00	70	80.0	81.5
55	0.80	73	80.0	81.5
60	0.75	73	80.5	82.0
65	1.25	80	80.5	81.0
70	0.55	73	80.5	82.0
75	1.00	75	80.5	81.0
80	1.20	78	80.5	82.0
85	1.30	81	80.0	81.0
90	1.25	79	80.0	80.0
Av.	1.02	71		

TABLE XXII

Data Sheet on Absorption of Nitrosyl Chloride in Solvay Waste
at Approximately 90°C

Vol. of Waste - 250 cc
Wt. of Waste - 280 gm
Wt. of NOCl - 14.11 gm
Absorbing Time - 120 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)	Heating Water Temp. (°C)
0	1.00	42	79.5	83.0
5	1.70	48	81.0	81.5
10	1.00	43	80.0	79.0
15	0.95	47	78.5	79.0
20	1.00	51	78.5	80.0
25	1.05	54	79.0	80.5
30	1.00	55	80.0	81.0
35	1.00	58	80.5	82.0
40	1.05	60	80.0	80.0
45	1.10	62	79.5	80.0
50	0.85	65	79.0	80.0
55	0.85	65	79.5	80.0
60	1.05	67	80.0	81.0
65	0.95	68	80.5	82.0
70	1.15	69	80.5	80.0
75	1.15	70	79.0	79.5
80	1.25	72	79.0	80.0
85	1.20	71	79.0	80.0
90	0.75	71	80.0	81.0
95	0.85	75	81.0	81.5
100	0.80	75	80.0	80.0
105	1.00	76	79.0	79.0
110	1.10	78	79.0	79.0
115	1.20	81	80.0	80.0
120	0.50	75	81.0	80.0
Av.	1.01	64		

Tables III to XXII give the necessary data for calculating the amount of chlorine recoverable from nitrosyl chloride at various reacting times, which results are recorded in Tables XXIII to XXIV inclusive. By reacting time is meant the length of time that the nitrosyl chloride was bubbled through the waste. The reacting time, in each case, was taken from Tables III to XXII. The manometer readings were also taken from Tables III to XXII.

The volume of nitrosyl chloride through the manometer was determined by taking from the manometer calibration curve shown in figure 2, the volume of nitrosyl chloride per minute corresponding to the average manometer reading. This value was then multiplied by the length of the run to determine the volume of nitrosyl chloride reacting. This volume must be corrected for temperature and pressure.

The temperature of the nitrosyl chloride was taken as the average of the corresponding readings in tables III to XXII. From this temperature and the barometric pressure, the theoretical density of the nitrosyl chloride was calculated. This value of density multiplied by the volume gives the amount of nitrosyl chloride through the manometer which is also the weight of nitrosyl chloride reacting.

The total chlorine in the unreacted waste was determined by multiplying the weight of nitrosyl chloride by the theoretical percentage of chlorine.

The weight of waste was determined by multiplying the density of the waste by the volume.

The weight of chlorine in the unreacted waste was determined by multiplying the weight of waste by the per cent chlorine in the unreacted waste.

The weight of chlorine in the reacted waste was determined by multiplying the weight of waste by the per cent chlorine in the reacted waste as determined from analysis. The difference between these values gives the weight of chlorine absorbed in the waste. The weight of chlorine absorbed subtracted from the weight of chlorine in the nitrosyl chloride which reacted gives the quantity of chlorine liberated as free chlorine and represents the chlorine in the nitrosyl chloride recoverable as free chlorine.

Tables XXIII to XXVI may be taken as an indication of the chlorine recoverable from the nitrosyl chloride as free chlorine. The chlorine absorbed may be either in the form of chlorides or as hydrochloric acid. If this be the case, the addition of oxides of nitrogen should liberate more chlorine. Consequently, Tables XXIII to XXVI do not necessarily mean that the chlorine absorbed by the waste is not recoverable. The tables do, however, indicate that approximately 40 per cent of the chlorine in the nitrosyl chloride may be recovered as free chlorine by the action of the oxides of nitrogen produced by the decomposition of nitrosyl chloride alone and the remainder converted into some chloride.

TABLE XXIII

Effect of Reacting Time on Chlorine Recoverable from Nitrooyl Chloride
at Approximately 28°C

Run No.	I	II	III	IV	V
Reacting Time (Min)	15	30	60	90	120
Manometer Reading (in-HCl)	0.96	0.89	1.00	0.99	0.93
Vol. of NOCl thru Manometer (Liters)	0.76	1.41	3.18	4.70	5.76
Temp. of NOCl (°C)	40	53	59	72	62
Barom. Press. (mm-Hg)	713	713	713	713	714
Density of NOCl (g/l)	2.39	2.29	2.25	2.17	2.24
Wt. of NOCl thru Manometer (gm)	1.81	3.23	7.15	10.19	12.90
Total Chlorine in NOCl(gm)	0.98	1.75	3.88	5.53	7.00
Wt. of Waste (gm)	560	560	560	560	280
Rel. Conc. as gram NOCl per 1000 gm Waste per hour	12.7	11.5	12/7	11.9	23.0
Wt. of Chlorine in unreacted Waste (gm)	42.89	42.89	43.29	42.89	21.64
Wt. of Chlorine in reacted Waste (gm)	43.24	43.51	45.86	46.51	26.12
Chlorine Absorbed in Waste(gm)	0.45	0.62	2.57	3.02	4.45
Recoverable Chlorine (gm)	0.43	1.13	1.51	2.51	2.55
Percent Recoverable Chlorine	43.8	64.6	53.7	45.4	36.4

TABLE XXIV

Effect of Reacting Time on Chlorine Recoverable from Nitrosyl Chloride at
Approximately 40°C

Run No.	I	II	III	IV	V
Reacting Time (Min)	15	30	60	90	120
Manometer Reading (in-HCl)	1.06	1.00	0.97	0.97	0.95
Vol. of NOCl thru Manometer (Liters)	0.80	1.59	3.06	4.59	6.00
Temp. of NOCl (°C)	64	74	56	76	62
Barom. Press. (mm-Hg)	714	714	715	715	717
Density of NOCl (g/l)	2.29	2.22	2.28	2.17	2.25
Wt. of NOCl thru Manometer (gm)	1.83	3.54	6.89	9.96	13.50
Total Chlorine in NOCl (gm)	0.97	1.92	3.79	5.40	7.52
Wt. of Waste (gm)	560	560	560	560	290
Rel. Conc. as gram NOCl per 1000 gm Waste Per hour	13.0	12.6	12.5	11.8	27.6
Wt. of Chlorine in unreacted Waste (gm)	43.29	43.29	43.29	43.29	21.64
Wt. of Chlorine in reacted Waste (gm)	43.90	44.24	43.53	43.80	25.68
Chlorine Absorbed in Waste(gm)	0.61	0.95	2.24	2.51	4.04
Recoverable Chlorine (gm)	0.36	0.97	1.55	2.89	3.28
Percent Recoverable Chlorine	57.1	50.1	40.9	53.5	44.8

TABLE XXV

Effect of Reacting Time on Chlorine Recoverable from Nitrosyl Chloride at
Approximately 60°C

Run No.	I	II	III	IV	V
Reacting Time (Min)	15	30	60	90	120
Manometer Reading (in-HCl)	0.94	0.95	1.03	1.00	0.93
Vol. of NOCl thru Manometer (Liters)	0.74	1.30	3.18	4.77	5.88
Temp. of NOCl (°C)	38	52	68	57	65
Barom. Press. (mm-Hg)	715	715	715	712	712
Density of NOCl (g/l)	2.41	2.39	2.20	2.26	2.22
Wt. of NOCl thru Manometer (gm)	1.78	3.89	7.00	10.78	13.10
Total Chlorine in NOCl (gm)	0.96	1.94	3.79	5.85	7.09
Wt. of Waste (gm)	280	280	280	280	280
Rel. Conc. as gram NOCl per 1000 gm Waste per hour	25.4	25.6	25.0	24.7	23.4
Wt. of Chlorine in unreacted Waste (gm)	21.64	21.64	21.64	21.64	21.64
Wt. of Chlorine in reacted Waste (gm)	21.50	22.48	24.05	24.67	25.79
Chlorine Absorbed in Waste (gm)	0.00	0.84	2.41	3.03	4.15
Recoverable Chlorine (gm)	1.10	1.14	1.38	2.82	2.94
Percent Recoverable Chlorine	—	58.7	36.9	48.2	41.5

