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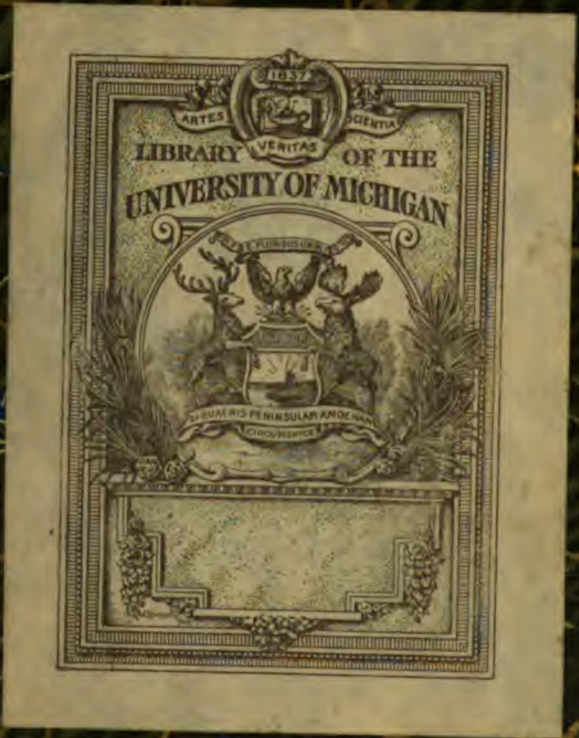

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EXAMPLES AND THEIR SOLUTIONS

SULPHURIC ACID
ALKALIES AND HYDROCHLORIC ACID
MANUFACTURE OF PAPER

SCRANTON:
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PREFACE.

The International Library of Technology is the outgrowth of a large and increasing demand that has arisen for the Reference Libraries of the International Correspondence Schools on the part of those who are not students of the Schools. As the volumes composing this Library are all printed from the same plates used in printing the Reference Libraries above mentioned, a few words are necessary regarding the scope and purpose of the instruction imparted to the students of—and the class of students taught by—these Schools, in order to afford a clear understanding of their salient and unique features.

The only requirement for admission to any of the courses offered by the International Correspondence Schools, is that the applicant shall be able to read the English language and to write it sufficiently well to make his written answers to the questions asked him intelligible. Each course is complete in itself, and no textbooks are required other than those prepared by the Schools for the particular course selected. The students themselves are from every class, trade, and profession and from every country; they are, almost without exception, busily engaged in some vocation, and can spare but little time for study, and that usually outside of their regular working hours. The information desired is such as can be immediately applied in practice, so that the student may be enabled to exchange his present vocation for a more congenial one, or to rise to a higher level in the one he now pursues. Furthermore, he wishes to obtain a good working knowledge of the subjects treated in the shortest time and in the most direct manner possible.

In meeting these requirements, we have produced a set of books that in many respects, and particularly in the general plan followed, are absolutely unique. In the majority of subjects treated the knowledge of mathematics required is limited to the simplest principles of arithmetic and mensuration, and in no case is any greater knowledge of mathematics needed than the simplest elementary principles of algebra, geometry, and trigonometry, with a thorough, practical acquaintance with the use of the logarithmic table. To effect this result, derivations of rules and formulas are omitted, but thorough and complete instructions are given regarding how, when, and under what circumstances any particular rule, formula, or process should be applied; and whenever possible one or more examples, such as would be likely to arise in actual practice—together with their solutions—are given to illustrate and explain its application.

In preparing these textbooks, it has been our constant endeavor to view the matter from the student's standpoint, and to try and anticipate everything that would cause him trouble. The utmost pains have been taken to avoid and correct any and all ambiguous expressions—both those due to faulty rhetoric and those due to insufficiency of statement or explanation. As the best way to make a statement, explanation, or description clear is to give a picture or a diagram in connection with it, illustrations have been used almost without limit. The illustrations have in all cases been adapted to the requirements of the text, and projections and sections or outline, partially shaded, or full-shaded perspectives have been used, according to which will best produce the desired results. Half-tones have been used rather sparingly, except in those cases where the general effect is desired rather than the actual details.

It is obvious that books prepared along the lines mentioned must not only be clear and concise beyond anything heretofore attempted, but they must also possess unequaled value for reference purposes. They not only give the maximum of information in a minimum space, but this information is so ingeniously arranged and correlated, and the indexes are so full and complete, that it can at once be made available to the reader. The numerous examples and explanatory remarks, together with the absence of long demonstrations and abstruse mathematical calculations, are of great assistance in helping one select the proper formula, method, or process and in teaching him how and when it should be used.

Four of the volumes of this library are devoted to subjects pertaining to Applied Chemistry. The present volume contains treatises on the manufacture of sulphuric acid, the manufacture of alkalies and hydrochloric acid, and the manufacture of paper. The manufacture of sulphuric acid, a comparatively new industry in the United States, is increasing rapidly. The subject is thoroughly treated and liberally illustrated with detailed plans of the most approved constructions. The section on Alkalies and Hydrochloric Acid treats of the manufacture of sodium chloride, soda, ammonia recovery, cryolite soda process, sodium sulphate, sodium thiosulphate, sodium hydrate, hydrochloric acid, chlorine, bleaching powder, etc., including the latest electrolytical processes and a description of the analytical methods of intermediate and finished products. The manufacture of paper occupies an important place in our industrial life, and the steady progress that this industry has made has been taken into careful consideration.

The method of numbering the pages, cuts, articles, etc. is such that each subject or part, when the subject is divided into two or more parts, is complete in itself; hence, in order to make the index intelligible, it was necessary to give each subject or part a number. This number is placed at the top of each page, on the headline, opposite the page number; and to distinguish it from the page number it is preceded by the printer's section mark (§). Consequently, a reference such as §16, page 26, will be readily found by looking along the inside edges of the headlines until §16 is found, and then through §16 until page 26 is found.

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SULPHURIC ACID

(PART 1)

INTRODUCTION

1. General Remarks and Definitions.—Before considering the technology of *sulphuric acid*, it is of the greatest possible importance to have a clear idea as to just what sulphuric acid is and the place it occupies among the oxides and acids of sulphur. The technical processes to be described, instead of seeming complicated will then appear consequent and logical, and the bewildering chemical and commercial terminology with which the evolution of the manufacture has incrusted the subject will be cleared away, or at least will be more readily understood.

2. Hydrates and Solutions of Sulphur Trioxide.—It was stated in *Inorganic Chemistry* that sulphur trioxide SO_3 when absolutely pure is a colorless, mobile liquid of 1.940 sp. gr. at 16° C., and when cooled it solidifies into long, transparent prismatic crystals. If a little water is added, a mass of opaque, white, asbestos-like crystals will result, which melt at about 50° C.

If 10.11 per cent. of water is added to the pure sulphur trioxide, a transparent crystalline mass is obtained, melting at 35° C. and readily decomposing at moderate heat into H_2SO_4 and SO_3.

If 18.37 per cent. of water is added to pure sulphur trioxide, a limpid, colorless, oily fluid is obtained of 1.8372 sp. gr.

at 15° C. (Lunge 1.8385), which solidifies at 0° C. into large, plate-shaped crystals and readily decomposing at moderate heat into H_2O and SO_3.

If 31.04 per cent. of water is added to the pure sulphur trioxide, large, clear, hexagonal, columnar crystals that melt at 8.5° C. are obtained.

All these mixtures of pure sulphur trioxide and water, or solutions of sulphur trioxide in water, possess characteristics, such as crystallization, melting points, change of volume, etc., that show them to be definite chemical compounds or hydrates of sulphur trioxide.

Again, if from 14 to 18 per cent. of water is added to pure sulphur trioxide, a thick, oily liquid that throws off dense white fumes on exposure to the air is obtained. These fumes are the vapor of sulphur trioxide combining with the moisture of the air and forming a non-volatile hydrate.

If 23.67 per cent. of water is added to the pure sulphur trioxide, a thick, oily liquid is obtained of 1.835 sp. gr. and stable at ordinary temperatures. This is the oil of vitriol of commerce, or 66° Baumé sulphuric acid (in the United States).

In the same way, water may be added in other percentages; in some cases hydrates, but nearly always simply solutions, result.

3. If these hydrates exist at low temperatures as definite crystalline compounds, and if on a rise of temperature they all decompose with more or less ease with the disengagement of either sulphur trioxide or water, and if in their ordinary form they present all the properties of simple solutions, it follows that between sulphur trioxide SO_3 and water H_2O there exists a consecutive series of homogeneous liquids or solutions, among which must be distinguished definite compounds, or hydrates; therefore, it is quite justifiable to look for other definite compounds between sulphur trioxide and water, which are distinguished by the variation of properties of any kind uniformly occurring with a solution of any uniform percentage of sulphur trioxide and water. Few of

TA

SULPHURIC

° Bé. U. S.	Sp. Gr.	Per Cent. SO_3	Per Cent. H_2SO_4	Weight of 1 Cu. Ft. in Lb. Av.	Per Cent. O. V.
0	1.0000	To reduce percentages of H_2SO_4 to terms of SO_3 multiply by .81636.	0.000	62.37	0.00
1	1.0070		0.935	62.81	1.00
2	1.0140		2.337	63.24	2.50
3	1.0210		3.422	63.68	3.66
4	1.0280		4.675	64.12	5.00
5	1.0360		5.610	64.62	6.00
6	1.0430		6.545	65.05	7.00
7	1.0510		7.480	65.55	8.00
8	1.0580		8.415	65.99	9.00
9	1.0660		9.584	66.49	10.25
10	1.0740		10.752	66.99	11.50
11	1.0820		11.687	67.48	12.50
12	1.0900		12.716	67.98	13.60
13	1.0980		13.744	68.48	14.70
14	1.1070		14.960	69.04	16.00
15	1.1150		15.895	69.54	17.00
16	1.1240		17.064	70.10	18.25
17	1.1330		18.326	70.67	19.60
18	1.1420		19.635	71.23	21.00
19	1.1510		20.570	71.79	22.00
20	1.1600		21.739	72.35	23.25
21	1.1690		22.907	72.91	24.50
22	1.1790		24.310	73.53	26.00
23	1.1880		25.479	74.10	27.25
24	1.1980		26.647	74.72	28.50
25	1.2080		28.050	75.34	30.00
26	1.2180		29.219	75.97	31.25
27	1.2290		30.621	76.65	32.75
28	1.2390		31.790	77.28	34.00
29	1.2500		33.192	77.96	35.50
30	1.2610		34.595	78.65	37.00
31	1.2720		35.876	79.33	38.37
32	1.2830		37.166	80.02	39.75
33	1.2950		38.569	80.77	41.25
34	1.3060		39.850	81.46	42.62
35	1.3180		41.140	82.20	44.00
36	1.3300		42.542	82.95	45.50
37	1.3420		43.945	83.70	47.00
38	1.3550		45.347	84.51	48.50
39	1.3680		46.750	85.32	50.00
40	1.3810	39.3080	48.152	86.13	51.50
41	1.3940	40.4530	49.555	86.94	53.00
42	1.4080	41.5970	50.957	87.82	54.50
43	1.4210	42.7430	52.360	88.63	56.00
44	1.4360	43.8870	53.762	89.56	57.50
45	1.4500	45.0330	55.165	90.44	59.00
46	1.4650	46.1770	56.567	91.37	60.50
47	1.4790	47.3230	57.970	92.25	62.00
48	1.4950	48.4670	59.372	93.24	63.50
49	1.5100	49.6120	60.775	94.18	65.00
50	1.5260	50.7570	62.177	95.18	66.50
51	1.5420	51.9020	63.580	96.17	68.00
52	1.5590	53.1990	65.169	97.23	69.70
53	1.5760	54.4200	66.665	98.30	71.30
54	1.5930	55.7180	68.255	99.36	73.00
55	1.6110	56.9400	69.751	100.48	74.60
56	1.6290	58.1610	71.247	101.60	76.20
57	1.6480	59.4350	72.808	102.79	77.87
58	1.6660	60.6790	74.332	103.91	79.50
59	1.6860	62.0530	76.015	105.16	81.30
60	1.7060	63.3510	77.605	106.40	83.00
61	1.7260	64.8770	79.475	107.65	85.00
62	1.7470	66.4040	81.345	108.96	87.00
63	1.7680	67.9310	83.215	110.27	89.00
64	1.7900	69.9300	85.665	111.64	91.62
	1.8010	71.0750	87.067	112.33	93.12
	1.8070	71.7470	87.890	112.70	94.00
65	1.8120	72.2810	88.544	113.01	94.70
	1.8180	73.0140	89.442	113.39	95.66
	1.8240	73.8840	90.508	113.76	96.80
	1.8300	75.0520	91.939	114.14	98.33
66	1.8350	76.3265	93.500	114.45	100.00

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CID TABLES

ounds . *V*. in Cu. Ft.	Per Cent. 60°	Pounds 60° in 1 Cu. Ft.	Per Cent. 50°	Pounds 50° in 1 Cu. Ft.
0.00	62.05	53.44	77.44	66.70
0.63	63.85	55.51	79.70	69.29
1.58	65.66	57.66	81.95	71.97
2.33	67.47	59.80	84.21	74.64
3.21	69.28	62.05	86.47	77.44
3.88	71.08	64.28	88.72	80.24
4.55	72.89	66.60	90.98	83.13
5.24	74.70	68.91	93.23	86.00
5.94	76.50	71.33	95.49	89.03
6.82	78.31	73.75	97.74	92.05
7.70	80.12	76.26	100.00	95.18
8.44	81.93	78.79	102.26	98.34
9.25	83.98	81.65	104.81	101.91
10.07	85.90	84.44	107.22	105.40
11.05	87.95	87.39	109.77	109.07
11.83	89.88	90.31	112.18	112.72
12.79	91.81	93.28	114.59	116.42
13.85	93.82	96.44	117.10	120.37
14.96	95.78	99.52	119.55	124.22
15.79	97.95	103.00	122.26	128.57
16.82	100.00	106.40	124.81	132.80
17.86	102.41	110.24	127.82	137.60
19.12	104.82	114.21	130.83	142.55
20.19	107.23	118.24	133.83	147.57
21.30	110.39	123.24	137.77	153.81
22.60				
23.74				
25.10	114.10	128.94	142.41	160.94
26.28				
27.68				
29.10				
30.44	120.48	137.89	150.38	172.11
31.81				
33.32				
34.72				
36.17				
37.74				
39.34				
40.99				
42.66				
44.36				
46.08				
47.86				
49.63				
51.50				
53.36				
55.28				
57.20				
59.21				
61.22				
63.29				
65.40				
67.77				
70.09				
72.53				
74.96				
77.42				
80.04				
82.61				
85.50				
88.31				
91.50				
94.80				
98.14				
102.29				
104.60				
105.94				
107.02				
108.47				
110.12				
112.23				
114.45				

PRINCIPAL HYDRATES OF SO_3

$SO_3 = 100.00\%\ SO_3$

$4SO_3 + H_2O = 94.68\%\ SO_3$

$2SO_3 + H_2O = 89.89\%\ SO_3$

$4SO_3 + 3H_2O = 85.56\%\ SO_3$

$SO_3 + H_2O = 81.63\%\ SO_3$

$SO_3 + 2H_2O = 68.97\%\ SO_3$

$SO_3 + 3H_2O = 59.70\%\ SO_3$

$SO_3 + 5H_2O = 47.07\%\ SO_3$

$SO_3 + 151H_2O = 2.86\%\ SO_3$

STANDARDS

Baumé Hydrometer

Modulus = 145
66° = 1.835 Sp. Gr.
at Standard Temperature 60° F.

1 cu. ft. water = 62.37 lb. av.

$H_2SO_4 = 100$

O. V.	H_2SO_4	*O. V.*	60° Bé.
60°	93.500	100.0	120.48
50°	77.605	83.0	100.00
	62.180	66.5	80.12

these variations of properties of definite solutions have been determined with sufficient accuracy.

In other words, the term **sulphuric acid** is the generic name of a series of solutions of sulphur trioxide in water, some of which are chemical hydrates of the sulphur trioxide and most of which are merely solutions of convenient strength for use in the arts.

4. In Table I are given the principal characteristics of the various commercial solutions of sulphur trioxide in water. The best known hydrates are also shown. It will be noticed that none of the hydrates are recognized commercially.

5. Nomenclature of Solutions and Hydrates of Sulphur Trioxide.—The term sulphuric acid is usually applied to the monohydrate of sulphur trioxide SO_3, H_2O, and yet at the same time it covers the whole range of hydrates and solutions containing a smaller percentage of SO_3 than the monohydrate, and also the hydrates and solutions containing more SO_3 than the monohydrate. As the moment that moisture is added to sulphur trioxide it becomes an acid, the term sulphuric acid therefore applies to the whole range of hydrates and solutions of SO_3 in water. There is no reason why the monohydrate should monopolize the term sulphuric acid other than the fact that it marks the margin of the acids of sulphuric trioxide that are stable in liquid form at ordinary temperatures; and even this is not quite correct, as the actual monohydrate itself, even at 40° C., begins to give off fumes of sulphur trioxide, and even in a dry atmosphere becomes weaker until it contains 1.5 per cent. of water. At this point, however, it really becomes stable, so far as the separation of the sulphur trioxide is concerned, and in a dry atmosphere will remain unchanged.

It is this sulphuric acid that contains not more than 98.5 per cent. of H_2SO_4, or 80.41 per cent. of SO_3 and 19.59 per cent. of water, that it has been possible to make by the so-called *chamber process*, aided by concentration (evaporation of water) and by distillation, and which has therefore been commercially available. If stronger acid were required, recourse to the fortification of this acid by sulphur trioxide made at great cost was necessary. The 80.41-per-cent. SO_3, or 98.5-per-cent. H_2SO_4, or as near to it as possible, was fortified with sulphur trioxide until it became 81.63-per-cent. SO_3 acid (monohydrate), and if a greater strength or a so-called fuming acid were required, more sulphur trioxide was added, and the acid thus fortified considered as the monohydrate plus a certain percentage of free sulphur trioxide.

6. Nordhausen or Fuming Sulphuric Acid.—As until comparatively recently the only commercial sulphur trioxide was produced as a **fuming** or **Nordhausen acid** (i. e., an acid containing a greater percentage of sulphur trioxide than the monohydrate) and very costly to make, every effort was made to bring the chamber acid to its greatest strength (to eliminate by evaporation as much water as possible). For, as the proportion of sulphur trioxide to water in monohydrate is 81.63 to 18.37, every part of water in the acid to be fortified first requires 4.444 parts of sulphur trioxide to form the monohydrate before any so-called free sulphur trioxide or $H_2SO_4 + SO_3$ is obtained. With the one exception of pyrosulphuric acid, disulphuric acid, or solid oleum, terms applied to the hydrate $H_2S_2O_7$, or $2SO_3 + H_2O$, there is no nomenclature that covers the whole range of acids from the monohydrate, or 81.63-per-cent. sulphur trioxide, to the sulphur trioxide itself, except the terms fuming or Nordhausen acids; the first is descriptive of a characteristic of these acids and the second is the name of a town in Prussian Saxony where a warehouse for the storage of these acids was located, the factories being at Braunlage, Goslar, and other places.

As, therefore, the term sulphuric acid is used not only to define the actual sulphuric monohydrate, but also to describe the whole range of hydrates and solutions of sulphur trioxide, it becomes necessary for *accurate* expression to define the hydrate or solution referred to in terms of percentage of sulphur trioxide contained in it. When acids stronger than commercial oil of vitriol (76.33 per cent. of SO_3) were rare and acidum sulphuricum distillatum (80.41 per cent. of SO_3) was the strongest commercial acid known, it was, of course, natural that the strength of all acids should be referred to the monohydrate, or nearest, hydrate.

7. Commercial Methods for Determining the Strength of Solutions Weaker than the Monohydrate. For ascertaining the strength of those solutions weaker than the monohydrate, recourse is had to their specific gravity—a fairly accurate method up to a certain point, but uncertain just about the reference point (monohydrate), as in passing from 79.99 per cent. of SO_3 (98 per cent. of H_2SO_4) to 81.63 per cent. of SO_3 (100 per cent. of H_2SO_4) the specific gravity decreases from 1.8415 to 1.8372. The specific gravity, however, rises just so soon as the monohydrate point is passed and SO_3 is slightly in excess.

In commercial acids a further cause of inaccuracy exists, owing to the effect on the specific gravity of the almost constant impurities present. Furthermore, commercial methods of observing the specific gravity are neither uniform nor accurate, even apart from the inaccuracy of the instruments themselves.

8. Specific-Gravity, or Density, Determinations.—The hydrometer used in connection with sulphuric acid is simply an instrument for determining its specific gravity, or density, in comparison with distilled water at 15° C. (or 60° F. in the United States). With commercial acids the use of the hydrometer should be limited to the solutions containing up to 76.33 per cent. of SO_3 (93.5 per cent. of H_2SO_4). Specific-gravity determinations beyond this point are unreliable on account of impurities in the acid, and all determinations above this point should be made alkalimetrically. Apparently, it should be easy to make the hydrometric scale an exact basis of universal calculation, but in practice there are many different hydrometer scales. One of the difficulties is the uncertainty as to the standard of maximum density. In Europe this is generally understood to be 1.842 sp. gr. at 15° C., or 66° Baumé. As this specific gravity would correspond to a fuming acid, it is difficult to see on what this standard is based. The specific gravities of solutions of sulphur trioxide, just between 97 and 100 per cent. of H_2SO_4 (79.19 and 81.63 per cent. of SO_3), are given in Table II.

TABLE II

SPECIFIC GRAVITY OF SOLUTIONS OF SULPHUR TRIOXIDE

H_2SO_4	SO_3	Specific Gravity
97.00	79.19	1.8410
97.70	79.76	1.8415
98.20	80.16	1.8410
98.70	80.57	1.8405
99.20	80.98	1.8400
99.45	81.18	1.8395
99.70	81.39	1.8390
99.95	81.59	1.8385
100.00	81.63	1.8372

9. In England, the Twaddell scale starts with a maximum specific gravity of 1.850, or 170°. Each intermediate degree represents a difference of .005 in specific gravity. In the United States, the Baumé scale is also used, the 66°, however, corresponding to 93.5 per cent. of H_2SO_4, or 76.3265 per cent. of SO_3, or a specific gravity of 1.835.

The modulus, or formula of division, where d = specific gravity and n = the number of degrees, for the European Baumé is

$$d = \frac{144.3}{144.3 - n},$$

and for the United States Baumé is

$$d = \frac{145}{145 - n}.$$

Throughout this work, the United States Baumé is used, as it is the one universally adopted by sulphuric-acid manuturers in this country. In addition to these scales, those of Gerlach and others are used in different parts of Europe and in different factories in the same country. All of which tends to show that the only precise and accurate way of describing the acids of sulphur trioxide is in terms of percentage contents of such oxide.

PRINCIPLES GOVERNING THE MANUFACTURE OF SULPHURIC ACID

10. When sulphur dioxide SO_2 and oxygen are brought together under certain conditions, they combine to form sulphur trioxide SO_3. This in the presence of water vapor becomes hydrated, and these hydrates are known as sulphuric acid. The conditions under which sulphur dioxide and oxygen may combine are varied. For the commercial manufacture of sulphuric acid, this combination is brought about in two ways.

1. By what is known as *contact* or *catalytic action*, the two gases are brought together in the presence of certain substances, as finely divided platinum, and other substances described farther on, that have the peculiar power to cause them to unite chemically. The dry sulphur trioxide thus formed is absorbed in the proper amount of water, to give an acid of the desired strength.

2. The two gases are brought together in the presence of steam and some of the higher oxides of nitrogen, as, for instance, N_2O_3. The oxide of nitrogen gives up oxygen to the sulphur dioxide and forms, in the presence of water vapor, sulphuric acid. The lower oxide of nitrogen formed immediately takes up oxygen from the air present and is regenerated.

The reaction is quite complicated but is continuous. A small amount of oxide of nitrogen serves to oxidize an indefinite amount of sulphur dioxide to the trioxide. This is the reaction used in the so-called *chamber process*.

In the discussion of the two processes for the manufacture of sulphuric acid, the above-mentioned reactions will be quite fully dealt with. Before discussing these, however, the various sources of sulphur and the preparation of sulphur dioxide will be taken up.

11. Raw Materials Used in the Manufacture of Sulphuric Acid.—Commercial sulphuric acid is derived from the following raw materials:

1. Brimstone (*a*) derived from sedimentary deposits accompanied by or derived from gypsum, found in Sicily, Louisiana, etc.; (*b*) derived to a limited extent from volcanic deposits (Solfatara).

2. Recovered sulphur (*a*) from alkali waste (Chance and Klaus processes); (*b*) from spent oxides from gas works.

3. Sulphureted hydrogen obtained as a by-product in the manufacture of ammonium sulphate, etc.

4. Iron pyrites, in which the principal value is the sulphur.

5. Iron pyrites with copper pyrites, in which the principal value is copper (sometimes also gold and silver) and the sulphur may be considered as a metallurgical by-product.

6. Zinc blende, in which the principal value is zinc.

7. Copper-nickel pyrrhotites, in which the principal value is the metal.

8. Copperas slate (*Vitriolschiefer*), which is oxidized to ferrous and then to ferric sulphate in the Nordhausen process for the manufacture of fuming sulphuric acid; also other acid sulphates of the alkalies, which, upon being heated, are first changed into pyrosulphates and then split up into neutral sulphates and sulphur trioxide.

It will be noted that these raw materials divide themselves into the following classes: (*a*) Where the sulphur is the principal or only value, as brimstone and most iron pyrites; (*b*) where the sulphur is a recovered or a by-product from a previous chemical process, and, therefore, only available locally or under special conditions, as hydrogen sulphide, alkali waste, etc; (*c*) where the sulphur is of secondary value and is virtually a waste product in a metallurgical operation; (*d*) where the sulphur is derived from sources that are only suited on account of their cost for special processes and products, as the various sulphates.

12. The history of the manufacture of sulphuric acid commercially shows, as may be expected, that at first brimstone, as being technically the simplest raw material, was exclusively used. This was, in turn, supplanted by iron pyrites. Iron pyrites are now being largely driven out by the waste gas produced in the desulphurization of copper, zinc, nickel, gold, and silver ores, and it is not difficult to see that in time the great bulk of acid will be produced as an adjunct to the various metallurgical processes. Literally, in the United States thousands of tons of sulphur are being delivered into the air as sulphurous gas every day of the year by the various metallurgical works. The capital invested in the present plants, the capital cost of making the necessary changes to render the gas available, remoteness from present markets, and other necessary costly adjustments alone prevent this sulphur from being recovered as sulphuric acid.

As to the use of sulphates for the manufacture of fuming acid, this industry is practically dead, having been replaced entirely by the catalytic or contact process described farther on.

13. Preparation of the Raw Material.—Brimstone or sulphur requires little or no preparation, as it comes to the market in suitable condition to be put into the burners. Crude sulphur in the Sicilian warehouses is graded according to its purity and also, in a way, according to the method employed in its extraction.

Grading is done by simple inspection, without sampling or assaying. Three qualities are recognized: *firsts*, *seconds*, and *thirds*. Light-colored sulphurs are included in the first two grades and darker varieties in the thirds. Seconds and thirds are subdivided into "vantaggiata," "buona," and "corrente." Firsts are nearly chemically pure and of a canary-yellow color, while seconds vantaggiata are but slightly inferior. Seconds buona have a fine chrome-yellow color; seconds corrente have a dirty yellow color; and thirds are chocolate brown on the exterior, shading to greenish brown inside.

14. For the American trade, two special classes are made, *seconda uso America*, best seconds, which is a mixture of seconds corrente and thirds vantaggiata; and *terza uso America*, best thirds, a mixture of terza vantaggiata and terza buona. The chemical purity of these classes differs comparatively little. The various grades of seconds range from 99.85 to 99.70 sulphur; and of thirds, from 99.64 to 99.58 sulphur. The principal difference—namely, that of color—is due to temperature and other points connected with the fusion.

15. The spent oxides of gas works, which contain sulphur, are first treated for the recovery of the salts of ammonia, ferrocyanides, and sulphocyanides, and are then roasted as if they were the fines, or dust, of the metallic sulphides and in the same class of furnaces.

16. **Sulphureted hydrogen,** when ignited in the air, burns with a blue flame, water and sulphur dioxide resulting

$$H_2S + 3O = H_2O + SO_2$$

with limited air access, or when the flame is cooled by the introduction of a cold body; only hydrogen burns and the free sulphur separates. Advantage is taken of this reaction to use the hydrogen sulphide produced in the Chance process for the utilization of alkali waste for the manufacture of sulphuric acid ; or by the Klaus process, for the recovery of sulphur. The hydrogen-sulphide gas is simply burned in a suitable combustion chamber and the resulting SO_2 passed to the lead chambers, or otherwise oxidized to SO_3.

17. The **metallic sulphides,** the bisulphides of iron, or iron and copper pyrites, can be roasted both in the form of small lumps or as dust, or fines, and by their own heat of combustion alone. The monosulphides, or copper- or nickel-bearing pyrrhotites and zinc blendes must be roasted as fines and with the aid of additional fuel. Many pyrites are so friable as to crumble to fines when being mined, and many pyrites carrying copper, gold, silver, and other valuable metals are in the form of concentrates, or fines; such ores are disseminated, when found, among large proportions of quartz or other gangue matter, or consist of the sulphides of several metals, which it is desirable to separate before further metallurgical treatment.

If these ores occur in massive form, they must first be broken into small pieces. This is done either by hand or by rock breakers. The method used will depend on local conditions, such as cost of labor, etc., and on the mechanical condition of the ore, such as friability, etc. The ore must then be screened and sized. As a rule, except in the case of a very free-burning iron pyrite or under special conditions, such as extreme friability of the ore and insufficient facilities for roasting the fines, the largest size produced should pass through a 3-inch ring; the next size should pass through a 2-inch ring; and so on. Too much emphasis cannot be given to the necessity for properly sizing the ore and burning one size only in the same burner. This applies not only to the lump ore but also to the smalls and fines.

18. In the first place, it is evident that for a "dead" roast, or a roast of equal efficiency, the capacity of any given furnace will be controlled by the time taken to roast the largest pieces. Therefore, to secure the efficient and economical use of costly apparatus, the economy of power and labor, or in other words, maximum output at minimum cost, it is necessary to have a reasonably close sizing of the charge of raw ore to any given furnace. Moreover, that serious class of troubles met with in roasting ores, called *clinkering*, *scarring*, etc., and much of the labor of breaking up and barring the bed of ore in a lump burner is the direct result of improper sizing. These scars, or clinkers, are really the formation of a fusible matte of ferrous sulphide FeS, owing to the irregular passage of air through the bed of ore on the furnace grates. If the ore is reasonably sized, air will be uniformly admitted through the bed and each piece of ore will get sufficient air for its complete oxidation. Moreover, the resulting regularity in the condition of the furnaces will tend to produce uniformity in the conditions of the burner-gas and the acid-making process.

19. Combustion of Sulphur and Its Thermochemistry.—When brimstone or a metallic sulphide is heated in the air, or burned, the following reaction takes place:

$$S_2 + 2O_2 = 2SO_2$$

In this respect, the combustion of sulphur appears to form an exception to the general rule of thermochemistry—viz., that where two or more compounds are possible as the products of chemical combination, that product will be formed which produces the greatest heat in the reaction; for example, C and O can form carbon monoxide CO or carbon dioxide CO_2, and carbon dioxide is the usual product of complete combustion; sulphur and oxygen can form sulphur dioxide SO_2 and sulphur trioxide SO_3, yet sulphur dioxide is the usual product of combustion. The reason for this is that the heat of the oxidation of sulphur to the trioxide is so great as to cause the dissociation of the trioxide into the dioxide and oxygen, or in other words, that the difference in the temperature of the production and dissociation of sulphur trioxide is so slight that unless some means are taken to carry off the heat of the reaction effectively it cannot exist. This fact becomes highly important in the consideration of the various contact processes.

As a matter of fact, the gas produced by the combustion of brimstone or the metallic sulphides *always* contains varying proportions of sulphur trioxide, so that technically the equation given above does not quite represent the reaction of the combustion of sulphur in air.

The fact that the burner gas contains varying quantities of sulphur trioxide is shown by the formation of free sulphuric acid, when such gases are washed in water or dilute sulphuric acid or passed over iron filings before being used in the manufacture of sulphite pulp.

20. Burner Gas.—Burner gas, whether derived from the combustion of brimstone or the metallic sulphides, forms the basis of the manufacture of sulphur trioxide and all its hydrates and solutions. It consists, according to the raw material used, of a mixture of sulphur dioxide and sulphur trioxide, nitrogen, oxygen, and many impurities, such as flue dust, iron, silica, arsenious and hydrofluoric acids, and compounds of selenium, thallium, zinc, lead, etc.

21. As air consists approximately of 79 parts, by volume, of nitrogen and 21 parts, by volume, of oxygen, and as 1 volume of oxygen on combining with sulphur forms 1 volume of sulphur dioxide, which in turn requires ½ volume of oxygen to form the trioxide, it is plain that 14 per cent. of sulphur dioxide in the burner gas is the highest theoretical percentage possible; as each 14 volumes of sulphur dioxide containing 14 volumes of oxygen requires 7 volumes of oxygen to form sulphur trioxide, or 21 volumes of oxygen in all, in which case the burner gas would contain the following:

Volumes of oxygen as sulphur dioxide..........	14
Volumes of oxygen to form sulphur trioxide....	7
Volumes of nitrogen..........................	79
Total..................................	100

In practice, however, even if pure sulphur is used to produce the burner gas, this percentage would not be practicable, as no matter what process is used a certain excess of oxygen is found necessary. This excess of oxygen is usually not less than 5 per cent. and the proportions therefore are about as follows:

Volumes of oxygen as sulphur dioxide........	14.0
Volumes of oxygen to form sulphur trioxide..	7.0
Volumes of oxygen excess..................	5.0
Volumes of nitrogen with the sulphur trioxide	79.0
Volumes of nitrogen with the excess of oxygen	18.8
Total..................................	123.8

From which it is evident that even when burning brimstone or pure sulphur, the percentage of sulphur dioxide in the burner gas should not exceed 11 per cent. As a matter of practice, 10 per cent. is rarely exceeded, as with less air sublimation of the sulphur is likely to take place unless great care is used.

22. When the question is one of roasting the metallic sulphides, it is evident that the matter is further complicated, as oxygen (and with it nitrogen) must not only be admitted to oxidize the sulphur to the trioxide and to provide for the necessary excess, but also to oxidize the metallic contents of the ore. The calculation will, of course, be different for the various ores used, but it may be stated in general terms that the burner gas produced when burning the metallic sulphides should range from 5 to 8 per cent. of sulphur dioxide. A less percentage than 5 per cent. can only be used (on account of its dilution with inert nitrogen) at the expense of a larger and, therefore, more expensive plant; nor, with reasonably well-constructed burners, need the percentage of sulphur dioxide fall below 5 per cent. unless under very exceptional circumstances.

23. Available Sulphur.—As all the raw material for the production of burner gas contains varying quantities of impurities, and as it is quite impossible, at the temperatures existing in the various furnaces used in sulphuric-acid manufacture, to entirely desulphurize any of these raw materials—various percentages of sulphur remaining in the ash or cinder—it is manifestly advisable to base figures relating to the process or yield upon the amount of sulphur actually available or existing in the burner gas as oxides of sulphur SO_2 or SO_3. The loss in the desulphurizing process is estimated separately, and it is to this available sulphur that all calculations will refer. Certain losses of sulphur occur in the process of desulphurizing by the escape of gas during charging and discharging and the various manipulations connected with the roasting. Losses also occur by partially roasted ore passing through the furnace; this is generally due to carelessness on the part of the burner men. Other quite unavoidable losses are caused by the temperature of the furnace being insufficient to convert the sulphides of certain metals occurring with the iron pyrites into oxides, they remaining in the cinder as sulphates.

TABLE III

Each per cent. contained in pyrites of......	Zn	ZnO	Cu	CuO	Pb	PbO	CaO	MgO	Fe_2O_3
Will render unavailable per cent. of sulphur	.5	.39	.5	.4	.15	.14	.57	.8	.6

24. Sources of Loss of Sulphur in Roasting.—As the metallic sulphides are sold to sulphuric-acid manufacturers on the basis of total sulphur contents, it is well, in comparing the relative values of any ores, to consider how much sulphur will be inevitably bound in this way as sulphates in the cinder and therefore, under no condition will be of value to the manufacturer or available for oxidation to the trioxide.

Table III is based on the assumption that all these sulphides are converted to sulphates, which is by no means the case.

25. The following illustrations show what is meant by "available" sulphur, the cause of loss of sulphur in roasting, and the relation of this loss to the yield or output of acid and to the value of any given ore to the manufacturer.

ILLUSTRATION 1.—An iron bisulphide of great purity, such as the Aguas Tenidas in Spain, contains:

Iron	46.60%
Sulphur	53.15%
Silica	.20%
Arsenic Copper Silver Gold	Traces

Such an ore with reasonable care can be roasted down so that the cinders will not contain more than .5 per cent. of sulphur. As the cinders will weigh only about 80 per cent. of the ore, the total loss of sulphur will be only .4 per cent., and this, so far as the metallic sulphides are concerned, would seem in practice to be the irreducible minimum, the manufacturer obtaining from the ore 52.75 per cent. of sulphur, or 99.24 per cent. of the sulphur for which he pays. In addition to this loss, there will be more or less loss from the escape of gas from the burners, varying with the excellence of construction of the burners and the care exercised by the burner men. Other losses at the burners will amount, say, in all to .6 per cent., making the total loss in ore buying and roasting 1 per cent. of the sulphur contents, leaving 98.12 per cent. of the sulphur *available* for acid making, or as sulphur oxides in the burner gas.

ILLUSTRATION 2.—A Norwegian pyrites contains by analysis:

Sulphur	44.50	Lime	2.10
Iron	39.22	Magnesia	.01
Copper	1.80	Oxygen, as Fe_2O_3	.50
Zinc	1.18	Insoluble	10.70

It is plain that on a complex ore of this nature the loss in roasting the bisulphide cannot be less than the loss in roasting the ore of the previous example, or .5 per cent., in addition to which the ore contains impurities that will hold sulphur in the cinders as sulphates, as stated in the above table. The roasting losses will stand as follows:

	Percentage of Sulphur
Roasting loss on bisulphide of iron in cinders	.40
Sulphate of zinc in cinders, 1.18 at .50	.59
Sulphate of copper in cinders, 1.80 at .50	.90
Sulphate of lime in cinders, 2.10 at .57	1.20
Sulphate of magnesia in cinders, .01 at .80	
Sulphate of iron in cinders, .50 at .60	.30
Total loss	3.39

In such an ore, therefore, the manufacturer will under no circumstances be able to obtain from the ore more than 41.11 per cent. of the sulphur, or 92.88 per cent. of the sulphur for which he pays. Adding the further loss of .6 per cent. of sulphur in gas, etc. in the roasting process, it brings his total loss up to 3.99 per cent. of sulphur, leaving 40.51 units of sulphur, or 91 per cent. of the sulphur, available for acid making or as sulphur oxides in the burner gas.

In purchasing ore, it is further necessary to consider the effect of low-sulphur contents on costs of freight, labor of handling, and room taken up in the furnaces and storage bins, etc.; for instance, in purchasing brimstone, 1 per cent. of these costs, at the outside, is on waste material, while in dealing with an ore containing 50 per cent. of available sulphur, 50 per cent. of these costs on the above accounts is on waste material, and so on.

26. Yield and Method of Calculating Yield of Sulphuric Hydrate.—The possible theoretical yield obtainable from 1 unit of actual sulphur, say 1 pound or 1 kilogram, is 2.5 pounds or kilograms of sulphur trioxide or 3.0625 pounds or kilograms of sulphuric monohydrate H_2SO_4, which corresponds to 100 per cent. of either of the above products; of course, such yields are never realized in practice. A yield of 98 per cent. (2.45 pounds of sulphur trioxide or 3.0013 of H_2SO_4) is probably the extreme average limit of even the best-managed and best-constructed acid works, while 97 per cent., or even 96 per cent., is considered extremely good average work.

As these figures are based on actual chemically pure sulphur, the importance of the above remarks becomes evident. At various factories, various and very loose data are used for the calculation of yield. Some factories express their yield in terms of sulphur shown by assay in the ore, without reference to the loss shown by sulphur held as sulphates, which can, under no circumstances, be recovered. Others neglect the gas losses in the desulphurizing furnaces. The safest way is to consider the available sulphur as that actually contained in the burner gas as sulphur oxides; or in practice to deduct from the assay value in sulphur of any particular ore a sufficient percentage to allow for the inevitable loss in the cinder and gas at the furnaces.

TABLE IV

YIELDS IN POUNDS OR KILOGRAMS OF SULPHURIC-ACID SOLUTION PER 100 POUNDS OR KILOGRAMS OF AVAILABLE SULPHUR OR SULPHUR OXIDES ACTUALLY CONTAINED IN BURNER GAS

Percentage of Theoretical	Sulphuric Anhydride $SO_3 = 100\%$	$SO_3 = 60\%$ $H_2SO_4 = 40\%$ $SO_3 = 92.65\%$	$SO_3 = 40\%$ $H_2SO_4 = 60\%$ $SO_3 = 88.98\%$	$SO_3 = 20\%$ $H_2SO_4 = 80\%$ $SO_3 = 85.31\%$	Monohydrate $H_2SO_4 = 100\%$ $SO_3 = 81.6326\%$	Distilled $H_2SO_4 = 98.5\%$ $SO_3 = 80.41\%$	Extra Concentrated $H_2SO_4 = 97\%$ $SO_3 = 79.18\%$	Oil of Vitriol 66° U. S. Bé. $H_2SO_4 = 93.5\%$ $SO_3 = 76.33\%$	Glover-Tower Acid 62° U. S. Bé. $H_2SO_4 = 81.35\%$ $SO_3 = 66.41\%$	Pan Acid 60° U. S. Bé. $H_2SO_4 = 77.6\%$ $SO_3 = 63.35\%$	Chamber Acid 50° U. S. Bé. $H_2SO_4 = 62.18\%$ $SO_3 = 50.76\%$
	Pounds	Pounds	Pounds	Pounds	Pounds	Pounds	Pounds	Pounds	Pounds	Pounds	Pounds
100	250.00	269.83	280.96	293.05	306.25	310.91	315.73	327.53	376.45	394.63	492.51
99	247.50	267.13	278.15	290.12	303.19	307.80	312.56	324.26	372.69	390.70	487.59
98	245.00	264.43	275.34	287.19	300.13	304.69	309.41	320.99	368.93	386.76	482.67
97	242.50	261.74	272.53	284.26	297.06	301.58	306.25	317.72	365.17	382.81	477.74
96	240.00	259.04	269.72	281.33	294.00	298.47	303.09	314.44	361.40	378.86	472.82
95	237.50	256.34	266.91	278.40	290.94	295.36	299.93	311.16	357.64	374.92	467.89

The same laxity is shown in estimating the consumption of nitrate of soda used in the chamber process. At one factory it will be expressed in terms of the actual available sulphur; at another, on the sulphur assay of the ore used; at another, even on the tonnage of pyrites burned. In the case, therefore, of a factory using an ore containing 42 per cent. of sulphur by assay, of which 38 per cent. only was actually available, the percentage of sodium nitrate is actually at different factories expressed as follows:

Sodium nitrate used per ton of ore	1.14%
Sodium nitrate used per ton of sulphur by assay	2.71%
Sodium nitrate used per ton of sulphur actually available	3.00%

27. Table IV covers the yields, on actual sulphur, of the principal solutions of sulphur trioxide in practical use.

The estimation of yield in a factory is not a very simple matter. In fact, it is impossible to obtain the actual yield except as the general average of a great number of observations and measurements extending over a considerable period.

28. Sometimes every day, though usually once a week, a record is taken of all the acid of various strengths in all the apparatus and storage tanks of the system. The dimensions of all this apparatus are usually tabulated, so that every inch in depth corresponds to a certain cubic capacity. The cubic contents of the acid of different strengths being thus ascertained, all these acids of different strengths are reduced by Table I to one strength — in a fertilizer factory, for instance, to terms of 50° Baumé; in other factories to terms of monohydrate, or 66° Baumé.

In reducing these acids, careful note should be taken of their temperature—although this is not usually done, the error probably being considered as a constant one. In this allowance for temperature, Table V is used by the Manufacturers' Association of the United States.

TABLE V

ALLOWANCE FOR TEMPERATURE

At 10° Baumé 46. Fahrenheit = 1° Baumé
20° Baumé 31.8 Fahrenheit = 1° Baumé
30° Baumé 30.25 Fahrenheit = 1° Baumé
40° Baumé 31.46 Fahrenheit = 1° Baumé
50° Baumé 34.69 Fahrenheit = 1° Baumé
60° Baumé 40.00 Fahrenheit = 1° Baumé
66° Baumé 43.24 Fahrenheit = 1° Baumé

From the total stock of acid obtained in this way is deducted the amount on hand at the previous time of stock taking; and the amount deducted from stock during the period, either for use in other departments or sold, is added. The result gives approximately the amount made during the intervening period, and the yield is deduced either from Table V or by calculation from the amount of sulphur used during that period, a record of which has also been kept. These records and measurements are usually taken by the superintendent or acid maker. and are checked by him at intervals, together with some one of the proprietors or general officers of the company. After a certain time, the general average of the work done at any given plant can be ascertained with fair accuracy so long as the same raw material is used and the sulphur available has been determined with sufficient accuracy.

29. Sometimes the yield is roughly estimated, especially in the contact process, by the difference in content of sulphur oxides contained in the burner and exit gases. The formula given in Art. **53,** for use in testing the burner gas, enables this calculation to be made.

30. Another calculation that must often be made by an acid maker is in connection with the mixing of acids of various strengths in such a way as to produce an acid of any desired strength. This is done by Gerster's formula for mixing a strong solution of sulphur trioxide with a weak solution of sulphur trioxide to produce an intermediate solution of sulphur trioxide of any desired strength. This formula is as follows:

$$x = 100\frac{b-a}{a-c}, \qquad (1.)$$

when x = quantity of weak solution required to mix with 100 parts of the strong solution;

a = total sulphur trioxide in 100 parts of the solution desired;

b = total sulphur trioxide in 100 parts of the strong solution;

c = total sulphur trioxide in 100 parts of weak solution.

When the percentages of the solutions are given in terms of monohydrate instead of sulphur trioxide, it is only necessary to multiply the percentages of the monohydrate H_2SO_4 by .816326 to reduce them to terms of SO_3 as mentioned in Table I.

THE PRODUCTION OF SULPHUR DIOXIDE OR BURNER GAS

31. General Remarks.—Commercial processes for the manufacture of sulphuric acid are not intermittent, but continuous. It follows, therefore, that to secure regularity in these processes all the separate factors must be as regular and uniform as it is possible to make them. Furthermore, the process consists of a series of chemical combinations, which in any given plant are proportioned as to volume to the size of that plant. If absolute regularity can be secured in the various chemical combinations, then the maximum work or output will be secured from such plant. Any irregularities will result either in an incomplete series of combinations and consequent waste of raw material, or a reduction in output and consequent waste of capital outlay, owing to incomplete utilization of the plant, or both.

The first requisite, therefore, in sulphuric-acid manufacture is a uniform steady stream of gas of constant composition and volume. This gas should be produced at the least cost for labor and repairs and with as complete an oxidation of the sulphur in the furnace as possible. Unfortunately, all furnaces, except some mechanical furnaces for desulphurizing fines and one or two furnaces for burning brimstone are intermittent in their action. That is, the brimstone or ore is fed to them and the desulphurized cinder discharged at intervals. It is only, therefore, by the most skilful and careful work and attention to numerous details that even an approximation can be had to the desirable condition of the burner gas above referred to.

