

## ADDENDUM

In discussion of this paper at the New Haven meeting of the AMERICAN CHEMICAL SOCIETY, R. E. Wilson suggested that the substance forming the gel might not be carbon, but a hydrocarbon of high molecular weight and relatively high carbon content. That the free carbon separated by Weiss and similar methods is not pure carbon, but is still contaminated with such hydrocarbons, is very probable; but experiments made during 1918 on destroying such hydrocarbons by activating heat treatment certainly pointed to the bulk of the material being pure carbon. The agree-

ment of the weight of the gel as free carbon (analytically) with the original free-carbon fraction also points to its identity with this. Specific investigation to determine the exact nature of the free-carbon fraction in such oils and tars seems desirable. On the other hand, the fact that in the present case petroleum coke is actually formed and deposited as a *Bodenkörper* certainly supports the view that some colloidal carbon is left in the liquid. The authors have modified the note somewhat to meet Dr. Wilson's valued criticism; while still presenting the facts observed, the interpretation is to be regarded as tentative.

## Sulfuryl Chloride<sup>1,2</sup>

### III—Hydrolysis to Sulfuric and Hydrochloric Acids<sup>3</sup>

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NEUMANN and Wilczewski have recently<sup>4</sup> published an exhaustive experimental study of the reaction

$$\text{SO}_2 + \text{Cl}_2 + 2\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HCl}$$

It is pointed out that the chemical change represented by this reaction can gain a new significance in Germany, because in the chlorine-alkali industry there has been a considerable excess of chlorine since the war. A Tobler tower<sup>5</sup> is recommended as suitable for producing concentrations of sulfuric acid the same as chamber or Glover acid (60 to 78 per cent). The sulfuric acid is practically free of chlorine and sulfur dioxide.

The simultaneous production of commercial hydrochloric and sulfuric acids has been proposed by other investigators. In 1903 Masson<sup>6</sup> patented a process for bringing chlorine, sulfur dioxide, and steam together in a heated chamber. Improvements on this process have been patented in Great Britain<sup>7</sup> and in Germany.<sup>8</sup> The last-named patent allows a mixture of chlorine and sulfur dioxide to meet with water, or better, hydrochloric acid flowing down in a reaction tower; at the bottom sulfuric acid of 65 to 80 per cent runs out and at the top gaseous hydrogen chloride escapes. It is stated that this process has given satisfactory results in practice, and that it can compete successfully with acids made in the ordinary way.

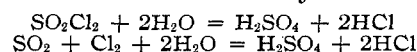
Coppodoro<sup>9</sup> gives a great deal of information concerning

*If all the hydrochloric acid used in the United States were made from chlorine, 150 tons of chlorine per day would be required. In 1918 the liquid chlorine-producing capacity of the United States was 22 tons per day. The writers propose combining chlorine with sulfur dioxide and shipping the anhydrous liquid sulfuryl chloride in iron drums to the place where the hydrochloric acid is wanted and there adding steam to produce pure hydrogen chloride gas and 60 to 78 per cent sulfuric acid. The writers do not claim that this new process can compete in all localities with present processes, but there are some local conditions and special uses for which this process is especially adapted. The production of dry hydrogen chloride gas and dilute mixtures of sulfuric acid and hydrochloric acid are two special uses.*

the process and includes estimates of costs. He recommends that the temperature in the apparatus should exceed 70° C. if over 70 per cent sulfuric acid is to be produced. Considerable heat (81.6 large Calories) is developed by the reaction. The process was in operation in 1909 in a plant at Ravenna, Italy. Welsh<sup>10</sup> uses electrical precipitation to remove sulfuric acid mist from the hydrogen chloride gas.