TABLE XXVI

Effect of Reacting Time on Chlorine Recoverable from Nitrosyl Chloride at
Approximately 80°C

Run No.	I	II	III	IV	V
Reacting Time (Min)	15	30	60	90	120
Manometer Reading (in-HCl)	1.05	0.99	0.96	1.02	1.01
Vol. of NOCl thru Manometer (Liters)	0.84	1.57	3.05	4.86	6.36
Temp. of NOCl (°C)	34	49	57	71	64
Barom. Press. (mm-Hg)	710	710	712	712	713
Density of NOCl (g/l)	2.43	2.31	2.26	2.17	2.22
Wt. of NOCl thru Manometer (Gm)	2.04	3.62	6.86	10.53	14.11
Total Chlorine in NOCl (gm)	1.11	1.96	3.22	5.73	7.65
Wt. of Waste (gm)	280	280	280	280	280
Rel. Conc. as gram NOCl per 1000 gm waste per hour	29.1	25.9	24.5	25.2	25.2
Wt. of Chlorine in unreacted Waste (gm)	21.64	21.64	21.64	21.64	21.64
Wt. of Chlorine in reacted Waste (gm)	21.73	22.62	23.10	25.00	25.34
Chlorine Absorbed in Waste (gm)	0.09	1.18	1.46	3.36	3.70
Recoverable Chlorine (gm)	1.02	0.78	1.76	2.37	3.95
Percent recoverable Chlorine	—	39.8	54.7	41.4	51.6

Effect of Temperature. Tables XXVII to XXXI inclusive are taken from Tables XXIII to XXVI in order to show more clearly the effect of temperature on the chlorine recoverable from nitrosyl chloride. Each table is for some constant time of absorption with the temperature as the variable. The percentage recoverable chlorine in Table XXVII for 60° and 80°C was considerably higher than the percentages found for longer periods of absorption and were evidently in error. It is believed that this error may largely be attributed to errors in determining the chlorides in the reacted waste and in reading the manometer.

Tables XXVII to XXXI indicate for comparative purposes the chlorine recoverable and the percentage chlorine recoverable as free chlorine at approximately 28°, 30°, 60°, and 80°C and absorbing times of 15, 30, 60, 90 and 120 minutes. These tables seem to indicate that temperature has little effect on the quantity of chlorine recoverable from nitrosyl chloride since there is no consistent noticeable change in either the quantity of chlorine or the percentage chlorine recoverable in either of Tables XXVII to XXXI.

This belief is further substantiated by figure 3 which is a plot of reacting temperature against recoverable chlorine. Figure 3 also shows the total chlorine present in the nitrosyl chloride.

Figure 3 then, shows a tendency towards only a very slight increase in recoverable chlorine with temperature. This plot does show that there is a considerable increase in recoverable chlorine with an increase in absorbing time.

TABLE XXVII

Effect of Temperature on Chlorine Recoverable from Nitrosyl Chloride
(Reacting Time-15 Min.)

Approx. Reacting Temp. (°C)	NOCl Reacting (gm)	Total Chlorine in NOCl (gm)	Recoverable Chlorine (gm)	Percentage Recoverable Chlorine
26.5	1.81	0.98	0.43	43.8
40.0	1.83	0.97	0.36	37.1
60.0	1.78	0.96	1.10	-----
80.0	2.04	1.11	1.02	-----

TABLE XXVIII

Effect of Temperature on Chlorine Recoverable from Nitrosyl Chloride
(Reacting Time-30 Min)

Approx. Reacting Temp. (°C)	NOCl Reacting (gm)	Total Chlorine in NOCl (gm)	Recoverable Chlorine (gm)	Percentage Recoverable Chlorine
26.5	3.23	1.75	1.13	64.6
40.0	3.54	1.92	0.97	50.1
60.0	3.59	1.94	1.14	58.7
80.0	3.62	1.96	0.78	39.8

TABLE XXIX

Effect of Temperature on Chlorine Recoverable from Nitrosyl Chloride
(Reacting time - 60 Min)

Approx. Reacting Temp. (°C)	NOCl Reacting (gm)	Total Chlorine in NOCl (gm)	Recoverable Chlorine (gm)	Percentage Recoverable Chlorine
29	7.15	3.88	1.31	33.7
40	6.98	3.79	1.33	40.9
60	7.00	3.79	1.38	36.9
80	6.86	3.22	1.76	54.7

TABLE XXX

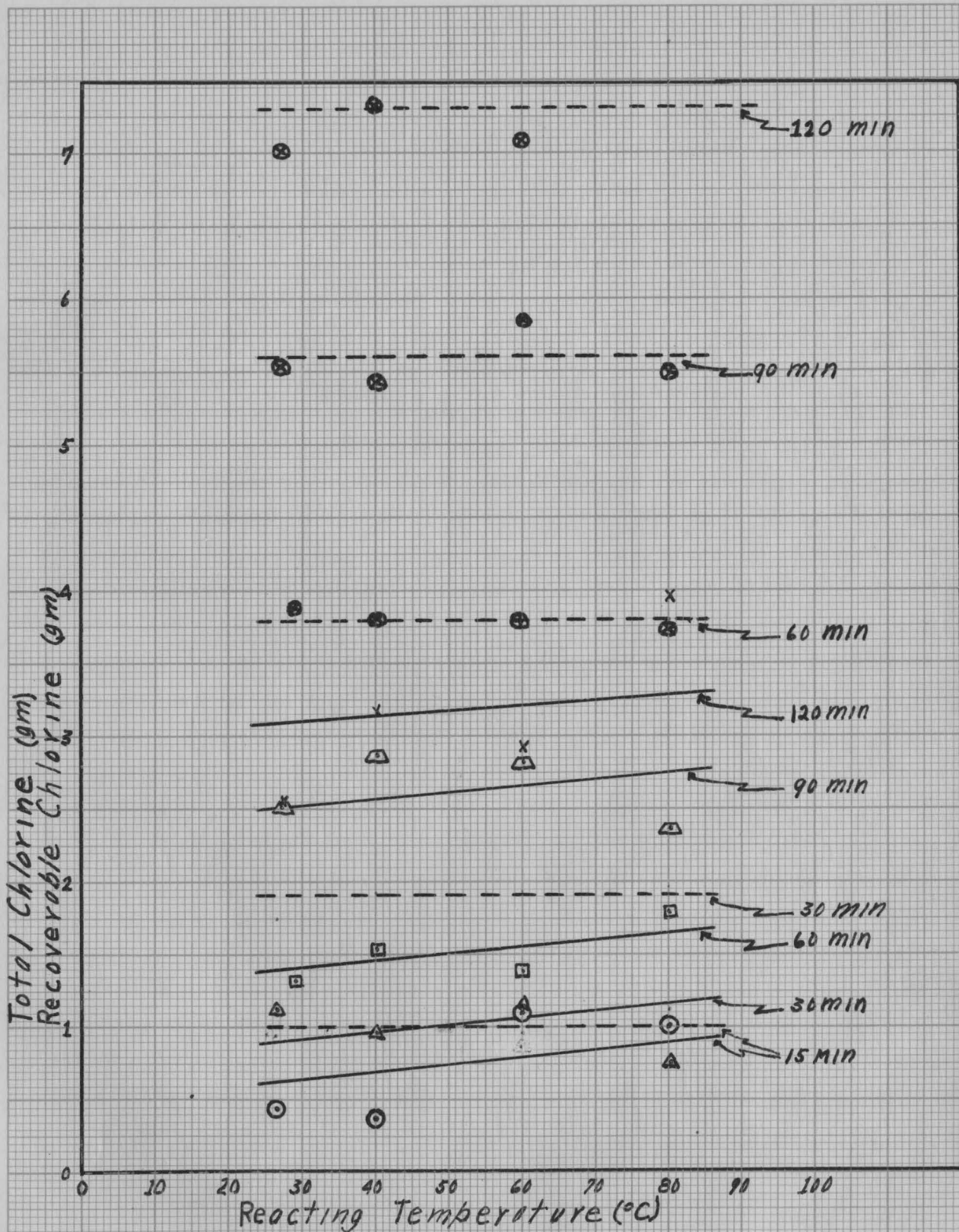
Effect of Temperature on Chlorine Recoverable from Nitrosyl Chloride
(Reacting time-90 Min)