32. To counteract the intermittent character of the individual furnace, the following points must be observed:

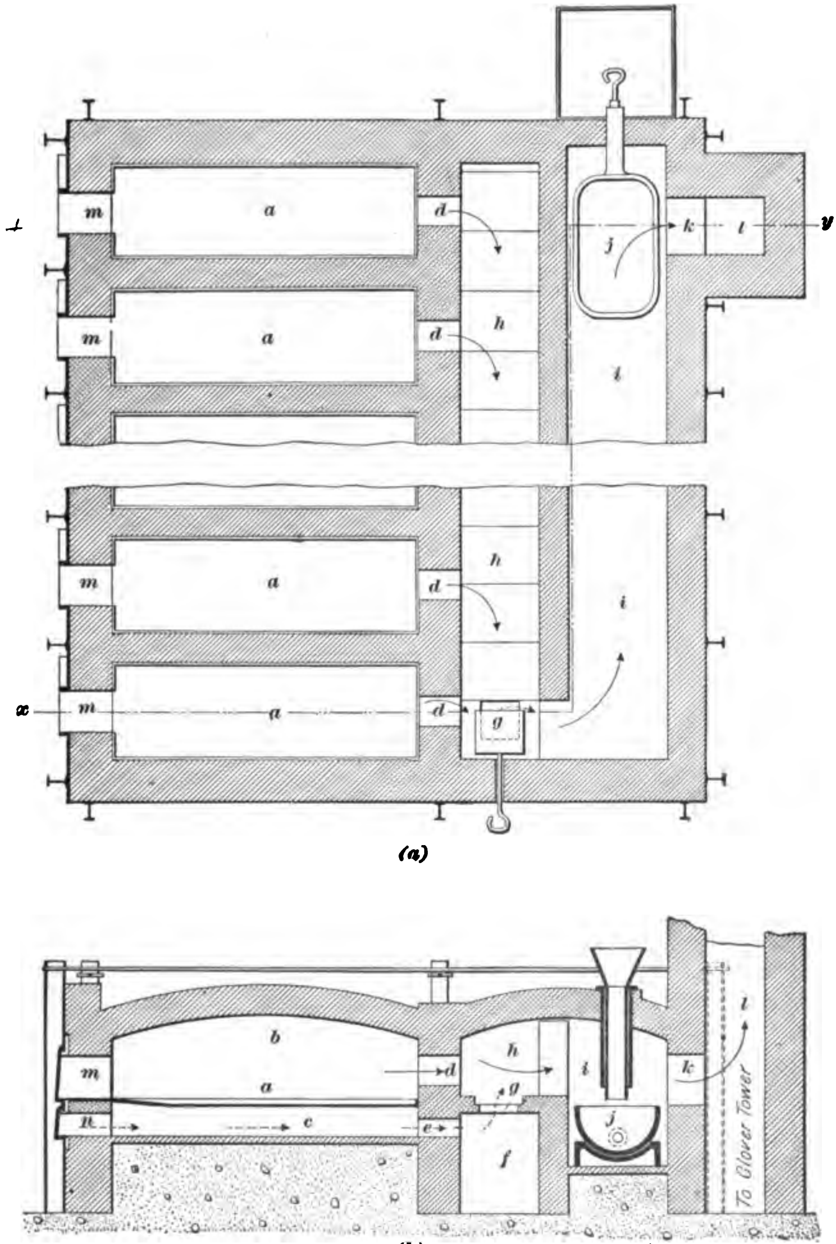
1. A considerable number of furnaces of small capacity are used, and are charged and discharged in series. For example, a sulphuric-acid works is designed to oxidize in 24 hours 14,000 pounds of actual sulphur to the trioxide. The ore available is iron pyrite in lump form, containing 50 per cent. of sulphur, about 1.5 per cent. of which will be lost either by being retained in the cinders or on other accounts, making the ore contain 48.5 per cent. of available sulphur; 28,800 pounds of ore will be required daily. To roast this ore, twenty-four burners will be used, each having a capacity for roasting 1,200 pounds in 24 hours. This ore is charged to each furnace in two charges of 600 pounds each, one every 12 hours, or the whole charge is divided up into forty-eight charges of 600 pounds each, so that one furnace of the twenty-four will be charged with 600 pounds of ore every half hour during the 24 hours. Furnaces are selected to be charged in rotation in such a way as to preserve as nearly as possible even conditions in every part of the bench of burners.

2. The furnaces are so constructed that the amount of air admitted to each furnace may be under as complete control as possible. It is evident that when any furnace has received a new charge of ore containing 50 per cent. of sulphur, it will require more air than it will 6 hours later, when much of the sulphur is burned off, and still more than it will when the sulphur is almost entirely burned off. In fact, the admission of much air when the ore only contains a small percentage of sulphur merely tends to cool the furnace and so prevent the thorough roasting of the ore. By judiciously regulating the admission of air to the individual burners, the general average of the gas in the flue common to all the burners is kept reasonably strong; and by the subdivision of the whole charge as above, a general average of gas is maintained that is as near an approach to continuous, uniform work as is possible under the circumstances.

FURNACES AND BURNERS FOR THE PRODUCTION OF BURNER GAS

33. General Remarks.—In the production of the burner gas and the efficient desulphurization of the various raw materials by the different furnaces now to be described—while various points peculiar to the management of each furnace will be pointed out—nothing but actual experience will secure satisfactory results. The minutest details tending to secure regularity must be insisted on in the management of the furnaces. Each ore or material has its own peculiar behavior in the furnaces, which when understood must be attended to.

When natural draft is used, meteorological conditions must be constantly considered and the drafting of the furnaces modified accordingly. Much trouble and anxiety is saved in this respect by the use of fans, or other apparatus devised to make the draft positive and controllable. Above all, it must be kept constantly in mind that the desired



(a)

(b)

FIG. 1

object is a uniform stream of burner gas of constant composition and volume, with as complete desulphurization of the ore as may be possible.

If the further oxidation of the sulphur dioxide of the burner gas to the trioxide is to be carried out by means of the chamber process, it is necessary to mix the burner gas at this point with nitric-acid fumes. The nitration of the gas will only be mentioned here in so far as it forms an adjunct to the desulphurizing furnaces; in other words, when the nitric acid is supplied by the decomposition of sodium nitrate and sulphuric acid by the heat of the burner gas. This method of adding the nitric acid is called *potting*, as it is done in large cast-iron pots, placed in a chamber or enlargement of the main gas flue of the furnaces, which is called the *niter oven.*

BRIMSTONE BURNERS

34. One of the simplest forms of **brimstone burners** is shown in Fig. 1 (*a*) and (*b*), (*a*) being the plan showing several burners connected with the common flue *h*, and (*b*) a vertical section on the line *x y*. The sulphur is charged through the door *m* upon the cast-iron pan *a*, where it is burned. The supply of air to the burning sulphur is carefully regulated. The gases containing the sulphur dioxide collect in the chamber *b* and pass through the flue *d* into the common flue *h*. To prevent overheating pan *a*, air is admitted under it through *n*, passing through *c*, *e*, *f*, and *g*, where it finally mixes with the gases and sublimed sulphur coming from *h*, as shown in (*a*). These mixed gases now pass into the combustion chamber *i*, where the combustion is completed.

If the burner gas is to be used for making sulphuric acid by the chamber process, it is mixed with fumes of nitric acid evolved in the pot *j* by the action of sulphuric acid on niter. The gas now passes through the flues *k* and *l* to the Glover tower. If it is to be used in the contact process, the nitrating is omitted.

35. Harrison-Blair Brimstone Burner.—This burner, which is of the continuous-feed and intermittent-discharge type, is shown in plan and longitudinal section in Fig. 2 (*a*) and (*b*). The brimstone is fed into the burning pan *a* through the funnel *d*, which is kept full. The brimstone settles as fast as that on the pan melts. Air for the combustion is supplied through the door *c*. The sulphurous gases pass from the chamber *b* through the flues *e* and *f* into the flue or chamber *i*; additional air for completing the combustion is supplied to *f* through the openings *f′*. In passing from *f* to *i*, the gases are led through a series of baffle walls lined with pigeonholed brick, shown at *g*, and over the niter pots *h*. From the flue *i* the nitrated gases pass through the flues *j* and *k* to the Glover tower. About once in 24 hours the ashes are removed through the door *c*.

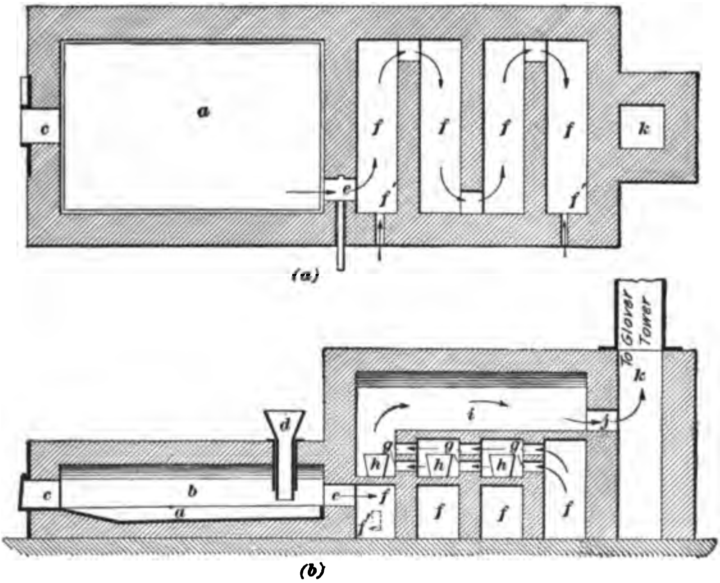
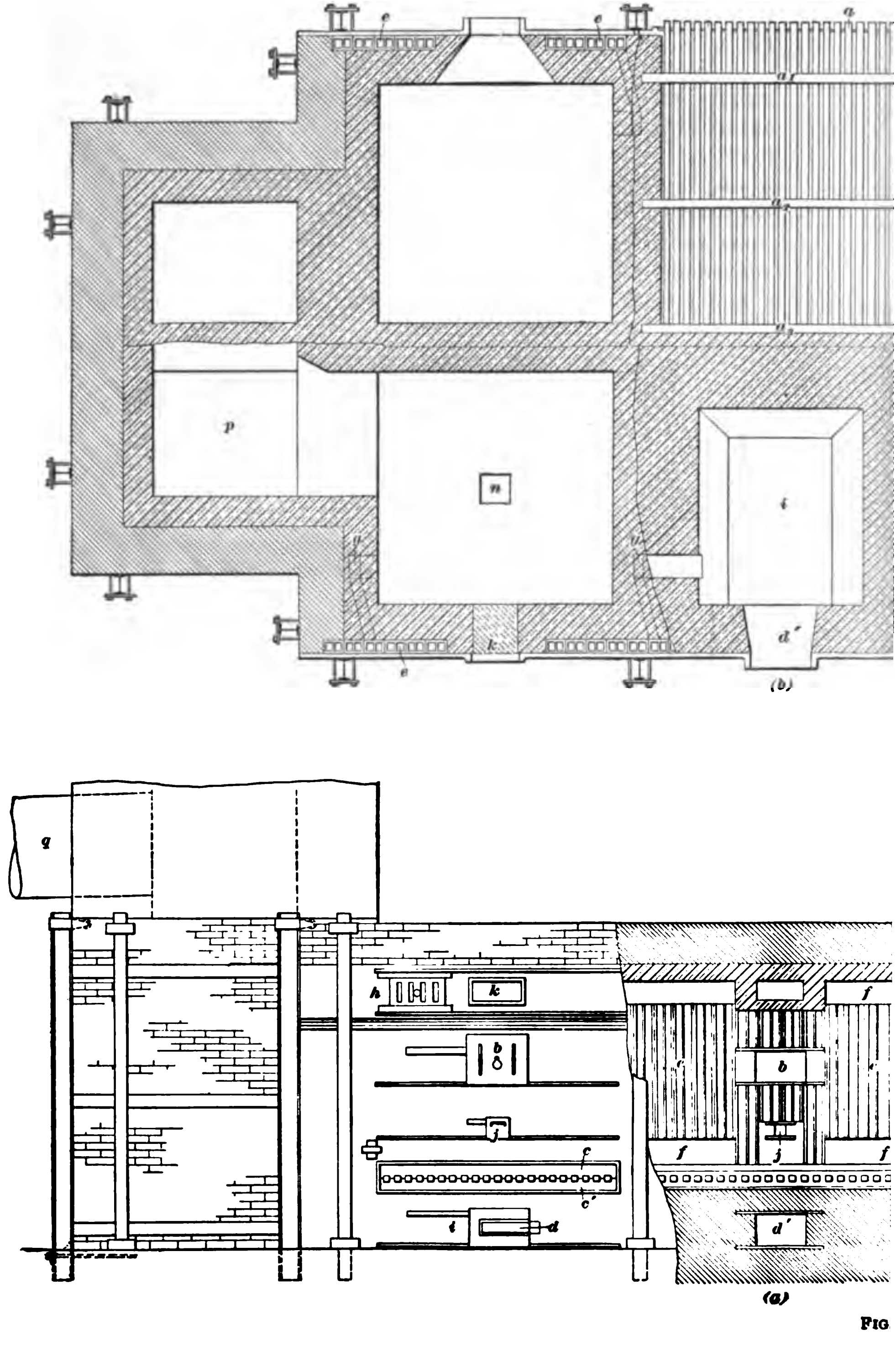
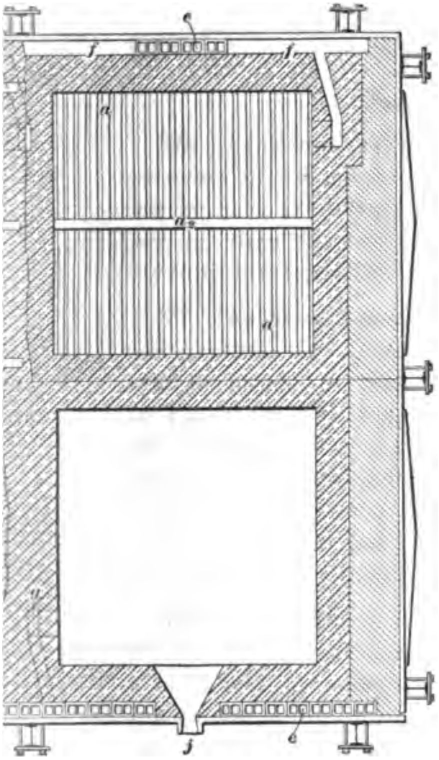
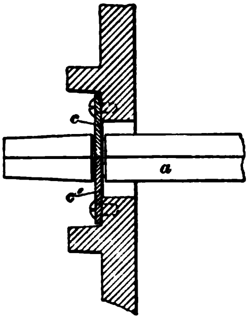


FIG. 2

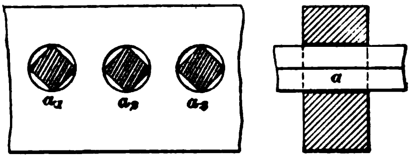


FIG

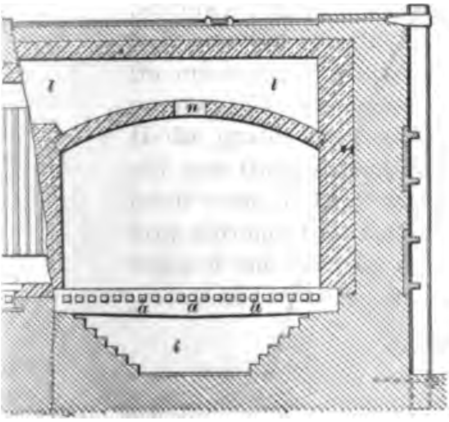


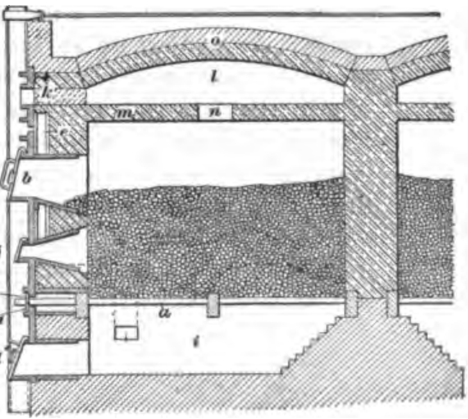


(e)



(d)





(c)

8

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PYRITES BURNERS

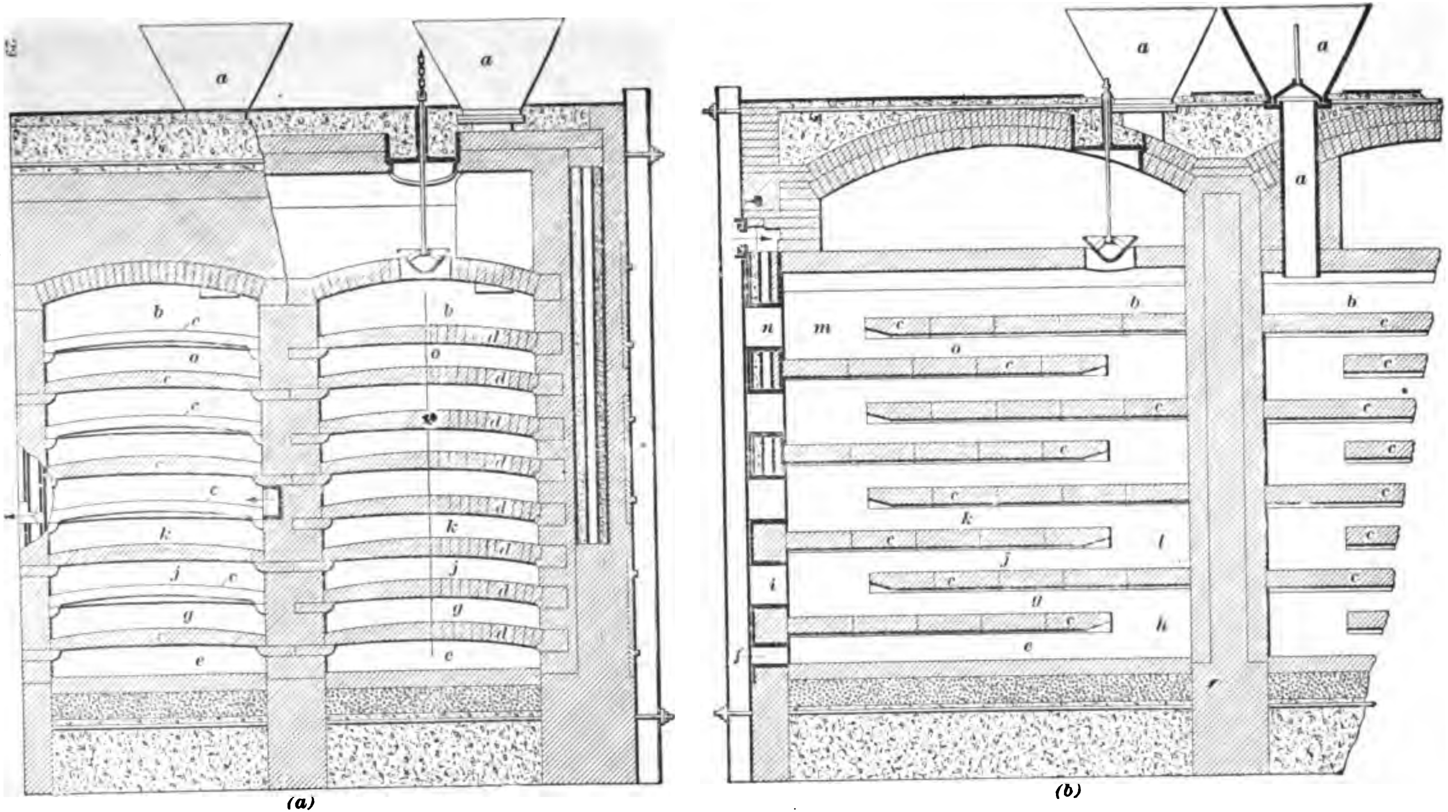
36. Furnaces, or burners, for roasting pyrites for the recovery of the sulphur, as SO_2, are of many styles, depending both on the nature of the pyrites used and on the manner of their operation. The following descriptions will serve to illustrate the most important forms.

37. Falding Lump Burner.—This furnace is used for self-roasting ores. It has an intermittent feed and is operated by hand. A bench of six furnaces is shown in detail in Fig. 3 (*a*), (*b*), (*c*), (*d*), and (*e*). (*a*) is a side elevation, also showing vertical sections through several parts; (*b*) is a plan showing horizontal sections through several different parts; (*c*) shows a vertical section from front to back through the center of an individual furnace; (*d*) and (*e*) will make themselves clear in the following description:

38. At *a* is the grate upon which the ore is burned. The thickness of the bed of ore carried on the grates will be from 2 to 2½ feet, as shown in (*c*), but will vary somewhat according to the sizing and character of the ore. It must in any case permit a passage of the air uniformly through its mass and not in spots or against the furnace walls. The ore is shoveled into the furnace through the charging door *b*, and must be spread as evenly over the surface of the bed as possible, being slightly deeper against the walls of the furnace, as shown in (*c*). The grate bars *a* are usually bars of square wrought iron from 1½ to 2 inches square, slightly rounded where they pass through the supporting cast-iron bearers a_1, a_2, a_3. These bars must be spaced so as to be best adapted for the size of the ore to be burned. When the ore is sized by screens, it is a good plan to have a certain number of furnaces spaced to accommodate each size of ore. If the grates are spaced too closely, the larger lumps will not pass through and the draft will soon be seriously interfered with; if they are spaced too far apart, the bed will drop through too rapidly and be difficult to control. At the front of the furnace the bars pass through a wrought-iron plate *c* and *c'*, that can be removed in two sections; as the bars are turned down to a circular section where they pass through the plates, the plates fit closely and prevent the entrance of "false" air into the furnace; the plates also tend to steady the grate bars. In order to drop the roasted ore through the grate, use is made of a large wrench, or key, fitting on to the square end of each grate bar. Each grate bar is by this means twisted backwards and forwards a few times, until an amount of roasted ore has been dropped through the grate into the cinder pit *i* equivalent to the amount of ore about to be charged through the charging door *b*. The roasted cinder is removed by means of the door *d'*. The cinder-pit door *d'* is provided with a slide or gate valve *d* for regulating the admission of air for combustion.

39. The furnace illustrated has hollow front walls *e*, which serve to prevent radiation of heat from the furnace, permitting the burner gas to be passed to the Glover tower at a high temperature; or, if desired, permitting the air supply for combustion of the ore to be preheated. The air passes through the regulator *h* into the air duct *f*, hollow tiles *e*, and side channels *g*, beneath the furnace grate. The door *j* is used for inserting a bar in case of bad clinkering low down in the bed. The bricked-up opening *k* enables the flue *l* to be cleaned when obstructed with flue dust. Each furnace has a roof *m*, in which is an opening *n*, through which the burner gas finds its way into the main flue *l* formed by the longitudinal arch *o*, and thence into the flue *p* common to both sides of the furnace bench, whence it is carried by the cast-iron pipe *q* to the Glover tower. In case nitration by means of potting is to be used, the niter oven will be placed in *p*, which also serves as a dust collector for coarse flue dust that may be carried over.

40. To start this furnace, about 2 feet of roasted ore is put upon the grates. (Incompletely roasted ore and brickbats broken so that they can be passed through the grates may be used.) A light wood or coke fire is then lighted on


23
a
a
b
c
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c
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f
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r

(a)

(b)

FIG. 4

the bed of each furnace. When the furnace is heated to a dull-red heat, the coke or wood ash may be removed and ore charged and the gas turned into the acid plant.

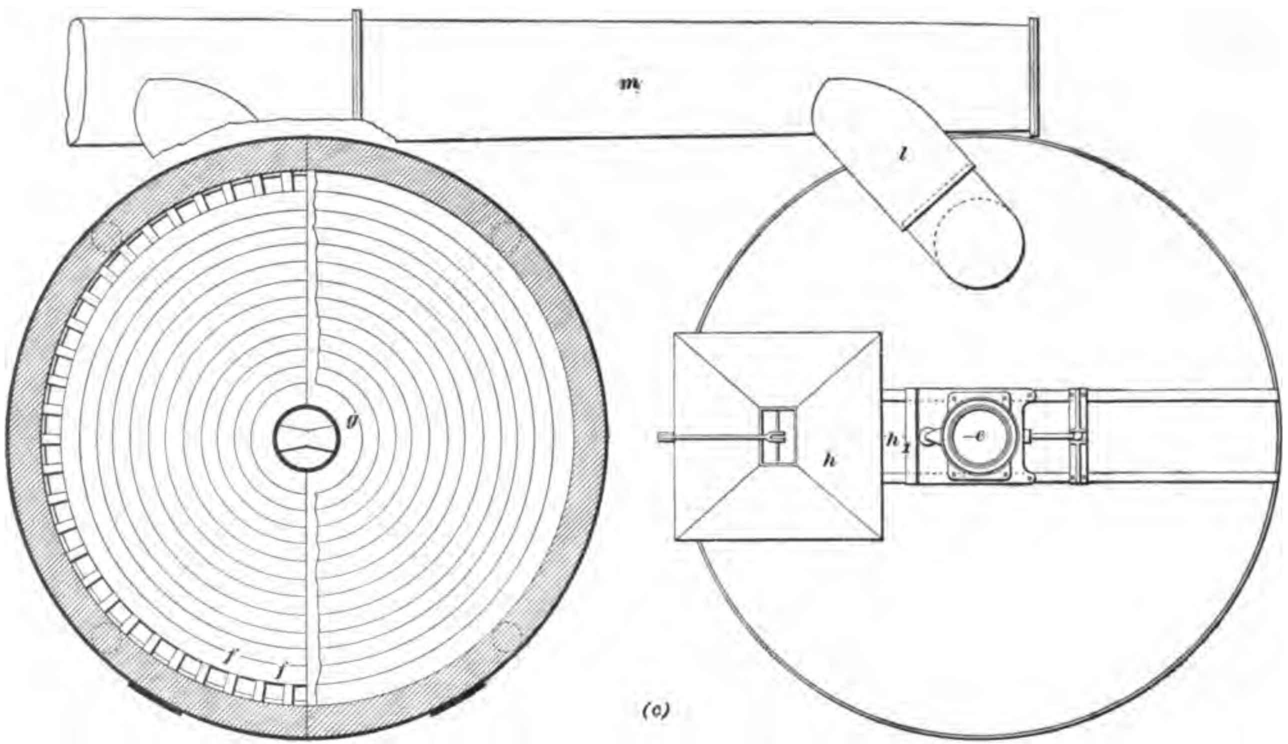
41. Maletra-Falding Furnace.—This type of furnace is adapted to the roasting of fines. It is worked by hand and has an intermittent feed. Fig. 4 (*a*) and (*b*) shows two sectional views of it, corresponding parts being lettered alike in both views.

Ore is introduced by means of the hopper and bell *a* on to the back end of the upper shelf *b*. These shelves can be constructed either with fireclay slabs *c*, *c*, *c*, or brick arches, as shown at *d*, *d*, *d*. After the furnace has been brought to a red heat ore is spread over all the shelves. After the expiration of a certain time the ore is raked off the lower shelf *e* through the door *f*. The ore from shelf *g* is then pushed through the opening *h* on to shelf *e*, through the door *i*, and spread over shelf *e*. The ore from shelf *j* is raked forwards on to shelf *g*, over which it is spread. The ore from shelf *k* is pushed through the opening *l* and spread on shelf *j*, and so on until the ore from shelf *b* is finally raked through the opening *m* by means of door *n* and spread on shelf *o*. Every shelf in the furnace is now covered with ore except the upper shelf *b*. A charge of ore is now introduced through the hopper and bell *a* on to the upper shelf *b* and spread over it. The furnace is now left for from 6 to 12 hours, when the lower shelf is discharged and the whole operation repeated.

These furnaces are generally constructed in groups of from four to sixteen, each of which has a capacity of from 1,600 to 2,000 pounds of pyrites in 24 hours.

42. Herreshoff Furnace of the MacDougall Type. This furnace is provided with mechanical rotary stirrers and has a continuous feed. It is designed for burning fines, and is illustrated in Fig. 5 (*a*), (*b*), and (*c*).

This furnace has five shelves, or hearths, *a*, *a*, *a*, *b*, *b*. The rotating, central, hollow, cast-iron column *c* carries a



(c)

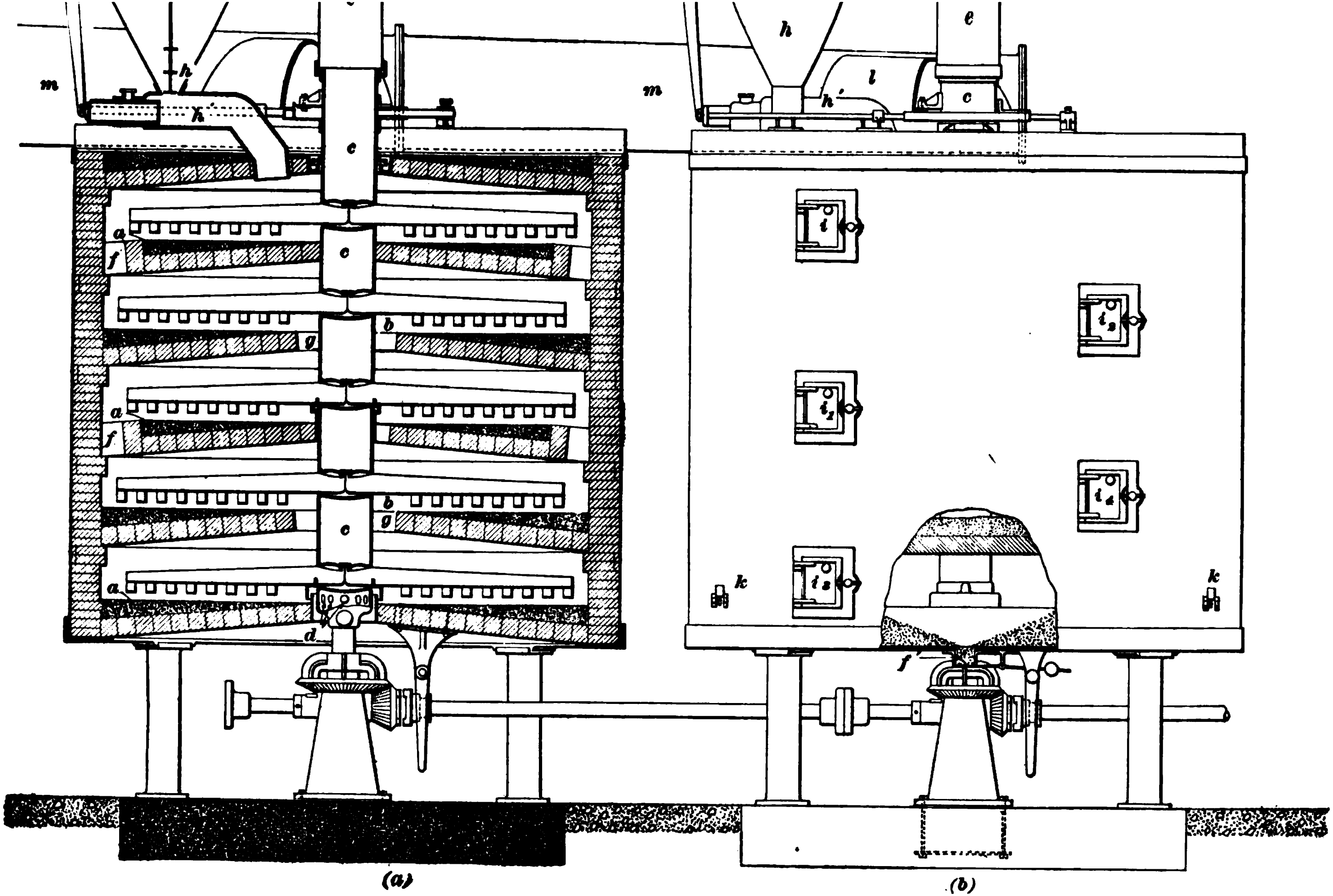


FIG. 5

pair of arms on each shelf. The column and arms adjacent to the column are kept safely cool by a current of cold air drawn through the holes d by natural draft created by the 30-foot stack e. The teeth, or stirrers, operating on hearths a, a, a are set at such an angle as will gradually work the ore from the center to the periphery, where it falls through ports f on to the hearths b, b and finally through discharge port f', which is closed by a balance valve suitably weighted to control the discharge. The teeth on the stirrers, operating on hearths b, b, are set at such an angle as to gradually work the ore from the periphery to the center, where it falls through the annular ports g. The ore is fed to the furnace by means of the hopper and plunger feed h, h', which is operated by the central revolving column c in such a way as to supply a desired quantity of ore at each revolution of the stirrer arms. These usually make a complete revolution once in 2 minutes and can be taken out and replaced by means of the doors i, i_1, i_2, i_3, i_4.

43. The air for supplying the necessary oxygen for the combustion of the ore and the production of a suitable burner gas is admitted on the lower shelf through gate valves k, k, etc., and passing through the furnace over the roasting ore, finally leaves the furnace as burner gas through the cast-iron pipe l, which connects with the common, or main, cast-iron burner-gas flue m.

If the mechanical construction of this furnace has been properly attended to, it can be readily started by first removing the arms, covering the hearths with a bed of roasted ore or cinder, then heating it to a dull-red heat by means of light wood fires on each shelf, then replacing the arms and feeding the ore in the usual way.

44. Spence Reciprocating Type of Furnace.—This style of furnace is designed for self-roasting fines. It has a continuous feed, the ore being carried from one shelf to another by means of a reciprocating device. Its mechanism is

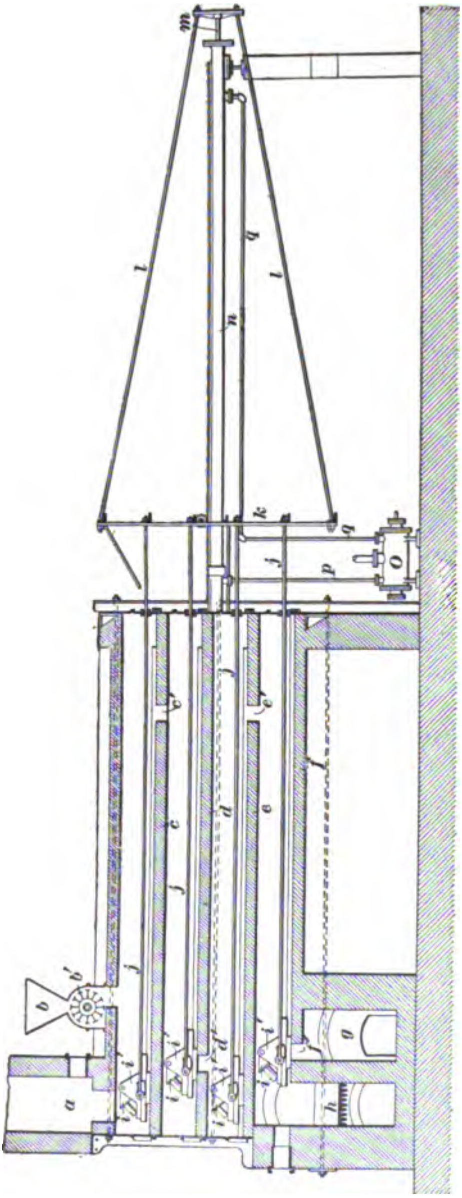


Fig. 6

shown in Fig. 6. The exit flue *a* is for the burner gases. The hopper *b* is kept full of ore, which is fed into the furnace in front of the rake *i* upon the hearth *c* by the continuous feed *b'*: As the rake *i* is drawn over the hearth *c* by the reciprocating mechanism shown at the right of the figure, it draws and spreads the accumulated ore over the hearth and causes part of it to fall through the opening *c'* upon the next lower hearth *d*. On its return stroke the rake on hearth *d* carries this ore over the hearth in the opposite direction, it then falling through the opening *d'*. From the lower hearth *f* it falls through *f'* into the pit *g*. A similar operation takes place on each hearth.

45. The ore rakes have triangular cast-iron teeth and extend

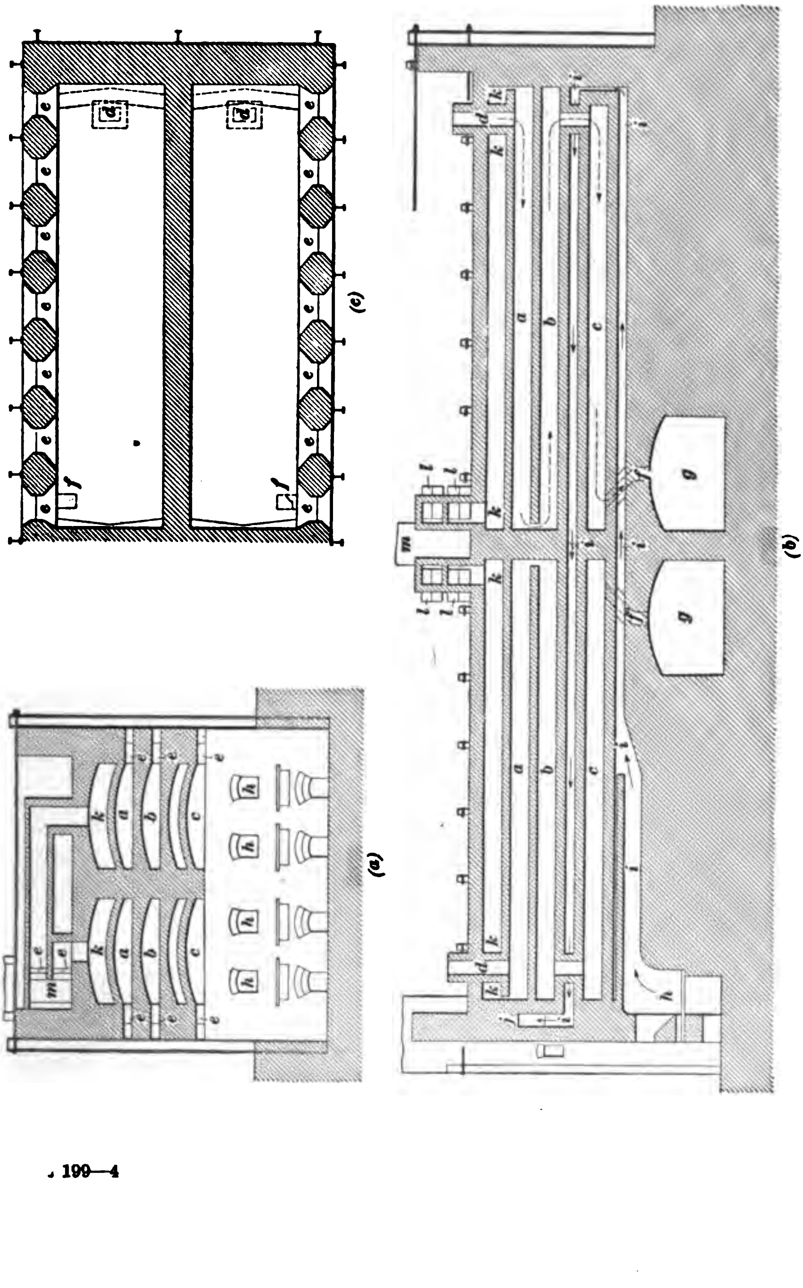


FIG. 7

across the furnace; they are attached to the skids *i'*. The reciprocating mechanism consists of a hydraulic cylinder *n* with a piston and piston rod *m*. The motion of the piston is transmitted to the rakes by means of the rods *l* and *j* and the frame *k*. Water is furnished to either end of the cylinder through the pipes *p* and *q* by the pump *O* by means of automatic valves.

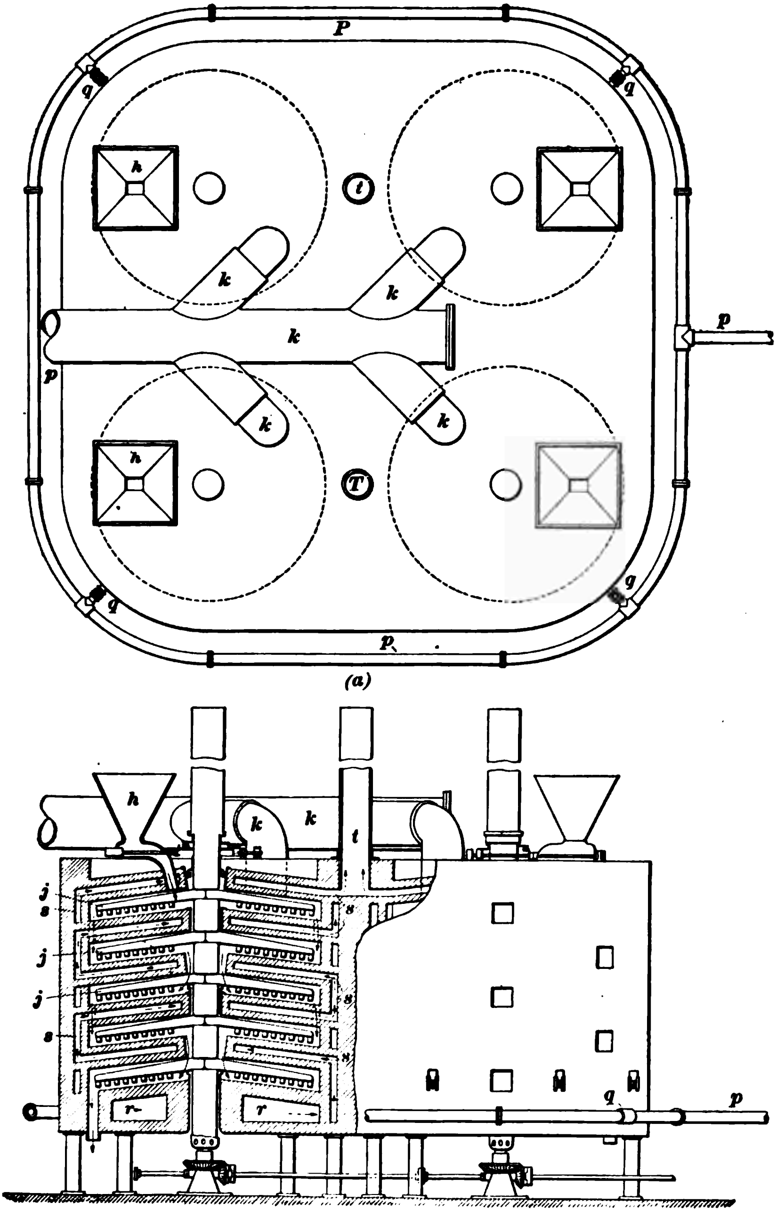
When the furnace is to be started up, a fire is built in the fireplace *h*, but after the furnace is well under way it is bricked up, the sulphur of the ore being the only fuel necessary for the continuation of the operation.

46. Rhenania Muffled Type of Furnace.—This furnace is for roasting refractory ores; the feed is intermittent. It is illustrated in Fig. 7 (*a*), (*b*), and (*c*). *a*, *b*, and *c* are the hearths, or shelves, upon which the ore is burned. Ore is fed upon the hearth *a* from time to time through the openings *d*. The ore is worked from shelf to shelf by means of slice bars introduced through the doors *e*, and finally passes through the ports *f* to the cinder pits *g*, from which it is periodically removed.

Heat for combustion is supplied by the fireboxes *h*; this heat passes through the whole length of the double furnaces and returns by means of the flues *i*, passing into the stack at *j*. The products of combustion of the ore pass over the ore and in the opposite direction into a flue *k*, on the top of the furnace, and thence by dampers *l* into the stack *m* connecting with the Glover tower.

These furnaces are built in blocks of four, fired by means of two fireboxes with two doors each, at one end of the block of four; the fire flues *i* pass from end to end of all four furnaces and back again

47. MacDougall Type of Muffled Furnace. — This furnace closely resembles in structure and operation the Herreshoff furnace already described. When these furnaces are muffled, that is, supplied with separate and distinct combustion chambers and flues for the purpose of introducing heat into the furnace other than that produced by



(a)

(b)

FIG. 8

the combustion of the ore itself, and the products of combustion are kept separate and distinct from the burner gas, they are constructed in groups of four. The feed is continuous. The fuel used may be oil, natural, or producer gas.

Fig. 8 (*a*) and (*b*) shows this furnace in plan and vertical section. The revolving arms *j* are operated in the same manner as in the Herreshoff furnace. Ore is fed in through the hopper *h* to the upper hearth and gradually worked outwards by the revolving arms and down to the next lower hearth, then towards the center and through another opening to the third hearth, etc. The fuel is supplied by means of the pipe *p* and branches *q* to the combustion chamber *r*, and thence to the flues *s* around the muffles. The products of combustion pass off through the stacks *t* and the burner gas through the pipes *k*.

TESTING THE BURNER GAS

48. Collecting the Sample.—Gas is aspirated from the flue common to all the furnaces at a point chosen so as to secure a reliable average of the gas. If there is any doubt as to the gas being an average, it should be aspirated at several points until a point yielding a satisfactory average is obtained.

49. Reich's Test for Sulphur Dioxide.—This test, which is described fully in *Quantitative Analysis*, is generally used, but is modified for sulphuric-acid works as follows: The deci-normal solution of iodine, containing 12.65 grams of iodine per liter, and the starch solution are prepared in accordance with the instructions given in *Quantitative Analysis.* The solutions must be kept in a dark, cool place. It is a good precaution to use small bottles, holding just sufficient for the day's tests, for use in the works, leaving the stock in the laboratory.

As in practice it is often necessary to make tests in several different parts of the works, it becomes necessary, for making the test, to fit up a simple cheap apparatus that can be left at each place. The apparatus shown in Fig. 9 can be readily put together and arranged on a rough shelf or shelves, in almost any place, so as to be ready for instant use. A pipette being left on the shelf, it is only necessary to carry around the two small bottles of solutions. A spare 2-liter jar being kept on the shelf, the aspirating water can be saved, or in case many tests must be made and water-supply pipes are available, a water aspirator can be used; failing this, a steam aspirator. In some works the pipes through which the gas is aspirated are all led to the laboratory, and being supplied with valves and a steam aspirator, tests can be made in the laboratory without going to the different parts of the works. This is a very convenient though somewhat costly plan.

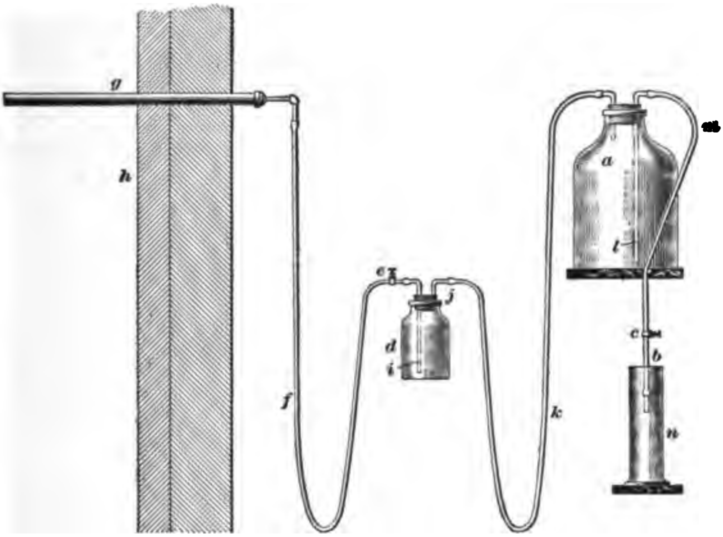


FIG. 9

50. This apparatus consists of a 1-inch iron pipe *g* penetrating the flue *h*, the gas in which is to be tested. This pipe is connected by means of the rubber tube *f* and pinch cock *e* with the absorption bottle *d*. The glass tube *i* penetrates the rubber stopper and extends nearly to the bottom of the bottle. The exit tube *j* extends just through the stopper. By this arrangement, the gas drawn through *f* bubbles through the reagent in *d*. The rubber tube *k* connects *d* with the 4-quart aspirating bottle *a*. In construction, this aspirator is similar to the absorption bottle, the positions of the tubes being reversed. When filled with water, the latter is siphoned off through *l* and *m*, creating a partial vacuum in the upper part of *a*. During operation, the volume of water (which is equal to the volume of gas used) drawn from *a* is measured in the graduated cylinder *n*.