All these processes have two serious disadvantages. First, it is necessary carefully to regulate the proportions of chlorine and sulfur dioxide used. If there is an excess of either substance the large amount of inert gas from the sulfur burner would carry it straight through the absorption system, thereby causing a loss and creating a nuisance. Second, the expense of shipping hydrochloric acid away from the chlorine plant to the place where it is to be used quickly becomes prohibitive. To ship 1 ton of hydrogen chloride it is necessary to pay freight on 2.4 tons of water. The corrosive nature of hydrochloric acid adds greatly to the shipping cost. It is necessary to purchase and maintain expensive shipping containers, and to pay return freight on them.

These disadvantages would be eliminated by combining the sulfur dioxide and chlorine before the water is added. The preceding paper of this series<sup>3</sup> describes a low cost method for the manufacture of sulfuryl chloride from sulfur burner gas and chlorine. Sulfuryl chloride,  $\text{SO}_2\text{Cl}_2$ , is a liquid boiling at 70° C. and does not attack iron at ordinary temperatures. This anhydrous material could be shipped in iron drums to the place where hydrochloric is wanted and there water added to produce sulfuric acid and hydrochloric acid. This process has not yet been tried out in commercial apparatus. In the description of the experimental work it will appear that the following two reactions are chemically identical:



<sup>10</sup> U. S. Patent 1,285,856 (1918).

<sup>1</sup> Received March 3, 1924.

<sup>2</sup> Submitted by Miss Salls in partial fulfillment of the requirements for the degree of doctor of philosophy, Department of Chemical Engineering, Columbia University.

<sup>3</sup> Part I, THIS JOURNAL, 16, 279 (1924); Part II, *Ibid.*, 16, 351 (1924).

<sup>4</sup> *Z. angew. Chem.*, 36, 377 (1923).

<sup>5</sup> U. S. Patent 1,332,581 (1920).

<sup>6</sup> French Patent 324,859 (1903).

<sup>7</sup> Askenasy and Mugdan, British Patent 14,342 (1903).

<sup>8</sup> Consortium für electrochemischen Industrie, German Patents 157,043 and 157,044 (1902).

<sup>9</sup> *Gazz. chim. ital.*, 39, 616 (1909).

## HYDROLYSIS AT ORDINARY TEMPERATURE

When sulfuryl chloride is added to an excess of water (1 volume to 10 volumes) at room temperature and the mixture is stirred, the reaction soon becomes so violent that the liquid mixture is forcibly expelled from the containing vessel.

The violent reaction is easily explained. Sulfuryl chloride is not miscible with water or with sulfuric acid, and is much heavier than water. It does, however, become cloudy when brought in contact with water, showing that a small quantity of water dissolves in the sulfuryl chloride. This water reacts to give sulfuric acid, hydrochloric acid, and heat. The sulfuric acid and the hydrogen chloride immediately take on water, generating more heat. The hydrogen chloride gas agitates the sulfuryl chloride, bringing a greater surface in contact with the water. The heat increases the reaction velocity. Soon enough heat is being liberated to boil the sulfuryl chloride, and these vapors coming in contact with the hot water cause still more favorable conditions for the hydrolysis. Then the reaction goes to completion in a few moments.

If, however, the heat is removed so that the mixture is kept at room temperature and the mixture is not stirred, sulfuryl chloride will remain in contact with a large excess of water for several days. A layer of sulfuric acid is formed at the surface of the sulfuryl chloride and the reaction does not proceed until the sulfuric acid slowly diffuses into the water layer.

These two simple experiments indicate that the rate of hydrolysis of sulfuryl chloride decreases with increasing concentration of sulfuric acid in the aqueous layer.

## HYDROLYSIS AT CONSTANT TEMPERATURES

This conclusion was tested out quantitatively by hydrolyzing sulfuryl chloride with a limited amount of water. Since it is known that at least a part of the water in a sulfuric acid solution exists as water of hydration, and furthermore, since it is known that hydrates of sulfuric acid are decomposed by a rise in temperature, these experiments were carried out at four different temperatures.