Approx. Reacting Temp. (°C)	NOCl Reacting (gm)	Total Chlorine in NOCl (gm)	Recoverable Chlorine (gm)	Percentage Recoverable Chlorine
27	10.19	5.53	2.51	45.4
40	19.96	5.85	2.82	53.5
60	10.75	5.85	2.82	48.2
80	10.53	5.73	2.37	41.4

TABLE XXXI

Effect of Temperature on Chlorine Recoverable from Nitrosyl Chloride
(Treating time-120 Min)

Approx. Reacting Temp. (°C)	NOCl Reacting (gm)	Total Chlorine in NOCl (gm)	Recoverable Chlorine (gm)	Percentage Recoverable Chlorine
27	12.90	7.00	2.55	36.4
40	13.50	7.33	3.28	44.8
60	13.10	7.09	2.94	41.5
80	14.11	7.65	3.95	51.6



Effect of Temperature on Chlorine Recoverable from Nitrosyl Chloride

○ 15 min	— Recoverable Chlorine
△ 30 min	
□ 60 min	- - - Total Chlorine
◇ 90 min	
× 120 min	

Fig 3

Effect of Absorbing or Reacting Time. Tables XXXII to XXXV inclusive are taken from Tables XXIII to XXVI to more clearly show the effect of reacting time on chlorine recoverable from nitrosyl chloride. In these tables the temperature is considered as the constant and the time of reaction as varying. By the time of reaction is meant the time that the nitrosyl chloride was bubbled through the waste.

Tables XXXII to XXXV indicate that the weight of chlorine recoverable from nitrosyl chloride increases with the absorbing time. While, again, the percentage recoverable chlorine varies somewhat, there is no consistent tendency toward either a decrease or increase with absorbing time in the percentage recoverable chlorine.

Figure 4 further substantiates the belief that the weight of recoverable chlorine increases with reacting time. Figure 4 is a plot of reacting time against recoverable chlorine and also shows the total chlorine present in the nitrosyl chloride.

This plot indicates a tendency toward an increase in the chlorine recoverable as free chlorine with an increase in reacting time. Figure 4 also indicates that reacting temperature has little effect on recoverable chlorine.

Thus, the results seem to indicate that the time the nitrosyl chloride is reacted with the waste increases the amount of recoverable chlorine but does not materially affect the percentage recoverable chlorine. The foregoing results also seem to indicate that the reacting temperature has very little effect on either the quantity of chlorine recoverable from nitrosyl chloride or the percentage chlorine recoverable from the nitrosyl chloride.

In the foregoing results, by recoverable chlorine is meant only that

chlorine which is liberated as free chlorine in the reaction between nitrosyl chloride and Solvay waste. Based on the results given, there is positive evidence that the nitrosyl chloride is first decomposed into some chloride and oxides of nitrogen. In order for any chlorine to be set free there must have been some nitric acid produced by the nitrosyl chloride which reacted with the chlorides in solution. Thus, the above results not only indicate tendencies in the reaction with respect to reacting time and temperature but they also indicate at least a partial utilization of the oxides of nitrogen in the nitrosyl chloride.

TABLE XXXII

Effect of Reacting Time on Chlorine Recoverable from Nitrosyl
Chloride at Approximately 28°C

Reacting Time (Min)	Reacting Temp. (°C)	NOCl Reacting (gm)	Total Chlorine in NOCl (gm)	Recoverable Chlorine (gm)	Percent Recoverable Chlorine
15	26.5	1.81	0.98	0.43	43.8
30	26.5	5.23	1.75	1.13	64.6
60	29.0	7.15	5.88	1.31	33.7
90	27.0	10.19	5.53	2.51	45.4
120	27.0	12.90	7.00	2.55	36.4

TABLE XXXIII

Effect of Reacting Time on Chlorine Recoverable from Nitrosyl Chloride at
Approximately 40°C

Reacting Time (Min)	NOCl Reacting (gm)	Total Chlorine In NOCl (gm)	Recoverable Chlorine (gm)	Percent Recoverable Chlorine
15	1.83	0.97	0.36	37.1
30	3.54	1.92	0.97	50.1
60	6.98	3.79	1.55	40.9
90	9.96	5.40	2.89	53.5
120	13.50	7.32	3.28	44.8

TABLE XXXIV

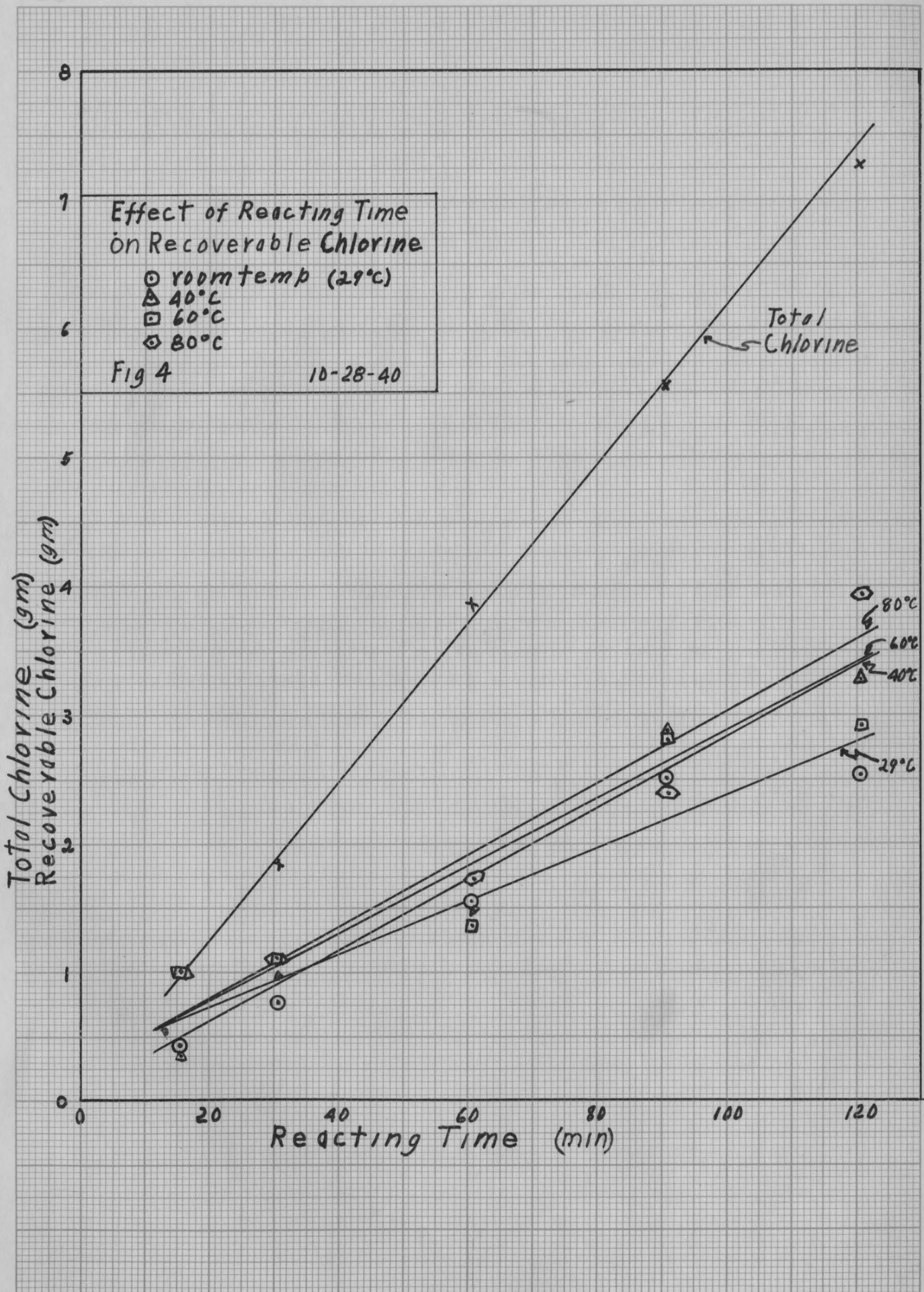
Effect of Reacting Time on Chlorine Recoverable From Nitrosyl Chloride at
Approximately 60°C