51. To make the test, fill the large bottle *a* with water; see that the stopper is perfectly tight; start the siphon by slight suction through the nozzle *b* and close the pinch cock *c*; fill the 8-ounce bottle *d* about one-quarter full of clean water (slightly warmed in winter); and pour into this about a teaspoonful of the starch solution. Then, by means of the pipette take 10 cubic centimeters of the deci-normal iodine solution and add to the water and starch solution in the 8-ounce bottle; replace the rubber stopper tightly and close the pinch cock *e* between the flue and the small bottle. Then open the pinch cock *c* at the nozzle and allow the water to waste; when the water ceases to run, proving the tightness of corks and connections throughout the apparatus, open the pinch cock *e* between the flue and the small bottle *d*. Take the small bottle in the left hand, keeping the right hand on the pinch cock *c* at the nozzle, and shake the bottle not too violently, holding it to the light in such a way that any change in color can be readily noted; when a considerable change occurs in the color, stop the flow of water with the right hand. If the color does not entirely disappear, aspirate a little gas carefully until it does; then close the pinch cock *e* between the flue and the small bottle. The tube *f* between the flue and this pinch cock is now filled with the gas to be tested. Remove the stopper from the small bottle and add 10 cubic centimeters of the iodine solution with the pipette; replace the cork tightly; open the pinch cock nearest the flue; then, with the pinch cock *c* in the right hand carefully waste water until the liquid in the glass tube, terminating the tube from the flue, is depressed to the bottom; or, in other words, until the tube is filled with the gas to its extreme end in the small bottle. Just before the first bubble of gas would escape and pass through the solution, allow the water to commence running into the graduated measuring jar; shake the small bottle as before and stop the water running the instant the color is discharged. The number of cubic centimeters of water that the jar holds at the point of discharge of color from the solution represents the volume of gas required to decolorize the solution, from which the percentage of sulphur dioxide in the burner gas is calculated.

52. The reaction taking place is as follows:

$$2I + SO_2 + 2H_2O = 2HI + H_2SO_4$$

Omitting any correction for temperature and pressure, the percentage of sulphur dioxide is calculated by means of the following formula:

$$p = \frac{111.4 \times n}{m + 1.114 \times n}. \qquad (2.)$$

p = percentage of SO_2.
n = the number of cubic centimeters of $\frac{1}{10}$ normal iodine solution used;
m = the number of cubic centimeters of water run into the measuring jar.

If the percentage of sulphur dioxide in the gas is very small, and, thus, m is very large in proportion to n, the formula may be simplified into

$$p = \frac{111.4 \times n}{m}. \qquad (3.)$$

In testing exit gas, using 10 cubic centimeters of a $\frac{1}{100}$ normal or centi-normal solution of iodine, formula **2** becomes

$$p = \frac{111.4}{m + 1.114}. \qquad (4.)$$

As in the case of formula **3**, when the percentage of SO_2 is very small and m is very large in proportion to n (as it usually is), the formula becomes

$$p = \frac{111.4}{m}. \qquad (5.)$$

By means of the following tables, the percentage of sulphur dioxide in burner and exit gases can be read directly from the volume of water in the measuring jar.

53. To calculate the yield of sulphur dioxide from the difference in content of SO_2 in the entering and exit gases, the following formula is used:

$$\text{Yield} = \frac{2a - 2b}{2a - 3ab}, \qquad (6.)$$

where a = the percentage of SO_2 in the entering gas;
b = the percentage of SO_2 in the exit gas.

CALCULATION OF VOLUME OF BURNER GAS

54. The general principles contained in *Theoretical Chemistry* regarding corrections for temperature and pressure and the corrections of gaseous volumes treated in *Physics*, *Theoretical Chemistry*, and *Quantitative Analysis* apply to burner gas. A rough approximation of the volume of burner gas at 0° C. and 960 millimeters barometric pressure, or at 32° F. and 29.92 inches barometric pressure may be made as follows:

55. One liter of sulphur dioxide weighs 2.86336 grams, or 1 cubic foot weighs .1787 pound. Therefore, 1 pound of sulphur burned in 24 hours produces 11.191968 cubic feet of sulphur dioxide, or .0077722 cubic foot per minute; therefore, neglecting the sulphur trioxide formed,

$$\frac{(.77722 \times \text{actual available sulphur burned in 24 hours})}{\text{average per cent. of } SO_2 \text{ in burner gas produced}} =$$

the cubic feet of burner gas per minute;

TABLE VI

TABLE FOR FINDING THE PERCENTAGE OF SO_2 IN BURNER GAS WHEN USING 10 CUBIC CENTIMETERS OF DECINORMAL IODINE SOLUTION (CALCULATED BY FORMULA 2)

Per Cent. of SO_2	Cubic Centimeters of Water	Per Cent. of SO_2	Cubic Centimeters of Water	Per Cent. of SO_2	Cubic Centimeters of Water	Per Cent. of SO_2	Cubic Centimeters of Water
.0	....	3.2	337.0	5.5	191.0	7.8	132.0
1.0	1,103.0	3.3	327.0	5.6	188.0	7.9	130.0
1.1	1,002.0	3.4	317.0	5.7	184.0	8.0	128.0
1.2	917.0	3.5	307.4	5.8	181.0	8.1	126.0
1.3	846.0	3.6	298.0	5.9	178.0	8.2	125.0
1.4	785.0	3.7	290.0	6.0	175.0	8.3	123.0
1.5	732.0	3.8	282.0	6.1	172.0	8.4	122.0
1.6	685.0	3.9	275.0	6.2	169.0	8.5	120.0
1.7	644.0	4.0	267.0	6.3	166.0	8.6	118.0
1.8	608.0	4.1	261.0	6.4	163.0	8.7	117.0
1.9	575.0	4.2	254.0	6.5	160.0	8.8	116.0
2.0	546.0	4.3	248.0	6.6	158.0	8.9	114.0
2.1	519.0	4.4	242.0	6.7	155.0	9.0	113.0
2.2	495.0	4.5	236.0	6.8	153.0	9.1	111.0
2.3	473.0	4.6	231.0	6.9	150.0	9.5	106.0
2.4	453.0	4.7	226.0	7.0	148.0	10.0	100.0
2.5	435.0	4.8	221.0	7.1	146.0	10.5	95.0
2.6	417.0	4.9	216.0	7.2	144.0	11.0	90.0
2.7	402.0	5.0	212.0	7.3	142.0	11.5	86.0
2.8	387.0	5.1	207.0	7.4	139.0	12.0	82.0
2.9	373.0	5.2	203.0	7.5	137.0		
3.0	360.0	5.3	199.0	7.6	135.0		
3.1	348.0	5.4	195.0	7.7	134.0		

or, letting x = cubic feet of burner gas per minute at 0° C.;

a = available sulphur in pounds burned in 24 hours;

b = average percentage of sulphur dioxide in the burner gas produced;

then,
$$x = \frac{.77722 \times a}{b}. \qquad (7.)$$

TABLE VII

TABLE FOR FINDING THE PERCENTAGE OF SO_2 IN EXIT GAS WHEN USING 10 CUBIC CENTIMETERS OF CENTI-NORMAL IODINE SOLUTION (CALCULATED BY FORMULA 4)

Per Cent. of SO_2	Cubic Centimeters of Water	Per Cent. of SO_2	Cubic Centimeters of Water	Per Cent. of SO_2	Cubic Centimeters of Water	Per Cent. of SO_2	Cubic Centimeters of Water
.05	2,226.9	.55	201.5	1.05	105.0	1.55	70.8
.10	1,112.9	.60	184.6	1.10	100.1	1.60	68.5
.15	741.6	.65	170.3	1.15	95.8	1.65	66.4
.20	555.9	.70	158.0	1.20	91.7	1.70	64.4
.25	444.5	.75	147.4	1.25	88.0	1.75	62.6
.30	370.2	.80	138.2	1.30	84.6	1.80	60.8
.35	317.2	.85	130.0	1.35	81.4	1.85	59.1
.40	277.4	.90	122.6	1.40	78.5	1.90	57.5
.45	245.5	.95	116.2	1.45	75.0	1.95	56.0
.50	221.7	1.00	110.3	1.50	73.2	2.00	54.6

For example, 10,000 pounds of available sulphur is burned in 24 hours with the production of a burner gas containing 7.5 per cent. of sulphur dioxide, substituting in formula **7**,

$$x = \frac{.77722 \times 10}{7.5} = \frac{7{,}772.2}{7.5}$$

= 1,036.3 cubic feet of burner gas per minute, containing 7.5 per cent. of sulphur dioxide.

This quantity of gas at normal pressure is corrected for a temperature of, say, 60° F. or 15.6° C. by the following formula:

$$V_t = V_o + \frac{t\,V_o}{273}. \qquad (8.)$$

V_t = volume at the given temperature;
V_o = volume at 0° C.;
t = temperature in degrees C. at which volume is to be calculated.

Substituting, $V_o = 1{,}036.3$ cubic feet, $t = 15.6°$ C.,

$V_t = 1{,}036.3 + \frac{1{,}036.3 \times 15.6}{273} = 1.095.5$ cubic feet per minute.

The approximate temperature at which the burner gas leaves the common flue of a bench of burners is about 1,000° F., or, say, 538° C., and at this temperature the volume of burner gas produced as above would be 3,078.5 cubic feet per minute. With gas containing only 5 per cent. of sulphur dioxide, the quantities at 0° C. and 538° C. would be, respectively, 1,554.4 and 4,617.6 cubic feet per minute.

56. It is evident, therefore, that great economy in the size of the apparatus is effected by keeping the gas as strong as possible; and also that in order to prevent unnecessary obstruction in the flues and apparatus, attention must be given to designing them of suitable capacity to handle the volumes of gas in accordance with the approximate temperature of the gas at the different stages of the process.

THE CATALYTIC, OR CONTACT, PROCESS

57. Preliminary Remarks Concerning Contact Phenomena.—In considering the so-called contact phenomena in chemistry, it must not be forgotten that contact is a necessary condition for every chemical reaction. Other conditions remaining constant, the rate of progress of a chemical reaction is accelerated by increasing the number of points of contact. To insure complete reaction between solids, it is necessary to reduce them to very fine powder and to mix them as thoroughly as possible. These considerations may throw some light on the large class of contact reactions; that is, such as appear to proceed from the mere presence of certain special substances. Porous or powdery substances are very prone to act in this way, especially spongy or very finely divided platinum and charcoal. A number of other substances, such as finely divided silica, act in a similar way.

Another consideration is the action, by contact, that two substances rich in oxygen have upon each other, in that so long as they are separate they retain their oxygen; but upon contact oxygen is liberated from both of them. As, for example, a solution of bleaching powder, which does not evolve oxygen when heated by itself, but upon the addition of a small quantity of certain oxides, for instance, cobalt oxide, first oxidizes the cobalt oxide to a higher oxide, which in contact with the bleaching powder decomposes into oxygen and the lower oxide. This resulting lower oxide, on contact with the bleaching powder, again results in the higher oxide, which again gives up its oxygen and produces the lower oxide, and so on

58. The action of nitrogen oxides in the chamber process is noteworthy as showing that intermediate forms of reaction may be found in the contact, or catalytic, phenomena. In this case a small quantity of nitrous oxide induces a definite chemical reaction between large masses of sulphur dioxide, oxygen, and water, forming sulphuric acid, the N_2O_3 being finally again liberated, as will be seen when considering the chamber process.

In the case of the combination of sulphur dioxide and oxygen by contact action, it is possible that either on account of an electrical action induced by the contact, or for some other obscure cause, a polarization or increased activity of the oxygen in the air is procured, enabling it to combine with the sulphur dioxide.

59. Richter suggests that as all bodies having a high heat of formation, and also those being decomposed at a high heat, must have their heat of formation removed or conducted away in order that their production may be at all possible; the catalytic action of many metals, for example, platinum, in this reaction, may be due to their conducting off the heat; or else that the bodies in question forming a galvanic chain, the chemical energy is removed as electricity, just as in the union of hydrogen and oxygen at ordinary temperatures due to the formation of a polarization current.

60. Contact Mass or Material Used in the Manufacture of Sulphuric Acid by the Contact Process. Broadly speaking, there are four contact masses in commercial use for the manufacture of sulphuric acid, viz.: (1) Asbestos, clay, pumice, or other porous material impregnated or coated with platinum. (2) Porous or fibrous material as above impregnated with cupric sulphate (blue vitriol). (3) Mass composed of crusts formed of an earthy or alkaline water-soluble salt impregnated or coated with platinum. (4) Ferric oxide (roasted pyrites).

For the first class of contact masses, where the platinum is combined with a fibrous or porous material insoluble in water, there are two principal methods of preparation, the first being to add finely divided platinum (platinum black), previously prepared, to the fibrous or porous material; and the second, to add either a dry or liquid salt of platinum to the inert material and then subject the mixture to a process that will reduce the platinum.

61. The usual methods for preparing the first class of contact masses are as follows:

1. The powdered fibrous or porous material is mixed with platinum black, a combustible material required to secure porosity (flour, bran, sawdust, cork dust, etc.), and an agglutinative substance (gelatine, gum, etc.).

2. The fibrous or porous material is mixed with an oxide or dry salt of platinum, a combustible material, and an agglutinative. It is then dried and reduced by calcination.

3. The fibrous or porous material is soaked in a platinum-salt solution, reduced by one of the methods described in the paragraphs immediately following, and after the addition of the combustible organic matter and agglutinative, is molded, dried, and calcined.

4. The fibrous or porous material is first impregnated with a platinic chloride and then reduced by one of the following methods: (*a*) By plunging the saturated material into a solution of ammonium chloride, ammonium-platinic chloride $(NH_4)_2PtCl_6$ is formed. The whole is then dried and calcined. (*b*) By plunging the material into a bath consisting of an alkaline solution of soda and of platinum chloride containing sufficient sodium formate to reduce the platinum, evaporating, washing, and drying. (*c*) The material saturated with platinum salts can be dried and submitted to the action of hydrogen or of gas rich in hydrogen, such as ordinary illuminating gas or even of hydrocarbon compounds. (*d*) The following methods for the preparation of platinum black may also be used.

62. Platinum black or finely divided platinum can be made as follows: (*a*) Platinic chloride $PtCl_4$ is treated in a concentrated potash lye with alcohol. The resulting powder is washed successively with alcohol, hydrochloric acid, potash, and water. (*b*) Platinum sulphate can be reduced by alcohol. (*c*) By the calcination of a platinic chloride, as calcium-platinic chloride $CaPtCl_6$, or ammonium-platinic chloride $(NH_4)_2PtCl_6$. (*d*) By precipitating platinic chloride with zinc. (*e*) By heating an ammoniacal salt of platinum, mixed with shreds of cork, in an open crucible. (*f*) By the reduction of platinic chloride with admixture of sodium carbonate, sugar, etc. (*g*) If 50 grams of platinic chloride be dissolved in 60 cubic centimeters of water and 70 cubic centimeters of a 40-per-cent. solution of formaldehyde be added, the mixture cooled, and then a solution of 50 grams of sodium hydrate in 50 grams of water added, the platinum is precipitated. After washing with water, the precipitate passes into solution and forms a black liquid containing soluble colloidal platinum. If the precipitated platinum be allowed to absorb oxygen on the filter, the temperature rises 40° C. and a very porous platinum black is obtained that vigorously facilitates oxidation.

Instead of the second class of contact material, some manufacturers use cupric sulphate at a red heat as contact mass. The salt is mixed into a paste with finely ground clay, molded into the desired shape, and dried.

63. In the third class of contact masses (under the Schroeder-Grillo patents), instead of the solid or integral insoluble bases above referred to, use is made of the soluble salts of the alkalies and of the alkaline earths, and of the heavy metals, which salts, for the production of the contact mass, are dissolved in water and then mixed with a solution of the finely divided platinum salt, especially platinic chloride. It can be used in a solution so diluted that in 100 parts of the salt, serving as base or vehicle, less than 1 part of platinic chloride is sufficient. Even contact bodies of .1 per cent., and less, of platinum contents are very efficacious. This mixture of solutions is then evaporated and the resulting salt crusts dried and broken up to about a uniform granular size. The powder that is formed in this reducing, or breaking-up, operation is dissolved afresh in water and treated as before until all the material has been converted into uniform granular size. The reduction of the metallic platinum in the finest subdivision between the molecules of the salts serving as vehicles for the platinum takes place automatically upon heating. In practice, the salts are always sulphates.

The technical advantage of this contact mass lies partly in the simplicity of its preparation; in its activity, on account of the extremely fine division of its platinum; and on the relatively small quantity of platinum required, both because of its fine division and because the base used also possesses catalytic activity. It is also regenerated readily and the platinum can be easily and completely recovered, on account of the solubility of its base, or vehicle, in water.

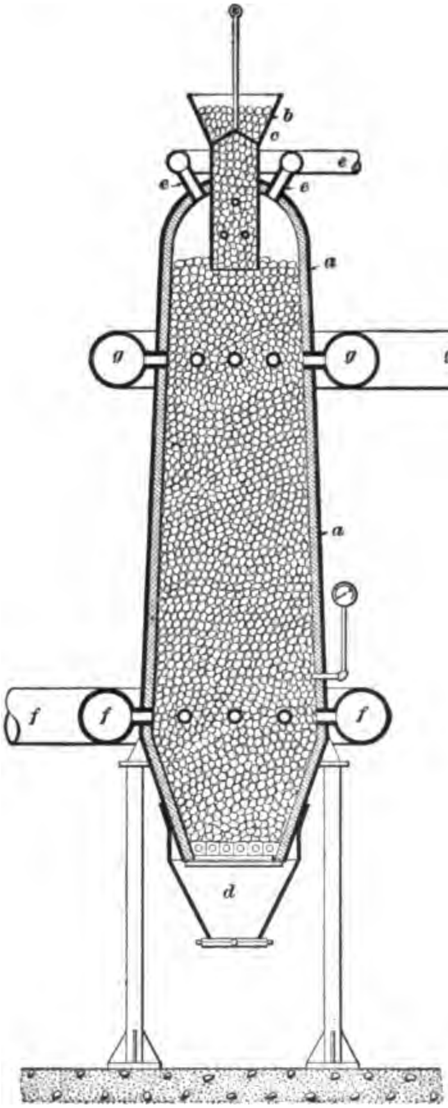


FIG. 10

When ferric oxide, the contact mass of the fourth class, is used, it is in the form of pyrites cinders (desulphurized iron pyrites), and these cinders must be porous and fresh. One advantage claimed for this mass is the removal of the arsenic from the burner gas in its passage through the cinders. It is also necessary to dry the air supplied to the roasting furnaces and to dilute the gas with further admissions of dry air after combustion and before it passes through the contact mass of cinders.

64. Frasch Converter.—A further elaboration of this process is the Frasch converter, which serves to dispense with the necessity for furnaces of special construction and to render it possible to use the burner gas produced by any furnaces of ordinary construction, including the gas from roasting zinc blendes or pyrrhotites, or, in fact, any metallurgical gas.

This converter is based on the fact that in comparison to the amount of pyrites desulphurized to produce the sulphur dioxide, a much smaller quantity of ferric oxide than the ore produces will suffice to oxidize the sulphur dioxide produced to sulphur trioxide; so that the heat produced by roasting the larger part of the ore can be avoided or regulated by roasting the ore in ordinary burners and conducting the burner gas, at a comparatively low temperature, to a converter in which only enough pyrites is burned to maintain the proper temperature and at the same time produce sufficient ferric oxide for the contact substance.

65. The Frasch converter, shown in Fig. 10, consists of a steel cylinder *a*, similar to a cupola furnace, lined with firebrick. Pyrites are charged into the converter through the hopper *b* by means of the bell *c*. The ferric oxide is discharged at the bottom into the double-valve hopper *d*, so as to prevent the admission of air during discharging. This converter is on the down-draft principle. Air is admitted through the pipes *e* and the products of combustion carried away through the pipes *f*. When the furnace is lighted and supplied with iron pyrites, a bed of burned pyrites (ferric oxide) is formed, in which there will be various zones of temperature from the upper to the bottom layer of its contents. These zones of temperature can be largely governed by the quantity of pyrites charged to or discharged from the furnace, but in any case a zone of fresh ferric oxide of suitable temperature can be maintained in the furnace at some point. Burner gas (containing sulphur dioxide) from outside sources, whether ordinary pyrites burners or metallurgical furnaces, are now admitted through the pipe *g*, and in passing through the zone of ferric oxide of suitable temperature, the sulphur dioxide is converted into the trioxide.

66. Purification of Burner Gas.—The burner gas, as it comes from the desulphurizing plant, always contains some, and often many, impurities. Of these, flue dust, hydrofluoric acid, arsenic, and selenium have a most detrimental effect upon the contact mass, partly chemical but principally mechanical, as they tend to glaze over and destroy the porosity of the mass, thus rendering it inert. It is further desirable to prevent the formation of dilute sulphuric acid, and its corrosive effect on the apparatus and connections, by at once extracting the sulphur trioxide and moisture contained in the burner gas.

This can be readily accomplished by first passing the gas through a tower constructed in every respect as a Glover tower, which is described later, except that it is packed with smaller pieces of quartz. This tower acts as a scrubber and collects most of the impurities, at the same time cooling the gas to a point where it will more readily deposit the impurities still remaining, in the next purifying apparatus. The heat of the gas also concentrates such weak acid as is formed by the sulphur trioxide and moisture contained in the gas, together with such additional water as may be found necessary to run down the tower. A necessary proportion of this acid, when concentrated sufficiently (to 62° Baumé), and separated from solid impurities by settlement, may be used in the next apparatus to absorb the moisture driven from the first scrubbing tower. After absorbing this moisture in its dilute condition, it is again run over the first tower and again concentrated, together with the new acid formed in the first tower. The unused increment, ultimately representing the daily quantity of sulphur trioxide contained in the burner gas, is, if pure enough, passed on to be further strengthened by the addition of sulphur trioxide in the main part of the contact plant. If impure, it is sold or used for purposes for which it may be suitable.

67. This first tower also serves another valuable purpose, in that the heat from the burner gas concentrating the dilute acid in the tower forms a considerable volume of steam, which is intimately mixed with the burner gas passing through it. This admixture with steam prevents the formation of volatile hydrogen compounds of the impurities, especially of arsenic, phosphorus, or their compounds, which would otherwise be formed by the action of the concentrated sulphuric acid on the metal of the coolers and the impurities, and which could only be removed with difficulty.

After passing through this first tower, the gas is taken through a long connection to the bottom of a second tower, through which it ascends, meeting a flow of sulphuric acid of at least 62° Baumé (concentrated acid from the first tower). This tower is constructed exactly like a Gay-Lussac tower, which is also described later, except that it is packed with very much smaller pieces of quartz or coke. In this tower the gas is dried and deposits nearly all the remaining impurities.

The burner gas is now passed through a tower of the same construction as the last, but which is dry (neither water nor acid being used) and serves as a final drying filter and cooling apparatus.

68. Other Methods of Purifying the Burner Gas. The above description of the tower system of scrubbing the gas sufficiently discloses the various purifying operations necessary. Other apparatus merely accomplish the same end by more or less approximate means. Just as in the purification and preheating of boiler feedwater, the requirements, partly chemical and partly mechanical, are accomplished by different forms of apparatus, although the underlying principles are practically the same in all.

In some cases, cooling is first accomplished by long flues between the desulphurizing furnaces and the purifying apparatus. This method is crude and unscientific, as it gives an opportunity for the sulphur trioxide and the water contained in the burner gas to condense, to the great deterioration of the flue and the loss of the acid so formed. Then, again, the steam (required as above) is added direct to the gas from a boiler, instead of utilizing the heat of the burner gas to produce it in the first tower.

69. It has further been proposed to absorb the burner gas in kieselguhr or diatomaceous earth. On the further application of heat, the gas is given off while the impurities are retained in the silicious filter.

The burner gas is now a pure mixture of sulphur dioxide, oxygen, and nitrogen, at about the average temperature of the atmosphere, and is consequently, since leaving the roasting furnaces, reduced in volume about two-thirds, or from 3 volumes to 1.

At this stage of the manufacture, in order to overcome the resistance to the gases likely to be met with in the succeeding apparatus, it is generally necessary to interpose either a compressor or blower. This resistance, according to the methods used, will later vary from a few millimeters of water to 5 or 6 pounds to the square inch. The resistance, in cases where it is small, may be overcome by a vacuum draft at the exit of the system.

If the gas is properly purified and *dried*, iron or phosphor bronze may now be used for the valves, pistons, cylinders, and various connections in contact with the gas.

70. Reheating the Gas.—The gas must now be reheated to the temperature necessary to start the reaction. This varies according to the contact mass used and according to the richness of the gas in sulphur dioxide. Generally speaking, it will vary from 300° C. to 360° C. with platinized asbestos or the Schroeder-Grillo mass, consisting, as previously stated, of finely divided platinum, with soluble alkaline salts as a carrier, or base.

This reheating can be done by the application of the direct heat of a special fire to coils of tubes through which the gas passes, as in a hot stove. It can also be passed through special apparatus or coils of pipes heated by the dried heat of the desulphurizing furnaces; in other words, utilizing the heat of the oxidation to sulphur dioxide. Or it can be made to pass around the ovens containing the contact mass, thus keeping the temperature of the contact ovens below the dissociation point of sulphur trioxide, and in this way utilizing the heat of the oxidation of the sulphur dioxide to the trioxide.

The above oxidations are exothermic and are as follows:

$$\begin{array}{rl} S + O_2 = SO_2 + & 71.0\ Cal \\ SO_2 + O = SO_3 + & \underline{32.2}\ Cal \\ \text{Total} = & 103.2\ Cal \text{ liberated.} \end{array}$$

The temperature of the gas about to enter the contact oven must be most carefully regulated.

71. Contact Ovens.—The usual form for contact ovens varies, but generally it consists of cylinders of varying diameters and lengths in which the contact mass is either filled solid, placed on perforated shelves, molded into special shapes, or otherwise disposed of so as to secure the most complete contact with the gas passing through, and at the same time to offer as little resistance to the passage of the gas as possible. Various means are taken to supply additional heat to the ovens at the entering point of the gas when necessary, and similarly to cool the ovens and prevent undue accumulation of heat near the exit of the gas.

If the gas is properly purified and the contact mass is therefore kept in active condition, the whole secret of success with the contact ovens is to maintain such temperatures as may have been found most advantageous in each individual plant, and with each special contact mass used, and, of course, under any circumstances, between the temperatures necessary to start the reaction and the dissociation point of sulphur trioxide. The gas issuing from the contact oven is now a mixture of sulphur trioxide, nitrogen, and excess of oxygen, and, with a properly working process, very small quantities of sulphur dioxide; and nothing remains but to absorb or dissolve the sulphur trioxide in water, allowing the inert nitrogen and oxygen to pass from the apparatus into the atmosphere.

72. This is usually done on the principle of the reflux cooler; that is, the gas is passed through or over and in the opposite direction to that of a stream of water or weak acid. Consequently, the strongest gas meets the strongest acid and the weakest gas meets the weakest acid, which more readily absorbs it. As the absorbing apparatus is generally of wrought iron, it is usual to start the process with acid not weaker than 60° Baumé.

The combination of sulphur trioxide and water is also exothermic.

$$SO_3 + H_2O = H_2SO_4 + 39.2\ Cal \quad \text{(Thomsen)}$$

73. Diagram of Contact Process.—In Fig. 11 is shown a diagram of the apparatus used in a sulphuric-acid plant employing the contact process. The course of the various materials and products is indicated by the arrows. A is a bench of pyrites burners. The burner gas passes through the flue a_1 to the first cleaning tower B. Weak sulphuric acid is constantly flowing down this tower, becoming concentrated by the hot burner gas and absorption of the sulphur trioxide contained in the burner gas, and finally flows out at the bottom into the cooler C at a strength of from 62° to 64° Baumé. From the cooler C, the strong acid passes to the tank D and is delivered by the pump D_1 to the storage tank T, or to the tank F over the second cleaning tower E. A constant stream of strong sulphuric acid from the tank F

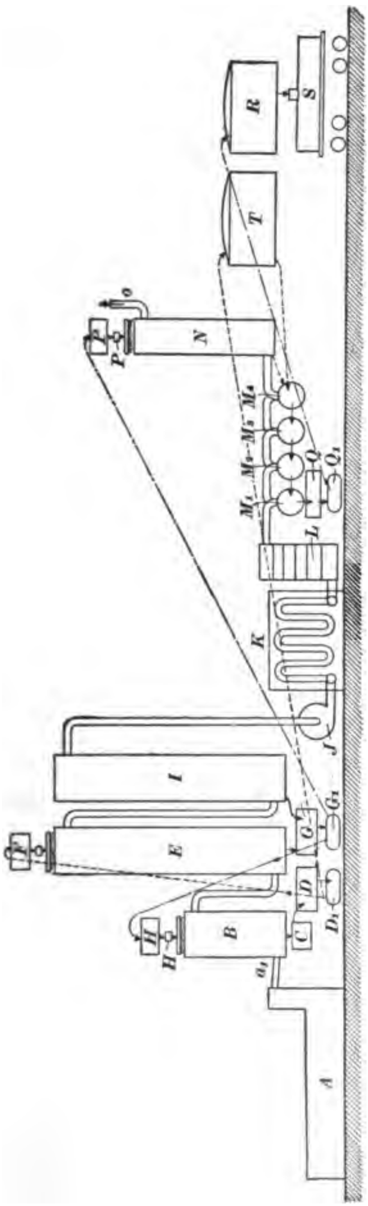


FIG. 11

is kept flowing down this tower. In this tower, the burner gas coming from the top of *B* is further cleaned and then passes to the drying tower *I*; the circulation of the gases through the train of apparatus is maintained by the fan *J*. Before entering the contact ovens, the mixed gases are reheated to the proper temperature for the combination of the sulphur dioxide and oxygen in the reheater *K*.

74. The contact oven *L* consists of cast-iron rings with perforated shelves, or diaphragms, upon which is placed the contact mass.

The sulphur trioxide formed in the contact oven now passes through the absorption cylinders M_1, M_2, M_3, M_4. These are cylindrical iron tanks connected in such a way that the gas passes from end to end, meeting the weak acid flowing in the opposite direction. Both the gas and the acid in M_1 are richest in sulphur trioxide, while in M_4 the gas and acid are weak, and such weak acid absorbs sulphur trioxide most readily. The strong acid, which is ready for the market as it comes from M_1, is collected in the tank Q and is delivered by the pump Q_1 to the storage tank R.

The gases coming from the last absorption tank M_4 contains still a small amount of unabsorbed sulphur trioxide. In order to recover this, the gases are passed through the tower N, which is supplied with weak acid from the tank P, which absorbs the last traces of sulphur trioxide. The nitrogen and oxygen remaining pass into the air through the pipe o. The tank car S receives acid for shipment from the storage tank R.

SULPHURIC ACID
(PART 2)

THE CHAMBER PROCESS

INTRODUCTION

1. We have seen that the oxidation of sulphur, under ordinary conditions, produces so much heat as to render the existence of the trioxide possible only to a limited extent, except in the presence of a third material possessing so-called "contact" properties, such as pyrites, cinders, spongy platinum, cupric sulphate, etc. Also, that some of these so-called contact substances, while producing a chemical reaction, remain themselves in the end unchanged, whatever intermediate reactions they may or may not have taken part in. In some of the contact phenomena, such intermediate reactions can be traced, or, at any rate, such is the only way of accounting for them. In the case of contact phenomena connected with the complete oxidation of sulphur into the trioxide, it is apparently possible that electrical action is set up, which permits the formation of the trioxide either by converting the excessive heat into another form of energy, or which renders the oxygen, free or combined with the sulphur dioxide, more active. In any case, the contact substance in the final result appears to suffer no chemical change or deterioration, but only the inevitable mechanical loss in handling.

2. It will now be seen that the **chamber process** is in nature a contact process, inasmuch as a definite chemical reaction between large volumes of sulphur dioxide, oxygen, and water is induced by a small quantity of nitrous oxide N_2O_3, which is recovered unchanged save for mechanical loss; and yet without which the reaction would not have taken place. In this case of contact action, however, the intermediate reactions have been studied and are fairly well understood.

When using the nitrous oxides as contact substance, or oxidizer, of sulphur dioxide, the presence of water is absolutely necessary and, consequently, only a hydrate or solution of sulphur trioxide can be formed. If water were not present, sulphur trioxide would be formed, but it would combine with the nitrous acid to form nitrososulphuric acid, or chamber crystals, $(HO)(NO_2)SO_2$. Water dissolves these crystals, forming sulphuric acid and releasing the oxides of nitrogen. Furthermore, water must be largely in excess of the quantity required to produce the hydrate H_2SO_4, as otherwise the oxides of nitrogen would be absorbed and retained in the sulphuric acid; in fact, it must be so much in excess as not to produce an acid stronger than about 69 per cent. of the monohydrate (54° to 55° Baumé).

3. Reactions of the Chamber Process.—The following explanation of the reactions that take place appears to be the most rational and the one that coincides most closely with the conditions of the actual chamber process.

(1) $SO_2 + HNO_2 + O = (HO)(NO_2)SO_2$

(2) $2(HO)(NO_2)SO_2 + H_2O = 2H_2SO_4 + N_2O_3$

If, in the above reactions, sulphur dioxide, nitrous acid, oxygen, and water be simply taken in definite quantity, then a definite quantity of sulphuric hydrate and nitrous oxide will be formed according to the above equations. The reaction would end and the excess of sulphur dioxide, if any, would pass on unchanged; but in the presence of excess of air and water the nitrous oxide is converted into nitrous acid, according to the following equation :

$$(3) \qquad N_2O_3 + H_2O = 2HNO_2$$

which again combines, according to equation (1) with the sulphur dioxide so long as the latter is present in sufficient quantity.

Or, in the presence of excess of oxygen (air) and water (vapor or steam), sulphur dioxide, nitrous acid, and oxygen form nitrososulphuric acid (chamber crystals). This is immediately decomposed by water into sulphuric hydrate and nitrous oxide N_2O_3. The sulphuric hydrate condenses in the apparatus as a stable compound, while the nitrous anhydride, with the water, forms nitrous acid, and the above reactions are repeated until the sulphur dioxide is practically all converted into sulphuric hydrate H_2SO_4.

4. In addition to the above principal reactions, another set of reactions appears to take place in the Glover tower and the first part of the first chamber, that is, where the sulphur dioxide is largely in excess, and in which the nitrososulphuric acid is partially decomposed by it.

$$(4) \quad 2(HO)(NO_2)SO_2 + SO_2 + 2H_2O = 3H_2SO_4 + 2NO$$

the oxide thus formed combining directly with the sulphur dioxide, oxygen, and water to form nitrososulphuric acid.

$$(5) \quad 2SO_2 + 2NO + 3O + H_2O = 2(HO)(NO_2)SO_2$$

which is converted into sulphuric hydrate and nitrous oxide according to equation (2).

If the above reactions could be started with the exact quantities of nitrous acid, sulphur dioxide, water, and oxygen necessary, it is evident, to secure a continuous process, all that would be necessary would be to secure a continuous supply of the exact quantities of sulphur dioxide, oxygen, and water, and return to the beginning of the process the nitrous oxide accumulated at the end of the process by simply supplying any mechanical loss common to all commercial processes.

This is approximately what is done in the chamber process. The nitrous oxide cannot, however, be returned direct, as the oxygen, being supplied as air, carries with it a very large proportion of inert nitrogen, which must be gotten rid of. It becomes necessary, therefore, to separate

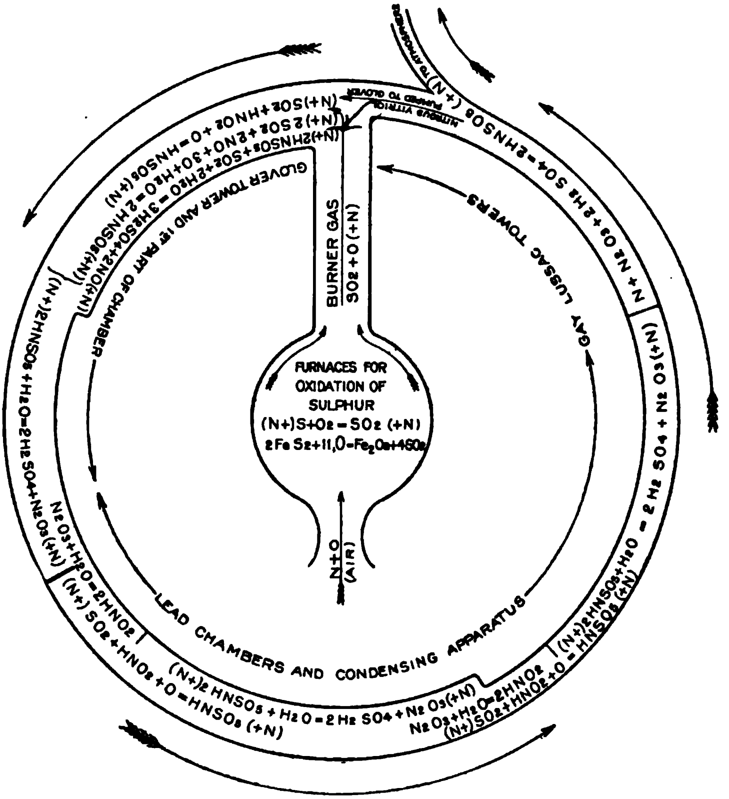


Fig. 1

the nitrous oxide from the inert nitrogen in such a way that the N_2O_3 can again be made available and the inert nitrogen wasted into the atmosphere.

Advantage is taken of the power of the stronger solutions of sulphur trioxide from 60° to 66° Baumé, to absorb and retain the nitrous oxide in fairly stable solution.

(6) $2H_2SO_4 + N_2O_3 = 2(HO)(NO_2)SO_2 + H_2O$

In other words, nitrososulphuric acid is formed. When dissolved in a large excess of the sulphuric-acid solution, the product is termed *nitrous vitriol*. The nitrous anhydride so absorbed can be set free, however, on dilution of the acid and especially in the presence of sulphur dioxide. When this nitrous vitriol is diluted, in the presence of sulphur dioxide at the beginning of the process, so as to set free the nitrous anhydride and complete the cycle, the reaction is represented by equation (4) above given. The diagram in Fig. 1 shows the chemical reactions that take place during a complete cycle. To read it, begin at the center and follow the direction of the arrows.

APPARATUS EMPLOYED IN THE CHAMBER PROCESS

5. In the manufacture of sulphuric acid by the so-called chamber process, the first essential piece of apparatus is a sulphur or pyrites burner provided with some means of nitrating the burner gas. Any of the burners previously described may be used.

6. Nitrating Oven.—Fig. 2 (*a*) and (*b*) shows an attachment to the burners by which nitrating by potting may be accomplished. Fig. 2 (*a*) is a horizontal section through the niter pots *d*, and Fig. 2 (*b*) is a vertical longitudinal section through one of these niter pots. The extreme end of a bench of lump pyrites burners is shown at *a*. The flues *b* from the burners enlarge into the niter ovens *c*, in which are placed the cast-iron niter pots, or "pigs," *d*. The cast-iron dishes *e* underneath the niter pots catch any acid material boiling over from the pots and prevent its penetrating the brickwork of the furnace. A cast-iron hopper, or funnel, *f* provides for the introduction of niter and sulphuric acid into the niter pots, the acid being stored in the tank *g* and conducted by a lead pipe and cock to the

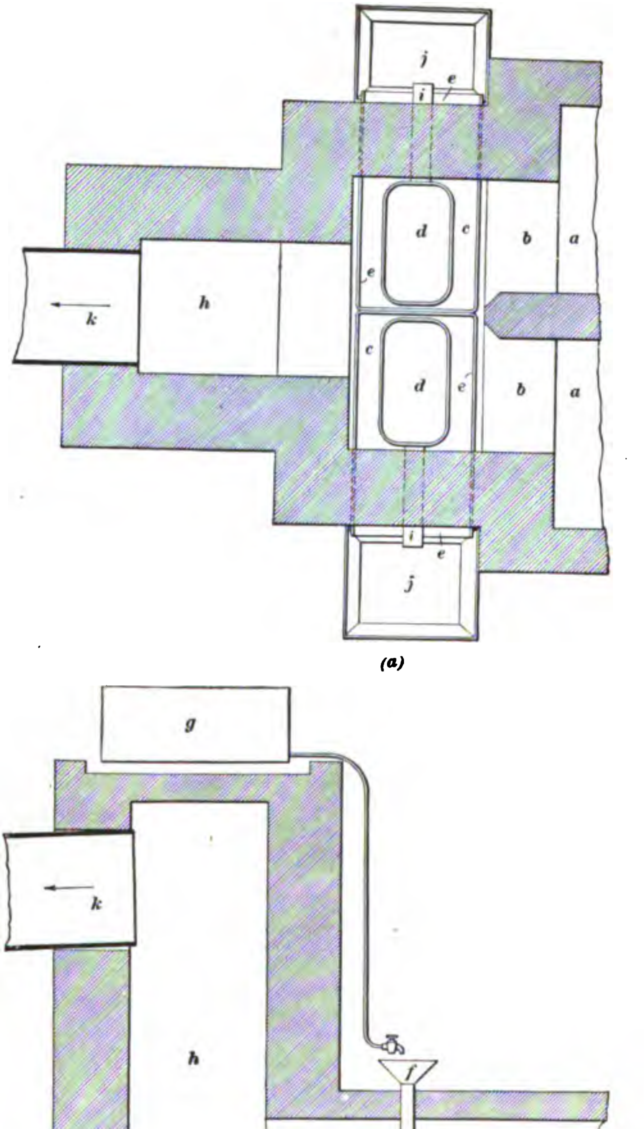


FIG. 2

hopper. The common flue and dust chamber *h* leads to the cast-iron flue *k*, through which the gas is carried to the Glover tower.

When the burners are in operation, the pots *d* are supplied with niter and a regulated amount of sulphuric acid added. The fumes of nitric acid thus formed mix with the hot burner gas and pass to the Glover tower. The sodium sulphate formed in the pots is removed through the cast-iron neck *i*, which is usually kept closed with a wooden plug, into the cast-iron dishes *j*. When cold and solid, it is broken up and removed.

7. This method of nitrating by "potting" is by no means satisfactory, because it adds another element of periodic irregularity to what should be a continuous process, and because, unless in the hands of careful and skilled workmen, it is a wasteful and a dirty process. It is also difficult in this way to supply the chambers with nitrous oxide just in the quantity and at the time when it is most wanted—that is, when something in the process is going wrong. Sometimes, also, on account of faulty construction, there is insufficient heat to decompose the niter rapidly enough or else the heat is too great and too direct and the sulphuric acid is evaporated before it has reacted completely with the sodium nitrate.

Wherever, therefore, the size of the plant justifies the manufacture of nitric acid on a small scale or where it is in any way possible, nitration should be secured by the use of nitric acid run into the Glover tower with the nitrous vitriol. This is accomplished by means of a small glass siphon from the nitric-acid tank or carboy, fitted with a glass cock and discharging from the cock into a glass funnel with a bent neck, so as to form a seal or lute and fixed into the center of the top lead of the tower. It does not matter how weak or impure the nitric acid may be for this purpose; indeed, in some works, the spent acid from the manufacture of nitroglycerin is used, as the acid is almost instantly decomposed upon entering the tower.

8. Glover Tower.—The apparatus in which the sulphur dioxide, oxygen, and nitrogen of the burner gas are mixed with the nitrous oxide N_2O_3, derived from the nitrous vitriol used in this stage of the process, water vapor and the nitrous fumes from the nitrating ovens, which after the process is once under way is only sufficient to make up for the mechanical loss, is known as the **Glover tower.** In this tower, the gases and vapors are not only thoroughly mixed, but the dilute sulphuric acid constantly flowing down is both denitrated and concentrated by the hot gases, rendering it strong enough to be again used for absorbing N_2O_3 at the end of the process.

9. The heat of combustion of the sulphur to SO_2 in the furnaces is usually more than sufficient to concentrate the whole of the make of chamber acid if entirely utilized to 66° Baumé, or to 93.5-per-cent. H_2SO_4. In a well-constructed plant, that is, where the heat is fairly well utilized, the Glover tower will concentrate from one and one-half times to twice the entire make of chamber acid to 60° or 62° Baumé (~~62~~ 78- to 80-per-cent. H_2SO_4), or, in other words, this quantity of chamber acid can be used to dilute the nitrous vitriol and will leave the Glover tower at 60° Baumé, or over. Of course, if it is not desired to keep this amount of acid in circulation between the Glover and Gay-Lussac towers, the nitrous vitriol may be diluted in whole or in part with water.

The temperature of the burner gas entering the Glover tower will vary, of course, with the construction and length of connections, but will average probably about 550° C. The greatest possible temperature produced by the combustion of sulphur will, of course, vary with the nature of the raw material. Mendeléeff estimates the highest possible temperature of actual sulphur burning in air to be 1,974° C. and in oxygen 7,258° C.