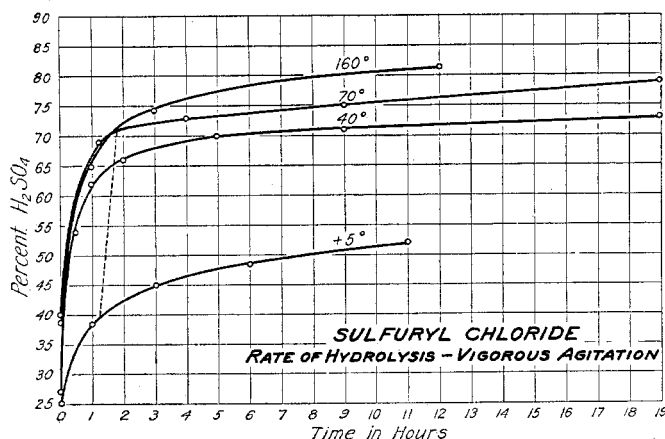


FIG. 1

A 200-cc. portion of water was stirred at a constant rate with an excess of sulfuryl chloride in a liter flask fitted with a reflux condenser and immersed in a thermostat at the specified temperatures. Analyses of the aqueous layer were made from time to time. The results are tabulated in Table I and plotted in Fig. 1.

Each of the curves shows an approximately constant rate of hydrolysis up to a certain concentration of sulfuric acid, and then another rate of hydrolysis—much slower—beyond that concentration. Furthermore, this change in the rate of

hydrolysis occurs at a different concentration of sulfuric acid at different temperatures.

Dilute sulfuric acid is a solution of hydrated sulfuric acid in water. The writers believe that the sulfuryl chloride reacts with free water but not with the water of hydration. The curves indicate that in 72 per cent sulfuric acid at 70° C. nearly all the water is combined with the sulfuric acid as water of hydration. A decrease in temperature to 40° C. causes more water to combine with the sulfuric acid, so that nearly all the water in 65 per cent sulfuric acid at 40° C. exists as water of hydration. A still further decrease in temperature apparently brings the line of complete hydration (dotted line) at 5° C. to 39 per cent sulfuric acid.

TABLE I—HYDROLYSIS OF SULFURYL CHLORIDE AT VARIOUS TEMPERATURES

Time Hours	Specific Gravity at 17° C.	H <sub>2</sub> SO <sub>4</sub> Per cent	HCl Per cent	Time Hours	Specific Gravity at 40° C.	H <sub>2</sub> SO <sub>4</sub> Per cent	HCl Per cent
At 5° C.							
1	1.400	38.5	25.0	0	1.300	27	21.0
3	1.44	45.0	14.5	0.5	1.473	54	6.5
6	1.47	48.5	12.0	1	1.538	62	3.1
11	1.49	52.0	10.5	2	1.580	66	1.2
				5	1.615	70	0.6
				9	1.630	71	0.5
				19	1.650	73	0.17
At 70° C.							
0	1.335	40	11.5	0	1.380	37	21.0
1.25	1.375	69	0.5	0	1.580	65	0.4
4	1.610	73	..	1	1.665	74	0.1
9	1.620	74	..	3	1.665	74	0.1
19	1.670	79	..	12	1.745	82	..
At 160° C.							

The fact that the hydrates of sulfuric acid are decomposed by rise in temperature indicates that in a solution of sulfuric acid there must be an equilibrium between the hydrates of sulfuric acid and free water. A hydrate of sulfuric acid will dissociate to give a lower hydrate and free water, and that lower hydrate will in turn dissociate to give a still lower hydrate and more free water. The concentration of free water in equilibrium with a highly hydrated sulfuric acid will be greater than that in equilibrium with a lower hydrate. This explains the shape of the curve obtained for hydrolysis at 5° C. The velocity of the hydrolysis reaction is proportional to the concentrations of the reacting components. As the concentration of free water decreases owing to its removal from solution by reaction with sulfuryl chloride the rate of hydrolysis gradually decreases. At the higher temperatures there is a large concentration of free water in the solution, and the rate of hydrolysis is not appreciably affected until the point is approached where nearly all the water is held as water of hydration of the sulfuric acid. Beyond this point the concentration of free water in equilibrium with the hydrate is so small that the rate of hydrolysis is severely repressed.