Reacting Time (Min)	NOCl Reacting (gm)	Total Chlorine in NOCl (gm)	Recoverable Chlorine (gm)	Percent Recoverable Chlorine
15	1.78	0.96	1.10	
30	3.59	1.94	1.14	58.7
60	7.00	3.79	1.38	36.9
90	10.78	5.85	2.82	48.2
120	13.10	7.09	2.94	41.5

TABLE XXXV

Effect of Reacting Time on Chlorine Recoverable from Nitrosyl Chloride at
Approximately 80°C

Reacting Time (Min)	NOCl Reacting (gm)	Total Chlorine in NOCl (gm)	Recoverable Chlorine (gm)	Percent Recoverable Chlorine
15	2.04	1.11	1.02	—
30	3.62	1.96	0.78	39.8
60	6.86	3.22	1.76	54.7
90	10.53	5.73	2.37	41.4
120	14.11	7.65	3.95	51.6



Effect of Relative Concentration of Nitrosyl Chloride and Solvay Waste on Recoverable Chlorine. Tables XXXVI to XL inclusive give the laboratory data taken while making runs using different quantities of waste and approximately the same quantity of nitrosyl chloride for each run.

At the top of each table, there is given the volume and weight of waste used in that run as well as the weight of nitrosyl chloride reacting. The other data was taken in the same manner, as that in Tables III to XXII.

Table XLI gives the results calculated from Tables XXXVI to XL. Each column in Table XLI was calculated in the same manner as those of Tables XXIII to XXVI.

Table XLI indicates that the quantity of recoverable chlorine as well as the percentage recoverable chlorine is constant for varying relative concentrations of nitrosyl chloride and waste.

Table XLII was compiled from Table XLI in order to better show the effect of relative concentration on recoverable chlorine. It will be noticed that at a relative concentration of 17.88 grams of nitrosyl chloride per 1000 grams waste per hour, the percentage recoverable chlorine is much lower than for any other concentration. It was noticed that during this run, the nitrosyl chloride temperature was rather high (83°C). At an increased temperature, the nitrosyl sulfuric acid and salt begin to produce large quantities of hydrogen chloride which will be absorbed in the waste as hydrochloric acid without the liberation of any chlorine. This increases the chlorine in the waste which in turn decreases the percentage recoverable chlorine.

Figure 5 is a plot of relative concentration as grams nitrosyl chloride per 1000 grams waste per hour against recoverable chlorine. This plot

also shows the total chlorine present in the nitrosyl chloride which reacted.

Figure 5 further tends to substantiate the statement that the relative concentration of nitrosyl chloride and Solvay waste has little or no effect on the chlorine recoverable from nitrosyl chloride.

TABLE XXXVI

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 30°C

Vol. of Waste - 100 cc
Wt. of Waste - 112 gm
Wt. of NOCl - 6.90 gm
Absorbing time - 60 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)
0	0.85	60	34.5
5	1.05	66	38.0
10	0.85	68	39.5
15	1.05	69	39.0
20	1.05	70	39.0
25	0.80	71	39.0
30	1.50	71	39.0
35	1.05	73	39.5
40	0.75	73	39.5
45	1.00	75	39.5
50	1.25	74	39.5
55	0.85	76	39.5
60	0.95	77	40.0
Av.	1.00	68	

TABLE XXXVII

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 34°C

Vol. of Waste - 200 cc
Wt. of Waste - 224 gm
Wt. of NOCl - 5.58 gm
Absorbing time - 60 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)
0	1.00	42	34.0
5	0.90	41	37.5
10	0.85	49	38.5
15	1.00	54	37.5
20	0.85	57	38.0
25	1.10	59	38.5
30	1.00	62	38.5
35	1.25	64	38.5
40	1.25	67	38.75
45	1.00	68	39.0
50	0.80	68	39.0
55	1.05	71	39.0
60	0.70	77	39.0
Av.	0.97	51	

TABLE XXXVIII

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 32°C

Vol. of Waste - 300 cc
Wt. of Waste - 536 gm
Wt. of NOCl - 5.98 gm
Absorbing time - 60 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)
0	0.65	74	32.0
5	1.00	74	33.5
10	0.95	74	34.5
15	0.90	76	35.5
20	1.10	81	35.5
25	1.10	82	36.0
30	1.10	81	36.5
35	1.25	78	36.5
40	0.80	76	37.0
45	0.55	75	37.0
50	0.85	76	37.0
55	1.25	83	37.5
60	0.90	93	38.0
Av.	0.90	83	

TABLE XXXIX

Data Sheet on Absorption of Nitrosyl Chloride in Solvay Waste
At Approximately 29° C Temperature

Vol. of Waste - 600 cc
Wt. of Waste - 672 gm
Wt. of NOCl - 7.35 gm
Approx. React. Temp. - 29°C
Absorbing time - 60 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)
0	1.50	34	29.5
5	0.95	36	30.5
10	1.00	39	31.0
15	0.70	43	32.0
20	1.00	47	32.0
25	0.90	50	32.5
30	1.00	52	33.0
35	0.90	54	33.0
40	1.10	56	33.5
45	1.35	58	34.0
50	0.95	58	34.0
55	0.95	58	34.5
60	0.90	61	34.5
Av.	1.01	61	

TABLE XL

Data Sheet on Absorption of Nitrosyl Chloride in Solvay
Waste at Approximately 29°C

Vol. of Waste - 1000 cc
Wt. of Waste - 1120 gm
Wt. of NOCl - 6.38 gm
Approx. React. Time - 29°C
Absorbing time - 60 min.

Time (Min)	Manometer Reading (in-HCl)	NOCl Temp. (°C)	Waste Temp. (°C)
0	0.90	58	29.0
5	0.90	61	29.5
10	1.15	66	30.0
15	1.10	68	30.5
20	1.10	67	31.0
25	1.25	68	31.5
30	0.75	67	31.5
35	0.80	69	32.0
40	0.80	68	32.0
45	1.00	70	32.0
50	1.15	73	32.5
55	0.60	72	32.5
60	0.60	73	32.5
Av.	0.92	72	