10. The construction of the Glover tower is clearly shown in Fig. 3. It consists of a circular brick-lined tower *e* covered with a lead sheathing *p* and lead pan *o* at the bottom, and is filled to near the exit pipe *g* with a packing *f*

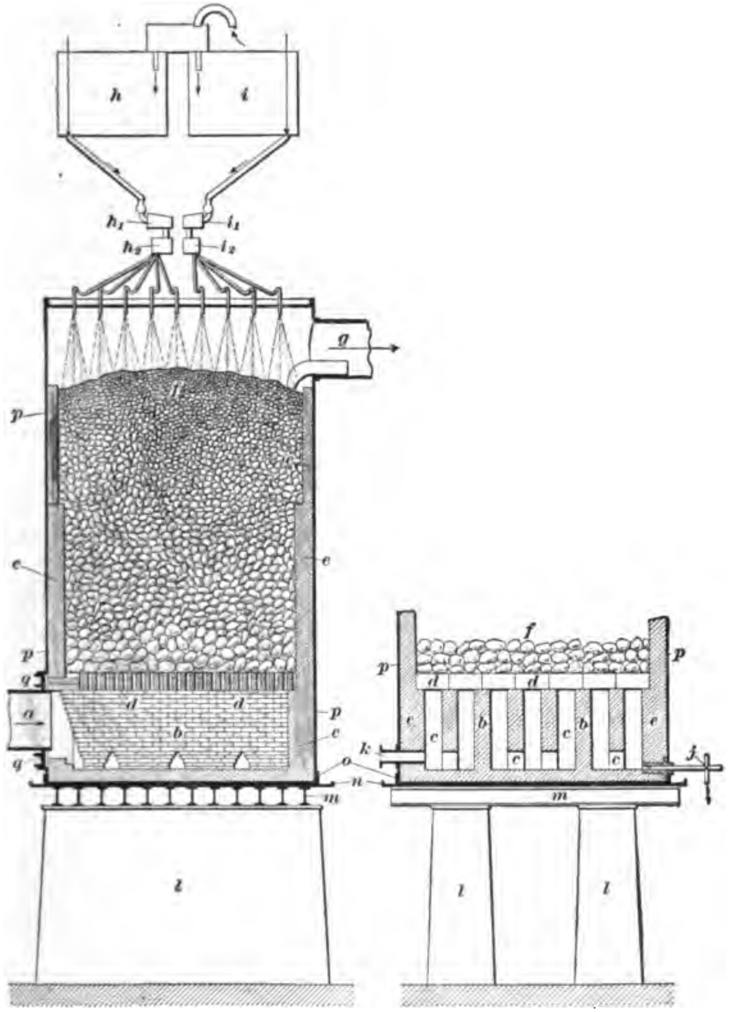


FIG. 3

consisting of broken quartz, the pieces being large at the bottom, but decrease in size towards the top. This packing

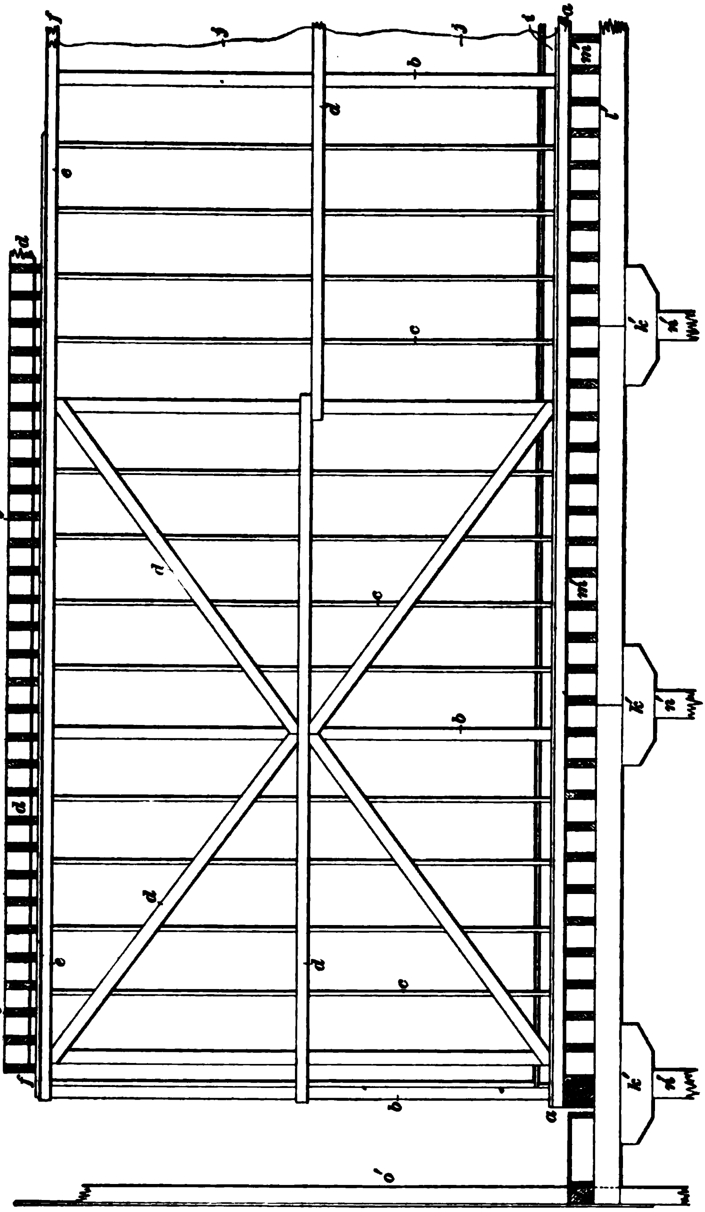


FIG. 4

rests upon the grill tiles *d*, which are supported by the walls *b*. The tank *h* contains dilute or chamber acid, which flows through the equalizer h_1 and the distributor h_2 over the top of the packing. On the other side is a similar arrangement *i*, i_1, and i_2 for the distribution of nitrous vitriol, which is strong sulphuric acid coming from the Gay-Lussac tower, described later, and heavily charged with nitrous oxide N_2O_3, this N_2O_3 being set free on dilution of the vitriol in this tower.

The burner gas enters the tower at the bottom by means of the pipe *a*, which is surrounded next the tower by the cast-iron cooling ring *q*, which prevents the heat from injuring the lead sheathing next the pipe. The gas is distributed through the gas spaces *c* and passes through the grill tiling up through the packing, coming in intimate contact with the dilute acids from above, which are giving up N_2O_3, and become mixed with the latter and also with steam formed by the hot burner gas on the dilute acid. This mixture of burner gas, nitrous oxide, and steam passes on through the pipe *g* into the first lead chamber.

As previously stated, the rapid evaporation of the moisture concentrates the down-flowing acid considerably. The denitrated and concentrated acid having a strength of from 60° to 62° Baumé is drawn off at *j*; the lead-covered cast-iron plate, or dish, *n* catches the acid or other leakage. The exit pipe *k* is for use when the tower is washed by flooding with acid in too large quantity to pass through *j*. The tower is supported on the foundation walls *l* and the **I** beams *m*.

In dimensions, the Glover tower will average about 24 feet in height and 12 feet in diameter. The construction is necessarily heavy, in order that it may withstand the high temperatures.

11. Lead Chambers.—The thoroughly mixed gases from the Glover tower containing nitrous oxide N_2O_3 and water vapor are allowed to pass to the chambers in which the oxidation of the sulphur dioxide to trioxide and the formation of sulphuric hydrates takes place. These chambers

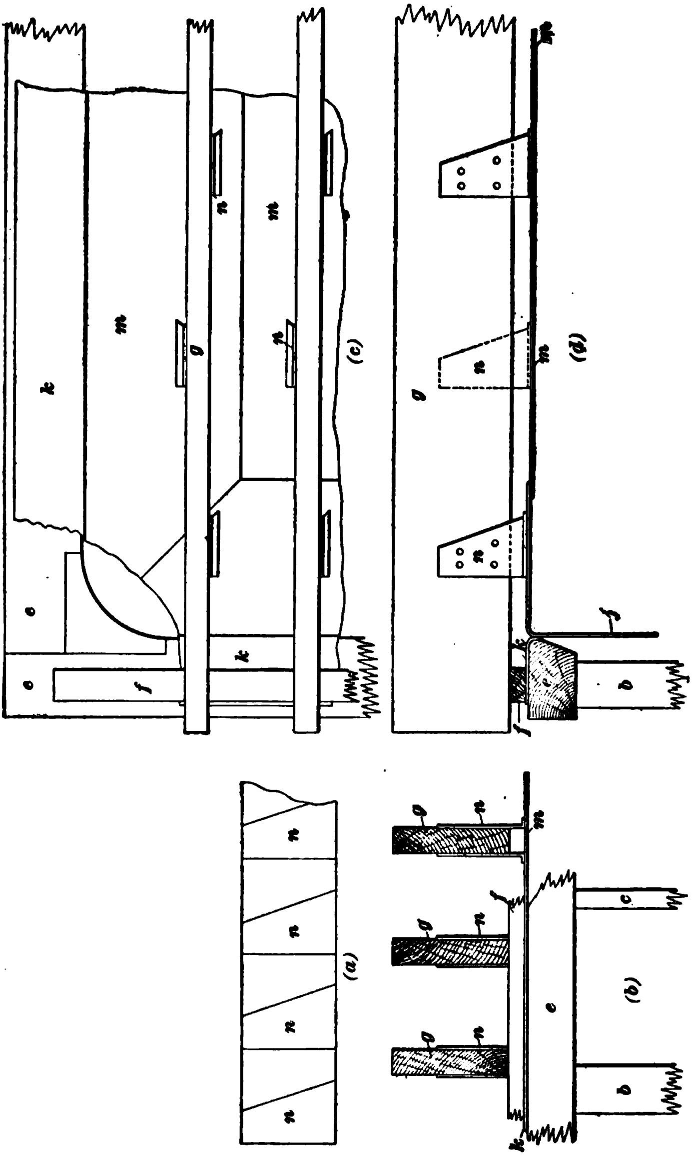


FIG. 5

are usually three in number, of greatly varying dimensions, but average between 50 and 100 feet long by from 20 to 30 feet wide and 20 to 30 feet high. They are connected together in series, the communication between them being comparatively small. The construction of the chambers is shown in Figs. 4, 5, 6, and 7.

Fig. 4 is a side elevation, showing the method of framing. The chamber building is built on posts *n'* upon which are the corbels *k'* supporting the stringers *l'*. The joists *m'* are laid on these stringers, and upon these are laid the sills *a* of the chambers. The posts *b* and the intermediate uprights *c* are erected upon the sills and stiffened by the braces *d*. The crown tree *e* surmounts the posts and intermediates, and on this the top joists *g* are laid. The floor of the chamber is covered with sheet lead, so as to form a pan whose edge is shown at *i*. The edge of the lead curtain forming the inside lining of the sides is shown at *j*. The end wall of the chamber building is shown at *o'*.

12. In Fig. 5 (*a*), (*b*), (*c*), and (*d*) is shown the method of attaching and supporting the lead lining. Fig. 5 (*a*) shows the method of cutting the lead straps for supporting the lead lining. Fig. 5 (*b*) shows the top joists *g* with the lead straps *n* attached, the lower ends of the straps being burned to the top lead *m*. Fig. 5 (*c*) is a plan of the top, showing the method of fitting the lead lining into the corners. The top lead *m* is supported from the top joists *g*. The crown tree is at *e*. A long horizontal strap *k* is nailed to the crown tree and supports the side lead at the top where it is attached to the top lead. The attachment of the top and side leads is best shown in Fig. 5 (*d*), which is self-explanatory.

In Fig. 6 (*a*), (*b*), and (*c*), further details of the attachment of the side and pan lead are shown. Fig. 6 (*a*) shows a horizontal section through the posts *b* and the uprights *c* at a corner, showing the attachment of the side straps *l* to both posts and lead. Fig. 6 (*b*) is a side elevation towards the bottom of the chamber, showing the method of attaching

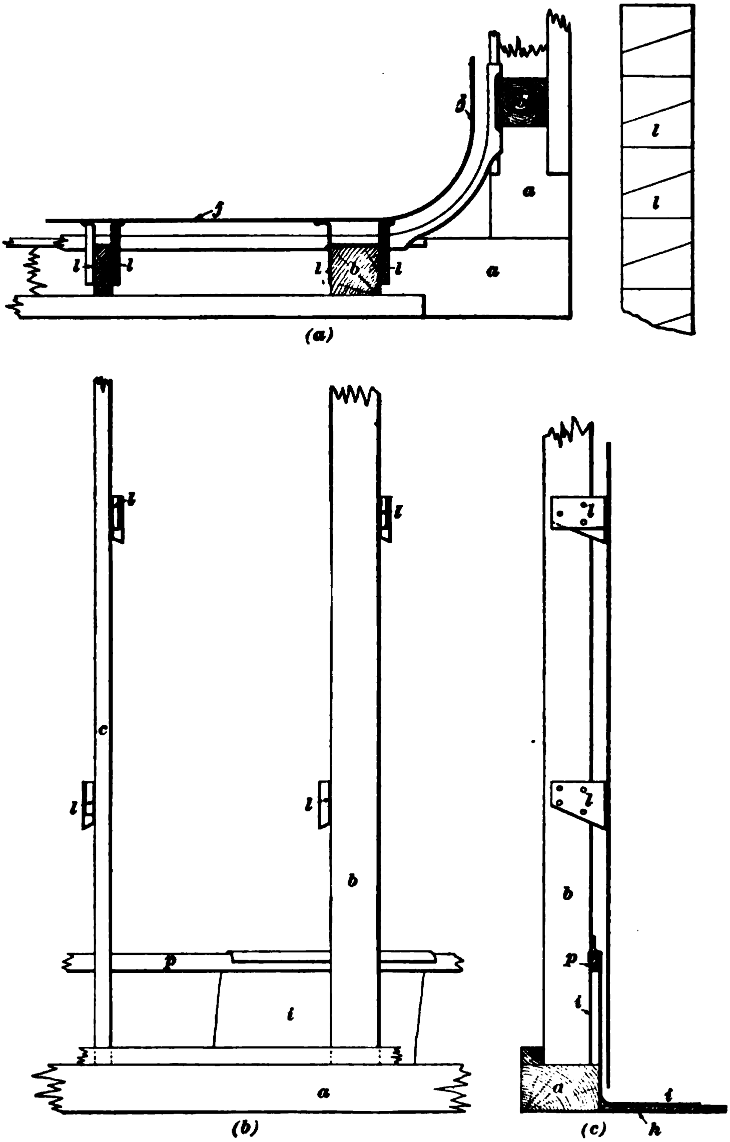


FIG. 6

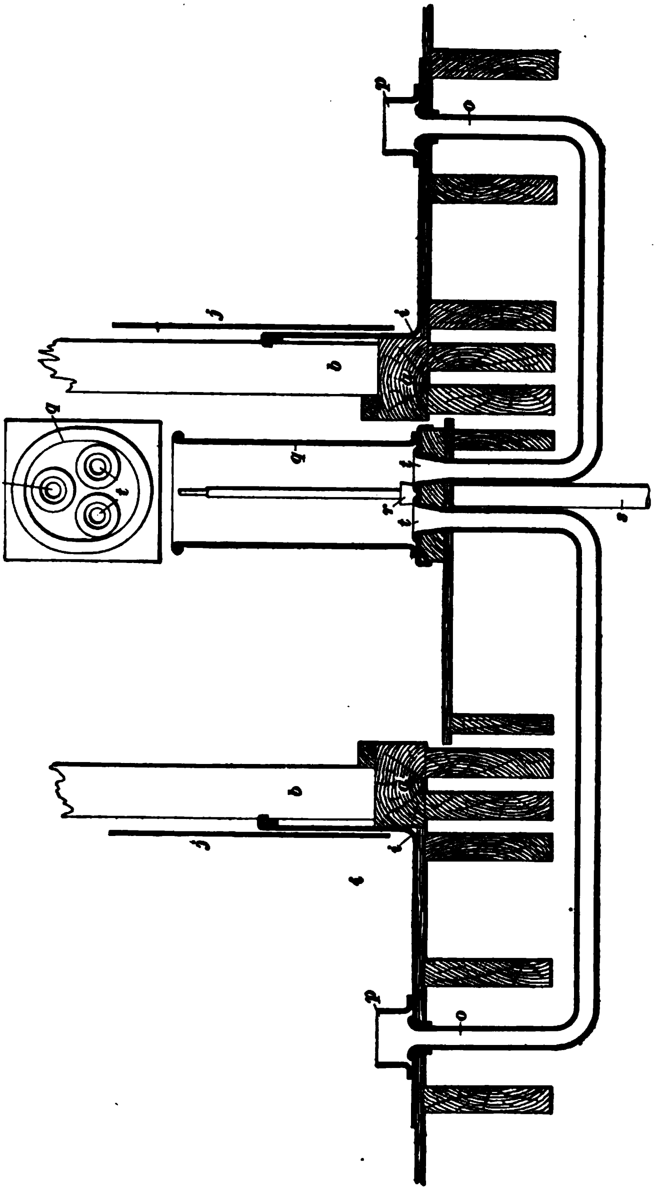


FIG. 7

the sides of the lead pan *i* by rolling the top over the strip *p*. Fig. 6 (*c*) is a vertical section through a side, showing the relative positions of the side lead *j* to the pan *i*.

This pan is kept about two-thirds full of acid and at all times the curtains or sides should dip at least 2 inches into the acid. When it is desired to draw acid from the chambers, it is done by means of the arrangement shown in section in Fig. 7. A pipe *o* is burned into the bottom of the chamber; the entrance to this pipe is protected from the wash of the flowing acid and a stratum of cool acid is kept on the bottom by means of a loose lead ring *p*, which may be removed when it is necessary to entirely empty the chamber. The pipes from two or more adjacent chambers meet in the cylindrical lead boot *q*. This boot is provided with a lead plug *r* or valve and seat communicating with a pipe *s* leading from the chambers to a tank or wherever it can flow by gravity. The entrances *t* to the boot from the chambers can also be plugged, so that acid can be drawn from either chamber or both, and the level in the two chambers can be regulated as desired.

SURFACE CONDENSERS

13. Immediately on the entering of the gas into the chambers, the formation of sulphuric acid commences. This acid is formed as a very fine mist. This mist gradually and slowly settles on the sides and bottoms of the chambers. As the gas leaves the first chamber it is very advantageous to condense this mist of already formed acid that it contains, so as to leave the gas free to enter into renewed activity upon entering the second chamber. The same thing may be said of the gas leaving the second chamber and entering the third chamber. Many proposals have been made to secure condensation at these points.

14. Lunge Condenser.—Lunge has introduced what he calls **plate columns** for this purpose, consisting of a lead tower, or column, fitted with flat, perforated, earthenware

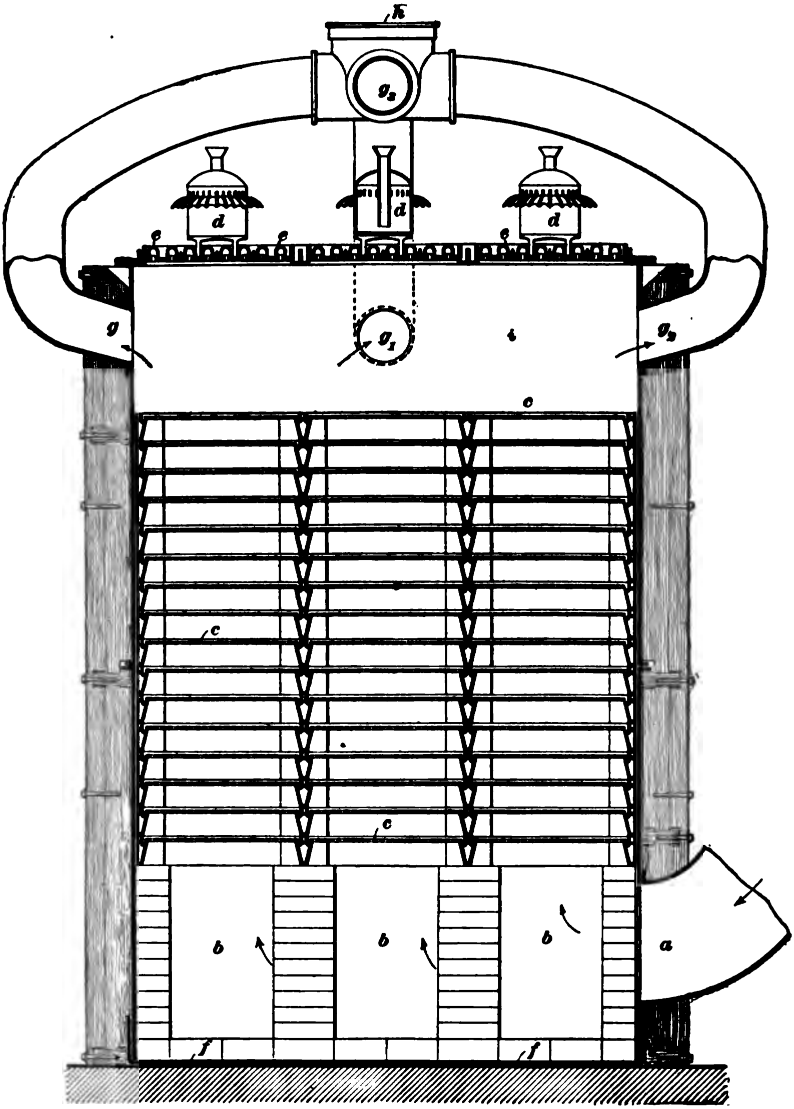


FIG. 8

plates in layers one above the other and about 2 inches apart. A stream of chamber acid is run over the plates. The perforations are so arranged that the acid in dropping through the perforations of one plate splashes upon the solid part of the plate below it and is thus broken into spray, upon meeting which the gas is cooled and deposits its mist of contained acid. This apparatus, therefore, may be considered as a type of spray condenser, similar to the well-known form used in steam engineering.

Fig. 8 shows the Lunge type of spray condenser. The gas is admitted at a into the lead-lined box b, whence it passes through the perforations in the plates c, c, meeting the stream of acid supplied by the distributors d and lutes e. This acid, together with the condensed mist contained in the gas, is collected in the pan f and either run back into one of the chambers or conveyed by lead pipe to storage. The gas passes on to the vent chamber i and through the collecting pipes g, g_1, g_2, g_3, and the main pipe h.

15. Gilchrist Condenser.—The Gilchrist pipe columns consist of an oblong tower, or column, of lead pierced in its smaller diameter by a series of lead pipes open to the air at each end. The lead column is surrounded by a wooden breaching and flue in such a way as to cause a current of air through these pipes, thus tending to keep them cool. The gas passing through this column is cooled by contact with these pipes and the acid mist is condensed on them. This apparatus may therefore be considered a type of air-cooled surface condenser.

Fig. 9 shows the Gilchrist air-cooled surface condenser. The gas is admitted at a into the lead box b. This box is pierced by numerous lead pipes c, c, c, open at both ends. The acid mist contained in the gas is condensed on these pipes and the comparatively cool surfaces of the lead box and runs to the bottom of the box b, whence it is carried to a chamber, or storage, by a pipe d. The gas then passes through the collecting pipe e to the vent chamber. The lead box is surrounded by a wooden breaching, so that the air entering *g* from below is drawn through the lead pipes *c*, *c*, *c* into the breaching *g'* and thence to the draft pipe *f*, thus tending to keep the apparatus cool.

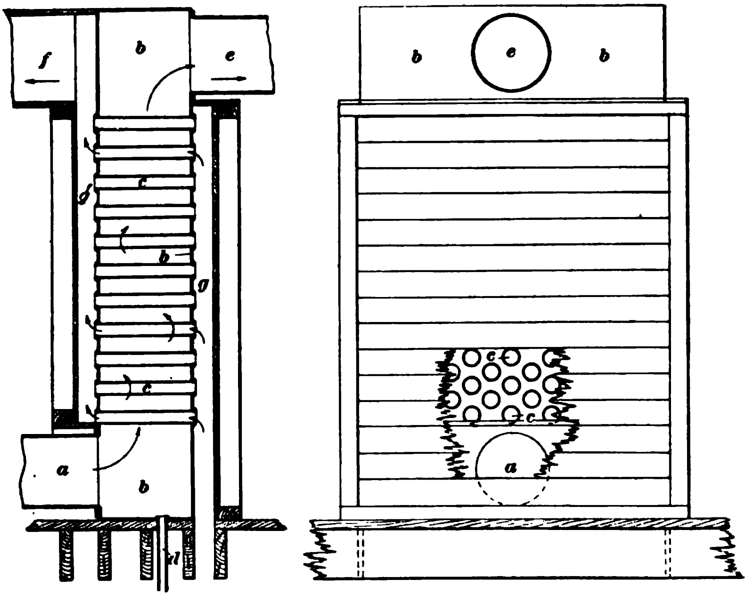


FIG. 9

16. The Falding Condenser.—The Falding surface condenser consists of a series of lead pipes surrounded by water as the cooling medium. They are arranged in such a way as to secure a maximum efficiency with a minimum use of water. This apparatus may therefore be considered as a type of water-cooled surface condenser.

Fig. 10 shows the Falding water-cooled surface condenser. In this condenser, the entering gas is broken up into a number of small streams through lead pipes *a*, *a*, *a*, *a*. These pipes dip almost to the bottom of a series of water-cooled lead pipes *d*, *d*, of larger diameter, with closed bottoms. The annular space between these pipes contains a strip of lead, which forces the gas to return in a spiral through acid to the top of the annular space, whence it

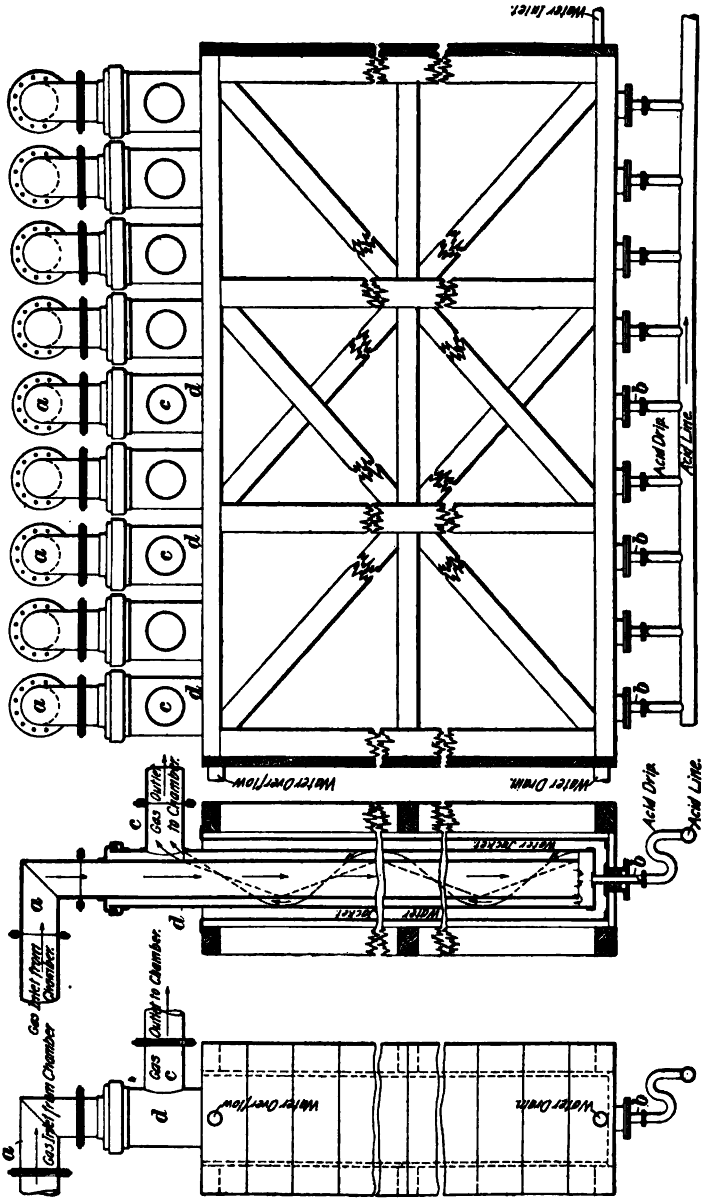

Water Inlet.
Water Overflow
Water Drain.
Acid Drip
Acid Line
a
b
c
d
Gas Outlet to Chamber.
Gas Inlet from Chamber.
Water Jacket.
Water Jacket.
Acid Drip
Acid Line
Gas Inlet from Chamber
Gas Outlet to Chamber.
Water Overflow
Water Drain.

FIG. 10

passes through pipes *c*, *c* into the next chamber or into a header or manifold and thence into the next chamber. The condensed acid mist runs from the apparatus at *b*.

17. Other Condensers.—Many manufacturers use simple lead towers filled with quartz, brick, or special earthenware shapes. These towers do not take sufficient account of the necessity for cooling, and while they are efficient to a certain extent, they are not sufficiently so when their cost relative to an equal amount of chamber spaces is taken into consideration.

If all operations have been properly conducted, the gases coming from the last lead chamber are practically free from sulphur dioxide, and consist of inert nitrogen, the excess of oxygen, and nitrous oxide N_2O_3. This latter gas, if freed from the other two gases, may be used over again as an oxidizer for more sulphur dioxide. This separation depends on the fact that nitrous oxide N_2O_3 is readily absorbed by concentrated sulphuric acid forming the so-called nitrous vitriol, while the other useless gases are unabsorbed. The apparatus in which this absorption takes place is called the *Gay-Lussac tower*.

18. Gay-Lussac Tower.—This piece of apparatus is in construction very similar to the Glover tower, but differs from it in that it is of somewhat lighter build. Its height is greater, the average height being about 50 feet, and its diameter is somewhat less, being about 8 to 10 feet.

The details of the Gay-Lussac tower are shown in Fig. 11. The brick walls *e* are of light weight and are covered with a lead sheathing *p*. Under the brick bottom is the lead pan *o* resting in the lead-covered cast-iron dish *n*. The tower is supported on the **I** beams *m* by the foundation walls *l*.

The filling *f* is of broken quartz, coarse at the bottom but becoming finer at the top, as in the Glover tower. The tank *h* contains strong, 62° Baumé, sulphuric acid, which flows through the equalizer *t* and the distributors *s* over the top of the packing.

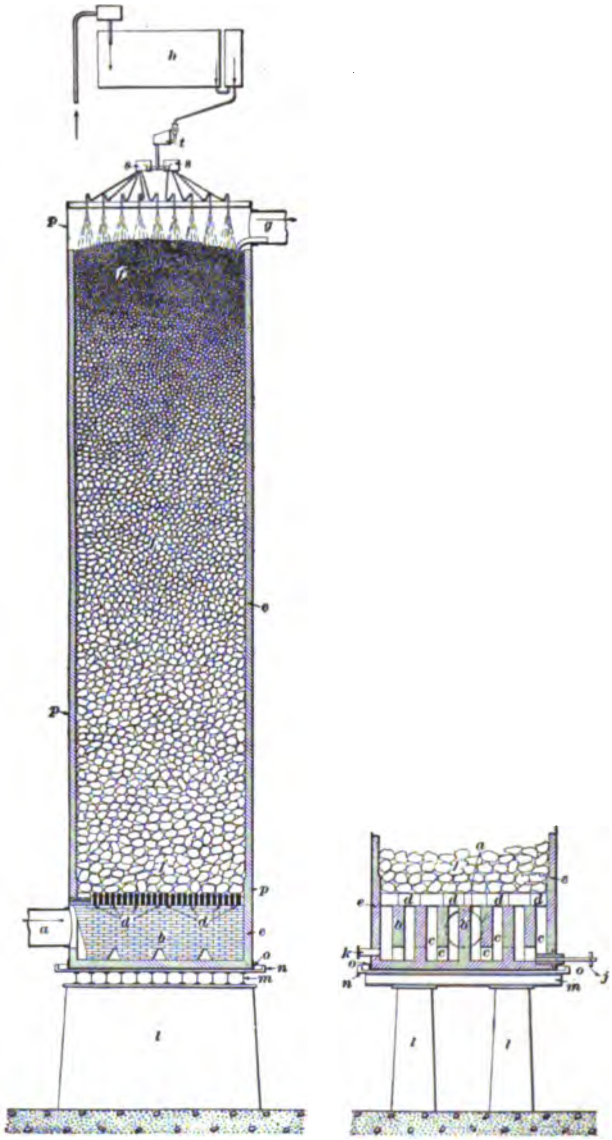


FIG. 11

During operation, the mixed gases from the chambers enter at the bottom through the pipe *a*, pass through the gas spaces *c* in the supporting wall *b*, and up through the grill *d* into the packing material. As the gases ascend, they come in contact with the descending concentrated sulphuric acid, which absorbs the N_2O_3. The unabsorbed gases pass through the pipe *g* into the air or, more commonly, into a second Gay-Lussac tower, which absorbs any N_2O_3 that may have escaped absorption in the first tower. The nitrous vitriol is drawn off at the bottom of the tower at *j*. The exit *k* is for flushing purposes.

The nitrous vitriol coming from the Gay-Lussac tower is pumped to the tank over the Glover tower and is used in the Glover tower, where it gives up its N_2O_3, which again passes through the system.

19. Diagram of Chamber Process.—The disposition of the various pieces of apparatus already described and the cause of the various materials and products is indicated in the diagram shown in Fig. 12. Reference to this diagram will enable one to keep a general idea of a plant in mind and better understand the process as the details are discussed.

In the figure, *A* is a bench of pyrites burners, niter oven, etc. The burner gas is conducted through the pipe *d* to the Glover tower *E*, where it meets the dilute acids and oxides of nitrogen. The fan *J* carries the gases through the pipe *i* to the first chamber *K*, where oxidation of the sulphur dioxide takes place, thence to the second and third chambers *M* and *N*, through the flues i_1 and i_2 and surface condensers *L* and L_1. The acid drained from the bottom of each chamber and the condensers is collected in the tank R_2.

The pump S_2 of one of the styles shown in Figs. 13 and 14 delivers this acid to the tank H_1, over the Glover tower, or to the storage tank *U*, whence it goes to the tank car *V*. The strong acid coming from the Glover tower is collected in tanks *Q* and R_1 and is delivered by the pump S_1 to the tank H_2 over the second Gay-Lussac tower *P* and to the

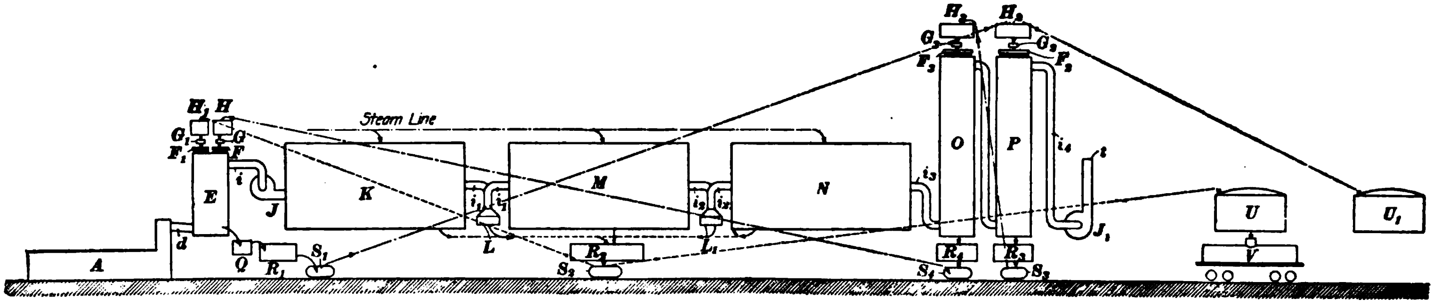

H_1
H
G_1
G
F_1
F
Steam Line
E
i
J
K
d
A
Q
R_1
S_1
i_1
L
M
R_2
S_2
i_2
L_1
N
i_3
H_2
G_3
F_3
O
R_4
S_4
H_3
G_2
F_2
P
R_3
S_3
i_4
t
J_1
U
V
U_1

FIG. 12

storage tank U_1. The gases from the last chamber N are conducted through the pipe i_2 to the first Gay-Lussac tower O and thence to the second Gay-Lussac tower P, their flow being maintained by the fan J_1. The exhausted gases pass to the atmosphere at t. The nitrous vitriol from the first Gay-Lussac tower is collected in the tank R_4 and is delivered by the pump S_4 to the tank H over the Glover tower. The nitrous vitriol from the second Gay-Lussac tower, containing but little N_2O_3, is collected in the tank R_3 and is delivered by the pump S_3 to the tank H_3 over the first Gay-Lussac tower. In different works, this scheme varies somewhat in detail, but not in its essential points.

20. Acid Pumps.—In both the catalytic and chamber processes, it is necessary to transfer large volumes of acid from one part of the works to another. This is done by means of pumps of peculiar construction, some of which are designed to act automatically, so as to give a continuous flow of acid. Two styles of pumps, the *Kestner automatic* and *Monteju's acid egg*, are here described.

21. Kestner Automatic Pump. — This apparatus, shown in Fig. 13, is automatic and works continuously; it is constructed of cast iron for strong acid, but is lead lined for weak acids. It is operated by compressed air. The acid chamber is connected by the vertical pipe b with the valve box c, which must be placed higher than the tank supplying the apparatus, so that in no case acid can rise within a foot or two of it. Acid is admitted from the supply to a by means of the pipe d and check-valve e. The float f connected with the counterbalanced compressed-air valve g by means of the rigid rod h running inside the vertical pipe b and stuffingbox i, is raised by the inflowing acid until it opens the compressed-air valve g. The compressed air from the pipe l communicating with i at j flows through the pipe b into the acid chamber a, driving the acid up through the pipe k to a receiving tank; for instance, on top of a tower. As soon as chamber a is empty the float falls, closing the air valve, and the operation is repeated. The air valve and float are so balanced that the total movement of the rod does not exceed $\frac{1}{16}$ inch. The great advantage of this apparatus is that it insures a steady flow of acid (which can be accurately controlled) over the towers.

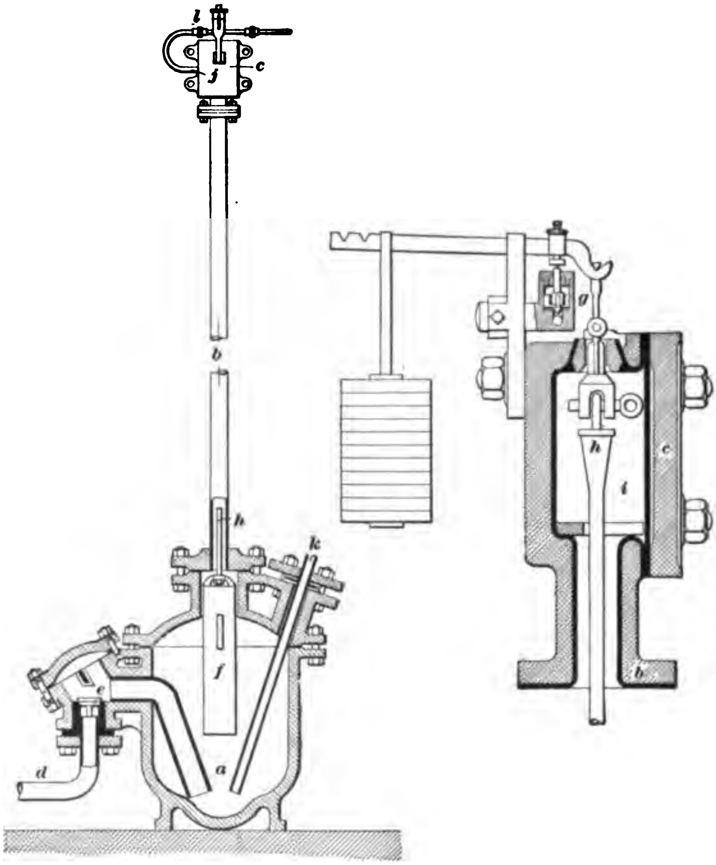


FIG. 13

22. Monteju's Pump With Acid Egg.—This pumping arrangement is illustrated in Fig. 14. The tank *A* containing the acid communicates at *e* with the receptacle or "egg" *G* by means of the pipe *b*, the flow being controlled

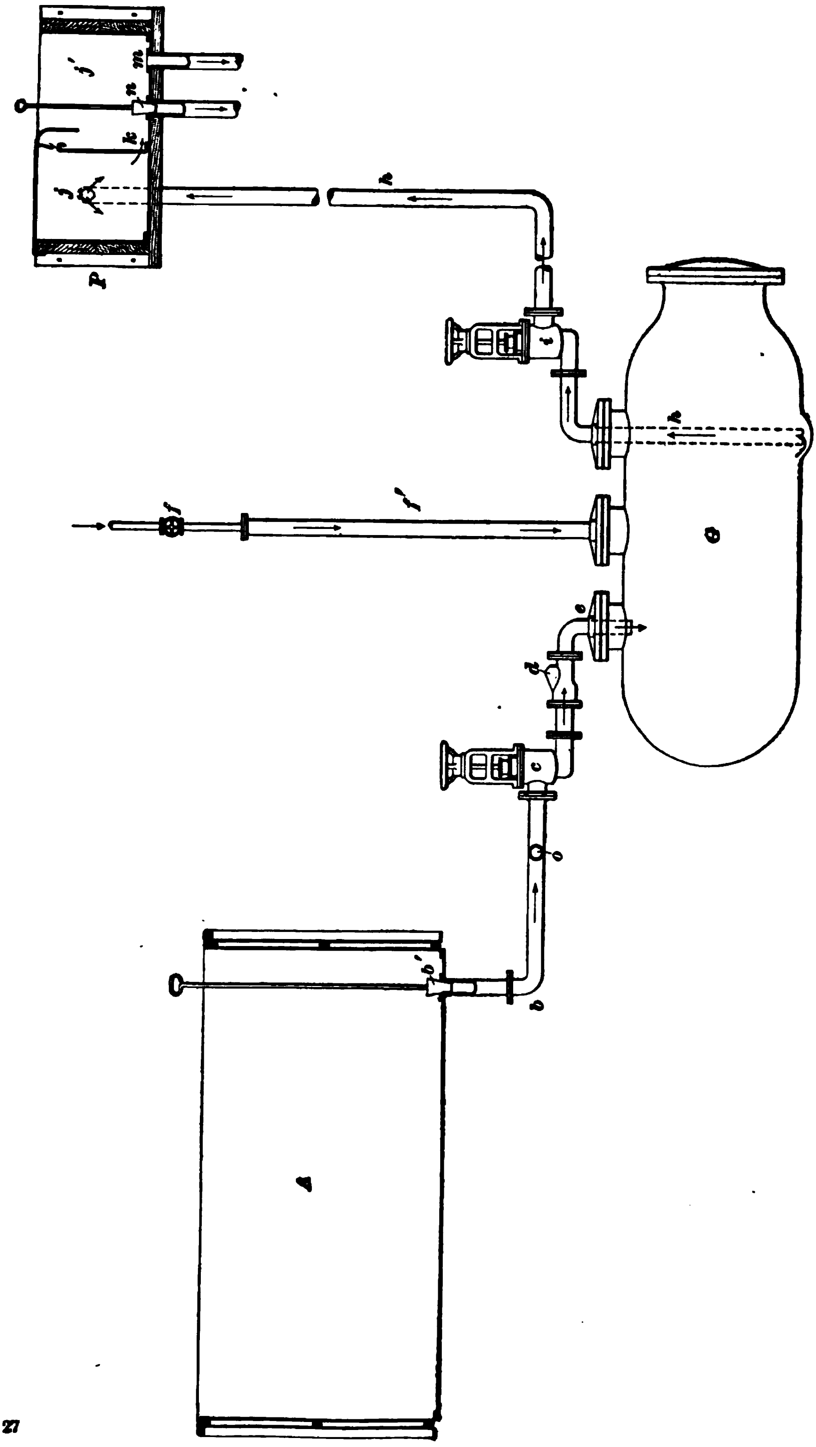


FIG. 14

by the globe valve *c*. The plug valve *b'* is merely auxiliary, and should not be relied on, as it can only with difficulty be made to withstand the back pressure. The check-valve *d* is used under ordinary circumstances. This valve permits the flow of acid into the egg until the acid rises to the level of the valve, which, when the compressed air is let into the egg, immediately seats itself and prevents the air from forcing the acid back into tank *A*.

Compressed air is admitted to the egg by means of the pipe *f'* and the valve *f*. The pipe *h* controlled by the valve *i* delivers the acid from the egg to the splash box *j* of the distributing tank *P*. When air is admitted to the egg, as it cannot pass valves *d* and *c*, and valve *i* being open, it forces the acid to a height of from 50 to 100 feet through *h* into the splash box *j*, which is a lead-lined box with two openings, through the lower of which the acid escapes into *j'*, an open part of the tank, and thence through the exit *m* into a receiving tank on top of the towers and an upper opening of large area, whereupon the air escapes into the atmosphere without splashing the acid over things. The exit *n* from *j'* into another receiving tank is provided in case the egg is used for pumping two kinds of acid, the plug being simply moved from *n* to *m* and a branch connection to a second supply tank being inserted at *o*, the flow of acid from either supply tank into the egg being then controlled by plugs *b'*.

OPERATION OF THE CHAMBER PROCESS

23. If the reactions involved in the chamber process have been understood, the importance of extreme regularity both as to volume and composition, of the supply of the substances entering into these reactions will appear obvious. For, although the process involving these reactions is a continuous one, and in fact more especially on this account, if loss is to be avoided and success attained, the supply of the necessary ingredients must be as exact as if the process were an isolated reaction involving the complete union of carefully weighed proportions. The materials in question are: (1) A constant stream of burner gas of uniform volume and percentage of sulphur oxides and free oxygen. (2) A uniform supply of finely divided water or water vapor of constant tension. (3) A uniform supply or circulation of nitrous vitriol containing a constant percentage of nitrous oxide N_2O_3. (4) A uniform supply of nitric oxide or acid for making good the oxides of nitrogen lost in the process (mechanically or otherwise).

It is only by careful watchfulness, honest work, and proper management, together with a rationally constructed plant, that a near approximation can be made to the requirements as to absolute uniformity called for. When, however, such approximation is reached, the difficulties of the chamber process disappear and the operation will proceed month after month with little, if any, variation, and with uniform results.

24. Conditions in the Glover Tower.—The burner gas, having an average temperature of about 550° C., in passing from below through the Glover tower meets a finely divided stream of nitrous vitriol $2H_2SO_4 + N_2O_3$ greatly diluted with chamber acid or with water, or both, and often carrying with it nitric acid, sufficient to supply the loss inevitable in the process amounting from 1.5 to 3 per cent. (The consumption of oxides of nitrogen is always given in terms of percentages of sodium nitrate $NaNO_3$ calculated on the available sulphur burned.) This stream of mixed acids enters the top of the tower at from 40° to 50° Baumé, according to the degree of concentration and denitration required and the concentrating efficiency of the tower. The hot, moist, sulphurous gas drives off the nitrogen oxides in the upper part of the tower, and as it descends to the lower and hot zone, the water is expelled from the dilute acid as steam. The acid is thus concentrated to from 60° to 62° Baumé, or in special cases to 64° Baumé, or even to 66° Baumé and flows from the tower, while a stream of gas containing a mixture of oxides of sulphur and nitrogen, steam, oxygen, and nitrogen, passes over to the first chambers.

25. Conditions in the Chambers.—The gas thus entering the first chamber contains all the elements necessary for the production of the hydrate or solution of sulphur trioxide and in a condition of maximum activity. At this point, the percentage of sulphur oxides is greatest, the free oxygen is in greatest excess, and the oxides of nitrogen NO and N_2O_3 are such as possess the most powerfully oxidizing effect. The temperature of the gas (80° to 100° C.) is also conducive to an active reaction. Therefore, it is at this zone of reaction that one would naturally look for a large make of acid, and such is actually the case, for between the Glover tower and the first forty feet of the first chamber, with all the elements and conditions of the process at their best, from 60 to 80 per cent. of the whole acid is made.

26. In a properly constructed plant, that is, a plant consisting of rightly proportioned Glover tower, chambers, and Gay-Lussac towers, a sufficient quantity of nitrogen oxides should be supplied to the gas by means of the Glover tower to raise the temperature of the reaction (as shown by the thermometers penetrating the sides of the chambers, say at a distance of 25 feet from the end that is nearest the Glover tower) to from 95° to 100° C. This, of course, does not apply to the oxides of nitrogen supplied to the system to replace the mechanical loss, but to the nitrogen oxides recovered at the end of the process and gradually accumulated as nitrous vitriol (nitrososulphuric acid dissolved in a large excess of 60° to 62° Baumé sulphuric hydrate or solution) and which is run over the Glover tower in dilute form to again utilize its contained oxides of nitrogen. The oxides of nitrogen so stored may be termed *niter in circulation*, and it is evident that, according to the quantity of this nitrous vitriol of uniform percentage contents of nitrogen oxides accumulated, put into circulation at the Glover and recovered at the Gay-Lussac towers, so will be the ratio of active nitrogen oxides to the sulphur oxides at this critical initial point; i. e., the Glover tower and first part of the first chamber.

27. Provided always that the towers are properly proportioned to fulfil their functions of denitration and absorption (or recovery), it is desirable to accumulate and put into and keep in circulation about 20 per cent. of niter (by niter is meant oxides of nitrogen calculated as nitrate of soda $NaNO_3$ on the available sulphur burned). This will secure an active process at the beginning and a rapid oxidation of the gradually lessening percentage of oxides of sulphur after the first active zone has been passed, owing to the large excess of active oxides of nitrogen in the chamber gas, and, consequently, a rapid change of these oxides of nitrogen to nitrous oxide N_2O_3, in which form it is capable of being at once absorbed in the Gay-Lussac tower. This will, on the other hand, prevent the process becoming sluggish and slow, with the consequent danger of sulphur dioxide escaping into the Gay-Lussac tower unoxidized, where it will decompose and so prevent the complete absorption of the nitrous oxide by the sulphuric acid, which takes place according to the following equations:

$$N_2O_3 + 2H_2SO_4 = 2(HO)(NO_2)SO_2 + H_2O$$
$$2(HO)(NO_2)SO_2 + SO_2 + 2H_2O = 3H_2SO_4 + 2NO$$

The oxide NO will not be absorbed, but passes with the inert nitrogen into the atmosphere. It will also avoid (by at once absorbing from the process) the danger of the N_2O_3 being changed to NO, or even to nitric acid HNO_3, when in the first case it would be lost as stated above, or in the second case it would not only be lost but would rapidly destroy the lead of the apparatus and contaminate the acid made.