## HYDROLYSIS AT HIGHER TEMPERATURES

The boiling point of sulfuryl chloride is 70° C. In order to take advantage of the higher concentration of free water at higher temperatures, an experiment was carried out in the same apparatus at 160° C. The concentration of sulfuryl chloride when in the vapor phase is much lower than when in the liquid phase. The effect of this lower concentration of sulfuryl chloride can be detected in the curve, but its effect is much less important than the repression due to the low concentration of free water beyond the point of complete hydration.

The conclusion to be derived from these curves is that the most efficient commercial apparatus will be one in which the hydrolysis is carried out in the gas-liquid phase, the sulfuryl chloride and steam being in the gas phase and dilute sulfuric acid in the liquid phase. A simple tower with large internal surface would appear to be a satisfactory type of apparatus. The other factors, considered below, point to the same conclusion.

It is possible to make a strong sulfuric acid by simply allowing sulfuryl chloride to stand in contact with dilute sulfuric acid at room temperature. The longer time required is offset by the simplicity of the operation and by the fact that both reacting substances are in the liquid phase. If

An 8-mm. T tube was sealed to the top of a 3-liter, round-bottom Pyrex flask. Connections to a manometer and to a vacuum pump were sealed to one arm, and connections to burets containing sulfuryl chloride and water, respectively, were sealed to the other arm. The flask was immersed in an air bath at 160° C. After evacuation the flask was two-thirds filled with