TABLE XLI

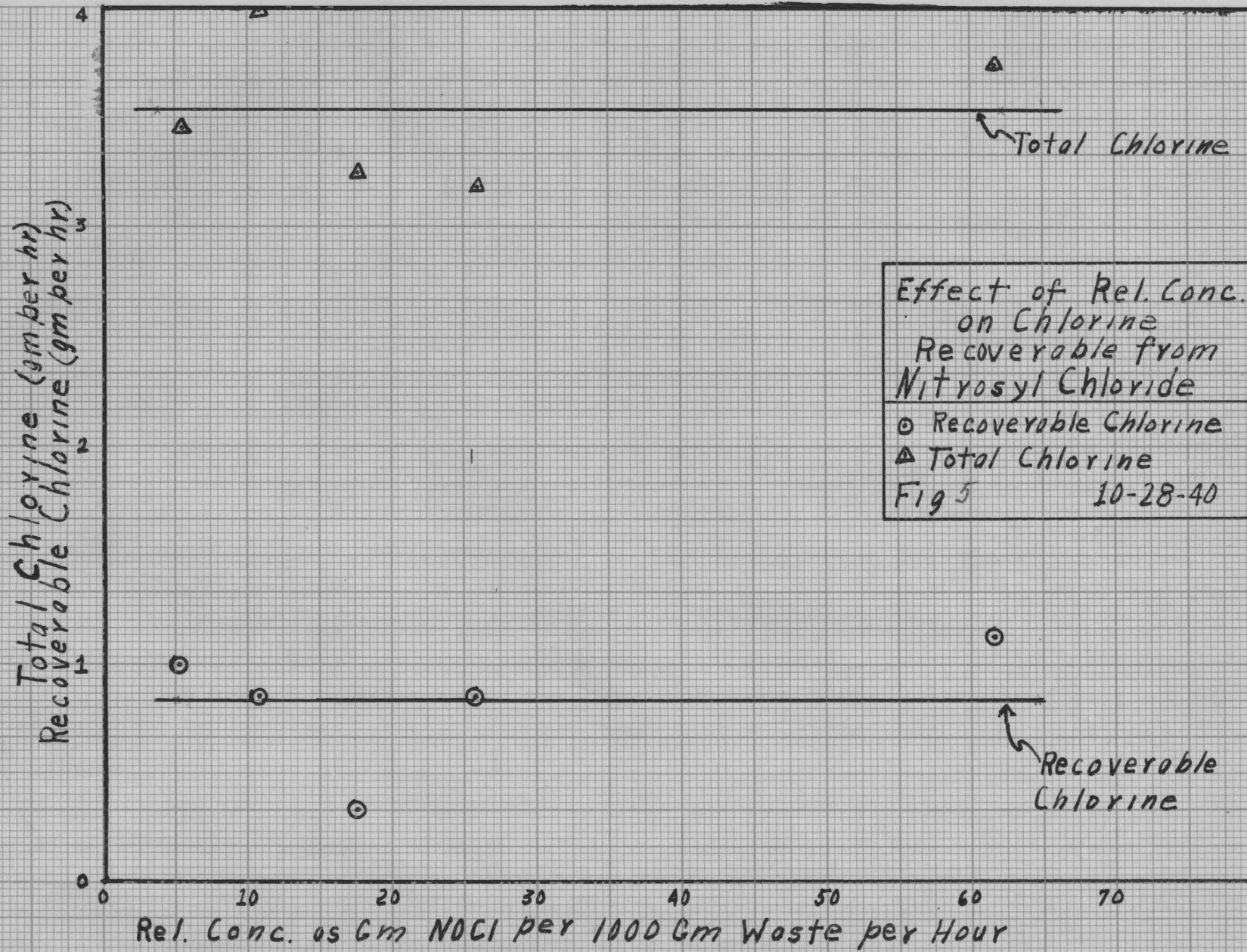
Effect of Relative Concentration of Nitrotyl Chloride on Chlorine Recoverable from Nitrotyl Chloride

Run No.	X	IX	VI	VII	VIII
Length of Run(Min)	60	60	60	60	60
Manometer Reading (in-HCl)	0.98	1.01	0.90	0.97	1.00
Vol. NOCl thru Manometer (Liters)	2.91	3.18	2.85	3.06	3.16
Temp. of NOCl (°C)	68	51	83	61	72
Barom. Press.(Mm-Hg)	714	714	712	712	712
Density of NOCl (G/L)	2.19	2.31	2.10	2.24	2.17
Wt. of NOCl Thru Manometer (Gm)	6.38	7.35	5.98	5.85	6.90
Rel. Conc. as Gm. NOCl per 1000 gm. Waste per Hr.	5.70	10.98	17.88	25.98	61.68
Total Chlorine in NOCl (gm)	3.46	3.98	3.24	3.17	3.74
Vol. of Waste (cc)	1000	600	300	200	100
Wt. of Waste(gm)	1120	672	336	224	112
Wt. of Chlorine in Reacted Waste (gm)	89.04	55.10	28.89	19.63	11.27
Wt. of Chlorine in Unreacted Waste (gm)	86.57	51.94	25.97	17.32	8.66
Chlorine Absorbed in Waste (gm)	2.47	3.16	2.92	2.31	2.61
Recoverable Chlorine (gm)	0.99	0.82	0.32	0.86	1.13
Percentage Recoverable Chlorine	28.6	20.6	9.9	27.1	30.2

TABLE XLII

Effect of Relative Concentration of Nitrosyl Chloride and Solvay Waste on Chlorine Recoverable from Nitrosyl Chloride

Rel. Conc. as Gm. NOCl per 1000 gm Waste per Hr.	Approx. Reacting Temp. (°C)	NOCl Reacting (gm)	Total Chlorine in NOCl (gm)	Recoverable Chlorine (gm)	Percentage Recoverable Chlorine
5.70	34	6.38	3.46	0.99	28.6
10.98	34	7.35	3.98	0.82	20.6
17.88	32	5.98	3.24	0.32	9.9
25.98	29	5.85	3.17	0.86	27.1
61.68	29	6.90	3.74	1.13	30.2



Effect of Rel. Conc.
 on Chlorine
 Recoverable from
 Nitrosyl Chloride
 ○ Recoverable Chlorine
 △ Total Chlorine
 Fig 5 10-28-40

Effect of Reacting Time on Carbonates and Bicarbonates. The effect of reacting time on the carbonates and bicarbonates contained in the waste is included in Tables XLIII to XLVI inclusive in the form of material balances across the reaction flasks. These tables also include a material balance on the insoluble material in the waste. The material balances were calculated by multiplying the percent of the material in the waste before and after reacting by the weight of waste used. The difference in each case was taken as the weight of that material reacting. The last two columns in each table give percent calcium and percent chlorine in the reacted waste. The calcium analyses were originally designed to determine the extent of volume change during the absorption of the nitrosyl chloride in the waste but due to the difficulty of sampling the waste because of insoluble material present no definite tendencies are indicated. Since the variation of percent calcium is not consistent, the general indication would be toward only a very slight volume change if any at all.

The acidity of the reacted waste is expressed as cc of 0.112 N sodium hydroxide required to titrate a 50 cc sample of the diluted waste using methyl orange indicator as described in the analytical procedure. Of course, as long as there are any carbonates or bicarbonates present, the reacted waste will be basic to methyl orange but as soon as all of these have reacted, the waste becomes acid. This means that the acidity is due to either hydrochloric or nitric acids or both. In general, it can be expected that the acidity can be attributed to the hydrochloric acid formed by the decomposition of the nitrosyl chloride.

TABLE XLIII

Effect of Reacting Time on Carbonates and Bicarbonates in Solvay Waste at
Approximately 28° C

Run No.	I	II	III	IV	V
Length of run (Min)	15	30	60	90	120
Wt. of thru Man. (gm)	1.81	3.23	7.13	10.19	21.90
Insoluble in Reacted Waste (%)	560	560	560	560	560
Insoluble in Reacted Waste (gm)	7.62	6.50	4.82	3.73	1.79
Insoluble in Unreacted Waste (gm)	7.62	7.62	7.62	7.62	7.62
Insoluble reacting (gm) Bicarbonate in Reacted Waste (%)	0.00	1.12	2.80	3.87	5.83
Bicarbonate in Reacted Waste (gm)	1.06	0.81	0.15	0.00	0.00
Bicarbonate in Unreacted Waste (gm)	5.94	4.54	0.84	0.00	0.00
Bicarbonate Reacting (gm)	4.93	4.93	4.93	4.93	4.93
Percent Chlorine in Reacted Waste	0.00	0.39	4.09	4.93	4.93
Acidity as cc 0.112 N NaOH to Titrate 50 cc Sample	7.74	7.77	8.19	8.27	9.33
Percent Ca in Reacted Waste	basic	basic	basic	1.4	2.5
	5.27	5.27	5.22	5.49	4.79