28. After the first 40 or 50 feet of travel of the gas in the first chamber, the temperature indicated by the side thermometers will rapidly diminish. This would naturally be expected as the reactions become less intense, on account of the lesser proportion of sulphur dioxide contained in the gas, and also its greater diffusion in the chamber and its saturation with a mist of already formed sulphuric hydrate. The length of the active zone, of course, varies according to the volume of burner gas passed into a chamber of any given size, and also to the intensity of the first reactions, depending on the proportion of nitrous vitriol kept in circulation; but sooner or later, and generally within the first 60 feet, the reactions, as indicated by the thermometers, will become sluggish and will so continue until the gases have been thoroughly mixed and the various elements brought into more intimate contact by passing them through a pipe connection and in their mixed condition allowing them to again expand in a second lead chamber. For this reason, it is now usual in the United States to limit the length of the first chamber to from 50 to 75 feet.

29. Where a positive method of controlling the currents of a gas (such as the use of fans, etc.) exists, it is preferable, in the case of large volumes of burner gas being handled, to divide the gas between two or more first chambers of limited length, so as to secure a large zone of great activity rather than an extended zone of rapidly diminishing activity or sluggish reaction.

The condition of the gases at the end of the first chamber, or after the zone of great activity, is such as to call not only for a thorough mixing but also for a cooling and a condensing of the mist of acid already formed. Radiation of heat from the surface of the chambers, while very considerable, is not sufficient by itself to conduct away the heat of the active zone so as to secure the best results. The towers, surface-, air-, and water-cooled condensers and plate columns employed have already been described. These apparatus, by bringing the gases again into intimate contact, also undoubtedly start the reactions into renewed activity.

30. The second chamber in a properly proportioned set and with sufficient nitrous vitriol in circulation (in other words, with a sufficiently active process) will almost entirely oxidize the remaining sulphur dioxide, so that with or without further surface condensers between the second and the third chamber, the oxidation will be completed at once on entry into the third chamber, which then acts merely to dry and cool the gas, now consisting of inert nitrogen, the excess of oxygen, and nitrous oxide, and render it fit for absorption in the Gay-Lussac towers. For cooling and drying the gas, a long pipe connection between the last chamber and the Gay-Lussac tower is of great advantage; it can, however, be replaced by a surface condenser of any of the types previously mentioned.

In this description of the passage of the gas through the sulphuric-acid plant, it must be remembered that while the gas enters the chambers containing a large proportion of water vapor derived from the concentration or evaporation of the dilute acid supplied to the Glover tower, this water is rapidly absorbed by the formation of the sulphuric hydrate and precipitated to the pans of the chambers.

More water, either as finely divided spray or as steam, must be added. Steam is the usual medium employed, either low-pressure steam (20 pounds per square inch) or exhaust steam from a neighboring engine, or both.

31. Admission of Steam to the Chambers.—It is well to have sufficient points of admission for the steam, either on the top or sides of the chambers, each point being supplied with an indicating valve, so that the steam may ultimately be supplied just at such points and in such quantities as experience may show to be the best in each individual case, and under varying conditions of conducting the process. Just as it is with the burner gas and the supply of nitrogen oxides, so must the flow of steam to the process be in every respect uniform. To secure this, the steam pipes must be well covered and trapped and the main line supplying steam to the branches must be supplied with steam gauges and an efficient reducing valve, which must be constantly watched and kept in order. The arrangement of

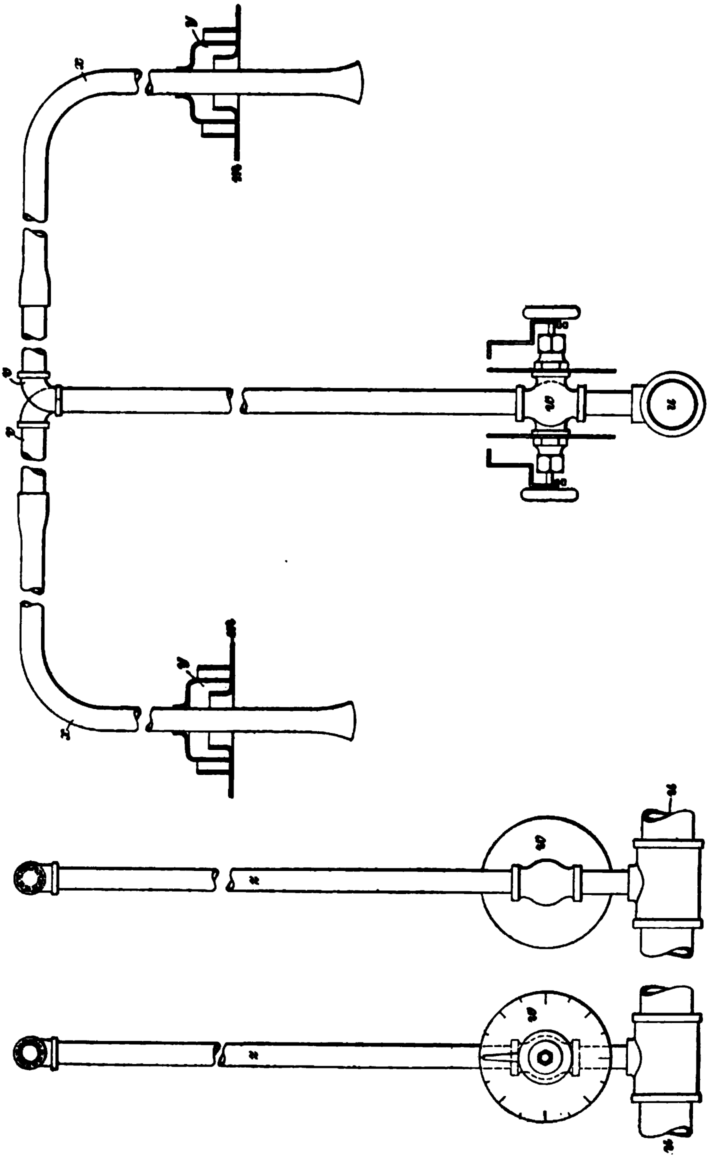


FIG. 15

the steam-pipe connections is shown in Fig. 15. The main supply pipe *u* is laid between the chambers, the vertical pipe *z* extending from it to the top and having branches *v* to the chambers right and left. The lead terminal pipes *x* enter the chambers by means of the hydraulic lutes *y*, which are ordinary water seals. At *m* is the top lead of the chamber. The indicating valves *w* serve to regulate the flow of steam to the chambers. If steam is admitted to the sides of the chambers, the lead terminal pipes enter the side leads or curtains through specially constructed stuffing-boxes.

With uniformity in the supply of gas, nitrogen oxides, and steam, and a draft subject to proper control once started, the chamber process becomes continuous and simply requires careful watching to maintain the regularity of the conditions. A careless burner man, by admitting too much air to the furnaces and thus reducing the percentage of sulphur dioxide in the burner gas, or a careless tower man in sending an irregular flow of nitrous vitriol over his Glover, will very quickly destroy the harmony of the reactions and too quickly disarrange the process to such an extent that first the supply of nitrogen oxides in circulation and then the sulphur dioxide itself will be pouring out into the atmosphere and the process will have resolved itself into the same, or almost the same, conditions, the acid maker has to confront when "starting up his chambers" or, in other words, at the beginning of everything.

32. Starting the Chamber Process.—This part of the operation requires the exercise of care and judgment, and it will take from 24 hours, where fans are used, to three or four times as long before the process is normal. The Glover tower, with its massive packing, absorbs much heat, and it will take considerable time for it to reach a temperature at which it will perform its double functions of denitration and concentration in a satisfactory manner, more especially as the acid that must be run into it from above has a constant cooling effect. At the same time, the Gay-Lussac towers become saturated with sulphur dioxide, which prevents the proper absorption of the nitrous oxide, and the formation, consequently, of a stock of nitrous vitriol for the Glover tower. These difficulties, of course, are exaggerated where no stock of 60° to 62° Baumé acid or of nitrous vitriol is on hand, and where the process has to be started with a supply of chamber acid alone (or even of water), as is generally the case in an isolated chamber system.

When such is the case, the chamber pans must be filled with sufficient acid of from 50° to 54° Baumé to form a hydraulic lute with the curtains or side and end sheets of the chamber lead.

A small quantity of acid must be run down the Glover tower until the packing is thoroughly moistened, and the Gay-Lussac towers should also be supplied with acid. Whether nitrogen oxides are to be supplied by "potting," or by the direct use of nitric acid on the Glover tower, arrangements must be made that will enable an abnormal amount to be used until such time as the towers are working properly and the stock of nitrous vitriol for circulation is secured. It will be advisable, at first, to supply an amount of nitrogen oxides equal to at least 8 or 10 per cent. of sodium nitrate, on the available sulphur.

The burner gas is then turned into the Glover tower and the chamber system. At first and until the Glover tower is performing its functions properly, it will be necessary to supply steam to the first part of the first chamber. This, however, will have to be done with extreme caution, as too great an excess of water is likely to cause the formation of nitric acid HNO_3, which will cause the rapid deterioration of the chamber lead.

33. As the Glover tower gets hotter it will concentrate the limited amount of acid with which it is supplied, to about 60° Baumé, and the quantity of acid can then be gradually increased. This stronger acid is at once supplied to the Gay-Lussac towers, which will then commence to absorb a little nitrous oxide; with patience and watchful care matters will gradually assume a normal condition. A sufficient stock of nitrous vitriol having been accumulated, and the steam admission, pumping arrangements, and the flow of acid over the various towers regulated, the extra niter supply will be reduced to a point where it is just sufficient to supply the daily loss and maintain the circulating supply of nitrous vitriol intact. The acid concentrated by the Glover tower should test 62° Baumé at 60° F. (66.4-per-cent. SO_3). Such part of it as is intended to be run over the Gay-Lussac towers should be run from the Glover tower into a cooler and cooled as thoroughly as the temperature of the cooling water will allow. It is then pumped to the supply tank on the second Gay-Lussac tower, where it meets with the gas just leaving the system and poorest in N_2O_3. It will run from this tower containing varying percentages of nitrososulphuric acid, and is known as the first, or weak nitrous vitriol. It is then pumped to the first Gay-Lussac tower, or the tower nearest to the last chamber, where it meets the gas strongest with N_2O_3. Sufficient acid should be supplied to these towers to permit a nitrous vitriol containing 2.5 to 3 per cent. of N_2O_3 to run from this first tower. This second, or nitrous vitriol, proper, is then passed to the stock tanks for nitrous vitriol, an exactly equal amount, both in quantity and percentage of N_2O_3, being taken from the stock tanks and pumped to the top of the Glover tower and run down the tower together with a sufficient stream of weak sulphuric acid to dilute it sufficiently to secure denitration and also to secure its concentration in the Glover tower to 62° Baumé.

34. All well-equipped plants are now being built with two Gay-Lussac towers, both because in this way it is possible to secure sufficient cubic capacity without undue height or diameter, and because if, for any reason, the process becomes irregular ("goes back") and sulphur dioxide gets into the first tower, decomposing the nitrous vitriol, then the second tower will still absorb and to a considerable extent take up the work which the first tower is doing badly, the first tower, in the meantime, assuming the functions which should have been performed by the last chamber. In this way, time is secured to find out just where the trouble is and remedy it before much harm is done. If, however, the trouble is not found and remedied, the sulphur dioxide will gradually get into the second tower and the process will be "lost," or in other words, with the exception that the Glover tower is hot, the acid maker will have to proceed as in starting up the system.

35. It must be borne in mind, and too great emphasis cannot be given to the statement, that when the chamber process begins to go wrong, *it is on account of a break in the uniformity of the supply of the various elements.* Either the burner gas is richer or poorer in sulphur dioxide, the nitrous vitriol is poorer in nitrous oxide on account of the acid supplied by the Glover tower being weaker than 62° Baumé, or too much or too little steam or higher or lower pressure steam is being supplied. When such irregularity is noticed, the acid maker must at once increase the flow of nitrous vitriol from his stock over the Glover tower. He will then immediately test his burner gas, nitrous vitriol, steam, etc. until he finds where the irregularity is occurring. This remedied in time, the process will rapidly become normal again and the increased supply of nitrous vitriol may be cut off gradually, in the meantime more 62° Baumé acid being run over the Gay-Lussac towers so as to recover as far as possible the nitrous vitriol temporarily taken from stock.

As the activity of the chemical reactions going on in the chambers is proportional to the heat produced by them, it is plain that in a regular normal process the temperature at the most active and least active zones will bear a constant ratio to one another, so long as the process is regular; this fact affords a very delicate indicator of the regularity of the process.

36. If a chamber thermometer, placed in the side of the first chamber about 20 feet from the entrance of the gas from the Glover tower, that is, in the zone of greatest activity, registers 100° C., and a thermometer placed in the side of the second chamber, or a zone of lesser activity, registers 70° C., *when the process is at its best and working with absolute regularity*, the difference between the two readings represents the relation between the greatest and lesser activity of that process when normal. If these temperatures vary so as to disturb *this difference of* 30° C. *so little as* 1° C., it is time for the acid maker to investigate his process and find out what is wrong. This will often enable him to save serious disturbance in his process before it has manifested itself in any other way. It must be noted that it is a disturbance of the difference or ratio, however, and not of the actual temperatures. The zones of most and least active reaction ebb and flow slightly in the chambers so that the actual readings of the thermometers may both be a degree or two higher or lower at various times of the day and especially at various seasons of the year.

In addition to the temperature readings, the manometer also affords a delicate test. Manometers registering the tension of the contents of the first and last chambers will show a constant *difference* of pressure when the process is regular and constant; such *difference* once determined when the process is at its best will be maintained so long as normal conditions prevail.

As a guide to the proper supply of steam at various zones of the process, drip pans are placed on the sides of the chambers, which enable a sample of the acid forming on the sides of the chambers to be taken and tested with the hydrometer and otherwise examined. This acid, being taken from the cool sides of the chambers, contains more water than the average of the acid being formed in the chamber. This difference is about 3° Baumé. A curtain or side drip reading of 50° Baumé would, therefore, represent approximately an average formation of 53° Baumé acid *in that portion of the chamber*.

37. Curtain Drip.—For taking these samples the device shown in Fig. 16 is employed. To the curtain or side lead is attached an inclined lead trough *a* about 4 feet long. At its lower end is attached the pipe *b*, which passes through the

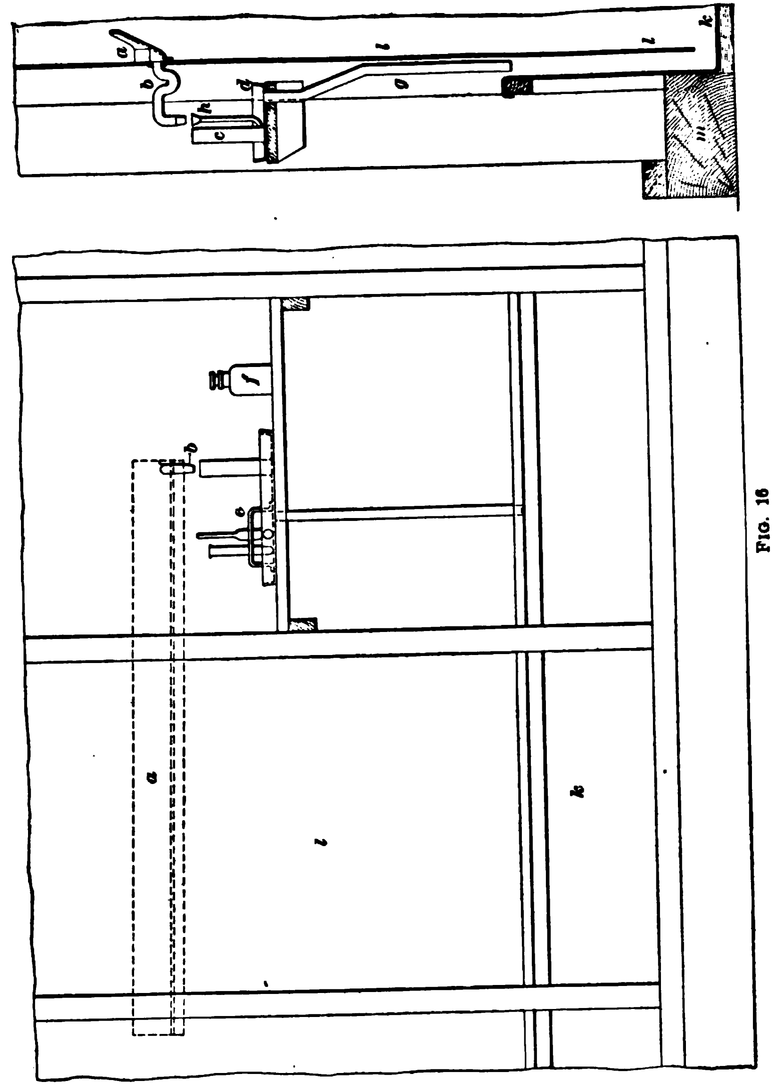


FIG. 16

curtain *l*, and is bent so as to form a lute or seal. Acid caught in the trough *a* runs through the pipe *b* and drips into the funnel *h*, communicating with the hydrometer jar *c*. This jar, together with a rack for the hydrometer, etc., stands in a lead tray *d* from whose bottom the drip pipe *g* leads to the chamber pan *k*. As acid is constantly dripping into *h* and overflowing from *c*, the acid in *c* varies according to that forming in the chamber, and hence tests of this give a fair indication of the condition of affairs in the chamber at that point.

Different acid makers prefer to keep the drips of the different chambers stronger or weaker. This is within certain limits immaterial. The acid in the first chamber, in spite of the large amount of water supplied by the Glover tower, will rarely fall below 52° Baumé. The acid formed in the chambers should, however, never be allowed to get strong enough to absorb and retain more nitrous anhydride than is absolutely inevitable, especially in so far as such chambers are concerned from which acid is withdrawn from the system. This strength will also be about 52° Baumé, and the tendency to absorb nitrogen oxide will increase with every degree Baumé above this point. Nor, on the other hand, must the acid get so weak as to permit the formation of nitric acid in the chambers. This strength will be about 45° Baumé. Therefore, the acid formed in the chambers must in no case be weaker than 44° or 45° Baumé, nor should it be much, if any, stronger than 52° Baumé.

Although the drips are highly useful adjuncts in controlling the chamber process, samples of the bottom acid should also be taken at intervals, and in each individual chamber the acid maker must learn in this way to compare the actual strength of the acid formed in the chambers as he finds it with the strength of the acid as shown by his drip tests. Such tests of the bottom acid are most satisfactory when taken from a tank that has been filled with acid drawn off from the chamber.

THE PURIFICATION OF CHAMBER ACID

38. General Remarks.—In addition to the impurities brought into the process with the burner gas, as was previously mentioned, some of which will not travel beyond the Glover tower, chamber acid will contain sulphates of lead derived from the slow deterioration of the lead apparatus, and also small quantities of nitrogen oxides and even nitric acid. From a commercial standpoint, the impurities that are most injurious are the arsenic and selenium compounds and even distillation will not entirely eliminate these, unless special precautions are taken. They will pass over into the products made from acid contaminated with them (for example, into muriatic acid and calcined salt cake made from salt and arsenical sulphuric hydrate). If acid contaminated with arsenic or selenium is used for "pickling" sheet iron or wire, preparatory to galvanizing or covering the sheets with zinc, tin, or lead, the galvanic action set up in the dilute acid bath will cause the arsenic or selenium to precipitate and become deposited on the iron sheets, which will prevent the adhesion of the zinc, tin, or lead, and result in "blistered" sheets.

39. Most other impurities, especially lead or iron sulphates, will separate in the tanks by sedimentation, or, at the worst, will produce a discoloration of the acid that does not unfit the acid for most commercial purposes. Fortunately, very few of the metallic sulphides contain selenium except in minute traces. Practically all the metallic sulphides contain arsenic, and many of these best adapted otherwise for sulphuric-acid manufacture contain it in considerable quantity. Arsenic, therefore, is the principal impurity of chamber acid, and on account of its poisonous characteristics, it becomes especially necessary to eliminate it. When sulphuric hydrate is used for refining crude petroleum, or for the manufacture of mixed acid for making nitroglycerin, arsenic is not detrimental, or at least the manufacturers do not object to arsenical acids. The arsenic contained in the enormous quantities of sulphuric hydrate used in the manufacture of superphosphates and fertilizers may even be of advantage in destroying insects, etc.; but for other purposes, and especially for processes connected with the manufacture of food products, its elimination becomes absolutely necessary. If the manufacturer is not prepared to thoroughly purify his product from arsenic and intends it for the general market, or for galvanizing, food products, or other similar purposes, then he must limit his choice of raw material, often to his great disadvantage as to cost, to such raw materials as are practically free from arsenic (as brimstone, some few of the iron bisulphides, etc.). If his ores contain only a little arsenic, he can sometimes obtain a fairly pure acid from the second chamber, using the acid produced in the Glover tower and first chamber for purposes less exacting of purity; this, however, is a dangerous makeshift.

40. Purification From Arsenic.—As all methods for the purification of acid from arsenic are based on its precipitation and ultimate removal by sedimentation, it is evident that this operation must take place when the acid is of least density; in other words, while it is still chamber acid (50° to 52° Baumé) and before further concentration.

This statement must, howexer, be qualified in regard to such manufacturers of 66° Baumé and extra-concentrated acid who are equipped to manufacture such acids by distillation, as will be hereafter described.

In many metallurgical plants, where the acid is a by-product and the principal value is in the metallic contents of the metallic sulphides, and in cases where the cheapness or other advantages outweigh the disadvantage of considerable arsenical contents in the raw material, the *whole output* must be treated for the elimination of the arsenic.

41. Freiberg Process for Removing Arsenic.—Where this is necessary, the only practical process is a modification of what is known as the **Freiberg process.** This process depends on the conversion of arsenious oxide into arsenious sulphide by means of sulphureted-hydrogen gas, the precipitation taking place according to the following equation: $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$. As sulphureted hydrogen will decompose strong sulphuric acid as follows, $3H_2S + H_2SO_4 = 4H_2O + 2S_2$, it is better to purify the acid as little over 50° Baumé as possible. By this process it is stated that at Freiberg, acid containing as high as .14 per cent. of arsenic can be purified until it contains only .0002 per cent. of arsenious oxide As_2O_3.

42. In chemical works, where sulphate of ammonia is prepared from the *gas liquor* of illuminating gas works, the sulphureted hydrogen is a troublesome by-product, but can be made readily available for purifying the acid in the Freiberg process. It contains, however, some pyridine bases that must first be eliminated if acid of good color is required. If this source of sulphureted hydrogen is not available, then it must be prepared by treating iron sulphide with dilute sulphuric hydrate $FeS + H_2SO_4 = FeSO_4 + H_2S$. The iron sulphide may be prepared in a simple little furnace by heating scrap iron or rails with brimstone. On the large scale, however, it can be very cheaply produced in a cupola furnace by smelting pyrites fines or inferior pyrites with silicious slag.

The iron sulphide so produced is broken into rather large pieces and filled into a generator, where it is treated with any available dilute sulphuric acid, such as is often produced about an acid works from the washings of tanks, tank cars, etc., and too dirty for general commercial purposes. These generators are all made on the same general plan (practically that of Kipp's apparatus, but they are constructed out of lead, wood, and iron, and are often made large enough to hold a charge of iron sulphide sufficient to last several weeks.

43. Freiberg Sulphureted Hydrogen Generator.—A simple and efficient generator for sulphureted hydrogen is shown in Fig. 17. It consists of a cast-iron generator *A* with flanged top and manhole *b* and an acid reservoir *c*. This generator, as well as reservoir *c*, is lined with lead. The generator is partially filled with iron sulphide *d* through the manhole *b* and the tank with weak sulphuric acid. The acid will then flow from the reservoir *c* to the generator *A*, and on coming in contact with the iron sulphide will form sulphureted hydrogen. The valve *e* and pipe are for carrying away the hydrogen sulphide; when the valve *e* is open, the hydrogen sulphide passes constantly away; when *e* is closed, the pressure in *A* rises until the acid is driven back into the tank *c*, and the evolution of hydrogen sulphide practically ceases. The weight of the acid in reservoir *c* being carried by the pressure in *A*, upon opening the valve *e* the acid again flows into *A* and generation of gas recommences. A cleaning vent is provided at *f*, from which the iron sulphate can be removed when the acid is spent—i. e., entirely converted into iron sulphate—and *g* is a screen of perforated lead.

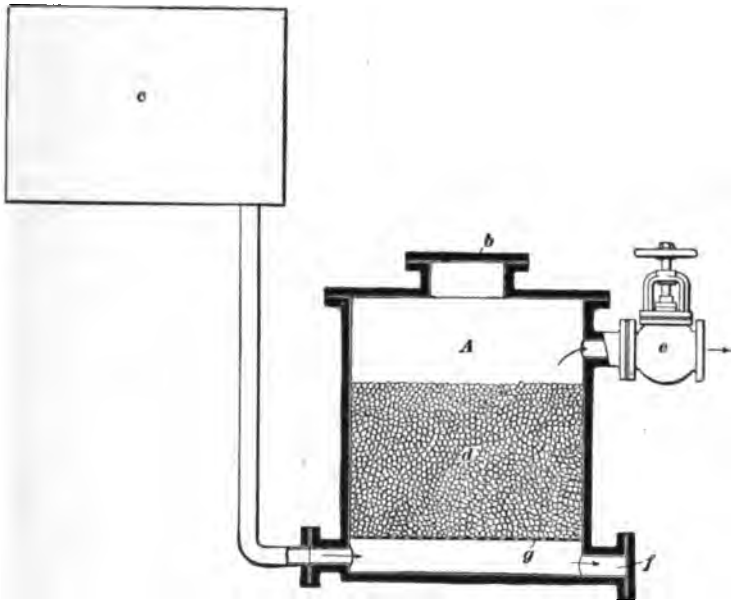
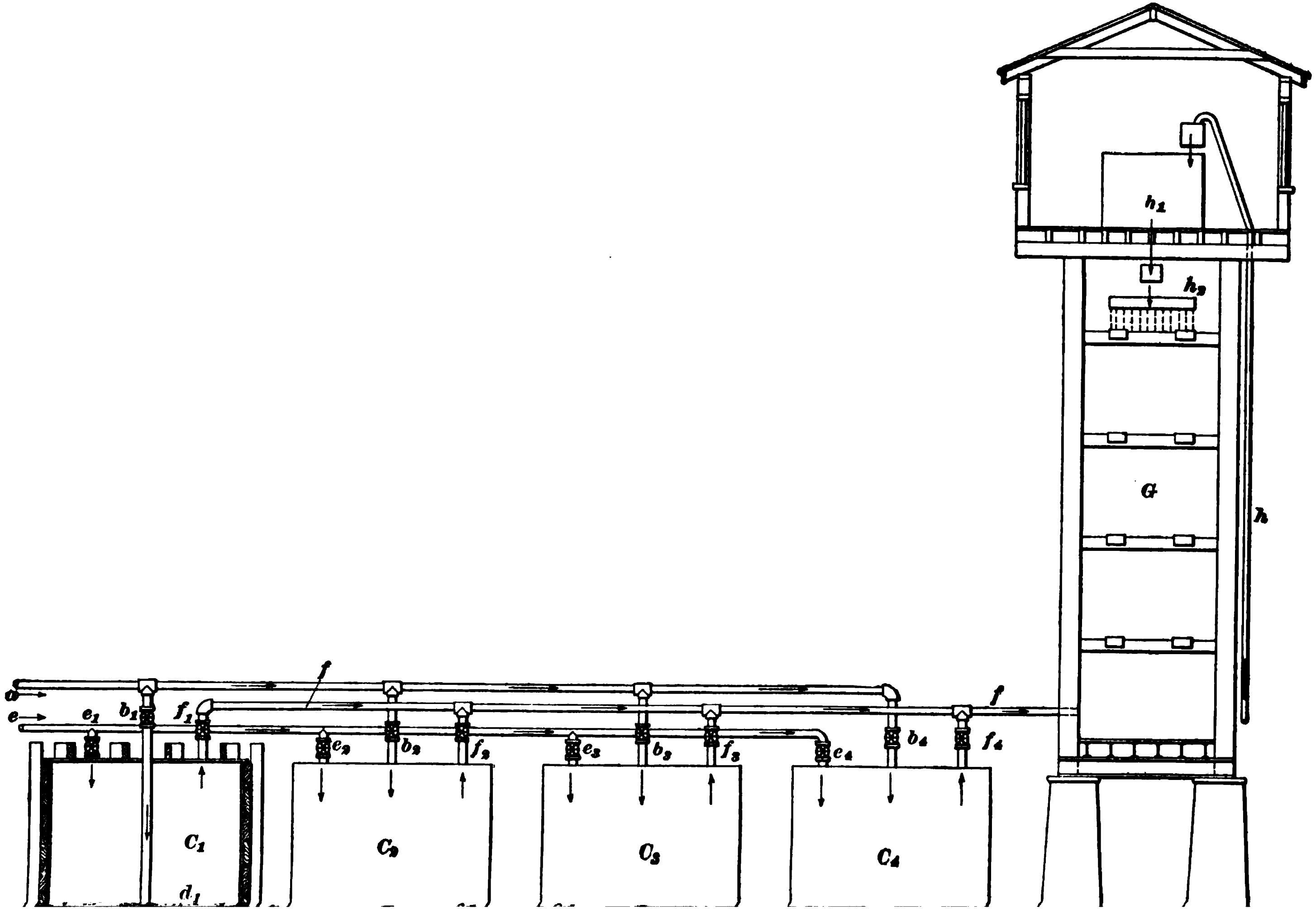


FIG. 17

44. Precipitation of the Arsenic.—The chamber acid is then run by gravity into a series of gas-tight lead-lined boxes or tanks. Each box in the series is provided with a perforated coil of pipe in the bottom connecting on the outside with the main supply pipe for sulphureted hydrogen and a valve controlling the admission of the gas; it is also connected at the top by means of pipes and valves with every other box in the series, in such a way that the gas may be made to pass through any one of the boxes first and then consecutively through the others; and, also, that any one of the boxes may be disconnected temporarily from the series. In this way, in a series of, say, four boxes, when the acid in box 1 has had sufficient treatment by the gas, it may be cut out and boxes 2, 3, and 4 remain. When box 2 has been treated sufficiently, then boxes 1, 3, and 4 remain in operation. The box so cut out is allowed to settle as long as necessary. The precipitation of arsenic sulphide has then taken place to such an extent that the upper stratum of acid, amounting to three-quarters or even more of the whole contents, may be decanted or drawn off by a siphon in a pure state, requiring no further treatment. The rest of the acid containing the precipitated arsenious sulphide must be filtered.

45. Each series of boxes is provided with two simple gravity filters, which consist of lead-lined boxes filled with broken quartz or sand of graduated sizes. The impure acid is run by means of a pipe and valve on to one of these filter beds, from which it will emerge practically free from arsenic. When one filter becomes foul the other filter is put into commission and the foul one cleansed by the removal of the arsenious sulphide from its surface.

The exit gas pipe from the last box of any one or more series of boxes enters the bottom of the tower shown in the construction. Just sufficient acid is run into this tower to prevent the escape of any sulphureted hydrogen that has not been absorbed in the boxes. The apparatus for the precipitation and filtration of the arsenic sulphide, together with all pipe connections, is illustrated in Fig. 18 (*a*) and (*b*).



h_1
h_2
G
h
b
e
e_1
b_1
f_1
f
e_2
b_2
f_2
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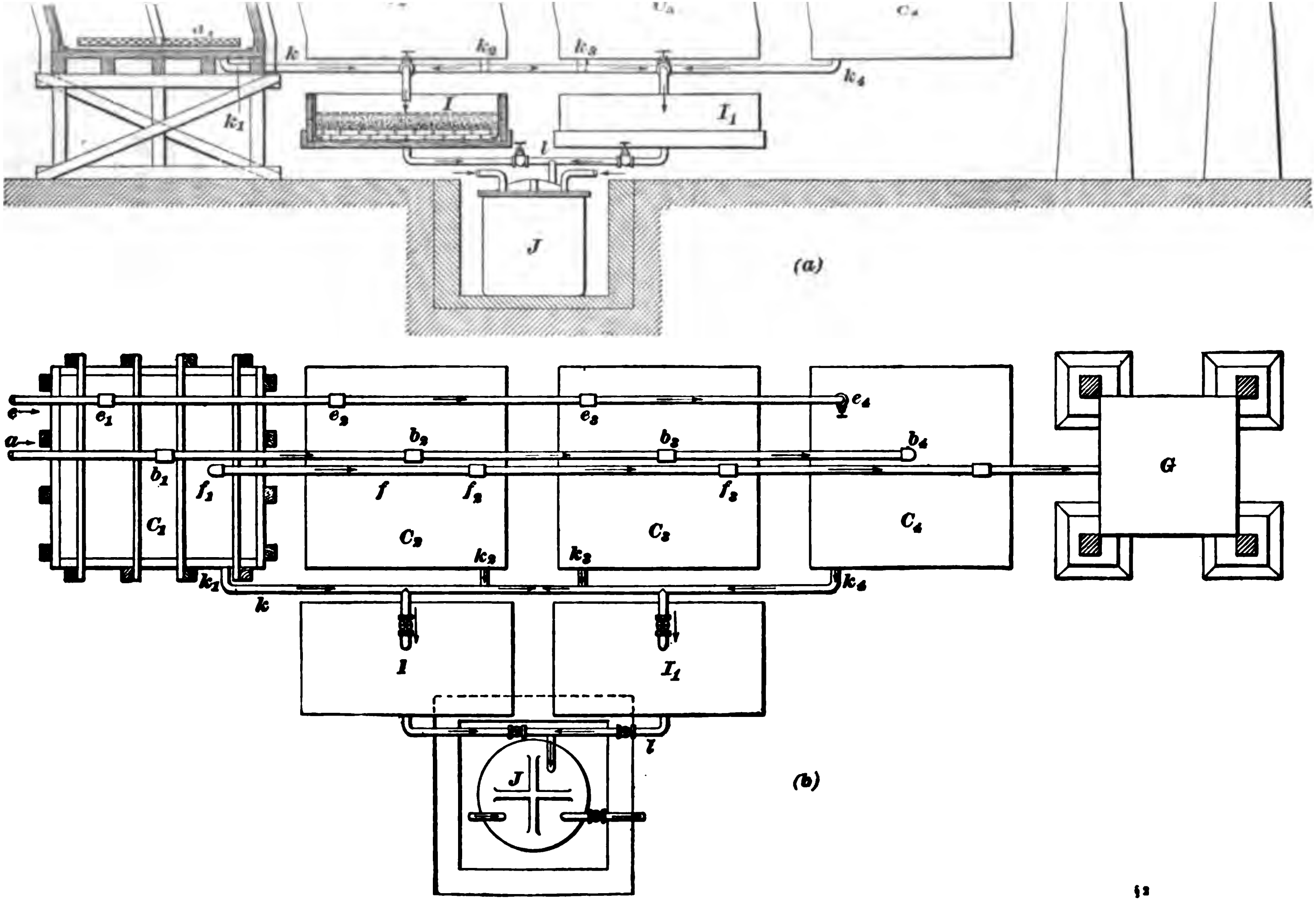
d_1
C_2
C_3
C_4


k
k1
k2
k3
k4
I
I1
l
J
(a)
e
a
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b1
f1
C1
e2
b2
f
f2
C2
e3
b3
f3
C3
e4
b4
C4
G
(b)

FIG. 18

The main pipe *a* brings sulphureted hydrogen from the generator shown in Fig. 17. The branches and valves b_1, b_2, b_3, and b_4 communicate with the gas-tight, lead-lined boxes C_1, C_2, C_3, and C_4, and the perforated coils d_1, etc.

The acid pipe line *e* is for filling the boxes C_1, C_2, C_3, and C_4 with chamber acid by gravity, fitted with branches and valves e_1, e_2, e_3, and e_4.

The return gas pipe *f* collects the hydrogen sulphide remaining after it has percolated through the acid in the boxes and conveys it to tower *G*. It is fitted with branches and valves f_1, f_2, f_3, and f_4.

The tower *G* is packed in various ways, and a stream of weak arsenical acid runs down through it, meeting the weak hydrogen sulphide not taken up by the arsenical acid in boxes C_1, C_2, C_3, and C_4. This stream must be regulated to completely utilize the hydrogen sulphide and prevent its loss into the atmosphere. The tower is fitted with acid supply line *h*, tank h_1, and distributor h_2.

The filters *I* and I_1 are used alternately. A blow case or acid egg *J* is used for pumping the purified acid to the storage tanks.

After a box is sufficiently treated with hydrogen sulphide the gas valve is closed and the manhole opened. The box is then allowed to stand for from 12 to 24 hours, when the arsenic sulphide will be found to have settled to such an extent that about three-fourths of the contents of the box may be decanted off by means of a siphon and passed direct to storage. The remaining quarter is drawn through pipe *k* and branches k_1, k_2, k_3, and k_4 into whichever one of the filters happens to be in commission. This filter strains out the arsenic sulphide, permitting the purified acid to run through pipe *l* into the pumping apparatus, whence it also passes to storage. The tank is then again filled with acid and another tank cut out for treatment.

46. Stahl Method for Removing Arsenic.—For the purification from arsenic of comparatively small quantities of acid, Doctor Stahl's method is very satisfactory. The acid is diluted to 40° or 42° Baumé heated to 80° C., and a solution of barium sulphide of 8.3° Baumé is run in at the bottom of the vessel in such a way that no hydrogen sulphide escapes. The arsenic trisulphide is filtered off on a sand bed placed on a layer of quartz lumps, and in this way the arsenic will be reduced to .01 per cent., but as the acid on standing in the filter again takes up a little arsenic, it is treated with gaseous hydrogen sulphide and is thus reduced to .005 per cent. arsenic.

Arsenic may also be precipitated as a sulphide by means of the sulphides of sodium, calcium, iron, and ammonium, and by sodium and barium thiosulphates, but for most purposes these substances are objectionable either on the ground of cost or because they leave objectionable impurities dissolved in the acid treated.

CONCENTRATION OF DILUTE ACID SOLUTIONS AND THE PRODUCTION OF SULPHURIC MONOHYDRATE

47. The acid solutions resulting from the reactions of the chamber process consist (1) of chamber acid averaging about 50° Baumé, rarely over 52° to 54° Baumé, and often diluted for purpose of purification as low as 40° Baumé; (2) of acid concentrated to 60° to 62° Baumé by the heat of the burner gas in the Glover tower.

The concentration of these two products varies materially and must be separately considered.

48. Concentration in Lead Pans.—The first concentration of the dilute chamber-acid solutions, varying from 40° to 54° Baumé, which come under the first class above, is always effected in shallow lead pans. Concentration in lead can only be made to 60° Baumé or slightly over, as the lead pans are rapidly acted on by hot acid of greater strength. The evaporation is carried on in these pans by means of (*a*) waste heat; (*b*) direct heat applied either (*c*) above or (*d*) below the pans, derived from coal, coke, natural or producer gas, oil or petroleum, tar, or applied as steam.

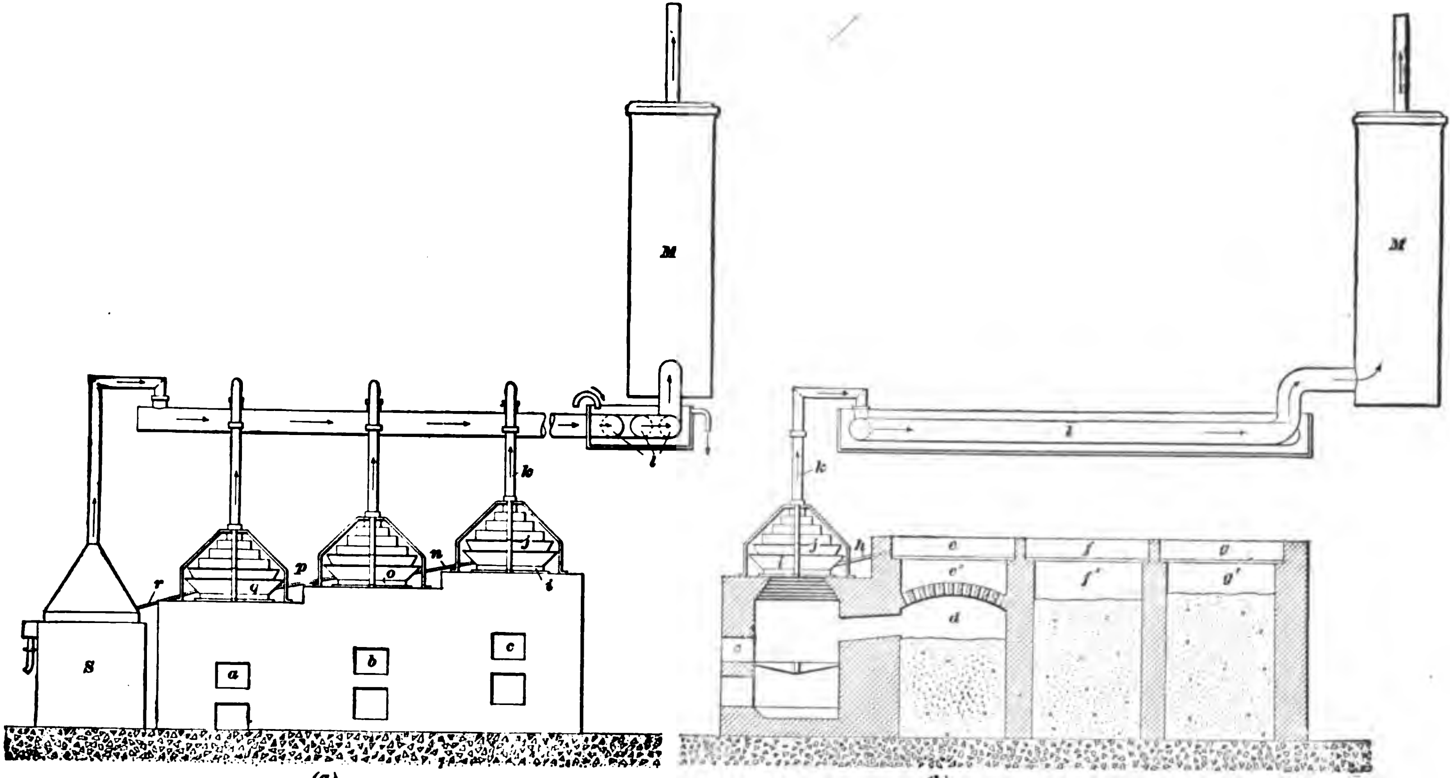
Practically, except in special cases, steam is not found satisfactory and the benches used are of two varieties, viz., those in which the heat is passed over and those in which the heat is passed under the pans.

Pans used to be placed over the brimstone burners, utilizing the heat of combustion. When pyrites began to take the place of brimstone, the pans were still placed above the burners. This practice is now almost entirely done away with, partly because of the large amount of dust involved by the use of pyrites and partly because of the trouble caused by leaks from the pans saturating the costly masonry of the furnaces with acid and of the difficulty of repairs to the pans when so placed, but principally because the introduction of the Glover tower utilizes the waste heat of the furnaces to much better advantage. Fig. 19 includes a pan bench arranged to be fired from below.

The dilute solution flows continuously through the pan bench in quantity to insure its leaving the bench a uniform density of about 60° Baumé. This acid must now be further concentrated, either in glass, porcelain, or platinum. After the acid reaches a strength of 64.5° Baumé, it may be further and finally concentrated in iron stills or the final concentration may be made in glass or platinum. Below this strength (64° to 65° Baumé) it acts too strongly on the iron. The concentration in porcelain cannot be carried beyond about 65.5° Baumé.

49. Concentration in Platinum, or Partly in Platinum and Partly in Iron.—In Fig. 19 is shown a bench of platinum pans or stills *i*, *o*, and *q*, also the bench of lead pans *e*, *f*, and *g*, in which the preliminary concentration is made.

Platinum stills of circular or oblong shape with rounded corners are made of many different patterns; some are provided with platinum covers; some have water-cooled leaden covers or hoods, as in Fig. 19. The principle, however, is the same in all; they are practically evaporating kettles for continuous service, provided with an inlet and



(a) (b)

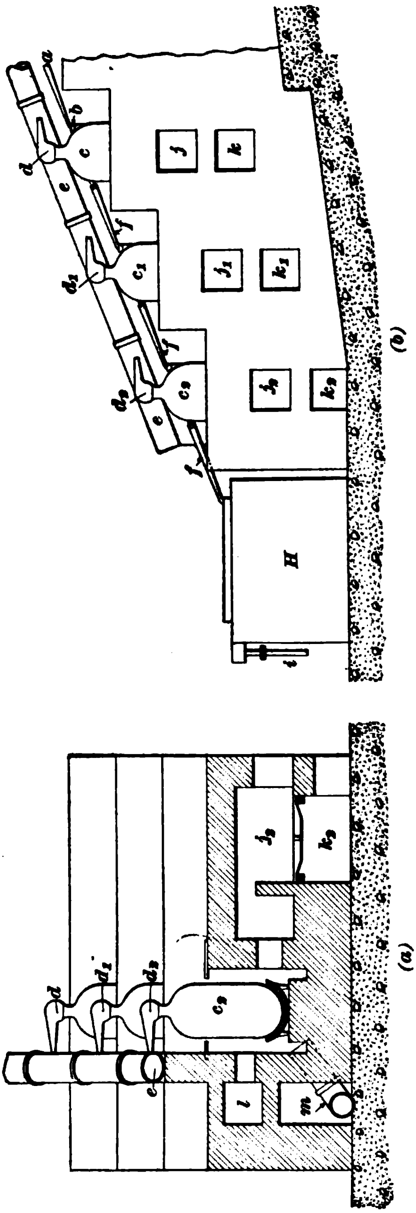
FIG. 19.

exit for the stream of acid and with means for eliminating and condensing the steam or weak distillate. During the gentle evaporation of these dilute hydrates in the lead pans, little but water, in the shape of steam, is driven off; after the solution reaches a density of 60° Baumé, more and more of the hydrate is driven off with the water; when the solution reaches a density of 66° Baumé (93.5-per-cent. H_2SO_4), the distillate will attain a density as high as 60° Baumé (77.6-per-cent. H_2SO_4). When the solution in the pans contains in the neighborhood of from 95- to 98-per-cent. H_2SO_4, the distillate will have a density of 66° Baumé (93.5-per-cent. H_2SO_4). Much of this distillate is too weak for a reconcentration. It is sometimes run into the drain, but should be used for diluting the nitrous vitriol on the Glover tower. The apparatus shown in Fig. 19 (*a*) and (*b*) is continuous in its operation.

The fireplaces *a*, *b*, and *c* communicate with the common flue *d*. This flue at one end is arched over with "pigeon-hole" or open brickwork, permitting the fire gas to pass into *e'*, under and from end to end of a lead pan *e*. The heated gas returns under lead pan *f* through flue *f'*, and then passes through flue *g'* under lead pan *g* to the stack.

Chamber acid is run into lead pan *g*, whence it flows to pan *f* and thence to *e*, from which it passes by platinum pipe *h* to platinum dish *i*, covered by a lead water-cooled hood *j*. The steam and acid vapors escape by pipe *k* into water-cooled condenser *l* and thence into the small condensing tower *M*. Acid then flows from platinum dish *i* by platinum tube *n* into platinum dish *o*, provided with water-cooled lead hood and exit to condenser. From platinum dish *o* the acid passes through platinum pipe *p* into platinum dish *q*, also provided with hood and exit to condenser. As the acid leaving *o* will have reached a strength of from 64.5° to 65° Baumé, an iron dish is often substituted for platinum dish *q*. The acid then runs through platinum pipe *r* into cooler *S*, and thence to storage.