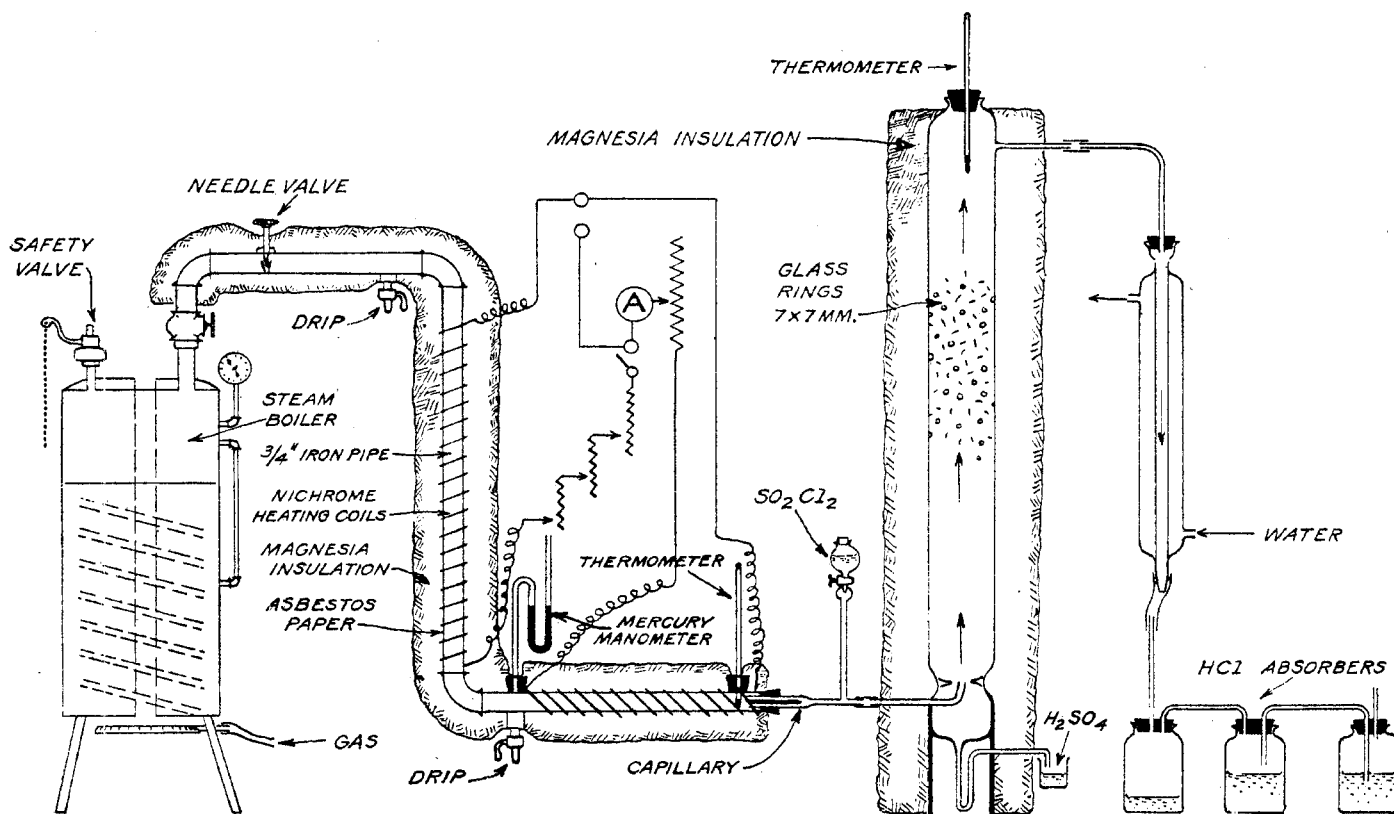


FIG. 2—HYDROLYSIS OF SULFURYL CHLORIDE

sufficient water is added to the sulfuryl chloride to dissolve all the hydrogen chloride, it is possible at room temperature to make a solution containing 35 per cent sulfuric acid, 25 per cent hydrochloric acid, and 40 per cent water. As soon as the solution becomes saturated with hydrochloric acid the hydrolysis proceeds more slowly. In one experiment water and sulfuryl chloride were allowed to stand together in a bottle at 40° C. The percentage sulfuric acid in the aqueous layer increased as follows: 1 day, 42 per cent; 3 days, 68 per cent; 7 days, 75 per cent; 12 days, 78 per cent; 3 months, 83.2 per cent.

For the production of pure acids, however, this type of operation is not recommended—first, because the sulfuric acid would have to be heated to drive out the sulfuryl chloride and hydrochloric acid; second, because the hydrogen chloride gas coming from the hydrolyzing vessel would carry along considerable quantities of sulfuryl chloride vapor; and third, because of the violence of the reaction in dilute solutions.

#### HYDROLYSIS IN THE GAS PHASE

Dixon<sup>11</sup> observed that at 100° C. oxygen and sulfur dioxide do not combine in the presence of water vapor, although when a particle of liquid water is introduced into the system oxidation takes place at once. The hydrolysis of sulfuryl chloride also requires the addition of an oxygen atom to the sulfur dioxide group. The following experiment indicates that the hydrolysis of sulfuryl chloride has something in common with Dixon's observation:

<sup>11</sup> *J. Gas Lighting*, **37**, 704 (1881).

steam and the connecting tubes heated to prevent any condensation. Sulfuryl chloride vapor was then added to make a total of one atmosphere pressure, being very careful at all times to keep the temperature of this vapor above 130° C.

Contrary to expectation, there was no evidence of reaction. The manometer showed no pressure change. The inlet tube was then allowed to cool below 100° C. in order to condense a drop of water. Immediately the manometer pressure began to fall and drops of liquid condensed in the flask. The condensed liquid contained 74.3 per cent sulfuric acid and 0.8 per cent hydrochloric acid. Some unchanged sulfuryl chloride remained in the flask. Apparently the drop of liquid water had catalyzed the hydrolysis of sulfuryl chloride.