TABLE XLIV

Effect of Reacting Time on Carbonates and Bicarbonates in Solvay Waste at
Approximately 40°C

Run No.	XI	XII	XIII	XIV	XV
Length of Run (Min)	15	30	60	90	120
Wt. of thru Man.(gm)	1.83	3.54	6.98	9.96	12.50
Wt. of Waste (gm)	560	560	560	560	280
Insoluble in Reacted Waste (%)	1.28	1.23	0.59	0.72	0.42
Insoluble in Reacted Waste (gm)	7.17	6.89	3.30	4.03	1.17
Insoluble in Unreacted Waste (gm)	7.62	7.62	7.62	7.62	3.81
Insoluble reacting (gm) Bicarbonate in Reacted Waste (%)	0.45	0.73	4.32	3.59	2.64
Bicarbonate in Reacted Waste (gm)	1.29	1.03	0.43	0.00	0.00
Bicarbonate in Unreacted Waste (gm)	7.22	5.77	2.41	0.00	0.00
Bicarbonate Reacting (gm) Percent Chlorine in Reacted Waste	4.93	4.93	4.93	4.93	2.46
Increase in Chlorine Percent	0.00	0.00	2.52	4.93	2.46
Acidity as cc 0.112 N NaOH to Titrate 50 cc Sample	7.84	7.90	8.13	8.19	9.17
Percent Ca in Reacted Waste	0.11	0.17	0.40	0.46	1.44
	basic	basic	basic	0.4	
	5.34	5.09	4.65	4.79	5.12

TABLE XIV

Effect of Reacting Time on Carbonates and Bicarbonates in Solvay Waste at Approximately 60°C

Run No.	XVI	XVII	XVIII	XIX	XX
Length of Run (Min)	15	30	60	90	120
Wt. of thru Man. (gm)	1.78	3.59	7.00	10.78	13.10
Insoluble in Reacted Waste (%)	280	280	280	280	280
Insoluble in Reacted Waste (gm)	1.32	1.28	0.85	0.70	0.67
Insoluble in Unreacted Waste (gm)	3.69	3.32	2.38	1.96	1.82
Insoluble Reacting (gm)	0.12	0.23	2.45	1.83	1.93
Bicarbonate in Reacted Waste (gm)	1.51	0.81	0.00	0.00	0.00
Bicarbonate in Reacted Waste (%)	0.54	0.29	0.00	0.00	0.00
Bicarbonate in Unreacted Waste (gm)	2.44	2.44	2.44	2.44	2.44
Bicarbonate reacting (gm)	0.93	1.63	2.44	2.44	2.44
Percent Chlorine in Reacted Waste	7.68	8.03	8.59	8.81	9.21
Increase in Chlorine per cent	0.00	0.30	0.36	1.08	1.48
Acidity as cc 0.112 N NaOH to Titrate 50 cc Sample	basic	basic	1.6	6.6	10.5
Percent Ca in Reacted Waste	5.42	5.50	5.51	5.36	5.51

TABLE XVI

Effect of Reacting Time on Carbonates and Bicarbonates in Solvay Waste at
Approximately 80°C

Run No.	XXI	XXII	XXIII	XXIV	XXV
Length of run (Min)	15	30	60	90	120
Wt. of thru Man. (gm)	2.04	3.52	6.86	10.53	14.11
Wt. of Waste (gm)	280	280	280	280	280
Insoluble in Reacted Waste (%)	1.36	0.93	1.50	1.34	0.72
Insoluble in Reacted Waste (gm)	3.81	2.60	4.20	3.75	2.02
Insoluble in Unreacted Waste (gm)	3.81	3.81	3.81	3.81	3.81
Insoluble reacting (gm)	0.00	1.21	0.00	0.06	1.79
Bicarbonate in Reacted Waste (%)	0.59	0.34	0.00	0.00	0.00
Bicarbonate in Reacted Waste (gm)	1.65	0.95	0.00	0.00	0.00
Bicarbonate in Unreacted Waste (gm)	2.44	2.44	2.44	2.44	2.44
Percent Chlorine in Reacted Waste	7.76	8.15	8.25	8.93	9.05
Increase in Chlorine Percent	0.03	0.42	0.52	1.20	1.32
Acidity as cc 0.112 N NaOH to Titrate 50 cc Sample	basic	basic	0.3	5.8	7.8
Per cent Ca in Reacted Waste	5.73	5.75	5.42	5.65	5.59

Effect of Relative Concentration on Carbonates and Bicarbonates.

Table XLVII shows the effect of relative concentration of nitrosyl chloride and waste on the carbonates and bicarbonates in the waste. The table was calculated in a similar manner to Tables XLIII to XLVI. This table shows that the carbonates and bicarbonates are more quickly decomposed as the relative concentration increases.

This table also shows that the waste may be expected to decompose the nitrosyl chloride for a considerable time after the carbonates and bicarbonates have disappeared since the solution continues to become acid. This acidity very probably is due to the hydrochloric acid formed in decomposing the nitrosyl chloride.

TABLE XLVII

Effect of Relative Concentration on Carbonates and Bicarbonates in Solvay Waste

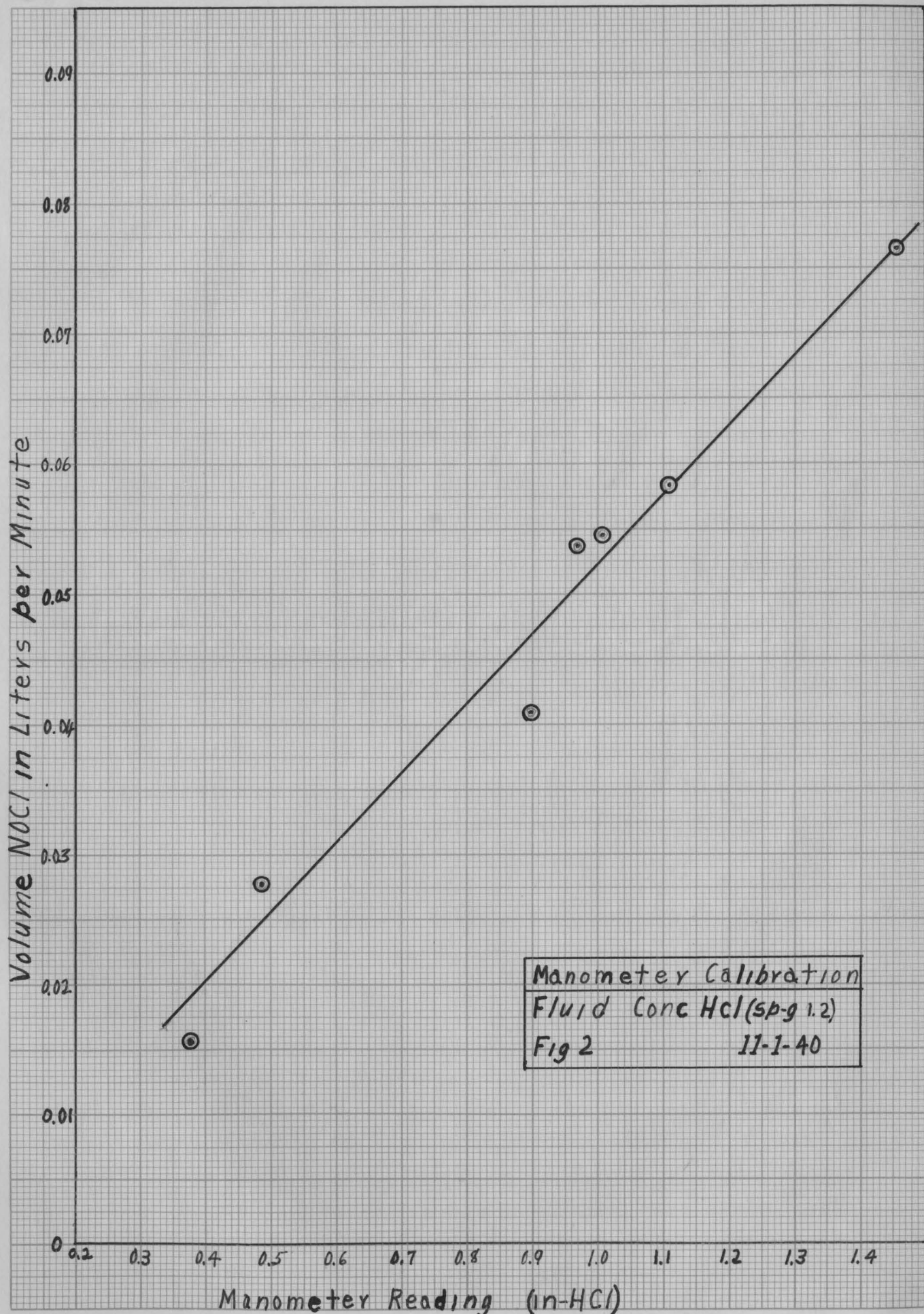
Run No.	X	IX	VI	VII	VIII
Length of Run (Min)	60	60	60	60	60
Wt. of NOCl thru Manometer (in-HCl)	6.38	6.35	5.98	5.85	6.90
Wt. of Waste (Gm)	1120	672	336	224	112
Rel. Conc. as Gm. NOCl per 1000 gm. Waste per Hr.	5.70	10.98	17.88	25.98	61.68
Insoluble in Reacted Waste (%)	0.93	0.87	0.40	0.60	0.62
Insoluble in Reacted Waste (Gm)	10.42	5.85	1.34	1.34	0.69
Insoluble in Unreacted Waste (Gm)	15.23	9.14	4.57	3.05	1.52
Insoluble reacting (Gm) Bicarbonate in Reacted Waste (%)	4.81	3.29	3.23	1.71	0.63
Bicarbonate in Reacted Waste (Gm)	0.90	0.62	0.00	0.00	0.00
Bicarbonate in Unreacted Waste (Gm)	10.03	4.17	0.00	0.00	0.00
Bicarbonate reacting (Gm)	9.86	5.91	2.96	1.97	0.98
Increase in Chlorides (%)	0.00	1.74	2.96	1.97	0.98
Acidity as cc 0.112 N NaOH to Titrate 50 cc Solution Calcium in Reacted Waste (%)	0.22	0.43	0.87	1.04	2.33
Chlorides in Reacted Waste (%)	basic	basic	2.0	7.2	17.0
Chlorides in Reacted Waste (%)	4.92	4.97	4.87	4.78	4.73
Chlorides in Reacted Waste (%)	7.95	8.20	8.60	8.72	10.06