50. Concentration in Iron.—Different manufacturers have different views as to the material best suited to this



(b)

(a)

FIG. 20

final concentration. Iron, if properly cast and of suitable composition, is but little acted on by acid of 64.5° Baumé, and it is, of course, very much cheaper than platinum. On the other hand, for the manufacture of the extra concentrated acid, from 97- to 98-per-cent. H_2SO_4 or 79- to 80-per-cent. SO_3 iron is also more suitable. Hot acid stronger than 94-per-cent. H_2SO_4 acts strongly on platinum, but has very little action on iron. In this country final concentration in iron may be said to be the rule and the practice is rapidly gaining ground in Europe.

51. Concentration in Glass Retorts or Stills.—This practice is practically obsolete in the United States, but the following description of the apparatus sometimes used will be of interest. In Fig. 20 (*a*) is shown a side view and section of the furnaces and retorts, and Fig. 20 (*b*) shows an end view of the same. The glass retorts c, c_1, and c_2 are arranged in steps as shown. The acid from the pan bench flows by gravity through the pipe a and funnel b into the highest retort c. The overflow from c flows through the pipe f to c_1 and so on down the series; the concentrated acid from the last retort c_2 flows to the cooler H, from which it can be drawn by means of the pipe i. The weak distillate is carried through the "goosenecks" d, d_1, and d_2 to the vapor flue e. A separate fire is maintained under each retort in the fireboxes j, j_1, and j_2. At k, k_1, and k_2 are the ash-pits. The flue l carries the fire gases to the stack. In case of breakage of retorts, their contents are carried off by means of the conduit m.

52. Concentration in Porcelain or Glass Beakers or Dishes: Systems of Negrier, Webb, Levinstein, and Others.—The principles involved in all these systems of concentration are very similar, and, generally speaking, are merely modifications in details of construction. The acid flows continuously from dish to dish or beaker to beaker. The firing is done from below and the acid vapor is carried away by a separate flue. Fig. 21 shows the Negrier

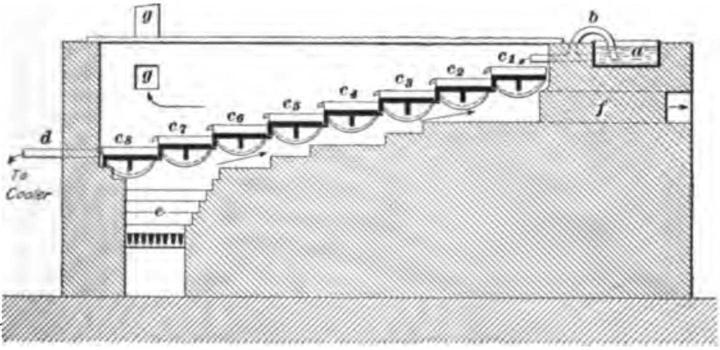


FIG. 21

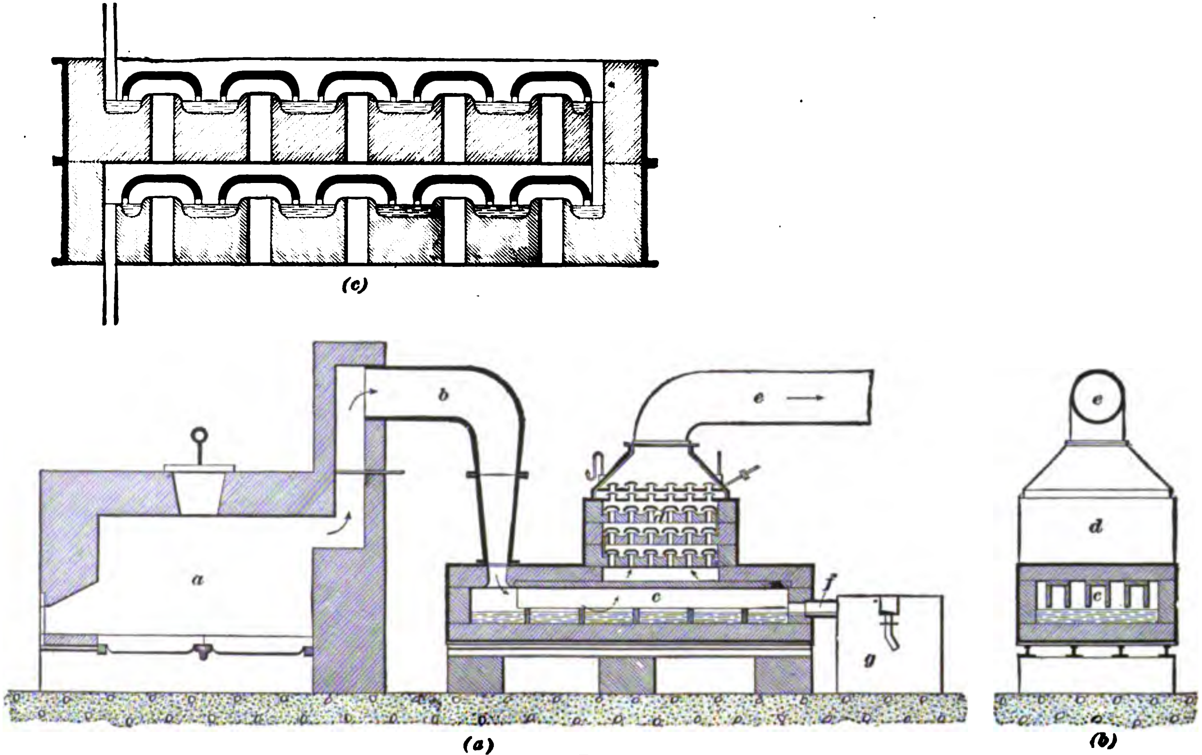


FIG. 22

apparatus and illustrates this method of concentration. All these methods, however, are open to the objection that it is very difficult to prevent the escape of acid fumes into the air.

The operation of the Negrier apparatus shown in Fig. 21 is as follows: Pan acid from *a* flows through conduit *b* into the first porcelain dish c_1 and so on by means of the lip on the dishes from one dish to the other c_1, c_2 . . . . c_8 until the strong, concentrated acid reaches the conduit *d*, through which it is taken to a cooler and the storage.

Heat is provided by fireplace *e*. The products of combustion pass under the porcelain dishes until they reach the flue *f* and are carried to the stack. The distillates and water vapor pass through the flue *g* and are carried to a suitable condensing apparatus or to the stack.

53. Concentration by the Kessler Process.—This method consists of the direct use of heated air or fire gas for evaporating the water from dilute sulphuric-acid solutions. The current of hot gas produced from a coke fire or producer is brought into immediate contact with the dilute acid. In this process, the following conditions must be fulfilled: The current of hot air or gas must be brought into contact with a sufficiently large surface of acid to immediately and considerably reduce its temperature. The air or gas must then be completely saturated with steam and acid vapor. The apparatus must not only be able to resist the action of hot acid and acid vapors, but must be so constructed that the crusts and deposits formed can either be readily removed or will not interfere with the efficiency of the apparatus. *Under these conditions, the acid can be concentrated at a temperature far below its boiling point.* In order to produce acid of 95-per-cent. H_2SO_4, boiling at 284° C., the temperature need not exceed 170° to 180° C.; for the most highly concentrated acid boiling at 320°, a temperature of 200° to 230° C. will suffice.

54. The Kessler still is shown in detail in Fig. 22 (*a*), (*b*), and (*c*). Apart from the coke fireplace *a*, the apparatus is divided into two parts, respectively, the saturator *c* and the recuperator *d*. The hot air enters the saturator at about 300° C. to 450° C. and leaves it at 150° C. The acid mist or vapor passing out of the saturator is retained in the recuperator, which acts as a dephlegmating or distilling column.

Fig. 22 (*a*) is a longitudinal section through the whole of the apparatus. A large coke fire in the furnace *a* supplies the hot air that passes through the flue *b* to the saturator *c*.

The saturator is constructed of lava (from the town of Volvic in France) with deflecting plates in such a way as to bring the hot gas into close and immediate contact with a large surface of acid, thus securing immediate reduction in temperature and saturation of the gas with the steam and acid vapors formed. The acid vapors contained in the gases leaving the saturator are recovered in the recuperator *d*.

The recuperator *d*, shown enlarged in Fig. 22 (*c*), is a dephlegmating column, also constructed of Volvic lava. It is supplied with weak acid. In the recuperator the gas leaving the saturator at 150° C. is reduced in temperature to 85° C., at which temperature all the acid vapor contained in the gas is condensed, while the steam or water vapor passes out of the apparatus at *e*. The concentrated acid passes from the apparatus at *f* into the cooler *g*.

The solutions can be concentrated to 98-per-cent. H_2SO_4 and Glover tower acid can be used. The fuel used to concentrate 100 parts of 95-per-cent. H_2SO_4 from 54° Baumé or 68.25-per-cent. H_2SO_4 is stated to be 8 parts of small gas coke for the hot-air producer and 3 or 4 parts of coal for power for the exhauster. No weak acid is made, and the product is clear and free from nitrogen compounds; no cooling water is required; the apparatus takes up little room and requires little repair.

55. Concentration and Distillation, Starting With the Glover Tower.—It has already been stated that the heat produced in the desulphurizing furnaces is sufficient, if properly conserved, to concentrate the whole of the acid made in any chamber plant to 66° Baumé.

This can be done in the Glover tower if the tower is constructed so as to stand the action of the hot, concentrated acid. There are, however, two drawbacks to this plan. The first is the impure condition of the concentrated acid, which thus contains most of the impurities of the burner gas, rendering it fit commercially for only a few purposes, and the second drawback is the danger of the Glover tower under these conditions not performing its denitrating function properly. The latter objection can be overcome in several ways. Two towers can be placed one above the other, the burner gas passing from the lower to the upper tower. The upper tower denitrates the nitrous vitriol and supplies a stream of hot acid from 58° to 60° Baumé to the lower tower, the function of the lower tower being simply one of concentration. If two chamber systems are near to each other, as is often the case in a chemical plant, then the Glover tower of one system may be employed as a denitrator and the Glover tower of the other as a concentrator; the burner gas from the two towers, the one intensely nitrous and the other not nitrous, being thoroughly mixed with a fan and passed on and distributed by the fan to the two-chamber systems. In this case all the nitrous vitriol is run down the ore tower and denitrated, the resulting denitrated acid of 60° to 62° Baumé being concentrated to 66° Baumé in the concentrating tower.

The drawback of impurity, however, still remains, and except when an unusually pure metallic sulphide is used as raw material, the acid is only fit for limited use.

56. A modification of this plan, however, has now been in use at several works for some years, producing a very pure acid at a very low cost. This consists in denitrating and concentrating the acid in a suitably constructed Glover tower until it has a density of 64.5° Baumé, at which point, it will be remembered, hot acid attacks iron but little.

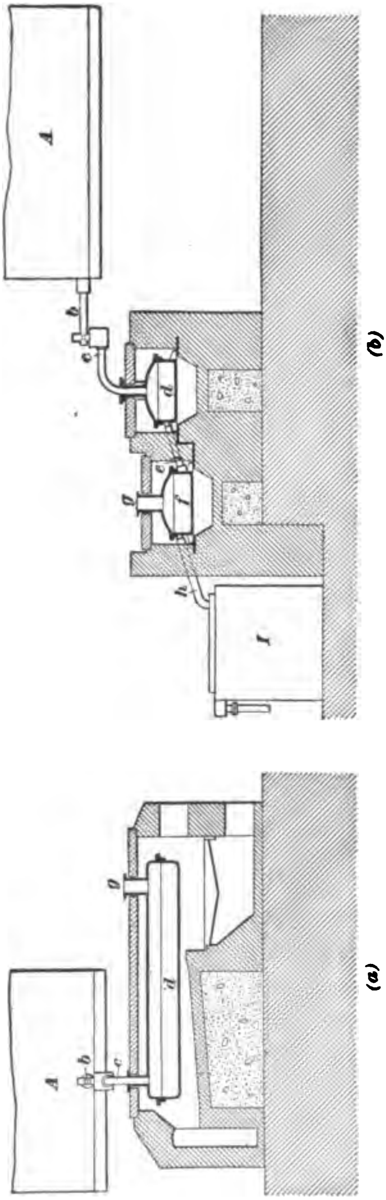
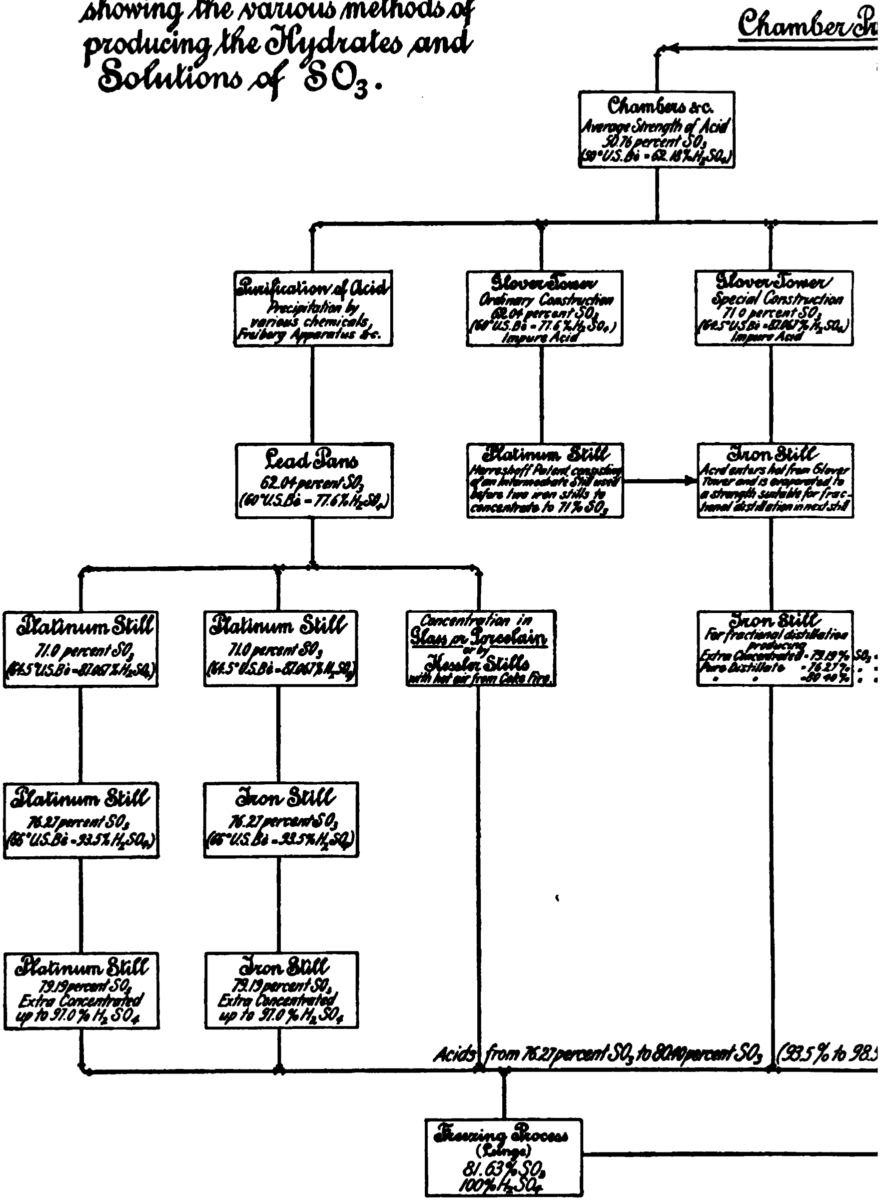


FIG. 23.

This acid, with the full heat imparted to it by the Glover tower (170° to 200° C.), is run from the tower directly into a large cast-iron still (about 8 feet × 2 feet × 6 inches). This still has a cast-iron cover and is so set in the brickwork of the fire that the fire gas plays all around it. In this still it is rapidly concentrated to about 95-per-cent. H_2SO_4 or some degree of strength higher than 93.5-per-cent. H_2SO_4 (66° Baumé). The 95-per-cent. H_2SO_4 acid is then run into a connecting iron still, also completely surrounded with the fire gases. In this still it is further concentrated to a very impure 98-per-cent. H_2SO_4. As nearly all the 98-per-cent. H_2SO_4 acid made in this country is made for the manufacturers of nitroglycerin, who do not call for a pure acid, and as after being mixed with nitric acid to make the so-called *mixed acid*, in which form it is sold to manufacturers of nitroglycerin, it is usually filtered to remove

Diagram showing the various methods of producing the Hydrates and Solutions of SO_3.



FIG

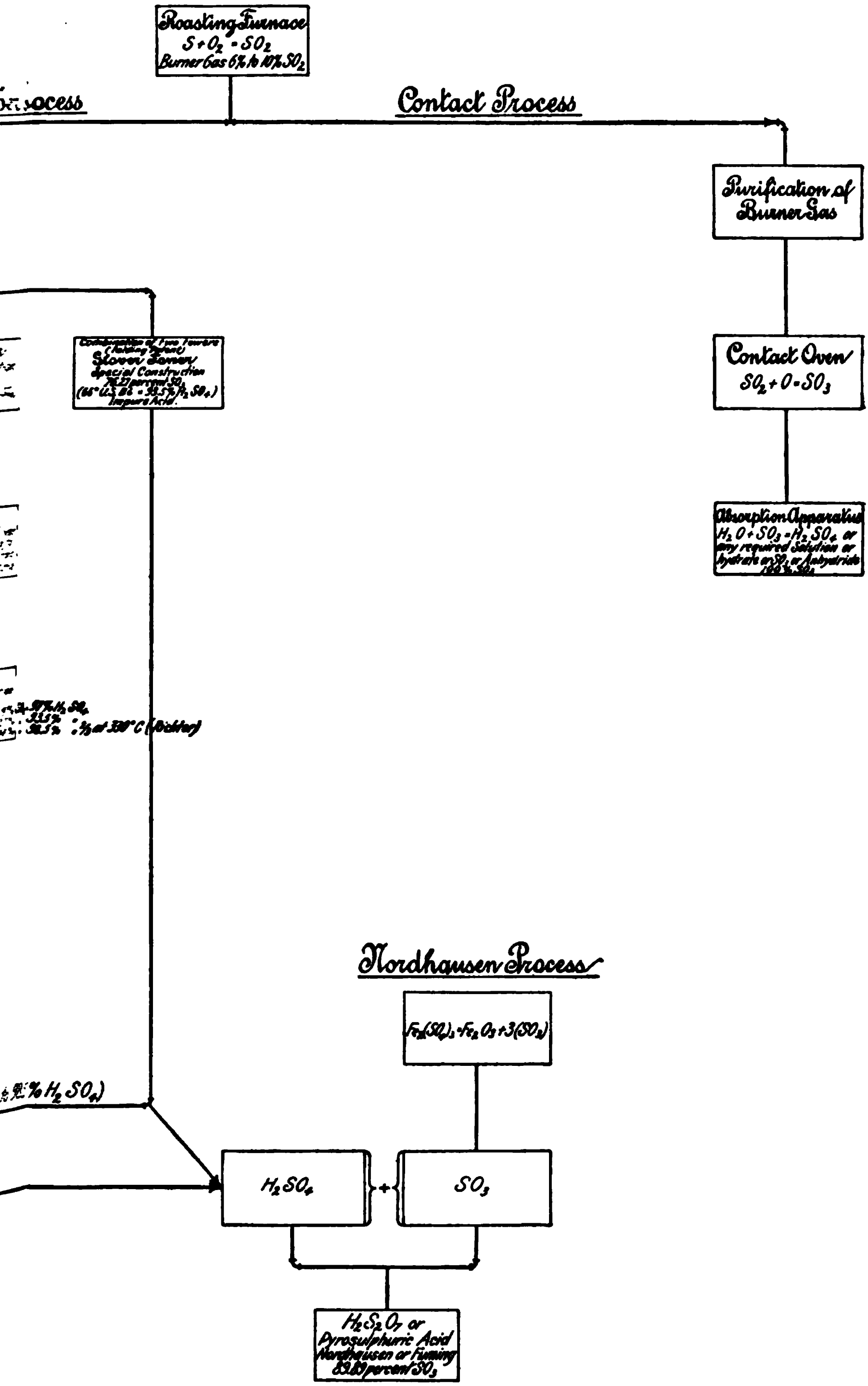

Roasting Furnace
$S+O_2=SO_2$
Burner Gas 6% to 10% SO_2
…rocess
Contact Process
Purification of Burner Gas
Contact Oven
$SO_2+O=SO_3$
Absorption Apparatus
$H_2O+SO_3=H_2SO_4$ or any required Solution or hydrate or SO_3 or Anhydride 100% SO_3
Combination of two towers (Glover Tower)
Glover Tower
Special Construction
76.27 percent SO_3
(66° U.S. Bé = 93.5% H_2SO_4)
Impure Acid
97% H_2SO_4
33.5%
93.5%
at 330° C (Bichler)
% H_2SO_4)
Nordhausen Process
$Fe_2(SO_4)_3=Fe_2O_3+3(SO_3)$
H_2SO_4
+
SO_3
$H_2S_2O_7$ or Pyrosulphuric Acid Nordhausen or Fuming 83.83 percent SO_3

FIG. 24

solid impurities, the impure condition of this acid is of little moment. The important fact is that the distillates produced by these two stills, respectively, are pure distillates of 60° Baumé and 66° Baumé, both of which are commercial solutions largely used in the arts in this country. Furthermore, as the acid runs hot from the Glover tower to the first iron still, means are taken to add very small quantities of ammonium-sulphate solution, .1 to .5 per cent. on the 66° Baumé acid produced. This not only destroys any nitrogen compounds remaining in the strong, hot acid, but also converts the volatile arsenious acid into non-volatile arsenic acid, which therefore either remains in the stills or the 98-per-cent. concentrate and does not pass over with the distillate of 66° Baumé and 60° Baumé acid.

The apparatus employed in this method of concentration is shown in Fig. 23 (*a*) and (*b*). The Glover tower *A*, Fig. 23 (*b*), is connected by the platinum pipe, or nozzle *b*, and the platinum box and tube *c* with the first iron still *d*. In this still the acid is concentrated to a strength higher than 93.5-per-cent. H_2SO_4, generally to about 95-per-cent. H_2SO_4. The distillate from this still will average about 60° Baumé.

The acid from the first still *d* flows to the second still *f* through the pipe *e*. In this still the acid is concentrated to 97.5-per-cent. H_2SO_4. The distillate passing out at *g* averages about 66° Baumé. The concentrated acid finds an outlet through the pipe *h* into the cooler *I*. A longitudinal section of one of the stills is shown in Fig. 23 (*a*).

57. Lunge Freezing Process for the Production of Sulphuric Monohydrate.—The solution employed should contain at least 97-per-cent. H_2SO_4, and in order to obtain a good yield of monohydrate should be stronger. The solution is first cooled and then charged into the iron cells of an ordinary ice plant. When the solution in the cells is properly frozen, the cells are dipped in warm water to detach the frozen solution from the sides of the cells. The frozen mass is then crushed and passed to a cast-iron centrifugal separator, in which the crystallized mass of monohydrate is separated from a solution of about 94-per-cent. H_2SO_4. The pure crystal monohydrate is then melted in a water-jacketed enameled pan and run into carboys or other packages.

58. By the above methods is produced the strongest acid which it is possible to produce by the chamber process. For obtaining the monohydrate or stronger solutions of SO_3, we have already seen that the old Nordhausen process has been replaced by the contact process.

59. The diagram, Fig. 24, shows the various methods of manufacturing and concentrating sulphuric acid, and also the relations of the several processes of manufacture.

A very useful function of the contact process is as an adjunct to an existing chamber process, where it can be used for strengthening the solutions of sulphur trioxide produced in the lead pans or the Glover tower, thus replacing the concentrating plant or enabling a stronger acid to be produced than is possible by concentration, and at the same time increasing the capacity of the plant.

ALKALIES AND HYDROCHLORIC ACID

(PART 1)

CHEMICAL METHODS

SODIUM CHLORIDE

OCCURRENCE OF SALT

1. Sodium chloride, or common salt, as the raw material from which practically all the compounds of sodium as well as hydrochloric acid, chlorine, and bleaching powder are more or less directly made, easily stands foremost in its importance to the human race among the substances occurring in nature. Fortunately, salt occurs in large quantities in the ocean, it issues from the earth in many places as brine from salt springs, and, most important of all, it occurs in large solid beds in nearly all countries.

SALT FROM SEA-WATER

2. The average amount of solid material in the Atlantic Ocean is about 34 grams per liter, of which a little more than three-fourths is salt, while the remainder consists of chlorides, bromides, iodides, and sulphates of potassium, magnesium, and calcium. The Pacific Ocean contains about the same amount of solids of approximately the same composition, while the waters of the various inland seas range from comparatively dilute to saturated solutions. Table I gives the composition of the more important large bodies of salt water.

TABLE I

COMPOSITION OF THE LARGE SALT-WATER BODIES

	Atlantic Ocean Per Cent.	Pacific Ocean Per Cent.	Mediterranean Sea Per Cent.
Solid salts . . .	3.63	3.50	3.37
H_2O	96.37	96.50	96.63
SOLID CONTENTS:			
$NaCl$	77.03	73.96	77.07
KCl	3.89		2.48
$CaCl_2$			
$MgCl_2$	7.86	13.19	8.76
$NaBr$ $MgBr_2$ . . .	1.30	1.01	.49
$CaSO_4$	4.63		
$MgSO_4$	5.29	4.63	2.76
K_2SO_4		3.18	8.34
$CaCO_3$ $MgCO_3$ . . .		3.85	.10

Salt is obtained from sea-water either by evaporating the water by means of the heat of the sun or by freezing out the water; it would not pay to use fuel for evaporating such a dilute solution. For this purpose, a low, level shore is selected, and a series of basins are formed and lined with beaten clay, which prevents the water from soaking away. The brine is kept circulating from one of these basins to the next until the sun's heat and hot winds have concentrated it to the crystallization point, when it is allowed to stand until about 50 per cent. of the salt has crystallized out. The remainder of the brine, which contains so much magnesium salts that they would separate out with the salt, is called *bittern*. This is run into another vat for the separation of the potassium and magnesium salts, or it is run back into the ocean. In the United States, large quantities of salt are produced by this method at Great Salt Lake, Utah, and at a few places in California. In Europe, the principal production is in Southern France and Italy; in Siberia, considerable salt is obtained by freezing the water instead of evaporating it.

ROCK SALT

3. The most important source of salt is the large, solid deposits that have been left by the partial or complete drying up of inland seas at some prehistoric period. The same process is going on today at the Dead Sea, the Great Salt Lake, and other places. In the course of time, these deposits have become covered with a layer of earth varying from a few feet to several hundred feet in depth. When this layer of earth is not too thick, the salt can be most economically obtained by sinking shafts and mining. The most important and extensive salt mines in the world are at Stassfurt, Germany. These mines produce not only large quantities of pure salt, but also the greater part of the world's supply of potassium salts. The Louisiana rock salt is very pure. Excellent salt is now mined in that state and also in New York and Pennsylvania. The salt from these places is used largely for manufacturing purposes, being crushed and screened to the several sizes required.

SALT FROM BRINE

4. Brines may be divided into two classes: *natural brines*, which flow from springs or wells from a natural reservoir, and may be quite dilute; and *artificial brines*, which are made by running water into a rock-salt deposit. These may always be made saturated if desired. In the United States, the processes used for evaporating brines are the following, being named in the order of the number of plants using the system: *grainers*, *solar evaporation*, *open pan*, *vacuum pan*, and *kettle*.

5. Solar Evaporation.—The **solar-evaporation method** depends on the direct heat of the sun. The brine as it is pumped from the wells first goes to a settling tank, where the iron, which is usually present in the form of acid ferrous carbonate, is precipitated as ferric hydroxide by the escape of the carbon dioxide and the oxidizing action of the air. Other sedimentary material also separates out at the same time. The brine is then run into shallow wooden vats, usually from 18 to 20 feet wide, from 100 to 400 feet long, and about 8 inches deep, where it is allowed to stand until salt crystals begin to separate out, by which time most of the calcium sulphate has deposited. Finally, the concentrated brine goes to the salt pans, which are similar to the vats just mentioned, but not quite so deep. Here the salt separates as crystals, and the brine is renewed from time to time until a salt layer about 3 inches thick is formed. The residue of the brine, which contains most of the chlorides of calcium and magnesium, is then run to waste, and the salt is "harvested" by scraping it together and putting it into tubs having perforated bottoms, where it is allowed to drain thoroughly.

The vats are built on piles and are arranged so that the brine, after being pumped into the settling tank, can run to the other vats by gravity. In countries where very little rain falls, especially during certain seasons of the year, as in California, and various tropical or semitropical countries, the vats can stand uncovered continuously. In the eastern part of the United States, however, where rains occur frequently, it is necessary to provide the vats with movable covers that can be rolled back during fair weather. The salt obtained by this process is in large, bulky, cubical crystals that occlude considerable quantities of mother liquor, and on account of the deliquescent calcium and magnesium chlorides thus mixed with the salt, it becomes moist in damp weather.

6. Kettle Evaporation.—In the **kettle process,** the brine is evaporated in cast-iron kettles that are about 4 feet in diameter by 2 feet deep and are heated either by direct fire or by a steam jacket. When necessary, for the removal of the iron, the brine is mixed with a little milk of lime and allowed to settle; it is then run into kettles and evaporated. The calcium sulphate, which separates out first, is removed from time to time until the salt begins to crystallize. The salt is removed from the kettle at intervals, drained into baskets, and then dumped into bins so as to dry thoroughly.

When heated by direct fire, the kettles are arranged in rows of from sixteen to twenty-five over the flues; and as those at the front end are the hottest, the brine evaporates most rapidly at that point, giving the finest crystals, while the kettles at the back end produce crystals more like the solar salt. With steam-jacketed kettles, the product is much more uniform.

7. Open-Pan Process.—The **open-pan process** is probably the oldest of all methods that use artificial heat, for the Romans at the time of their occupation of England used practically the same arrangement as the present, except that their pans were of lead and only about 6 feet square. The pans *a*, Fig. 1, now used are made of iron and are from 70 to 150 feet long, from 20 to 25 feet wide, and from 12 to 18 inches deep. They are heated by direct fire. The grates, of which there are three or four for each pan, with the doors *b* for charging, are situated at the front end of the pan and are connected to a chimney, which is placed at the rear end of each pan, by flues that lead under the pan. The brine, after having been purified by milk of lime and settled, is led into the back part of the pan, where it becomes slowly heated and concentrated so that it deposits its calcium sulphate as it slowly flows toward the front and hotter portion of the pan, where the greater part of the salt is deposited. At intervals the salt is scraped together and on to draining boards *c* by means of long-handled wooden hoes. The workmen pass between the pans on wooden walks *d*. The roof covering the pans and furnace is cut out at the peak in order to allow steam to escape, but it is covered with a cap to keep out rain.

8. **Grainers.**—An important modification of the pan process is the so-called **grainer.** The pans are made of either iron or wood and have the same general dimensions as those in the pan process, except that they are somewhat deeper. The evaporation is caused by steam circulating through pipes that are raised about 6 inches above the bottom of the pan and are kept constantly covered with brine; in other respects, the operation is practically the same as in the pan process.

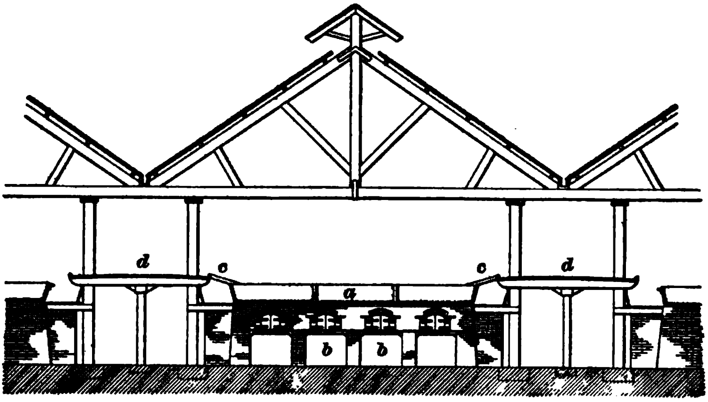


FIG. 1

9. **Vacuum-Pan Process.**—The **vacuum-pan process** leads to a very fine grade of salt, and on this account is used in several places. Since salt is about equally soluble in either hot or cold water, it is not possible to concentrate the solution in the pan and then run the solution outside to crystallize, as is done in many other cases; also, if the vacuum pan is used for anything more than bringing the brine to its saturation point, the salt must be allowed to deposit in the pan. This can, of course, be accomplished by using a simple pan that is covered over and partly exhausted, but it is then necessary to open the pan from time to time to remove the

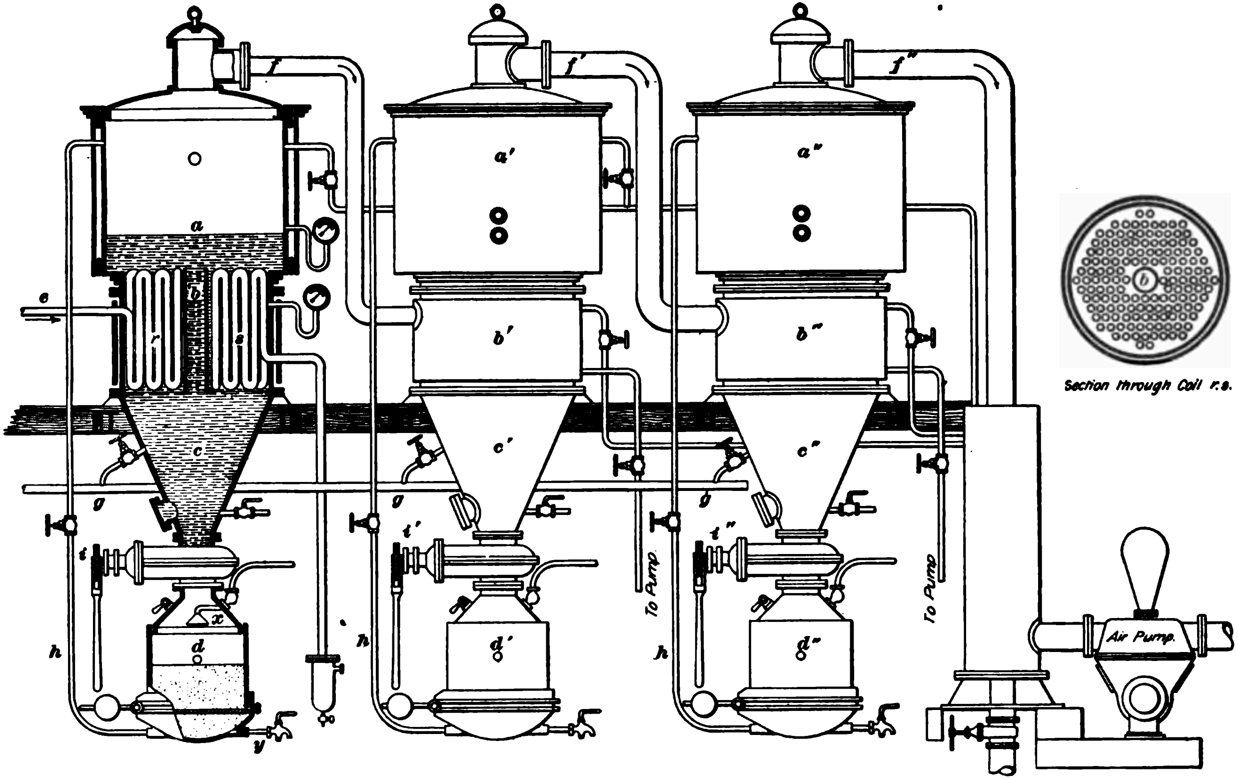

a
b
c
d
e
f
g
h
i
r
s
x
y
a′
b′
c′
d′
f′
g
h
i′
To Pump
a″
b″
c″
d″
f″
g
h
i″
To Pump
Air Pump
b
Section through Coil r.s.

FIG. 2

salt, which is an obvious disadvantage. To do away with this difficulty, several continuous-acting vacuum pans have been proposed, the best of which is **Pick's triple-effect evaporator,** which is shown in Fig. 2.

In this apparatus is followed the principle of keeping each element under less pressure than in the preceding one, and evaporating its contents by means of steam taken from the preceding element. The brine enters at *g*, and at *r s* is a vertical coil of pipes, which, in the first element, is supplied with steam through *e* and is sufficiently long to condense the steam so that it flows as water from the opposite end *s*. The heat from the steam coil evaporates the brine *a c*, and the steam passes through the pipe *f* into a similar vertical coil at b', where it condenses and boils the brine in $a' c'$, which stands under less pressure than that in *a c*; the steam from $a' c'$, in turn, evaporates the brine in $a'' c''$, which is under still lower pressure. The salt as it separates collects in the funnels c, c', c'', and can be brought into the filter chambers d, d', d'' when desired by turning the valves at i, i', i''. Each filter chamber has a filter in the bottom portion, from which a pipe *h* returns to the upper part of the element, so that the mother liquor may be returned if desired. The salt may then be washed by means of the rose *x*, and the wash water run off by the tap *y*. The salt can be withdrawn through an opening in the side of the filter chamber.

10. Frequently, in preparing fine table salt, the brine is first mixed with sodium carbonate to precipitate, so far as possible, the calcium as carbonate, and then with a little soap, or some similar substance, to remove the remainder of the calcium and magnesium as the insoluble soaps of these elements.

SODIUM CARBONATE

NATURAL AND ARTIFICIAL SODA

11. Natural Occurrence.—**Sodium carbonate** occurs in nature widely distributed. It is seldom found, however, as the normal carbonate, but as a partial decomposition product of sodium bicarbonate of the composition $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, commonly known as *Trona* or *Urao.* It has long been known in Egypt, where it is called *Wadi Atrium*, or *Natrium;* in Hungary it is called *Szekso.* Sodium carbonate is also found in Russia and other countries. Very large deposits are found in many parts of the United States, especially in Wyoming and California.

In Wyoming are found lakes that contain over 2 pounds of crystallized sodium carbonate per gallon of water and only a small amount of sodium chloride. Coal is mined within 15 miles of these lakes, so that it is estimated that from 98 to 99 per cent. of pure sodium carbonate can be made for one dollar a ton. A company has been incorporated to undertake its manufacture. Sodium carbonate is also obtained from springs located at Soda Springs in the same state. The waters of these springs carry about the same quantity of sodium carbonate, and the product supplies the local demand and part of that of California, but the total tonnage available is not large.

Probably the largest deposits of natural sodium carbonate in the world occurs in California. Mono Lake in that state has an area of 65 square miles and is estimated to contain 75,000,000 tons of sodium carbonate and 18,000,000 tons of sodium bicarbonate. This lake is situated high in the mountains, however, where fuel is scarce and solar evaporation is out of the question; besides, the difficulty of removing the finished product makes the working of this deposit impossible, for the present at any rate. Owens Lake, however, which has an area of about 110 square miles, contains a sodium-carbonate deposit of from 40,000,000 to 50,000,000 tons, and is constantly being added to at the rate of about 200,000 tons each year. The soda is here obtained by solar evaporation, and large quantities are produced.

A third large deposit, which has recently been discovered in Mexico, is located about 2½ miles from Adair Bay on the Gulf of California. This deposit covers an area of about 60 acres to a depth of from 1 to 3 feet, and is only covered by about 3 inches of sandy silt. The average sample of the dry soda showed 76 per cent. of sodium carbonate, 5 per cent. of sodium sulphate, 1 per cent. of sodium chloride, and about 18 per cent. of soluble matter.

The source of natural soda is probably feldspar rocks that are decomposed by atmospheric conditions. The sodium carbonate formed is washed by rains into lakes, and, lacking outlets, their waters become supersaturated. Probably some sodium carbonate is also made by transforming sodium chloride to sodium sulphate by calcium or magnesium sulphate, then reducing the sodium sulphate to sodium sulphide by certain algæ, and converting the sulphide into the carbonate by the action of carbon dioxide.

Notwithstanding these large natural deposits of sodium carbonate, they are the sources of very little of the soda of commerce. Owing to the cost of solution, evaporation, purification, and transportation, the product, except at points of consumption near the deposits, can be manufactured much more cheaply from salt by processes about to be described.

12. Until near the end of the 18th century, practically all the world's supply of soda was obtained from these natural deposits and from the ashes of certain plants that grow in or near the sea, most of it, however, coming from the latter source. For this reason, the potassium carbonate found in the ashes of land plants was much the cheaper and more commonly used alkali at that time. The plant soda was made in Spain, where it is called *barilla;* in France it is called *varil*, or *blanquette*.

13. Artificial Soda.—The artificial preparation of sodium carbonate, frequently called *soda ash*, dates back to the latter part of the 18th century and has now become one of the largest of the chemical industries. While many processes for the manufacture of soda have been proposed, the only ones in use on a large scale at present are *Le Blanc's process*, the *cryolite-soda process*, the *ammonia-soda*, or *Solvay*, *process*, and the *electrolytic process*. These processes are named in the historical order in which they became important, but they will be treated in the order of their present importance in the production of soda ash in America.

THE SOLVAY PROCESS

14. Historical.—The fact that when solutions of sodium chloride and ammonium bicarbonate are mixed, a part of the sodium separates out as sodium bicarbonate, was probably known in the early part of the 19th century. Not until 1838, however, was it recognized as a possible method for the manufacture of sodium carbonate. In that year, H. G. Dyar and J. Hemming took out an English patent for making sodium carbonate by means of the reaction

$$NaCl + HNH_4CO_3 = NaHCO_3 + NH_4Cl$$

and then heating the sodium bicarbonate to drive off the carbon dioxide and water, leaving sodium carbonate. This patent covered the chemistry of the process practically as it is worked at the present time, and also many of the mechanical principles. At that time, however, the cost of ammonia was so great that they did not succeed in keeping the loss low enough to make the process profitable. About 1855, Schloesing and Rolland patented in England some improvements on the preceding process, and at a factory in France actually manufactured about 25 tons of soda a month for nearly 2 years. They did not succeed in recovering the ammonia sufficiently well, however, and abandoned the method. Various other inventors worked on the process between 1838 and 1863, and fortunes in time and money were spent to no avail. In the latter year, Ernest Solvay, a Belgian, took up the process without knowing much about the other work that had been done on it. He worked on the process until 1873 before the mechanical difficulties were overcome and the method became an assured success. From 1873 until the present time, the process has been constantly growing in importance and strength, so that now more than half the world's supply of soda is made by this method.

15. **Outline of the Process.**—In brief, the **Solvay process** consists in preparing carbon dioxide from limestone, passing this gas into an ammonium-hydrate solution to form ammonium bicarbonate, mixing salt solution with the ammonium bicarbonate, and getting sodium bicarbonate, which precipitates, and ammonium chloride, which remains in solution. The sodium bicarbonate is then calcined to form soda ash. and the carbon dioxide, after being cooled, is let back into the process. The ammonium chloride is decomposed by milk of lime, the ammonia is set free so that it may be used over again, and the chlorine goes to form calcium chloride, which is mostly run to waste. The reactions are then

$$\begin{aligned} CaCo_3 &= CaO + CO_2 \\ NH_4OH + CO_2 &= HNH_4CO_3 \\ NaCl + HNH_4CO_3 &= HNaCO_3 + NH_4Cl \\ 2HNaCO_3 &= H_2O + CO_2 + Na_2CO_3 \\ CaO + H_2O &= Ca(OH)_2 \\ Ca(OH)_2 + 2NH_4Cl &= 2NH_3 + CaCl_2 + 2H_2O \end{aligned}$$

These reactions, however, do not take place in quite so many steps, for the sodium-chloride and ammonium-hydroxide solutions are first mixed and the carbon dioxide then run in. The reaction between the sodium chloride and ammonium bicarbonate is a reversible one, so that if sodium bicarbonate is used to start with and ammonium chloride is added to it, a certain amount of sodium chloride and ammonium bicarbonate will be formed. The reaction, therefore, can never be complete. It will be driven farther in the desired direction the more of an excess of salt there is present, and since salt is cheap, the customary method is to allow an excess of salt over the amount necessary to react with the ammonium bicarbonate. The latter substance is thus more completely used. Formerly, it was very common to employ solid salt, but this practice is now quite generally given up and an excess of saturated brine is used. It should also be remembered that sodium bicarbonate is much less soluble in brine or a solution of ammonium chloride than in water alone.

RAW MATERIALS

16. Limestone.—The nearer pure calcium carbonate the limestone is naturally, the better it is, although the impurities in this case are not so serious an objection as in the Le Blanc soda process. A percentage of silica, iron, or alumina that is too high is objectionable, as it causes the limestone to clinker if the heat is sufficient to burn the limestone rapidly. When the lime clinkers, that is, *dead burns*, it is almost impossible to slake it, and the lime is worthless. A high percentage of magnesium carbonate is also undesirable in a limestone, as it lowers the efficiency of the quicklime, for the magnesium oxide cannot be used with advantage to liberate ammonia from its salts nor to make caustic soda. The limestone from different parts of the same quarry varies considerably, as is shown in Table II, which gives the average analyses of the limestone used by one of the large United States ammonia-soda works for three consecutive months.

TABLE II

ANALYSES OF LIMESTONE

Constituents	October Per Cent.	November Per Cent.	December Per Cent.
SiO_2 (insol. in HCL)	2.95	5.60	3.95
Al_2O_3 and Fe_2O_3 . .	.80	.90	.30
$CaCO_3$	94.20	83.26	88.39
$MgCO_3$	2.36	10.41	7.75
Total	100.31	100.17	100.39

Although a hard, compact limestone requires a little more time for burning, it is the most suitable, as it gives a quicklime that is easier to slake thoroughly, and the slaked lime is usually of better quality.

17. Brine.—The salt used in the Solvay process is in solution, and the solution may be made from solid salt at the works. Usually, however, the soda works are so situated that either natural brine or artificial brine—made by dissolving the rock salt from its bed—can be used. A brine that is as pure as possible is desirable; however, the ordinary brine used generally contains more or less calcium and magnesia salts, and sometimes iron compounds are also present. The magnesium salts are the most injurious, for they are not precipitated so rapidly by the ammonium carbonate in the purification process (see Art. 24), and the magnesium carbonate separates out later when vat liquor is being cooled and is liable then to clog the conducting pipes. A sample of the Tully brine used by the Solvay Process Company, at Syracuse, New York, in 1892, gave the following analysis:

CONSTITUENTS	GRAMS PER LITER
Sediment	.020
$CaSO_4$	4.306
$CaCl_2$	2.718
$MgCl_2$	.250
Total impurities	7.294

This same brine contained at that time 292.88 grams of sodium chloride per liter. This is a good brine, although it is somewhat low in salt.

18. Ammonia.—Although the ammonia is used over and over in the preparation of ammonia soda, there is, nevertheless, always more or less loss that must be made up by adding more from the outside. The usual sources of ammonia are the coal-gas works and, at the present time, the by-product coke ovens. This ammonia comes to the works in the form of concentrated gas liquor, which is a solution of a mixture of ammonia salts, principally carbonate and acid carbonate. A good gas liquor should contain at least 15 per cent. of ammonia.

If the concentrated gas liquor is not available, sulphate of ammonium purchased on a basis of 25 per cent. of ammonia may be used when distilled with lime; but as a rule it is too expensive as a source of NH_3. The sulphate derived from ammonia by the destructive distillation of bones is not desirable for this purpose, owing to its strong and disagreeable odor.