#### HEAT OF REACTION

A large amount of heat is generated by the hydrolysis of sulfuryl chloride. The combination of sulfuryl chloride vapor with steam to make 70 per cent sulfuric acid and hydrogen chloride gives out 67 large Calories per mol of sulfuryl chloride, or 890 B. t. u. per pound. This is one-fifteenth the calorific power of a good coal. Upon the assumption that no heat is lost by radiation, this quantity of heat is sufficient to concentrate all the 70 per cent sulfuric acid to 100 per cent, then to dissociate this sulfuric acid completely into sulfur trioxide and water, and finally to raise the temperature of the sulfur trioxide and hydrogen chloride to 430° C. The sulfur trioxide and hydrogen chloride could combine to make chlorosulfonic acid. Since chlorosulfonic acid reacts vigorously with the water of hydration in all strengths of sulfuric acid—even

95 per cent—it should therefore be possible to produce any strength of sulfuric acid up to 100 per cent. This very desirable result has not yet been realized experimentally. The writers have not yet been able to realize the condition of no radiation losses in an apparatus for hydrolyzing sulfuryl chloride by steam.

#### TOWER FOR HYDROLYSIS OF SULFURYL CHLORIDE

A review of the foregoing results shows that a tower for the hydrolysis of sulfuryl chloride should be constructed in such a manner that the following conditions are efficiently met:

- 1—A large surface of contact between gas and liquid.
- 2—Constant relative motion at the interface of gas and liquid.
- 3—Absence of any stagnant areas in either gas or liquid.
- 4—Absence of any channels in the packed tower through which either gas or liquid can pass without adequate contact with the other phase.
- 5—A temperature high enough to obtain a sufficient concentration of free, liquid water in the circulating sulfuric acid.
- 6—Control of the violence of the reaction at the start.
- 7—Sufficient time for the completion of the reaction.
- 8—Removal of sulfuryl chloride and hydrochloric acid from the sulfuric acid.
- 9—Removal of sulfuryl chloride vapors and sulfuric acid mist from the hydrogen chloride gas.

A small tower which had satisfactorily reproduced the operating conditions and products that are realized in a commercial tower for the denitration<sup>12</sup> of waste acid was slightly modified to meet these requirements, and then used for the hydrolysis of sulfuryl chloride.

This laboratory denitrating column (Fig. 2) consisted of a 5.5-cm. Pyrex tube, 70 cm. long, with an inlet at the bottom for the mixture of sulfuryl chloride and steam, a trapped outlet at the bottom for sulfuric acid, a thermometer, and an outlet for hydrogen chloride at the top. The column was well insulated with magnesia. Steam under pressure was admitted through a needle valve into a superheater fitted with a mercury manometer and a petcock for removal of condensed water. Steam at 200° C. and atmospheric pressure passed through a 3-inch section of capillary tube in the end of the superheater. Sulfuryl chloride liquid was dropped into the superheated steam in the short section between the capillary tube and the column. The steam flow was measured by noting the manometer reading and was regulated by the needle valve. Winding the superheater with wire of high electrical resistance all the way from the needle valve to the capillary tube prevented condensation, and consequently a steady manometer reading could be obtained during the greater part of the experiment. The column was packed with rings 7 × 7 mm. which had 1-mm. walls and 71 per cent free space.<sup>13</sup> The cubic capacity of the column without packing was 1800 cc.; therefore the internal surface was 1.74 square meters.

Steam was passed through the tower until the thermometer at the top read 100° C. The sulfuryl chloride was then passed in and the rate increased until sulfuryl chloride began to appear at the exit. At a slightly lower rate than this the sulfuryl chloride was almost completely hydrolyzed. A small amount of sulfuryl chloride vapor in the hydrogen chloride can be detected by dissolving the hydrogen chloride in ice water. Oily drops of sulfuryl chloride appear in the ice water.