Nitrites in Solution. Each run gave a positive test for nitrites on the addition of ferrous sulfate. This fact indicates that the nitrosyl chloride is being decomposed into nitrites. These nitrites are very probably nitrous acid. Nitrous acid is very unstable at ordinary temperatures and consequently in the few instances in which it was tried, no nitrite test could be obtained on samples of the reacted waste after standing a few days but a nitrate test could be obtained. This indicates at least nitric acid was present and very probably metallic nitrates since chlorine was liberated.

Corrosion Due to Nitrosyl Chloride. The results seem to indicate that the nitrosyl chloride is readily decomposed when in contact with Solvay waste. If, in order to produce chlorine, the reaction between oxides of nitrogen and Solvay waste is carried on in an absorption column, the nitrosyl chloride would be continually decomposed in the column by the feed solution to the column and the solution already present in the column. On the basis of the results obtained in this investigation, it would seem that the nitrosyl chloride should not exist as a gas in the reaction at all. If the nitrosyl chloride does exist in a free state, it should be for a very short time only and in very small quantities. Any free nitrosyl chloride in the column, if any were present, should be evenly distributed throughout the column and there should be no points of severe attack. However, it is believed that the nitrosyl chloride will not exist in the reaction column as such and if this be true, provision must be made only for wet chlorine.

Calibration of Manometer

The procedure for the calibration of the manometer was the same as that for absorbing nitrosyl chloride in Solvay Waste except that the nitrosyl chloride was reacted with distilled water instead of waste. Seven 15-minute runs were made at different readings of the manometer, each time absorbing the nitrosyl chloride in 500 cc of distilled water. Readings were taken as outlined under "Method of Procedure" and ten cubic centimeter samples of the water in which the nitrosyl chloride was absorbed titrated for chlorides. The total chlorides contained in 500 cc of water was determined and calculated as grams nitrosyl chloride per minute. By means of the ordinary gas laws, the volume of nitrosyl chloride flowing through the manometer per minute was calculated for each reading of the manometer. A calibration curve for the manometer was drawn as shown in figure 2.



IV. DISCUSSION

Preparation of Nitrosyl Chloride. One of the main difficulties in carrying out this investigation was that of making a sufficient quantity of nitrosyl chloride to react with the waste. It was necessary to use at least 250 cc of waste for the reaction. The highest rate that the nitrosyl chloride could be produced for any length of time was 0.03 to 0.06 liters per minute. In the shorter runs of 15 and 30 minutes, this corresponded to only about 1.5 grams of nitrosyl chloride in 15 minutes and only about 3.0 grams in 30 minutes. This produced an increase in the percentage chlorides of from only 0.2 to 0.4 per cent. The available chlorine in the nitrosyl chloride is only 54.2 per cent of the weight of nitrosyl chloride or about 0.80 grams of chlorine in 15 minutes and 1.6 grams in 30 minutes. If an error, of say 0.05 to 0.10 per cent occurs in analysis of the reacted waste, the results may give an increase in chlorides of from zero to even above the total chlorine present after reacting. For these reasons the quantity of chlorine recoverable as well as the percentage recoverable chlorine may vary considerably in the short runs. In general, the 15 minute and 30 minute runs serve only to indicate that some free chlorine is liberated in as short a time as 15 minutes. When the length of the runs are increased to one hour and greater, the percentages in error in chloride content due to analysis decreases appreciably. This accounts for the fact that in some instances the percentages of recoverable chlorine in the first 15 and 30 minute runs was high, in one case exceeding 100 per cent while in the longer runs, the percentage recoverable chlorine is comparatively constant.

Data. The only difficulty encountered in taking the data was that of reading the manometer. The flow of nitrosyl chloride could not be regulated so as to prohibit fluctuation in the manometer readings. This necessitated reading the manometer while the fluid was gradually rising and falling. However, for each reading, the average reading of each arm for about 5 seconds was taken as the most correct reading.

Calculation of Results. The method of making material balances across the reaction flasks was that of subtracting the chlorides in the original waste from the weight in the reacted waste. The weight of waste was considered constant throughout the run. This did not, however, introduce an appreciable error because, at most, only about 12 grams of nitrosyl chloride was added. About 2.5 grams of chlorine were recovered from this much nitrosyl chloride. A decrease in carbonates of about one per cent would indicate the loss of about 2.5 grams of carbon dioxide. This makes 12 grams added and 2.5 grams lost besides the loss in weight due to the escape of nitric oxide. If the chloride content of the reacted waste was say 10 per cent, then the maximum error in chlorine balance would be 0.7 gram which is well within the limits of the accuracy expected.

Effects of Time and Temperature. The curves shown in figures 2, 3 and 4 indicate that temperature has little or no effect on the quantity of chlorine recoverable as free chlorine while the quantity recoverable gradually increases with reacting time.

It was expected that the quantity of chlorine released from the nitrosyl chloride would increase with reacting time since more nitrosyl chloride was being decomposed, producing hydrochloric and nitrous acids. Increased reacting time also gives more time for the production of nitric acid which

must react with the chlorides in the waste before any free chlorine can be liberated.

Judging from the waste temperature given in Tables III to XXII, it seems that there is a tendency for the reacting to produce heat since the waste temperature in many instances rose above that of the water surrounding the reaction flasks. This fact would also tend to indicate that it would not be necessary to heat the waste in order for the reactions to proceed.