19. Coal and Coke.—Coal is used entirely for heating the boilers, and any grade of coal that is suitable for firing can be used. Coke is used mostly in the lime kiln, and should be good oven coke that is as free from sulphur as possible; for with high sulphur, sulphur dioxide is liable to get into the gas, and at any rate it will yield a lime high in sulphates. Such lime if used for making caustic soda, will cause the formation of large quantities of sodium sulphate in the caustic liquor, which necessarily means a loss of soda as well as the necessity of fishing this salt from the caustic as it is boiled down.

DETAILS OF THE SOLVAY PROCESS

20. Carbon Dioxide and Lime.—Since lime is required for the recovery of the ammonia and carbon dioxide is necessary for the preparation of the bicarbonate, both are best made at the works from limestone. The gas must be at least 30 per cent. carbon dioxide, and, since the ash of the fuel does not especially interfere with the use of the lime, the coke, which is the fuel used for burning the lime, is charged in layers with the limestone.

The most suitable form of lime kiln to use is shown in Fig. 3. This kiln consists of a shaft from 24 to 40 feet high that tapers both ways to two-thirds the distance from the top. The outer shell of iron is lined with firebrick. In the larger furnaces, two rows of brick are used. The whole kiln is supported by iron pillars *e* that rest on iron bases set in brickwork. The top of the kiln is provided with a cover *a* that can be raised to charge the kiln and then lowered so as to rest in a lute of sand or water in *b*. At *d* is shown one of several 3-inch holes that are ordinarily kept closed with plugs, but which may be opened to serve as peepholes to observe the state of the kiln, to admit more air if necessary, and sometimes to break down the charge. At *f* the kiln is provided with grate bars that hold the lime in place until it should be removed, when a car is run under on the track *g*, and then, by turning the bars, the lime is emptied into the car. A platform is placed at *h* for the convenience of the workmen using the peepholes *d*, and another platform is located at *c* for charging purposes. All the limestone and coke are elevated to the platform *c*, from which point these materials are conveyed to the different kilns by means of cars running on the track *i* and charged in alternate layers. A pipe for carrying away the gas is located about 4 feet below the top of the kiln, as shown, the escaping gas being quite cool at this point, say not over 300° C. As has been previously stated, the limestone and coke are charged in alternate layers; the relative amounts of limestone and coke that should be charged vary at each place, depending on the composition of these materials. The considerations that follow will help in deciding the relative amounts of limestone and coke.

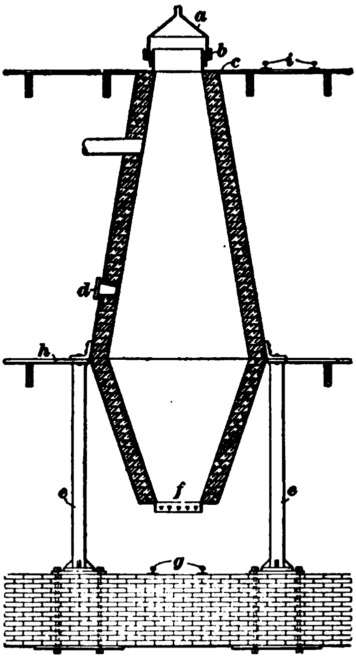


FIG. 3

21. The best temperature for burning limestone is about 850° C., but if, owing to impurities in the limestone or to too high ash in the coke, the limestone tends to fuse at this temperature, a lower one must be employed and a longer time spent in the burning. Damp limestone burns not only at a lower temperature than dry limestone, but it burns better, for the moisture aids the dissociation of the limestone into carbon dioxide and calcium oxide.

Theoretically considered, 1 kilogram of pure calcium carbonate requires 373.5 calories of heat for its decomposition, and in burning carbon to carbon dioxide, 1 kilogram of carbon yields 8,080 calories of heat. Therefore, 1,000 kilograms of calcium carbonate should be burned by about 46 kilograms of pure carbon. Considering that the escaping gases carry away heat from 1,000 kilograms of calcium carbonate, 440 kilograms of carbon dioxide remains. Furthermore, the 46 kilograms of carbon will give 169 kilograms of carbon dioxide, making in all 609 kilograms of carbon dioxide. Carbon has a specific heat of .22 calory, and if it escapes at 300° C., it will carry with it $609 \times 300 \times .22 = 40{,}194$ calories of heat. Then, in order to burn the carbon, air that is four-fifths nitrogen is used, so that the air necessary to burn 46 kilograms of carbon contains $490\frac{2}{3}$ kilograms of nitrogen. This has a specific heat of .244, and therefore will carry with it $490\frac{2}{3} \times 300 \times .244 = 35{,}917$ calories. Thus, the escaping gases will take a total of 76,011 calories of heat, which must be supplied by burning more carbon. This will require about 9.4 kilograms more of carbon, which in turn will furnish gas to convey heat, and the amount can be calculated as just shown.

It is then found that, theoretically, about 57 kilograms of carbon will burn 1,000 kilograms of calcium carbonate. However, there is still to be added the loss of heat through radiation from the sides of the kiln, from the quicklime, which is not quite cold when drawn, and also the heat required to evaporate the moisture in the limestone. Taking all of these factors into consideration, it has been found to be a pretty safe rule to allow 120 kilograms of pure carbon for every 1,000 kilograms of calcium carbonate. Then, if the limestone is 90 per cent. calcium carbonate, it will require 1,000 ÷ .90 = 1,111.1 kilograms of limestone to give 1,000 kilograms of calcium carbonate; and if the coke is only 95 per cent. carbon, it will require 126.3 kilograms of coke.

22. Having thus decided on the charge, the foreman must watch the results to learn if it is right. He must regulate the air supply, so as not to allow the temperature to get too high, or the lime will fuse, dead burn, nor to fall too low, or too much time will be required in the burning. If an insufficient amount of air is supplied, carbon monoxide will appear in the gas, and the air must be increased; on the other hand, too much air will show itself by oxygen in the gas. Ordinarily, the supply of air must be regulated to burn the coke properly and not have an excess. If the kiln tends to get too hot and thus dead burn the lime, the supply of coke should be reduced. It is often found necessary to allow part of the limestone to go unburned, in order not to dead burn the rest of the charge and at the same time to avoid carbon monoxide in the lime-kiln gas.

One of the most frequent mechanical difficulties with which the lime-kiln man must contend is *bridging;* that is, the charge tends to clog at some point in the lower part of the kiln, and the loose material underneath works out through the grate (at *f*, Fig. 3), leaving in the kiln an arch that prevents the remainder of the charge from feeding down. When this is observed, it must be remedied at once by breaking down the arch with iron rods. If the bridge is very low in the kiln, the rods can be inserted from below; otherwise, they must be used through the peepholes.

23. The carbon dioxide from the limestone and coke mixed with the nitrogen of the air used to burn the coke is removed from the kiln through the pipe previously mentioned. This waste contains, as especially undesirable impurities, sulphur dioxide from the sulphur in the coke and considerable dust. These are removed as far as possible by thoroughly washing the gas before sending it to the carbonating tower. The scrubber used for this purpose is shown in Fig. 4. The gas from the kilns enters the scrubber through the pipe *a*, which, inside of the apparatus, is perforated its entire length so that the gas will be uniformly distributed. The gas rises through the spray of falling water to the first plate *c*, where it must bubble through a column of water, then again through the spray to the second plate *c*, and so on until it passes out through *e*, to the carbonating tower. Meanwhile water is admitted through the pipe *b* in such quantity that it stands at a suitable height on each plate. Each plate *c* has a tube *f* leading to the next lower one, so that if the water enters too fast or the holes in *c* become stopped, the water can overflow through this tube. If necessary, the gas can also ascend by this tube to the next section of the washer. Finally, the wash water collects in the bottom of the washer and siphons off through pipe *d*.

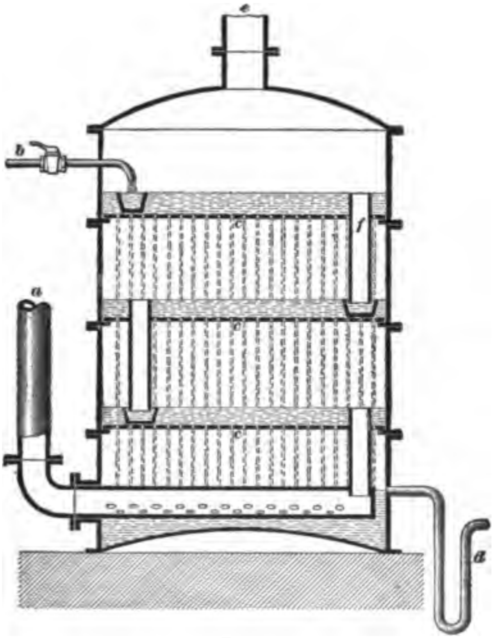


FIG. 4

The supply of carbon dioxide is often supplemented by the flue gases that arise from burning anthracite coal or coke under the boilers. These gases must also be cooled or washed, as in the case of burning lime. They are, of course, much poorer in carbon dioxide than the gases from the lime.

The lime as it comes from the kiln is slaked with just enough water to cause it to crumble, after which it is thrown into a large vat fitted with revolving paddles. In this vat the lime is churned with sufficient water to bring it to a specific gravity of 1.16, when it is pumped through a screen to remove the lumps of unburned limestone, and then to the ammonia distilling apparatus (see Art. **37**).

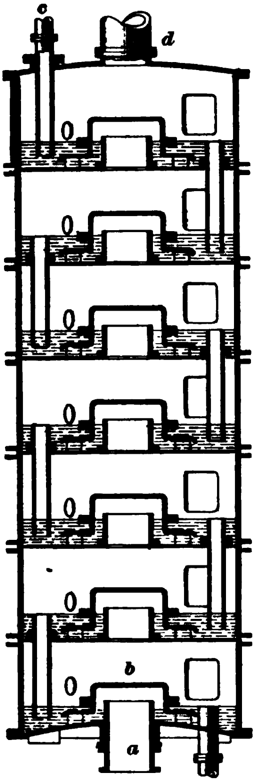


Fig. 5

24. Purification of the Brine. The brine must be freed from the calcium, magnesium, and other impurities as soon as possible after it enters the works. To do this, the brine is used to wash the gases that escape from the ammonia saturators (see Art. **25**) and from the carbonators (see Art. **26**). These waste gases contain ammonia and carbon dioxide, so that they form ammonium carbonate in the brine, and precipitate the iron as hydrate and the calcium and magnesium as carbonates.

For washing the gases, coke towers similar to those used in condensing hydrochloric acid are sometimes used. A more suitable style of washer, and one in much more common use, is shown in Fig. 5. In this apparatus, the brine enters at *c* and slowly overflows through corresponding pipes until it finally passes out at the bottom. Meanwhile,

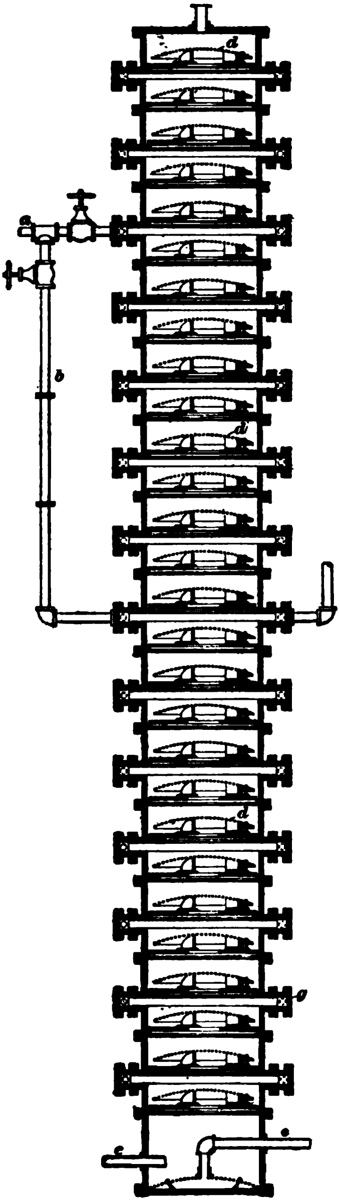


FIG. 6

the gases from the saturator and the carbonator enter at *a* under the cap *b*, which causes the gas to spread out and pass through the brine before going to the next section. The gas finally passes out at *d*.

25. Ammoniacal Brine. By washing the waste gas, the brine receives enough ammonium carbonate to purify it, and must now be treated with ammonia. This saturation of the brine with ammonia takes place in an apparatus similar to that shown in Fig. 5, except that not so many sections are required. For saturating enough brine to make 50 tons of sodium carbonate a day, a saturator 8 feet in diameter and made up of two or three sections like the foregoing, having a depth of 15 or 18 inches of liquor in each section, is sufficient. The brine must be run through the saturator at such a rate that it will contain from 65 to 70 grams of ammonia per liter when it leaves the tower. The ammonia and ammonium carbonate have now thrown out the calcium, magnesium, and iron, and this precipitate remains suspended in the liquid, which is run into the cooling and settling tanks. The settling tanks, or vats, are built with a conical bottom, so that the impurities will collect in the narrow part, from which place they may be drawn off at intervals by opening a valve in the bottom. If the brine does not settle, it must be filtered, but usually this will not be the case. In the vats, the brine is cooled to as low temperature as the available water will cool it, and should now be clear and contain 70 grams of ammonia and 270 grams of sodium chloride per liter.

26. Carbonating the Ammoniacal Brine.—From the settling tanks the ammoniacal brine goes to the carbonating towers, Fig. 6. These towers are of iron, and are from 60 to 65 feet in height and about 6 feet in diameter. They are made up of sections, each of which is about 3½ feet high and has in its interior two iron plates, one at the bottom and the other about half way up. Each plate is surmounted by a dome-shaped diaphragm *d* that is perforated with a large number of holes. Between each pair of plates are a number of pipes *g*, Fig. 7, which conduct water to regulate the temperature in the tower.

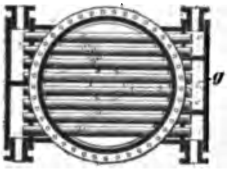


FIG. 7

27. The carbonating usually takes place in two similar towers. In the first, the ammonium hydrate is converted into ammonium carbonate, and then the brine is run to the second tower to be finished. In this way less ammonia is lost and the controlling of the temperature is easier. The temperature, in the second tower, especially, must be very carefully controlled. If the temperature is too cold, a fine, muddy precipitate of sodium bicarbonate is deposited, which is hard to filter and work with; while if it is too high, the yield of sodium bicarbonate is very much diminished. A temperature is therefore selected that gives the best mean course between the two difficulties; this temperature is between 30° and 40° C.

The ammoniacal brine, by standing in the settling tanks, becomes thoroughly cooled. The gas enters the carbonator against a pressure of 1½ to 2 atmospheres, and in being pumped against this pressure becomes heated. To make it easier to regulate the temperature in the lower part of the tower, this gas is cooled to about 28° C. before entering the carbonators. In this way, all the materials entering the towers are thoroughly cooled, and the increase in temperature in the tower is due entirely to the chemical reactions taking place there. The brine passes into the carbonating tower through the pipe *a b*, Fig. 6, which enters the tower about half way down, although a branch of this pipe is provided, which enters near the top of the tower and may be used when occasion demands. The advantage of introducing the brine at about the middle of the carbonator is that the ammonia has a chance to meet the carbon dioxide sooner and is thus converted into carbonate before the top of the tower is reached. As the ammonium carbonate is less volatile than the ammonia, less ammonia is lost from the carbonator by this method of working. The carbon-dioxide gas enters the tower through pipe *e*, which is arranged in a rose at the end, so as to distribute the gas uniformly over the bottom of the tower. This gas, rising through the ammoniacal brine, converts the ammonia and ammonium carbonate into ammonium bicarbonate, which, in turn, throws out the sodium bicarbonate in fine crystals. These, for the most part, pass to the bottom of the tower, in suspension in the liquid, and flow away through the pipe *c*.

A small amount of these crystals constantly adheres to the plates, and finally enough collect to clog the holes so much as to interfere with the free passage of the gas. For this reason, every 10 days or 2 weeks, the carbonating tower should be emptied and then cleaned by blowing in hot water and steam to dissolve these crystals. The tower must be cooled before using it again. Several towers are usually employed, so that the process does not stop, a clean tower being brought into use when it is necessary to renovate one.

Since ammonia is the most expensive substance entering into the process, an effort is constantly made to use it as completely as possible, even at a sacrifice of other materials. For this reason, only about two-thirds or three-fourths of the salt entering the carbonator is converted into sodium bicarbonate, the remainder being allowed to remain unchanged in the escaping liquid. A portion of the carbon dioxide also escapes unused, although the higher the percentage of carbon dioxide in the gas used, the better it is utilized.

A rough test to show that the carbonator is working properly is to draw a cylinder of the liquor as it runs from the tower and to allow it to stand for ½ hour. This liquor should then have a precipitate of sodium bicarbonate equal to from one-third to one-fourth its total volume. The bicarbonate should be coarse-grained, and when taken from the filters and crushed in the hand no water should run out of it.

28. Washing the Gases.—The gases that escape from the ammonia saturators contain considerable ammonia, and therefore cannot be allowed to escape directly into the open air. The gases from the carbonators consist mainly of nitrogen, carbon dioxide, and ammonia, and, of course, must also be washed. The general method of working with these gases is the same in each case, so that they can most conveniently be considered together. It has been found advantageous to keep the saturators as well as the washers under a slightly diminished pressure. Since the ammonia stills connect directly with the saturators, the effect is to give a reduced pressure in the stills; this causes the ammonia to be given off more easily and prevents leaks. Fig. 5 shows a suitable form of washer for this purpose. In order to reduce the loss of ammonia as much as possible, two of these washers are used. In the first washer, brine is used to absorb the ammonia and carbon dioxide; the brine then goes directly to the saturator. The second washer uses as a wash liquid dilute sulphuric acid, which removes the last traces of ammonia.

29. Filtration.—The liquor running away from the carbonating tower consists of sodium bicarbonate in suspension and salt, ammonium chloride, and ammonium bicarbonate in solution. The sodium bicarbonate in suspension is separated from the mother liquor by *vacuum filters* or centrifugal machines. Two forms of vacuum filters are in use; the older, the so-called *sand filter*, consists of a box about 10 or 15 feet long, 3 feet wide and about the same depth, with a perforated bottom. This bottom is covered with a layer of large pebbles, then smaller ones, and finally a coating of sand. This is covered with a cloth, and a series of slats is laid on so as to protect the filter when the bicarbonate is shoveled out. The filter is fastened tightly to a large receptacle, from which the air can be exhausted, thus producing suction and more rapid filtration. A vacuum of from one-half to two-thirds of an atmosphere is maintained. This receiver also serves to catch the mother liquor. Above each filter is suspended a water pipe that extends the whole length of the filter and is sufficiently free to swing the width of the trough. This pipe is perforated with fine holes and enables the workman to wash the precipitate easily. When one of these filters has been filled and the precipitate is washed, it is necessary to shovel out the material by hand. This operation requires a number of men.

30. For this and other reasons, another form of filter has been introduced into many of the most progressive establishments. This filter consists of a cylinder about 4 feet long and 3 feet in diameter, the sides of which are finely perforated and covered with cloth. This cylinder revolves in a large trough filled with the liquor from the carbonating tower, and as a vacuum is maintained on the inside of the cylinder, the mother liquor passes to the inside and away, while the sodium bicarbonate is held to the cloth by the outside pressure of the atmosphere. As the cylinder revolves, the portion with the precipitate comes up out of the liquor and meets a fine spray of water, which thoroughly washes it. The cylinder then passes on until it meets a scraper, which removes the precipitate from the filter and starts it on its way toward the calciner.

31. Another form of filter, which is used somewhat for the crude bicarbonate, but more especially for the purified bicarbonate, is the *centrifugal*. This filter produces a rapid and complete separation of the mother liquor from the crystals, but has the same disadvantage as the sand filter in that the crystals must be shoveled out by hand. The centrifugal filter consists of an inner shell, the sides of which are made of wire gauze or perforated metal, and an outer casing. The inner portion is free to swing about its axis; and when a liquid is brought into it, the centrifugal force throws the contents to the outside, where the solid part adheres, and the liquid passes through to the outer compartment, where it drains off.

Quite recently a form of centrifugal has been introduced that has a large opening at the bottom, through which the contents of the so-called basket of the centrifugal is discharged. This opening is kept closed when desired by means of a flange and clamp.

32. The crude bicarbonate from the filters contains considerable water, but otherwise it is remarkably pure. Its average composition is as follows:

	Per Cent.
$NaHCO_3$	70.0 to 75.0
Na_2CO_3	3.0 to 5.0
$NaCl$	.2 to .7
NH_3	.51
H_2O	20.0 to 26.0

33. Calcination.—The next step in the process is the drying of the bicarbonate and its conversion into soda ash; at the same time, the small amount of ammonia contained in the crude bicarbonate is driven off and saved. Of the large number of arrangements for calcining the bicarbonate, only the two in most general use will be described.

34. The pan form of drying and calcining apparatus is shown in Fig. 8. It consists of an iron pan *a* covered tightly by an iron cover *b*. Through the top of the cover, an iron shaft runs in a gas-tight box and bears the scrapers *c*. These scrapers are set at an angle to the bottom of the pan, so that when they revolve they scrape the bicarbonate and carbonate away and prevent it from burning fast; they also mix the charge thoroughly. The pan is heated from the outside by a fire in the grate *f*. The damp bicarbonate is charged in through the door *e*, which is then closed, and the gases escape through the pipe *d*. When the calcination is complete, the soda ash is withdrawn through the same door *e*.

35. A second form of calciner is shown in Fig. 9. This is superior to the pan form in that it requires comparatively little labor to operate it. The moist bicarbonate is charged into the hopper *a*, is fed into the conveyer *d* by the wheel *c*, and is carried forwards by the worm *e*. At the same time, a suitable amount of calcined soda ash is fed in by the worm *b* so as to keep the bicarbonate in a condition to move. The mixture is carried forwards to *f*, where it falls to *g* and then passes into the iron cylinder *h*, which is heated by the fire in the grate *i*. The flames from the grate surround the cylinder

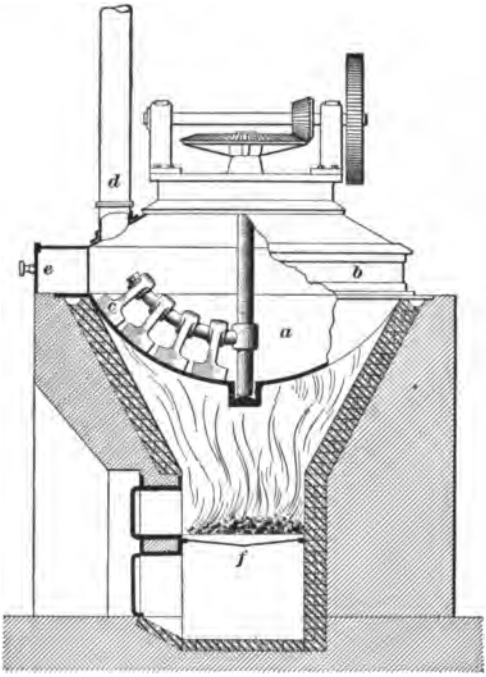


FIG. 8

and finally go to the chimney through the flue *j*. The cylinder *h* revolves about its long axis on the rollers *k*. The chain *l* scrapes the charge loose from the sides and mixes it. At *m* a scoop arrangement is caused to dip periodically into the charge and bring a portion of it to the worm *n*, which conveys it outside to carriers. The liberated gases and vapors pass out through *g*, *f*, and *o*.

36. A modification of the Thelan pan is sometimes used. This pan is covered over, and the gases escape through a pipe in the top cover. The scrapers, instead of revolving, move back and forth over the bottom. With this apparatus, it is found most practical to drive off only the ammonia and three-fourths of the carbon dioxide and to finish the calcination in a reverberatory furnace.

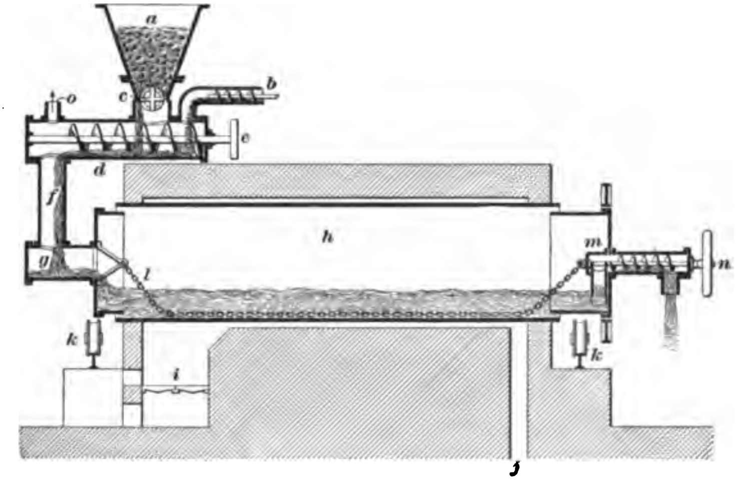


FIG. 9

The gases from the calciner are passed through condensers to condense the water and to recover the ammonia as a solution of ammonium bicarbonate, which is then run to a special distilling apparatus. The carbon dioxide from the decomposition of the sodium bicarbonate should, theoretically, be almost 100 per cent. pure, and for this reason it should be especially good for finishing the carbonating of the ammoniacal brine; but, owing to unavoidable leaks in the apparatus, it is but little better than the lime-kiln gas and is usually mixed directly with that gas.

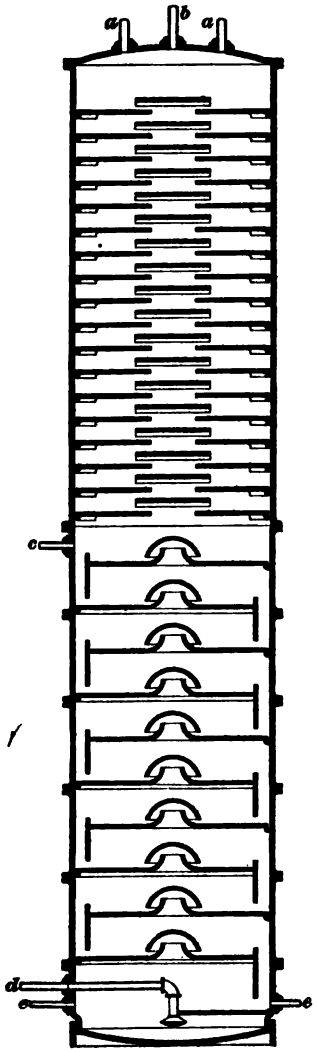


FIG. 10

37. Ammonia Recovery.—The mother liquor that comes from the bicarbonate filters contains the greater part of the ammonia that was contained in the ammoniacal brine. From 15 to 20 per cent. of this total ammonia is present as ammonium bicarbonate, and the remainder as ammonium chloride. This mother liquor is run into storage tanks, where enough gas liquor is added to make up for the loss of ammonia in the process. The gas liquor contains free ammonia, ammonium carbonate, ammonium sulphate, sulphide, etc. By the addition of this liquor, the solution going to the still is kept as nearly uniform in composition as possible. Besides the ammonium salts, this mother liquor contains the sodium chloride from the brine that is unacted on, sodium bicarbonate, and small quantities of other salts.

38. The old system of managing this liquor was to use a common still and to run in a charge of liquor and a charge of lime and then heat. This has, however, been given up for a continuous system in practically all works of importance. A still of this latter type is shown in Fig. 10. The lower part is built up of wrought-iron rings, and is divided into compartments by iron plates having a hole in the center, which is covered with a hood-shaped piece of iron. The upper part is built up of cast-iron sections, and is also divided by plates, which serve to break up the liquor as it passes down the tower. The liquor to be distilled comes from the storage tanks and enters the upper part of the distiller at *b*; it then passes down over the baffle plates, meeting the ascending current of hot gases from the lower part of the apparatus. In this upper half, which is called the *heater*, the ammonium carbonate is decomposed and driven off, together with the free ammonia. All the gases escape through the exit pipes *a*, *a*. At *c*, a carefully regulated stream of milk of lime enters and mingles with the descending solution of ammonium chloride and other ammonium salts. Steam is blown in at *d* through a rose and carries the ammonia set free by the lime into the upper part of the apparatus, where it mingles with the other gases and passes out through *a*. At *e* are the waste-liquor outlets, from which the liquor that is free from ammonia escapes.

The gases from the distiller consist mainly of ammonia and carbon dioxide saturated with water vapor at 80° or 85° C. These gases must be cooled and dried before they go to the saturators for the ammoniacal brines. This is accomplished by passing the gases through a long pipe coiled in running water. The gases then pass into the saturators, and the condensed liquor is either returned to the still or sent to a special still along with the condensed liquor from the calciners.

39. Distiller Liquor.—The composition of the liquor running from the distiller is somewhat variable, depending on the quality of lime used in making the milk of lime and on other conditions. It may be stated in general, however, that this liquor contains as magnesium hydrate or oxide all the magnesium that was in the lime, for it is found to be inadvisable to attempt to use little enough lime to utilize the magnesium oxide, and in the presence of lime the magnesium oxide will not act. The liquor also contains calcium hydrate, calcium carbonate, and, principally, calcium chloride and sodium chloride. The clear liquor does not vary so much. The clear liquor used for making paper filler, taken from a series of distillers at the Solvay Process Company's works at Syracuse, New York, in 1897, had the following composition:

CONSTITUENTS	GRAMS PER LITER
$CaCl_2$	75 to 85
$NaCl$	50 to 75
$CaSO_4$	1
$Ca(OH)_2$	1

In this distiller waste, the chlorine of the salt is lost, and in addition, it occupies valuable land and pollutes streams. The pollution of the streams by distiller waste, however, is not to be compared with that from tank waste (see Art. **104**), neither does it suffer decomposition, yielding offensive products, as does tank waste. Apparently, the best way to dispose of this waste is to build tight earth walls around an area and run in the waste. In this way, the water and most of the substances in the solution leach away; as the lime becomes carbonated, the residue does comparatively little damage. Many efforts have been made to utilize the waste, or at least to obtain the chlorine contained in it, but they have met with little success. Also, numberless methods have been proposed for liberating the ammonia in such a manner that the chlorine will be left in a little more accessible form, but these too are of little value.

A small amount of calcium chloride produced by this process is used for circulating in pipes in cold-storage and ice machines, and it has also been utilized somewhat in the manufacture of artificial stone. An important use for the calcium chloride would be in the manufacture of paper filler, if there were sufficient demand for the material; but, compared with the amount produced, the demand for paper filler is insignificant.

40. Ammonia Lost.—When the ammonia-soda process was first tried, 20 and more parts of ammonium sulphate per 100 parts of sodium carbonate was lost, so that it is small wonder that it did not pay. This loss has been considerably reduced, although previous to 1890 it was as high as 4 parts of the sulphate per 100 parts of carbonate. It has since been steadily reduced until, in England, in 1897, the loss was about 2 parts per 100; and now, in the best-managed works in the United States, it is without doubt reduced to from ½ to 2 parts per 100. This loss of ammonia plays a very important part in the process, as will be realized when it is considered that ammonium sulphate costs about four times as much as sodium carbonate.

41. Properties of Ammonia Soda.—The sodium carbonate made by the Solvay process is remarkably pure, having an approximate composition as follows:

CONSTITUENTS	PER CENT.
Na_2CO_3	98.40
$NaCl$	1.28
Na_2SO_4	.07
SiO_2	.02
Fe_2O_3 and Al_2O_3	.01
$CaCO_3$	.12
$MgCO_3$	.04

Some purchasers, having become accustomed to the less pure Le Blanc soda, still demand that sort of soda ash. This leads the ammonia-soda manufacturer to add salt or sodium sulphate, or both, to the ash and to sell it as a lower grade of soda ash. The soda ash made by the ammonia-soda process is of considerably lower density than that made by the Le Blanc process, so that in equal bulk there is only about 2 parts, by weight, of ammonia soda to 3 parts, by weight, of the Le Blanc soda. For making soda solutions, the lighter soda dissolves more readily, and for this purpose is preferable. On the other hand, the denser soda is much to be preferred for use in furnaces where the charge must be fused, for it is not so easily carried away by the fire gases. The denser kind is also better for packing to ship, as it does not require so much space. The light ammonia soda can be concentrated into the more dense form by calcining in a Mactear, or reverberatory, furnace.

CRYOLITE-SODA PROCESS

42. In the southern part of Greenland there occurs a mineral of the composition Na_3AlF_6, called **cryolite**, and, so far as is known, it does not occur in any quantity in any other place. In Greenland, however, it is found in large quantities. The quarry now being worked is 300 feet long by 150 feet wide and 120 feet deep, and shafts have been sunk 120 feet farther without showing any sign of diminution of the supply of material. Cryolite can only be mined in the summer, however, and this short season tends to limit the output. This mineral was first considered as a source of soda by Julius Thomsen, a Dane, in the first half of the 19th century. He developed a method for working the material, and in 1854 obtained the exclusive right to mine the cryolite and work it up into sodium carbonate and other materials in Denmark. He afterwards sold his right to a company, and in 1865 the Pennsylvania Salt Manufacturing Company obtained the right to two-thirds of all the cryolite mined. At the present time, there is one soda works in Denmark using cryolite, but the greater part of the mineral mined is worked up by the American company at its works at Natrona, Pennsylvania.

The method of working cryolite at the present time, even to the furnace used, is practically the same as that proposed by Thomsen 50 years or more ago. The cryolite is first decomposed by calcining it with limestone, when the following reaction takes place:

$$Na_3AlF_6 + 3CaCO_3 = Na_3AlO_3 + 3CaF_2 + 3CO_2$$

43. The calcination of the mixture takes place in a reverberatory furnace. This furnace must be of special construction, however, for the mixture must be kept at red heat; but the temperature must not get so high that the mass fuses, for the fused mass is very difficult to lixiviate. The furnace is built with flues under the hearth, so that the charge can be heated from the bottom as well as from the top, and the temperature can, by this means, be carefully regulated.

44. According to the preceding reaction, 100 parts of the cryolite would require 143 parts of calcium carbonate; but in practice about 150 parts of pure calcium carbonate is used for 100 parts of cryolite, as the excess renders the mixture less liable to fusion and increases its porosity when calcined. Of course, quicklime can be used in place of the limestone, and at Natrona this is partly done. The mix at that place, by weight, is 100 parts of cryolite, 20 parts of limestone, and 80 parts of quicklime. A charge for a furnace is 950 pounds of this mixture, and during calcination it loses 75 pounds. About 1 hour is required to finish a charge of this size. After calcination, the charge is allowed to cool, and it is then lixiviated. A solution of sodium aluminate is obtained, and the insoluble calcium fluoride is left in the tank.

45. Calcium Fluoride.—Calcium fluoride is of comparatively little value, although it is used in the manufacture of hydrofluoric acid and fluorides of the other metals. It is also sometimes employed by glass manufacturers, but must never exceed from 6 to 9 per cent. of the mix, for otherwise too much silica will be volatilized and the silicon tetrafluoride will act on the furnace to too great an extent. Calcium fluoride is also employed as a flux in certain metallurgical operations.

46. Sodium Aluminate.—The sodium aluminate is carbonated by carefully washed lime-kiln gases; sodium carbonate is left in solution, while the aluminum is precipitated as the hydrate. If the carbonation takes place at the ordinary temperature, the aluminum hydrate separates in a gelatinous condition, from which it is almost impossible to wash the soda. If, however, a suitable higher temperature is selected, the precipitate obtained is granular and can be easily filtered and washed on a filter press. The soda solution is then evaporated and allowed to crystallize. The crystals are sold as such, dehydrated and sold as soda ash, or converted into bicarbonate; they are especially suited for this latter purpose on account of their high purity. Sometimes, the soda solution is converted into caustic soda.

The aluminum hydrate is calcined and sold as aluminum oxide for the manufacture of metallic aluminum; or, it is treated with sulphuric acid for aluminum sulphate or for alum.

47. **Other Uses of Cryolite.**—Owing to the limited quantity of cryolite available, and its higher price compared with that of common salt, the cryolite-soda process of manufacturing sodium carbonate is going out of use. The mineral is more economically used as a flux in enameling ironware, etc.; it is also employed in the recent beautiful process for manufacturing aluminum electrolytically from bauxite. In the latter process, the alumina of this mineral is dissolved to a limited extent in fused cryolite, which either leaves the ferric oxide and other impurities floating on the top or settled on the bottom of the container. From this fused solution of the alumina, the metallic aluminum is deposited by the electric current.

SALT CAKE

48. **Sodium Sulphate.**—In Egypt, Spain, and other European countries, **sodium sulphate** occurs naturally, while in the United States, immense deposits are found in Wyoming and in some parts of California. It is so extremely cheap, however, and these deposits are at present so inaccessible that it does not pay to use them. In this country, and more especially in California, an attempt is now being made to utilize these natural deposits of sulphate of sodium, but it is doubtful whether it will be successful, unless the expense of gathering and transportation to the coast is materially reduced. There is some prospect of this, however, as a railroad, known as the Tonopah and Tide-Water Railroad, is now in course of construction. This may permit a successful exploitation of these deposits and their utilization on the Pacific Coast, possibly in the neighborhood of San Francisco, but so long as salt can be obtained for the mere cost of pumping, as it is in parts of New York, Michigan, and West Virginia, the eastern manufacturer can successfully compete with these deposits and carry the manufactured

resulting products, as soda ash, or caustic soda, around the Horn to Pacific ports.

The native anhydrous sodium sulphate is called *thenardite;* the hydrated, *mirabilite.*

Sodium sulphate was first described by Glauber in 1658, although it was probably known before that time. He prepared it by the action of sulphuric acid on salt and recommended it as a medicine for internal and external use. He gave it the name *sal mirabile*, and later it was called *sal mirabile Glauberi.* Even at the present time, the crystallized salt is called *Glauber's salt.*

The manufacture of this substance, which, when artificially prepared, is usually known as **salt cake**, depends almost entirely on the reaction between sodium chloride and sulphuric acid. The latter may be used ready made or formed at the instant of its action. In the first case, acid sodium sulphate is first formed; afterwards, the normal salt, so that the reactions are:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$
$$NaCl + NaHSO_4 = Na_2SO_4 + HCl$$

In the second method, instead of sulphuric acid, sulphur dioxide, oxygen, and steam are brought together with the salt, giving the reaction

$$4NaCl + 2SO_2 + 2H_2O + O_2 = 2Na_2SO_4 + 4HCl$$

The first method is the older and at the same time the one most used for making salt cake, although large quantities of it are made now in England by the latter method, which is known as the *Hargreave process.*

CRUDE MATERIALS

49. Salt.—The salt best suited for making salt cake is what is known in the United States as *cattle salt.* The coarse crystals form a spongy mass that readily absorbs the acid and this aids the decomposition. The fine-grained, so-called *table salt* is totally unsuited for this purpose.

If made by evaporation, the salt as it comes to the works usually contains about 95 per cent. of sodium chloride and about 5 per cent. of water, with other minor impurities. However, very much the larger proportion now used in this country for manufacturing purposes is *mined*, or *rock*, *salt*, which is ground to pass through a $\frac{1}{16}$- to a $\frac{1}{8}$-inch mesh screen. It is free from moisture and tests 99 per cent. or over of sodium chloride.

50. Sulphuric Acid.—The impurities usually occurring in sulphuric acid have quite an important bearing on the resulting product. Iron, arsenic, selenium, and nitric or hyponitric acids should be entirely absent, or, if present, should be in minute quantities only for the following reasons:

If the salt cake is used for glass making, iron to the extent of .2 per cent. (determined as Fe_2O_3) is permissible, but more than this is objectionable. This iron is derived from the decomposing pan and iron tools. If additional iron is present in the sulphuric acid, as when iron sulphide is added to it to precipitate arsenic, this excessive amount renders the salt cake unfit for glass making. If the salt cake is used only for soda ash, or caustic soda, the iron is of no importance. Arsenic, if present in the sulphuric acid, is found entirely in the resulting hydrochloric acid, and is very objectionable in nearly all uses to which the same is put, as is also selenium. Nitric or hyponitric acid derived from the nitrate of soda or nitric acid used in the chamber process for the manufacture of sulphuric acid, develops free chlorine in the hydrochloric acid, which is generally objected to. Want of attention to these details has made the product of some manufacturers difficult to sell, or it has to be sold at reduced prices to fertilizer manufacturers.

The concentration of the acid should be from 60° to 61.5° Baumé. Weaker acid acts on the decomposing pans and, in turn, gives weak hydrochloric acid. If stronger, the acid does not penetrate nor readily act on the salt, and the resulting hydrochloric acid is more difficult to condense, owing to the smaller percentage of aqueous vapors present.

APPARATUS AND METHOD OF MANUFACTURE

51. The apparatus used in the manufacture of salt cake varies considerably in detail, but according to its essential features may be divided into *open roasters*, *blind roasters*, or *muffles*, and *mechanical furnaces*.

52. Open Roasters.—The **open roaster** shown in Fig. 11 consists of two parts, the *pan a* and the *roaster b*.

53. The Pan.—Since the pan must withstand the action of sulphuric acid, it was at first assumed that lead was the only material that could be used. But this material has the decided disadvantage of soon wearing out by the action of the tools used in mixing the salt and acid and in transferring the product to the roaster *b*. A very low and carefully regulated temperature must also be employed on account of the low melting point of the lead. Lead has therefore been almost entirely discarded in favor of iron for pans, although even now, when it is desired to make a salt cake free from iron, lead pans are used. The iron pans are from 9 to 11 feet in diameter and from 1 foot 9 inches to 2 feet 6 inches in depth. They are made about 6 inches thick on the bottom and taper to about 2 inches at the edge, and are covered with a brick arch having an outlet pipe *c* for the escape of the hydrochloric acid. The pans are supported at their edges by supporting walls, and are heated by direct fire from a grate *d*. This grate is covered by a section of an

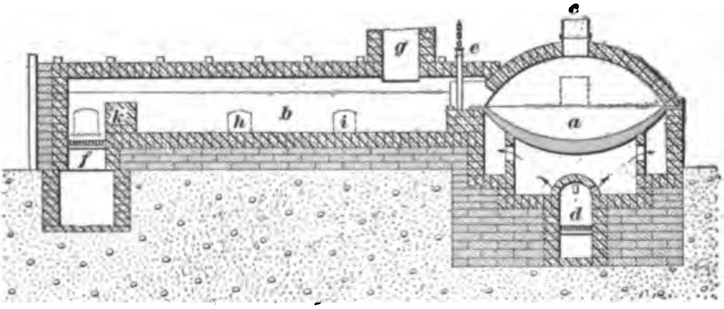


FIG. 11

arch so as to spread the flame and prevent overheating in one place and so burning the iron. The pan must be able to withstand considerable temperature changes as well as the action of the acids, since they are nearly at red heat when the batch is transferred to the roaster, and in rapid work, a new charge of salt that is possibly damp is introduced before the pan has cooled very much.

Between the pan and the roaster is a slide *e*, which is best made of two thin sheets of iron placed a few inches apart, the space thus formed being filled with a packing of salt, so as to keep the hydrochloric acid from the pan separate from that of the roaster. By this means the condensation of the pan acid is easier, and a much purer acid is obtained than would result from the mixed gases. The passage between the pan and the roaster is kept open only long enough to permit the transfer of the batch of salt cake.

54. Management of the Pan.—Salt to the amount of from 500 to 1,000 pounds, depending on the preference of the management, but usually 800 to 900 pounds, is shoveled into the pan through the working door. Then enough sulphuric acid, of 60° to 61½° Baumé (taken cold), having been previously heated to from 100° to 125° C., is run in through a pipe in the cover of the pan and the mixture heated.

The amount of sulphuric acid used is naturally regulated by the charge of salt and the moisture in the salt. Theoretically, every 58.5 parts, or pounds, of salt should have 49 parts, or pounds, of sulphuric acid, H_2SO_4; that is, every 100 parts, by weight, of $NaCl$ requires 83.75 parts, by weight, of H_2SO_4. Sulphuric acid of 60° Baumé is 78 per cent. H_2SO_4, and therefore 100 parts of $NaCl$ requires 107.37 parts of sulphuric acid of 60° Baumé. Since, however, the salt used is only about 95 per cent. $NaCl$, the amount of 60° Baumé acid will be 102 parts, by weight, for every 100 parts, by weight, of salt. However, some allowance must be made for loss of sulphuric acid, by volatilization, in the pan and roaster. Thus, in most works, for making strong salt cake, about 2½ parts, by weight, of sulphuric acid in excess of the amount calculated is added for each 100 parts, by weight, of salt. The practice, then, is to add 104.5 parts, by weight, of 60° Baumé sulphuric acid to each 100 parts, by weight, of salt charged. If stronger or weaker acid is used, the calculation of the amount of acid can be carried out in the same way. Similarly, in using rock salt, its test must be taken into account.

The charge of acid is never weighed, but is measured so that it must be added each time at the same temperature. The salt and acid are analyzed daily in the laboratory, and tables are furnished the panman; thus, by determining the specific gravity of the acid coming to him, at a constant temperature, he can easily determine the amount of acid to add. The best temperature for the acid is a matter of opinion, but it should never be below 50° C. while some use it at 125° C. The hotter the acid, the less the action on the pan; but with acid that is too hot, the hydrochloric acid is given off too rapidly, and it is difficult to condense it. An acid of about 125° C. is considered the best.

55. Under the best conditions of working, the batch in the pan foams badly and has a tendency to boil over. This difficulty can be quite largely overcome by adding a small piece of paraffin as soon as the sulphuric acid is run in.

As soon as the acid is added to the salt, the mixture is thoroughly stirred by the panman, for which purpose he uses a long-handled iron rake that he inserts through a hole in the working door. At best, some hydrochloric-acid gas escapes during this operation, but by heaping salt about the rake handle where it passes through the door and moistening the salt, the escape of the gas is reduced considerably. When the mixture has been brought to the consistency of thin mud and all the lumps of salt have been broken, the rake is withdrawn and the door closed as tightly as possible by piling damp salt against it. The door itself is made of slate or of lead-covered cast iron and is set in a frame of acid-resisting stone. The workroom should be thoroughly ventilated to relieve the workmen, so far as possible, from the inconvenience of the acid that sometimes unavoidably escapes.

56. In this operation in the pan, the first half of the reaction takes place, and, theoretically, 50 per cent. of the total hydrochloric acid is evolved. Practically, the heating of the pan is continued until about 70 per cent. of the total hydrochloric acid is given off, for it is advisable to have as much of the hydrochloric acid evolved in the pan as possible. The pan hydrochloric acid is purer and easier to condense than that from the roaster. The batch in the pan is considered finished when the mixture offers considerable resistance to the moving backwards and forwards of the rake, owing to the stiffness of the mass. The finishing of the batch then requires a higher heat than can be obtained in the pan. Assuming the roaster bed to be empty, at a bright-red heat, and the batch in the pan finished, the slide *e* is raised and the pan door opened. The panman then transfers the charge to the roaster by means of a long-handled, spoon-like shovel, and it is at once spread out evenly by the roasterman. There is always a tendency for the acid salt cake to stick to the pan, especially if it is not set so as to be evenly heated. This is best remedied by carefully setting the pans so that the heating will be uniform and moderating the fire before transferring the charge. Where such cakes form, they should be removed before adding a new charge, otherwise the pan is liable to crack.

57. Open Roaster.—The **open roaster** *b*, Fig. 11, consists of a shallow basin from 12 to 15 feet long and narrow enough for the batch to be handled by the workmen using long-handled hoes. It is simply a form of reverberatory furnace, 8 feet wide by 16 to 20 feet long, inside measurements, and is lined with firebricks that are carefully laid. The material is heated by direct flame from a coke fire on the grate *f*, and the products of combustion, together with the hydrochloric acid, escape through the pipe *g*. Since all the fire gases mix with the hydrochloric acid in the open roaster, it is very much diluted, and its complete condensation to a stronger acid is very difficult. Fuel oil and producer gas have also been used to advantage.