The gases issuing from the top of the tower contained hydrogen chloride and steam together with a small quantity of sulfuric acid mist. The temperature at the top of the tower was 106° to 112° C., and increasing the rate for sulfuryl chloride decreased this temperature. The rate of sulfuryl

chloride addition was 65 grams per hour and a 25 per cent excess of steam at 200° C. and atmospheric pressure was used. The sulfuric acid running out of the bottom of the tower contained 58 per cent sulfuric acid and 0.38 per cent hydrochloric acid. The hydrochloric acid obtained by absorbing the exit gases after washing with a small quantity of water contained 33.58 per cent hydrochloric acid and 2.88 per cent sulfuric acid. The purity of the acids obtained in this experiment is therefore within the limits of purity of commercial acids produced in the ordinary way, but the improvements suggested below should remove all doubt as to the question of purity.

The data obtained on this small tower supply an experimental foundation for an opinion as to what may be reasonably expected from a large tower. Suppose that the Glover tower of a 25-ton chamber sulfuric acid plant were used for the hydrolysis of sulfuryl chloride. The dimensions of this tower would be about 7.3 by 3.66 meters (24 feet × 12 feet).<sup>14</sup> Assuming half the capacity per unit volume as obtained by the small denitrating column, this tower would hydrolyze 37 tons sulfuryl chloride per 24 hours, producing simultaneously 57 tons of 22° Bé. hydrochloric acid and 35 tons of sulfuric acid calculated as 60° Bé. It would require 19.5 tons of chlorine to make 37 tons of sulfuryl chloride. In other words, this Glover tower would make nearly one and a half times as much sulfuric acid as the entire chamber plant of which it was but a part; and at the same time would convert the total output of a very large chlorine plant into hydrochloric acid.

A smaller tower of the same height but 0.92 meter (3 feet) in diameter would produce, per 24 hours, 3.6 tons of 22° Bé. hydrochloric acid and 2.2 tons of sulfuric acid calculated as 60° Bé.

In order to produce 66° Bé. sulfuric acid it would probably be necessary to instal a small concentrating unit. Although the thermochemical data show that the hydrolysis of sulfuryl chloride gives out enough heat to raise the temperature of the acid in the bottom of the tower far above the boiling point of 66° Bé. sulfuric acid, it must not be forgotten that the hydrolysis proceeds very slowly in the strong acid. Consequently, it would probably be advisable to use the bottom of the hydrolyzing tower as a condenser for the concentrating unit. After starting, the concentrating unit would have little work to do. As alternatives it might be possible to heat the bottom of the hydrolyzing tower directly with an oil burner, as in a tower concentrator, or indirectly with highly superheated steam.

The greater part of the sulfuric acid mist can be removed by the scrubbing action of the dilute acid condensed in the top of the tower. This would produce hydrochloric acid of about the same degree of purity as is found in the market at the present time. If a still higher purity is desired, it can be readily obtained by removal of the mist by electrical precipitation.

Finally, it should be pointed out that this new process falls in line with the modern tendency to change plants and processes to conform with the fundamental principles of industrial hygiene. Charles F. McKenna, in a report of the New York State Division of Industrial Hygiene,<sup>15</sup> says, "One of the dangers in the manufacture of hydrochloric acid is the annoying fumes which come from the hot salt cake when it is drawn from the furnace \* \* \* the fumes of acid quickly cause the teeth to rot away." The manufacture of hydrochloric acid from sulfuryl chloride can be carried out entirely in closed apparatus, thus eliminating the discharge of these corrosive gases into the atmosphere.

<sup>14</sup> Lunge, "Sulfuric Acid and Alkali," Vol. I, 1913, p. 878.

<sup>15</sup> New York State Department of Labor, 2nd Report of the Factory Investigating Commission, 2, 1067 (1913).

<sup>12</sup> Pauling, U. S. Patent 1,031,864 (1912).

<sup>13</sup> Zeisberg, *Trans. Am. Inst. Chem. Eng.*, 14, 321 (1922).