The results do not only mean that the total chlorine recoverable from nitrosyl chloride is limited to the quantities given. It must be remembered that for free chlorine to be produced, the nitrous acid formed by the decomposition of the nitrosyl chloride must first break down into oxides of nitrogen and these oxides must produce nitric acid which liberates the chlorine from the waste, according to the following equations:



The chlorides added to the solution by the nitrosyl chloride may be in the form of calcium chloride or sodium chloride or in the longer run after all of the carbonates have been decomposed, in the form of hydrochloric acid. Either calcium chloride, sodium chloride or hydrochloric acid, is satisfactory as feed to a reaction tower for waste and nitric acid. Thus, the free chlorine in the nitrosyl chloride may be further recovered by the addition of oxides of nitrogen.

According to the above equations, two molecules of nitrous acid gives

one molecule of nitrogen dioxide and one molecule of nitric oxide. Since no oxygen was added, this nitric oxide was wasted. Nitric oxide is easily oxidized by air and it is believed that the addition of oxygen or air would have increased the chlorine recoverable as free chlorine.

On the basis of the results obtained by reacting the nitrosyl chloride with the waste, some of the oxides of nitrogen must have been recovered since it is these oxides which must have liberated the chlorine.

Effect of Relative Concentration. It was expected that relative concentration would have very little effect on the reaction and this was found to be the case. In very concentrated solutions of hydrochloric and nitric acids or of sodium chloride and nitric acid, there is not enough water to react with the nitrosyl chloride but in a solution which is very dilute such as Solvay waste, the nitrosyl chloride should be decomposed by the water and chlorine liberated. The results obtained seem to further substantiate this statement.

Chlorine Recoverable at 88°C. Runs were made at an approximate reacting temperature of 88°C for 15, 30, 60, 90, and 120 minutes. On analyzing the reacted waste, it was found that the per cent chlorides in the solution was much higher than for any of the previous runs. On calculating the recoverable chlorine it was found that it was considerably lower than for any previous runs. This meant that the curve for recoverable chlorine versus time would have fallen below all the other curves. It is believed that this was due to evaporation of water from the waste during the runs. It will be remembered that the chlorine balance was made by multiplying the per cent chlorides in the waste before and after reacting by the weight of the waste. If the volume of the waste is materially decreased

during the run, which was the case, then the per cent chlorides will be much higher than it should be and will necessarily give low values for recoverable chlorine.

Recommendations

1. The reaction between oxides of nitrogen and Solvay waste should be studied so as to determine whether any nitrosyl chloride escapes with the chlorine and unused oxides of nitrogen.

This investigation has lead to the belief that at least a portion of the chlorine and oxides of nitrogen contained in nitrosyl chloride may be recovered by causing a reaction with Solvay waste. It is further believed that with the addition of oxygen that all of the oxides of nitrogen in the nitrosyl chloride can be utilized and the chlorine either recovered as free chlorine or converted into some chloride which will react with the oxides of nitrogen and subsequently liberate the chlorine. If it could be definitely established that the time of contact between oxides of nitrogen, Solvay waste, and the nitrosyl chloride produced could be so regulated so as to completely utilize the nitrosyl chloride, then, quantitative data on the final products formed in the reaction between oxides of nitrogen and Solvay waste, chlorine and nitrate, would be all that is necessary for pilot plant design.

Limitations. The chief limitations of this investigation may be summarized as follows:

1. The production of sufficient quantities of nitrosyl chloride to react with the waste for an appreciable length of time without the use of

large quantities of hydrochloric and nitric acids was difficult.

2. The production of hydrochloric acid cannot be entirely eliminated.

3. Representative samples for calcium analysis were difficult to obtain due to the insoluble material present in the waste.

The production of large quantities of nitrosyl chloride requires unusually large quantities of nitric, hydrochloric and sulfuric acids. If larger quantities of nitrosyl chloride could have been reacted with the waste, much more accurate results could have been expected.

When salt is added to the nitrosyl sulfuric acid, some hydrogen chloride is produced, especially at temperatures over about 60°C. This hydrochloric acid is absorbed in the waste and will liberate no chlorine. The gas reacting with the waste was considered as pure nitrosyl chloride containing 54.2 per cent while an equal volume of hydrogen chloride at the same temperature and pressure would contain about 97 per cent chlorine by weight. This necessarily introduces an error in the chlorine added by the nitrosyl chloride gas which in turn diminishes the amount of recoverable chlorine.

The method of controlling the amount of nitrosyl chloride reacting was that of controlling the temperature of the nitrosyl sulfuric acid flask. This temperature was difficult to regulate so as to produce an even flow of gas through the manometer and fluctuations in the manometer reading could not be avoided.

Some errors necessarily crept into the analysis. The calcium and insoluble material was the most difficult to duplicate. Considerable quantity of the calcium was present in the insoluble material, consequently, it was difficult to get the same amount of solid calcium salt in each sample.

V. CONCLUSIONS

On the basis of the results obtained in this investigation, the following conclusions seem justified:

1. Causing a reaction between nitrosyl chloride and Solvay waste is a suitable means of decomposing the nitrosyl chloride produced in the reaction between Solvay waste and oxides of nitrogen.
2. Solvay waste will liberate free chlorine from nitrosyl chloride.
3. Reacting temperatures between 25°C and 80°C have little or no effect on the amount of chlorine recoverable from nitrosyl chloride and Solvay waste.
4. For reacting times of from 15 minutes to 120 minutes, the amount of chlorine recoverable from nitrosyl chloride and Solvay waste seems to increase with an increase in reacting time.
5. Between 5.70 grams and 61.68 grams nitrosyl chloride per 1000 grams waste per hour, the relative concentration of nitrosyl chloride and waste seems to have no effect on the amount of chlorine recoverable from nitrosyl chloride.
6. Nitrosyl chloride will decompose the carbonates and bicarbonates in Solvay waste.
7. By decomposing the nitrosyl chloride produced in the reaction between oxides of nitrogen and Solvay waste by causing a reaction with the waste itself, corrosion caused by the nitrosyl chloride should be reduced to a minimum.
8. Approximately 40 per cent of the chlorine contained in nitrosyl

chloride can be recovered as free chlorine.

9. At least a part of the oxides of nitrogen contained in the nitrosyl chloride may be recovered without the addition of oxygen.

10. The percentage recoverable chlorine is very nearly constant at temperatures of from 26°C to 80°C and for reacting times of from 15 minutes to 120 minutes.

VI. SUMMARY

Nitrosyl chloride, prepared by the action of sodium chloride on nitrosyl sulfuric acid, was reacted with Solvay waste by bubbling the gas through 250 cc of the waste contained in two 500 cc flasks. The reacting temperature was regulated approximately by surrounding the flasks with water heated by means of a hot plate.

Runs were made at approximately 28°, 40°, 60°, and 80°C and for reacting times of 15, 30, 60, 90 and 120 minutes. Nitrosyl chloride reacts with Solvay waste to liberate free chlorine. The chlorine recoverable from the nitrosyl chloride seems to be independent of reacting temperature but seems to increase with the reacting time.

Runs of one hour duration were also made using 100, 200, 300, 600, and 1000 cc of waste. On the basis of these runs, it seems that the quantity of chlorine recoverable from the nitrosyl chloride is independent of the relative concentration of nitrosyl chloride and Solvay waste.

From the results, it would seem that about 40 per cent of the chlorine contained in the nitrosyl chloride is recoverable as free chlorine. That is, the oxides of nitrogen contained in the nitrosyl chloride reacts with the chlorides in solution liberating free chlorine.

Nitrosyl chloride will decompose the carbonates and bicarbonates contained in Solvay waste.

The results seem to indicate that the nitrosyl chloride would react with the Solvay waste as fast as it is formed in the reaction between Solvay waste and oxides of nitrogen. Therefore, the corrosion caused by the nitrosyl chloride should be almost completely eliminated.

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