58. Management of the Roaster.—The batch is spread evenly over the bed of the roaster, and at intervals of from 10 to 15 minutes it must be turned over and all lumps broken. For this purpose, the furnaceman uses a wrought-iron rake and a bar of wrought iron flattened at the end into a blade. The tools are inserted into the furnace through the doors *h* and *i*, and are supported by hooks hanging from the ceiling and located in front of the furnace door. By thus supporting the tools, the furnaceman is relieved of part of their weight, but the work is hard and disagreeable at best. The furnace must be kept hot to get the batch off quickly, but it must not be allowed to get too hot or the batch will flux. A small amount of fluxing can be taken care of and the lumps broken, but if it once gets ahead of the furnaceman, especially next to the fire-bridge *k*, it is almost fatal to the charge, for it cannot be controlled and the salt cake is rendered almost useless for the black-ash furnace. The way to avoid this fluxing is to watch the fire carefully.

The furnace work is finished when no more vapors are given off, even on turning the batch and when it is quite red hot, but it must never flux at any point. The salt cake is then withdrawn by means of wrought-iron hoes into steel barrows and taken to the storeroom. The hydrochloric acid given off in the open roaster is mixed with the gases and dust from the grate, so that the operation of condensing it to a strong acid is difficult; there is also danger of the condensers becoming stopped by the dust. To obviate these difficulties, the *blind*, or *muffle*, *roaster* has been adopted by many manufacturers.

59. Blind, or Muffle, Roaster.—In the **blind, or muffle, roaster**, a pan of practically the same dimensions and setting as in the open roaster is employed. This pan is sometimes heated by the waste gases from the muffle heating, but a better method is to heat it by its own fire, as in the preceding case, for although some fuel is saved when waste heat is employed, direct firing makes the working of the pan independent of the muffle, and this in many cases is a decided advantage. The essential difference between this method and the preceding one is in the roaster. Here, instead of having the batch heated by direct fire, with its numerous disadvantages, the batch is brought into a closed muffle and heated by the heat conducted by the muffle walls from the outside flues. The muffle walls are made of brick and must be quite thin, or it will not be possible to get the charge sufficiently hot. Since the walls are thin, they are liable to be damaged by the tools used in working the material, or they may crack on account of the temperature changes. Also, since the pressure inside the muffle is greater than on the outside, if such a crack forms, large quantities of hydrochloric acid may escape into the chimney gases and cause great damage before the leak is discovered. These difficulties led Deacon to devise his *plus-pressure furnace.*

60. Deacon's Plus-Pressure Furnace.—In the muffle roaster just described, the fire-grade is nearly on the same level as the muffle, and a draft is produced by means of a chimney. Thus, the flues about the muffle are under diminished pressure, while, on account of the acid-absorption apparatus, the acid in the muffle is under greater pressure than the atmosphere. The result of this, is that, if there is a leak in the muffle, the hydrochloric acid will escape into the chimney. Deacon reverses this condition, not by diminishing the pressure in the muffle, but by increasing the pressure in the flues by placing the fire-grate *a*, Fig. 12, much lower than the muffle *c*. The hot gases in the vertical flue rising to the muffle flues *b*, *b*, produce a pressure on the latter, so that if there is a leak in the muffle, the flue gases go in and do comparatively little harm. It is practically putting the muffle at the top of the chimney instead of at the bottom, as in the other style. As shown in the illustration, the fire gases rise from the grate *a*, pass over the muffle and then through a series of flues on the under side of the muffle, and finally go to heat the pan or go direct to the chimney.

61. All that has been said about the working of open roasters applies equally well to muffle furnaces. The heating of the whole furnace bed is more uniform, and the danger of overheating is not so great.

Muffle furnaces are also rectangular in form and of about the same size as open furnaces, except that in some works the hearth is made longer, so as to allow a thinner layer of salt cake to be worked and thereby compensate for the heat lost from absorption by the muffle.

62. Advantages of Open and Muffle Furnaces. The advantages of the two styles of roaster may be summarized as follows: The open roaster works more rapidly because the charge can be made hotter, and therefore gives a larger yield of salt cake. For the same reason, it is possible to make a stronger salt cake; that is, one containing a higher percentage of normal sodium sulphate. Less repairs are needed, and it is impossible for the acid to escape by accident anywhere except through the condensers. The muffle roaster, on the other hand, makes possible a better condensation of the hydrochloric acid, and therefore produces a cheaper and stronger acid. It requires less sulphuric acid per unit of salt, and instead of the more expensive coke, coal

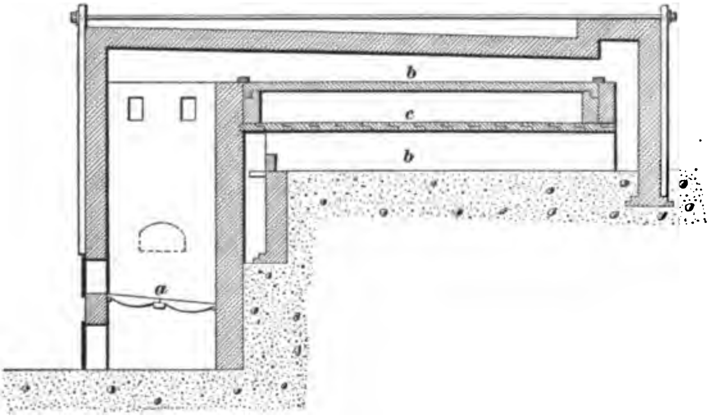


FIG. 12

can be used for firing. More fuel is required, however, so that the last item probably does not represent much saving. The system to be installed depends on the uses to which the resulting salt cake and hydrochloric acid are to be applied. If the salt cake is to be used for making soda ash and the hydrochloric acid for making bleaching powder, the open roaster is preferable on the ground of economy; but, if the salt cake is to be used in manufacturing glass, for which use it has to be white and free from dirt, and the hydrochloric acid is intended for purposes of sale, then the muffle roaster is to be preferred.

63. Mechanical Furnaces.—In the preceding methods of working, the batch must be transferred from the pan to the roaster, where it is carefully worked so as to prevent lumps of salt that are unacted on from getting into the finished product. It requires a certain amount of skill to do this properly, and the manufacturer is thus to a certain extent in the hands of his workmen. Furthermore, every time the furnace door is opened, acid gas escapes into the room and produces an unhealthful atmosphere for the workmen. These considerations have led to various attemps to perform all this work mechanically, but the only arrangement that is commercially successful is the **Mactear furnace,** which is shown in Fig. 13.

This furnace consists of the pan *a* in the center of the movable hearth *b*, and it is heated by gas from the grate *c*. The salt is fed in continuously through the hopper *d*, and at the same time the proper amount of acid flows in through the pipe *e*. The two substances mix and partly react in the pan, and then the mixture is slowly worked over on to the hearth by the stirrer *f*. The hearth revolves on small wheels running on the tracks *g*, and by this motion and the stirrers, which extend from *f* to the outer edge and are turned by the outside cogs, as shown, the charge is worked to the outer edge by the time the reaction is completed. The salt cake then flows into the annular trough *h*, by means of which it is conducted from the apparatus. All the joints of the

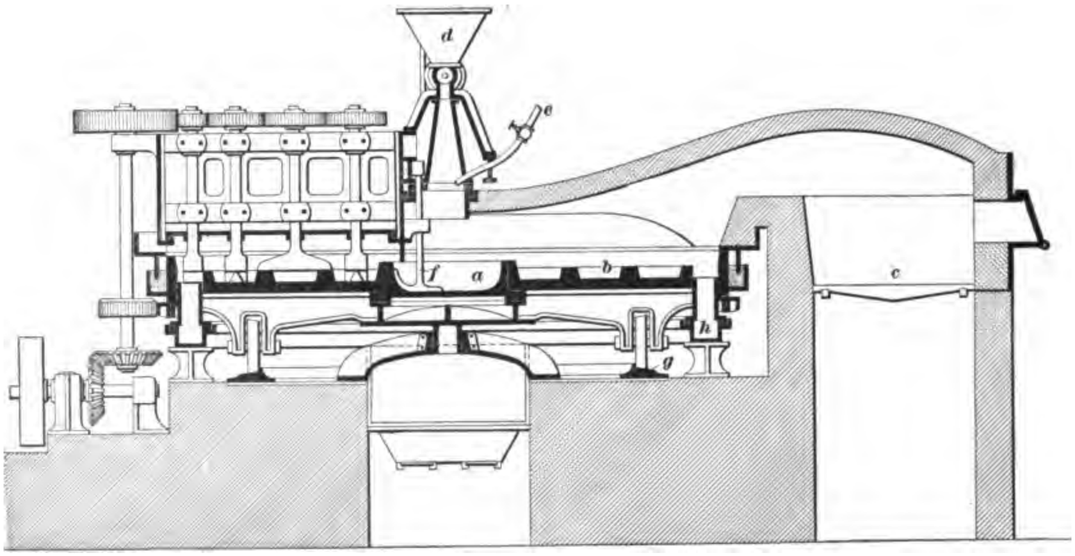


FIG. 13

apparatus are closed by aprons dipping into lutes of molten sulphate, but even this does not altogether protect the outside from the acid fumes.

64. Another furnace, that of Jones & Walsh, has been so improved as to serve a good purpose. The principle involved in this furnace is the same as in the Mactear, but its operation is not so cumbersome.

The salt cake from these mechanical furnaces is not well adapted for glass making. Very few mechanical furnaces are in operation in the United States, however, and the same may be said of the hand-worked, open-roaster furnaces. Muffler roasters are preferred in this country, as the chief use of sodium sulphate is for glass making, and the demand is for a concentrated and comparatively pure hydrochloric acid. In mechanical furnaces, it seems to be an assured fact that there is less waste of sulphuric acid.

65. Mechanical furnaces have the advantages that they do away with a large amount of manual labor, yield a continuous product, and allow the hydrochloric acid to be more easily condensed, for it comes in a continuous, uniform stream, while, in the hand furnace, the evolution of acid is variable. But they have the disadvantages that the hydrochloric acid cannot be made so strong as with hand work, and that the machinery is expensive and requires a large amount of repairs. These disadvantages have restricted the use of this furnace, so that probably not over 15 per cent. of the salt cake manufactured at the present time is made by mechanical furnaces.

66. Yield of Salt Cake.—The yield of salt cake will naturally vary in different works and with different apparatus, but the amount that may be expected with good work, etc. is about as follows: 100 parts, by weight, of pure salt should, theoretically, yield 121.5 parts, by weight, of salt cake. As already pointed out, the salt obtained by evaporation rarely contains over 95 per cent. of sodium chloride; and, of course, this must lower the yield of salt cake. If, however, the rational method of calculating the percentage yield on the sodium chloride actually used is adopted, the yield should be very near that determined theoretically. Works are in operation that produce 120 parts of salt cake for 100 parts of pure chloride used, the small, natural loss in working being made up by the presence of free sulphuric acid, iron, and insoluble matter obtained from the furnace hearth.

67. Properties of Salt Cake.—A good quality of salt cake should be finely granular and yellowish white or, better, pure white in color. A deep-yellow or reddish-brown color shows much iron, while a dirty-gray color indicates incomplete decomposition of the salt. The salt cake should not contain over 1 per cent. of free sulphuric acid, nor more than .6 per cent. of sodium chloride. When intended for use in glass manufacture, the iron should not exceed .2 per cent. Fe_2O_3, and it should contain not less than 96 per cent. of normal sodium sulphate, Na_2SO_4.

68. Uses of Salt Cake.—Sodium sulphate is most largely used in making sodium carbonate by the Le Blanc process. It is also used in the manufacture of glass and ultramarine, and in dyeing and coloring. It finds a smaller use in making sodium acetate and other sodium salts from the corresponding calcium salts, while the crystallized sodium sulphate (Glauber's salt) is used medicinally.

SODA BY THE LE BLANC PROCESS

69. Le Blanc's process for making sodium carbonate from salt consists in first making sodium sulphate, as already described, and then converting this into sodium carbonate by fusing the sulphate with a mixture of calcium carbonate and carbon.

The process includes the starting with sulphur in its elementary form, or the much less valuable iron pyrites, with calcium carbonate, carbon, and sodium chloride as raw materials, and ending with the sodium as carbonate, the chlorine free or as hydrochloric acid, the calcium carbonate as when starting, and the sulphur free, so that the only material used up is the carbon. There are no by-products.

This cycle is now practically realized and may be represented by the following reactions:

$$\begin{aligned} 2S + 3O_2 + 2H_2O &= 2H_2SO_4 \\ 4NaCl + 2H_2SO_4 &= 2Na_2SO_4 + 4HCl \\ 2Na_2SO_4 + 4C &= 2Na_2S + 4CO_2 \\ 2Na_2S + 2CaCO_3 &= 2Na_2CO_3 + 2CaS \\ 2CaS + 2CO_2 + H_2O &= 2CaCO_3 + 2H_2S \\ 2H_2S + O_2 &= 2S + 2H_2O \end{aligned}$$

Or, combining them,

$$2NaCl + C + O_2 + H_2O = Na_2CO_3 + 2HCl$$

That is, theoretically, for 117 parts, by weight, of salt, only 12 parts, by weight, of carbon, is required to convert the salt into sodium carbonate and hydrochloric acid, which makes the process apparently a cheap and simple one. The practice is, however, not nearly so close, for actually 400 to 500 parts of carbon is required to every 117 parts of salt. In addition, there is a large amount of money invested in the plant, which constantly requires a large outlay for labor and repairs; besides, the reactions do not go so smoothly as represented.

70. The reaction that takes place when carbon, sodium sulphate, and calcium carbonate are fused together has been the subject of almost endless discussion, especially with regard to the calcium compound, for it is well known that an insoluble calcium sulphide is not formed with either hydrogen sulphide or ammonium sulphide. Therefore, it was long held that the calcium compound formed in the reaction mentioned must be an oxysulphide, $CaO \cdot CaS$. It is impossible to go into a discussion of this subject, but it may be considered as definitely settled that the reactions take place practically as just represented, the calcium sulphide formed being insoluble. At the end of the operation the reaction

$$CaCO_3 + C = CaO + 2CO$$

begins, and it also serves as a signal for withdrawing the charge, for the carbon monoxide comes up through the material and burns with long, pointed flames, called *candles*, and thus indicates that the transformation is complete. This reaction continues for a long time after the charge is withdrawn and while it is cooling, so that the escaping gas leaves the material porous, and for that reason much easier to lixiviate in a later stage of the work.

RAW MATERIALS

71. Sodium Sulphate.—As the preparation of salt cake has already been described, repetition will be avoided by considering it here as one of the raw materials. The sodium sulphate should be fine and porous, not fluxed, and should contain 96 or 97 per cent. of sodium sulphate. It is better if the sodium sulphate contains a little free acid, as this lessens the probability of its containing much salt. The acid, however, should not exceed 2 per cent., and the salt not over ½ or 1 per cent.

72. Calcium Carbonate.—The calcium carbonate is usually chalk or high-grade limestone. All impurities are harmful, and magnesium and silica are especially so, because they form insoluble compounds with sodium and thus cause a loss of the latter. The limestone is crushed to the size of a pea or a bean before being used, but does not need to be fine, and is better if not too fine. Caustic mud (see Art. **10**, *Alkalies and Hydrochloric Acid*, Part 2) and calcium carbonate from the sulphur recovery (see Art. **104**, etc.) are also sometimes used, but they are so light that they do not flux well.

73. Carbon.—The carbon is supplied in the form of rather finely crushed coal, which should be low in ash—not over 7 per cent. being allowable—and one that gives a high yield of coke. The presence of a moderate amount of pyrites does not interfere, but the less nitrogen present the better, for it leads to the formation of cyanides, cyanates, and ferrocyanides, the latter introducing iron into the ash.

DETAILS OF THE LE BLANC PROCESS

74. The mixture varies considerably in the proportions of the constituents, probably partly on account of impurities in the coal and limestone; but even taking that into account there is a wide variation, since each works uses the mix that it considers will give the best result. The theoretically correct proportions can, of course, be calculated from the reactions given in Art. **69.** Leaving out the reaction

$$CaCO_3 + C = CaO + 2CO,$$

the proportion will be 100 pounds of salt cake, 70 pounds of calcium carbonate, and 17 pounds of carbon. Taking this reaction into account, it will be approximately 100 pounds of salt cake, 75 pounds of limestone, and 20 pounds of carbon. In practice, however, much more coal is required, for some burns and some is left in the product. On account of this coal that remains in the flux, the fused mixture is black, and it is called *black ash.*

In the hand-worked furnaces, about an average mixture is 100 pounds of salt cake, 98 pounds of good limestone, and 48 pounds of coal; but in the mechanical furnaces, which are now largely used, the charge is frequently cut down to as low as 100 pounds of salt cake, 80 pounds of limestone, and 30 pounds of coal.

75. Hand Furnaces.—The **hand furnaces** are simply reverberatory furnaces adapted to this special purpose. Fig. 14 shows a front elevation and vertical and horizontal sections of one of these furnaces. The fire-grate is at *a*. The hot gases pass over the bridge *g* on to the bed of the furnace *b c*, which is divided into two sections, and then over the liquid to be evaporated in the pan *d*. The fire-bridge *g* is built with a flue *h*, which permits the air to circulate freely and thus keep the bridge cool and retard its burning out. The bed of the furnace is usually about 15 feet long by 7 feet wide, and a charge of about 700 pounds, more or less, of the mixture is worked at a time.

76. Management of the Furnace.—The charge is first introduced on to the back half of the furnace through the hopper *e*, and it is then spread out and allowed to get hot and dry, being turned occasionally. When it is thoroughly heated and the front part of the furnace is hot, the charge is transferred to this part of the furnace and a new charge introduced in the back. The principal part of making the black ash takes place on this front bed of the furnace, and here also the work and skill of the furnaceman comes into play. Very soon after it is brought on to the working bed of the furnace, the mixture begins to melt in places; then the furnaceman must turn this mixture so that the melted portion

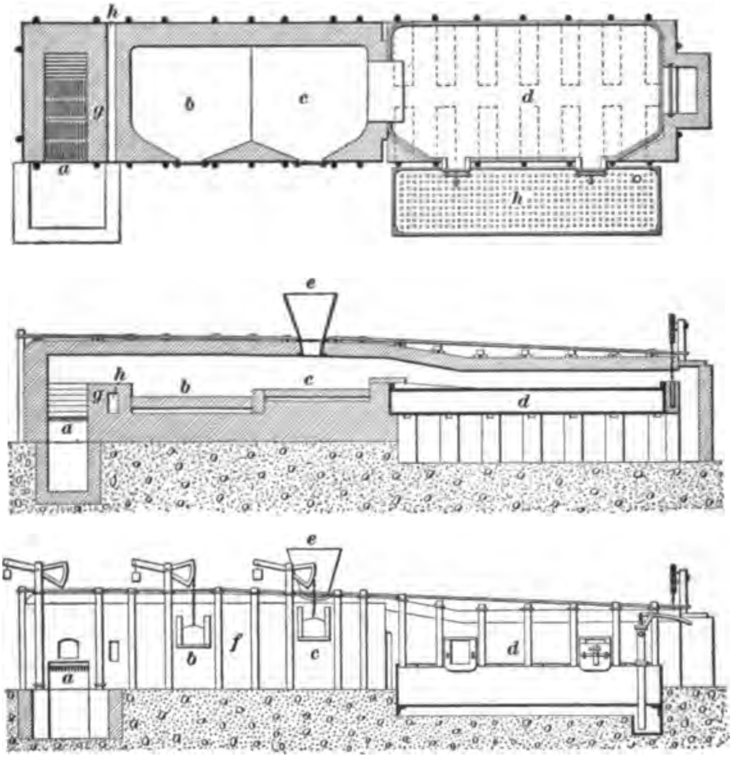


FIG. 14

of the material is turned under and the under part comes to the top. By working the mixture in this way, the furnaceman must gradually and thoroughly mix the whole mass of material and bring it to a rather soft state of fusion. This requires an almost white heat, and to get up the temperature, as well as to rest himself, the furnaceman up to this point works only for a few minutes at a time and then closes the furnace door for about 10 minutes before mixing again. The chemical action does not begin until the mixture is in a state of pasty fusion (it never gets past the pasty stage), and when this condition is reached, the reaction must be finished very rapidly. The furnaceman is busy from now on, stirring and mixing the mass and working it toward the door of the furnace. When the reaction is completed, flames of carbon monoxide, colored yellow by the sodium (so-called candles), will appear, and the black ash is then worked out into a barrow.

The proper time must be selected for "balling" together and withdrawing the charge, for otherwise it will be either underdone or overdone. If not allowed to remain in the furnace long enough, the charge will contain unchanged sodium sulphate, and also be dense and hard to lixiviate; when in this condition, it is called *soft ball*, for the last reaction, which gives the gas and causes the porosity, has not had an opportunity to start. On the other hand, if left too long, the gas of this last reaction will escape while the material is still in a soft condition, and it will then settle into a hard mass, called *burned ball*, which is difficult to lixiviate. Under proper manipulation, however, the material is balled together when candles appear; it is then brought into an iron barrow, where, by the continued action between the carbon and the limestone, gas constantly escapes as the material cools, and so leaves it porous. The slaking of the lime thus formed assists in the lixiviation. The greatest difficulties occurring in the black-ash furnace are the forming of these "soft" or "burned" balls, and the avoiding of them depends almost entirely on the furnaceman. The way to avoid them is to have the furnace hot, to keep the batch well mixed, and to bring the temperature well up at the end of the work; then, with proper judgment as to the time to withdraw the charge, good results are not difficult to obtain.

77. Mechanical Furnaces.—Although the tools are suspended by chains and hooks, the continuous handling of them at the high temperature that exists is very hard on the workmen, and much depends on the good-will of the furnaceman to get good results. For these reasons and to save the cost of the expensive hand labor, mechanical furnaces are very desirable. The first furnaces of this kind that were tried were very expensive to operate on account of the frequent repairs made necessary by the great wear and tear. Furthermore, it was difficult to watch for the candles and draw at the proper time to avoid overburned ash. The excessive repairs were finally overcome by adopting a *barrel-shaped furnace*, shown in Fig. 15, which revolves around its long axis.

The furnace proper *a* consists of an iron shell lined inside with firebricks. As just stated, the shape is that of a barrel; it either conforms to the outside shell, or, if that is cylindrical, the bricks are laid thicker at the ends than in the middle. Two rows of these lining bricks are laid higher than the rest, so as to break up the mass and mix it, and also better to expose it to the fire gases as it drips from these projections. These furnaces are from 15 to 30 feet long, and average about 6 feet in diameter at the ends and from 10 to 12½ feet in the middle. They are heated by the fire gases, which pass in at one end and out at the other. The furnace is heated by the gases from the grate *c*, or sometimes by producer gas, although for some reason the latter gas does not seem to be much used. The hot gases enter the furnace *a*, where they bring about the conversion of the salt cake into black ash, and then pass out through *e* to *g*, where they pass over the top of pans containing the liquor from the lixiviation of black ash and evaporate it. At *b* is shown the manhole through which the black-ash mixture is introduced, and from which, at the end of the process,

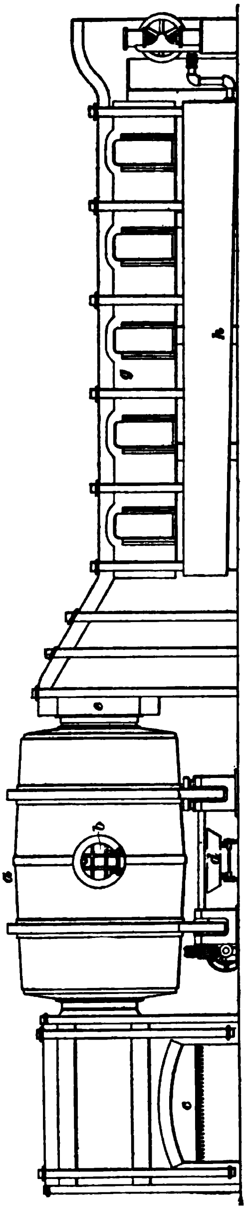


Fig. 15

the black ash is discharged into the cars *d*. The draining pan for the black salts is shown at *h*.

78. Charge for the Mechanical Furnace.—The theoretical charge for the mechanical furnace is naturally the same as that already calculated from the hand furnace, and the same conditions in regard to water and impurities in the limestone and coal rule here. It is found, however, that there is less burning of the mixing coal and less mechanical loss of the constituents of the mixture, so that not so large an excess over that theoretically demanded is now used for the mechanical furnace. The average proportions of the constituents of the black-ash mixtures to be used with a mechanical furnace are 100 parts of salt cake, 82 parts of limestone, and 30 parts of good coal. The size of the charge will naturally vary with the size of the furnace, but an average charge is from 1½ to 3 tons of the mixture.

79. Management of the Mechanical Furnace.—The operation consists in charging in all the limestone and about two-thirds of the coal, without drying. The cover is then put on, and the cylinders are slowly revolved (about one revolution in 3 or 4 minutes) until the appearance of a bluish flame of carbon monoxide around the manhole shows that at least a part of the limestone has been converted into lime. As soon as this operation is completed, which requires from 1 to 1½ hours, the cylinder is turned so that the charging hole is up, and the finely ground salt cake and the coal are dumped in. The cover is then replaced, the draft through the cylinder diminished, and the slow turning resumed. After about 15 minutes, the mixture is hot enough so that the danger of carrying away parts of the mixture is not too great, and the draft is restored. In a few minutes, the appearance of a bright-yellow flame around the manhole shows that a part of the charge is becoming fused. The rate of revolution of the cylinder is then brought up to three or four revolutions per minute. The charge is now watched through peepholes, and when yellow flames (candles) are seen to break from it, it is time to stop. The furnace is now revolved a few times as rapidly as possible to bring the mass together. It is then turned so that the charging hole is up, when the cover is removed and the furnace turned so that the charge runs out into the cars *d*. If the furnace is worked properly, the gas should continue to be given off while the material is in the cars. Thus a porous black ash is produced.

80. In some works, the method proposed and patented by Mactear is adopted. This consists in making a mixture of, say, 100 parts of salt cake, 73 parts of limestone, and 40 parts of coal. This mixture is put into the furnace and the reaction brought to an end, as shown by candles. Then from 6 to 10 per cent. of quicklime and from 14 to 16 per cent. of furnace cinders are added, and the furnace turned quickly two or three times to mix the materials thoroughly, when the whole is run out. This method saves considerable time in working, as the preliminary conversion of a portion of the limestone into lime is saved, and the material is left in a condition that is considered by many to be the best for lixiviation.

81. Advantages and Disadvantages of the Mechanical Furnace.—The mechanical furnace has the advantage over the hand furnace in that it makes the manufacturer more independent, as the only skilled man needed is the foreman, who can take care of several of these furnaces. It gives a large output with a comparatively small amount of manual labor, and at the same time a more uniform material is obtained. On the other hand, revolving furnaces are expensive to build, and as frequent repairs are necessary, they are expensive to maintain. But with all this, they are much more economical, and are now almost universally adopted.

82. Cyanides.—One of the most disagreeable impurities occurring in black ash is the sodium cyanide formed from the nitrogen in the coal. This cyanide will unite with iron, if opportunity is offered, and make sodium ferrocyanide, which is very hard to remove from the solution. However, at the end, when the soda ash is calcined, this sodium ferrocyanide decomposes into sodium carbonate and ferric oxide, coloring the soda ash. In the hand furnaces, usually no attempt is made to remove the sodium cyanide from the black ash; but for mechanical furnaces, the *Pechiney-Weldon method* works very well. This process depends on the fact that when sodium cyanide is fused with sodium sulphate the cyanide is decomposed. It is not known exactly what the reaction is, but probably the following equation very nearly expresses the truth:

$$Na_2SO_4 + 2NaCN = Na_2S + Na_2CO_3 + CO + N_2$$

The operation consists in adding a little salt cake to the first finished black ash in the furnace, giving the furnace a few turns to mix the charge thoroughly, and then discharging the black ash at once into barrows. The amount of salt cake required must be determined for each furnace and coal used, as the amount of cyanide will vary as these conditions vary. As there is no time to analyze the black ash just before adding the salt cake, a fixed amount must be decided on and then added to each charge of ash. This is best done by determining the amount of cyanides in several charges of black ash from a furnace, averaging these, calculating the amount of salt cake necessary by the preceding equation, and then adding from four to six times the theoretical amount to the charge each time just before emptying the furnace, as just stated. For example, if an average analysis shows ½ per cent. of sodium cyanide, there will be ½ pound of sodium cyanide in 100 pounds of the mixture, and from the equation

$$Na_2SO_4 + 2NaCN = Na_2S + Na_2CO_3 + CO + N_2,$$

$142 : 98 = x : .5$; or, theoretically, .72 pound of sodium sulphate will be required. It is not very easy to get material of this character in extremely close contact, however, so the excess is necessary, and if six times the theoretical amount is selected, 4.32 pounds of salt cake should be added for every 100 pounds of the mixture used. This is rather an extreme case, as usually the cyanide will not run so high.

Another method for attaining the same result, and one that is much preferred by many manufacturers, consists in adding regulated amounts of salt cake to each furnace charge until the amount is found that gives the most satisfactory result.

83. So far nothing has been said concerning the excess of salt cake added, and it might naturally be considered that there would be enough excess of lime and coal in the black ash to convert it into sodium carbonate, and there no doubt is. It has been found better practice, however, to add about an equal weight of finely ground limestone to the salt cake used before adding it to the mixture in the furnace.

A mixture that has given good results with this process is: Salt cake, 100 parts; limestone, 78 parts; coal, 37.5 parts; and, as a final addition, a mixture of 6 parts of salt cake and 7 parts of powdered limestone.

84. Properties of Black Ash.—A good black ash from a hand furnace should have on the fracture a brownish-black or dark slate-gray color, and a porous, pumice-like structure. It should be uniform in appearance throughout the ball, and should not have many black spots of coal or white spots of limestone. Balls that are pale pink or reddish are usually also dense and burned, and will be found on analysis to be high in sodium sulphide and sodium sulphate. Each man's work for the day should be tested in the laboratory for at least total alkali, sodium sulphide, and sodium sulphate.

Black ash from a mechanical furnace appears quite different from that from a hand furnace, being dense and of a higher color. This ash would be almost impossible to lixiviate were it not for the free limestone contained in it, which on slaking, breaks up the pieces of black ash, so that the water can get at it to dissolve out the sodium carbonate.

85. Composition of Black Ash.—Black ash naturally varies somewhat in composition, but it usually has about 40 per cent. of soluble matter, consisting of the carbonate, oxide, chloride, sulphate, sulphite, thiosulphate, aluminate, silicate, cyanide, and sulphocyanide of sodium; while the insoluble portion consists mainly of the sulphide, carbonate, and oxide of calcium, ferrous sulphide, aluminum oxide, silica, magnesium oxide, carbon, sand, and insoluble sodium compounds of aluminum and silicon. Of course, sodium carbonate, calcium sulphide, and calcium oxide are the preponderating substances.

86. Lixiviation of Black Ash.—The black ash when removed from the furnace is very hot, and must be allowed to lie and cool until it can be conveniently broken and handled. This usually requires about 2 days. Black ash should not, however, be allowed to lie longer than is necessary, for the moisture, carbon dioxide, and oxygen of the air act on it. The carbon dioxide converts the lime into calcium carbonate, and the calcium sulphide into calcium carbonate and hydrogen sulphide. The oxygen converts calcium sulphide into calcium sulphate and various intermediate oxidation products. Finally, the moisture aids in the formation of sodium sulphate, sulphide, etc., from the calcium salts and sodium carbonates, and thus causes a loss of the valuable sodium carbonate.

Various difficulties must be overcome in the lixiviation; for the lime is slaked and tends to react with the sodium carbonate, as just stated, while the calcium sulphide also reacts to form the sulphide of sodium. This takes place rapidly, especially if the solution is hot and dilute. Furthermore, unless the material is protected from the air, the oxidation of the calcium sulphide to sulphate and then a reaction between that and the sodium carbonate takes place here as well as in the preceding case. It is necessary then to lixiviate away from the air as rapidly as possible and to keep the liquid cold. These last two conditions seem to be and are directly opposed to each other, but a temperature is selected that will give the most rapid extraction with the least trouble in other directions.

87. Shank's Lixiviation System.—The system for lixiviating the black ash known as **Shank's lixiviation system** has practically displaced all other systems, as it is rational, simple, and efficient. The lixiviating apparatus consists of one large tank divided into from four to eight watertight compartments. Each compartment has a false bottom of perforated sheet iron, which serves to support the lumps of black ash and to act as a filter for the solution of sodium carbonate. A pipe leads from under the false bottom of each section of the apparatus to a point near the top of the other sections, so that the different sections may be connected together at will; each section has a pipe for supplying fresh water when necessary. Frequently, the sections are fitted with steam connections as well, so that the liquid may be warmed, if desirable.

88. In working, either water or dilute lye flows in at the top of the section, and as it dissolves more material, it becomes heavier and sinks to the bottom of the tank; it is then forced into the next tank by the fresh incoming lye. This process is continued until the liquid finally flows away sufficiently concentrated. The pipes are so arranged that the contents of the various tanks are always completely covered. The process is continuous, the water flowing into the tank containing the most nearly extracted black ash and flowing away from the last and most recently charged tank as long as the specific gravity does not fall below 1.25. As soon as the specific gravity of the lye from the last tank falls below 1.25, the water or a dilute solution of lye is turned into a tank recently filled with new ash, and the exhausted ash is washed with water until the wash water has a specific gravity of only 1.005. Then the waste is sent to the dump, and the tank is freshly charged to serve as the end tank in its turn. The best temperature for lixiviation to give concentrated solutions is about 50° C., which is usually reached by the heat from the slaking of the lime when the lye comes in contact with the fresh ash. If this does not occur, the temperature can be raised by blowing in steam. In the first one or two tanks of the series, where the lye is weak, the temperature is not allowed to get below 35° C. The black ash, as can be shown by extracting with alcohol, contains no sodium hydrate or sodium sulphide; the lye obtained from its lixiviation contains not only these substances, but various other soda compounds formed by interchange during the lixiviation.

Although the composition of the various lyes differs considerably, depending on the conditions of lixiviation, etc., the following analysis of a lye of 1.25 specific gravity will give an idea of the general character of such solutions. The solution contained 313.9 grams of solid substance per liter, and the solid had the following composition:

	PER CENT.
Sodium carbonate	71.30
Sodium hydrate	24.50
Sodium chloride	1.90
Sodium sulphide	.10
Sodium thiosulphate	.37
Sodium sulphate	.24
Sodium cyanide	.09
Alumina	1.51
Silica	.19
Iron	traces

89. Purification of the Lye.—The lye contains considerable finely divided suspended matter, and is therefore allowed to stand for a time in a warm place to allow it to settle and become clear. The iron compounds, if left in the lye, would decompose at a later stage of the process and color the ash. The sodium ferrocyanide may be decomposed by heating the lye to 180° C., the following reaction taking place between the sodium ferrocyanide, sodium thiosulphate, and sodium carbonate:

$$Na_4Fe(CN)_6 + 5Na_2S_2O_3 + 2Na_2CO_3 + 3H_2O = 5NaCNS$$
$$+ 5Na_2SO_3 + NaCHO_2 + NH_3 + 2NaHCO_3 + FeO$$

This method is difficult and expensive, however, so that it is far better to use the Peçhiney-Weldon method and thus exclude the ferrocyanide from the black ash and also from the lye. The iron sulphate may be separated by allowing the lye to stand exposed to the air, when the iron sulphide slowly separates out. This method is slow, however, and it is better and more customary to allow the lye to flow down ropes and chains in tall towers, up which are passing carbon dioxide and oxygen from the black-ash furnaces or from lime kilns. By this means, the caustic soda is carbonated, forming sodium carbonate; the iron is precipitated, and the sodium sulphide is converted into sodium carbonate with the liberation of the hydrogen sulphide. This last reaction is not complete under practical conditions, so that zinc hydrate is sometimes mixed with lye at this point to complete the removal of the sodium sulphide.

90. Paull's Method.—The method of purifying the tank liquor known as **Paull's method** consists in mixing it with a little Weldon mud (see *Alkalies and Hydrochloric Acid*, Part 2) and then blowing in air and steam until the sodium sulphide is thoroughly oxidized and the iron, silica, and alumina are precipitated. About 2 pounds of manganese dioxide to every 100 pounds of sodium carbonate in the solution is a suitable proportion.

If, for the sake of convenience, Weldon mud is considered as manganese dioxide, the reactions may be written as follows:

$$2Na_2S + 4MnO_2 + 5H_2O = 2NaOH + Na_2S_2O_3 + 4Mn(OH)_2$$
$$4Mn(OH)_2 + 2O_2 = 4MnO_2 + H_2O$$

Since the manganese dioxide is continuously recovered, except the small amount carried away mechanically, it may be used over and over until, through the precipitation of ferric hydrate, silica, aluminum hydrate, etc., the precipitate becomes too bulky to handle, when it must be thrown out and new Weldon mud supplied.

91. Evaporation of the Tank Liquor.—The tank liquor, after settling and purification, is evaporated to obtain the sodium carbonate. The methods of evaporating the tank liquor may be conveniently divided into three classes, that is, *in pans by surface heat*, *in pans by heat underneath*, and *in pans with mechanical stirrers*, by means of which the sodium-carbonate crystals are fished out as soon as formed. Of these three methods, the one using surface heat is the most common; it is very convenient, for it utilizes the waste heat from the black-ash furnace.

92. Surface-Heat Evaporation.—The pans for **surface-heat evaporation** are shown in connection with the black-ash furnaces illustrated in Figs. 14 and 15. They are of very simple construction and are made of about $\frac{3}{8}$-inch sheet iron. They are provided with two or three doors, as the case may be, and are so formed that the contents (crystals and mother liquor) can be drawn out on the draining table *h*, Figs. 14 and 15. During the evaporation of the liquor, the doors are closed, and, to make them tight, they are luted on with clay.

In working the pan after the doors are closed, the pan is filled with the clear settled liquor, and the waste gases from the black-ash furnace are allowed to pass over the surface of the liquor. This soon causes the liquor to boil, and the current of hot gas, by carrying away the vapor as fast as it is formed, rapidly concentrates the solution. From time to time fresh liquor is run in until the pan is nearly filled with crystals, when the evaporation is allowed to continue until the mixture of crystals and mother liquor has about the consistency of mortar. The doors are then removed, the mother liquor allowed to run off, and the whole mass brought on to the draining table. The mother liquor, called "red liquor," is allowed to drain off until another panful is nearly ready to run out, when the crystals are removed to a special drainer, where they are allowed to lie and drain for 24 hours.

The surface evaporation has the advantage that it is rapid, but the disadvantage that the sulphur dioxide from the fire gases is all absorbed here and causes a loss of sodium carbonate. Dust from the black-ash furnace is also carried over into the pan and thus makes the salts impure.

93. Pans With Heat Below.—Pans heated underneath have the disadvantages that they do not last so long and that they are neither so effective nor so economical; but, on the other hand, they give a purer product, and the loss of sodium carbonate, through the acids in the heating gas, is avoided. Various shapes of pans are in use for this purpose, but those built boat-shaped (that is, with sloping sides and a narrow bottom) and heated more along the sides than on the direct bottom, are the best; for in these, by the boiling, the sodium-carbonate crystals, as they separate, settle in the narrow, bottom portion of the pan, where they are away from the direct heat of the fire and from which place they can be scooped out. However, even with this style of pan, there is always more or less trouble through the crystals burning fast to the bottom of the pan.

94. Mechanical Pans.—The **mechanical pans** are also heated by outside fire, but they have mechanical stirring devices that not only prevent the crystals from sticking to the bottom of the pan, but save labor by working the crystals to the end of the pan and finally lifting them out to drain. By this system, fresh liquor can be run in continuously and the salts removed until the mother liquor gets too thick with caustic soda and sodium sulphide, when it is drawn off and fresh liquor started again.

The most satisfactory pan of this type is the *Thelan pan* shown in Fig. 16. This pan consists of a semicircular iron pan *a*, which is heated on the outside by the fire from the grate *d*. The hot gases circulate under the pan and escape to the chimney at the opposite end. The scrapers *b*, which are rotated by the shaft and gear *c*, prevent the separated salt from burning fast to the pan and move it to the end, where it is lifted to a draining apron. From the draining apron the salt is moved to a large draining table, where it is allowed to drain for 24 hours before being calcined.

95. Calcining the Crystals.—The salt that separates from the evaporating pan is dark in color and is known as the *black salt*. It consists mainly of monohydrated sodium carbonate, $Na_2CO_3 \cdot H_2O$, and must be calcined to remove the water and to oxidize any remaining sodium sulphide and organic matter. The calcining usually takes place in a reverberatory furnace, similar to a black-ash furnace, and the charge may be brought to a dull-red heat, but must not be fused. During the drying, the material should be turned over and the lumps broken up, but further than this the operation requires very little attention outside of charging and discharging the furnace and taking care of the fire.

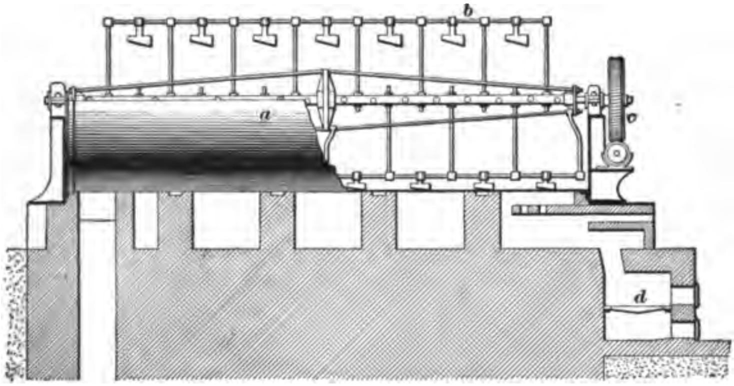


FIG. 16

96. Grinding the Soda Ash.—By calcining the black salt, the material is caused to cake together, so that it is necessary to grind it before putting it on the market. This operation is carried out in ordinary mills, such as are used for grinding grain in making flour.

SODA CRYSTALS

97. Sodium carbonate crystallizes at ordinary temperatures with 10 molecules of water, forming crystals that are generally known as *sal soda*, or *washing soda*. These crystals contain 63 per cent. of water, and many dealers consider the crystallized material so much better than the calcined soda ash that they are willing to pay the freight on all the water in order to have the crystals. This attitude was justified before ammonia soda came into the market in such large quantities, for the soda crystals were purer than any of the soda ash then available. At the present time, most of the crystal soda is sold for household purposes. It is better than soda ash for laundry purposes, for it dissolves quickly, and thus avoids the danger of particles of the undissolved soda getting on the linen and damaging it.

The soda crystals, $Na_2CO_3 \cdot 10H_2O$, are manufactured from the calcined soda ash. This substance is dissolved in hot water and allowed to stand and settle until quite clear, when it is run into iron crystallizing pans. The size and shape of these pans vary considerably, but these features are not of material importance; the essential thing is a pan that will cool slowly and not render the solution impure. These pans are allowed to stand from 5 days, in winter, to 15 days, in summer, to permit crystallization. When the crystallization is complete, that is, when no more crystals form, a hole is broken in the crust and the mother liquor is drawn off. The crystals are then drained and packed.

Soda crystals made from pure soda ash are soft and unsatisfactory. It has therefore been found advisable to have enough sodium sulphate in the solution so that the crystals will contain from 1 to 1½ per cent. of sodium sulphate. For some reason, this admixture of sodium sulphate renders the crystals hard.

98. Yield.—Owing to a number of causes, only about 82 per cent. of sodium sulphate occurring in 96-per-cent. salt cake is finally converted into sodium carbonate; or, from

100 tons of salt cake, 61 tons of real sodium carbonate is produced. Sometimes 63 tons is obtained under favorable conditions. The main sources of loss are a mechanical carrying away of part of the charge by the fire gases in the black-ash furnace, and a volatilization of another part by the high heat. A portion of the sodium sulphate fluxes with the brick lining of the furnace and the coal ashes, and forms insoluble sodium compounds. There is always a more or less incomplete conversion of sodium sulphate into sodium carbonate, and a further loss by necessarily incomplete lixiviation. Finally, the action of the water, by causing a reverse reaction, causes a loss of soda.

99. Finished Soda Ash.—The finished product from the Le Blanc method of the manufacture of soda ash should be white or nearly so, and should show very few reddish specks after grinding. It should not contain over 2½ per cent. of sodium hydrate (unless intended for special purposes), nor should the insoluble matter exceed 1 per cent. Neither should it be possible to detect sulphides in the finished soda ash, and the sulphate should not exceed .1 per cent. Sodium chloride and sulphate are always present and are harmless, but they should not exceed 4 per cent.

100. Uses of Sodium Carbonate.—Sodium carbonate is used for an almost unlimited number of purposes, for some of which sodium bicarbonate, or caustic soda, is also used and frequently to better advantage. The most important uses for soda ash may be enumerated as follows: (1) The manufacture of the various kinds of glass. In the place of soda, salt cake is frequently used for this purpose. (2) The making of various kinds of hard soap. Caustic soda is also used for soap making. (3) The manufacture of borax and various other sodium compounds. (4) In the preparation of starch, the manufacture of glucose, the preparation of the fatty acids, the purification of oils, and in the organic manufactures where an alkaline base is required, or where it is necessary to neutralize an acid. (5) For scouring, dyeing, etc., in cloth manufacturing.

101. Methods of Stating Strength of Soda Ash. Soda ash may contain varying amounts of sodium sulphate, sodium chloride, and various other substances that have no value as alkali. The methods of determining the amount of available alkali in a sample of soda are more suitably explained in a treatise on chemical analysis; but since the methods for stating this value vary considerably, it is desirable that they should be explained here.

The French express the value of their soda ash in degrees Descroizilles. This value is based on the reaction between sodium carbonate and sulphuric acid, and is expressed in terms of the number of parts, by weight, of 100 per cent. of sulphuric acid that is necessary to neutralize 100 parts of the substance. Since 53 parts, by weight, of sodium carbonate will neutralize 49 parts, by weight, of sulphuric acid, then 100 parts, by weight, of chemically pure sodium carbonate will neutralize 92.45 parts, by weight, of sulphuric acid; therefore, chemically pure soda is 92.45° Descroizilles. By the same reasoning, chemically pure sodium hydroxide is 122.5° Descroizilles.

The Germans very rationally report the percentage of sodium carbonate in the sample. Since, however, by the method of determining this percentage, caustic soda will also be determined and reported as carbonate, which may have the peculiar effect of showing a substance to be 120 per cent. pure, this method is not so suitable as the English method.

The English rate their alkali on the percentage of real or available alkali, that is, on the percentage of Na_2O, in the case of both sodium carbonate and hydrate. This method seems to be the most rational, for it is the real alkali that is of value, and it does not matter so much in what form it is; therefore, the percentage of the valuable constituent is given. This system is also somewhat used in France, and is there called the Gay-Lussac degree. Unfortunately, when this system was established in England, the values of the atomic weights were not exactly determined, and 32 was used as the equivalent weight of Na_2O, instead of the more correct value 31. Although this error is known to exist, it is still retained, either through dishonesty or neglect to make a change.

In the United States, the English system is quite generally adopted, using the correct equivalent for Na_2O, although in New York and some other large cities, where considerable soda is imported from England, the English and Liverpool degrees are also in use.

Soda ash is generally sold in the American, and always in the English, market on a basis of 48 per cent. Na_2O, Liverpool test. The corresponding true percentage may be readily determined by referring to Table III, and applying ordinary proportion.

TABLE III

VALUE OF SODA ASH BY VARIOUS METHODS

Percentage Sodium Carbonate, Na_2CO_3	Actual Alkali, Na_2O	English Alkali Test, Na_2O	Liverpool Alkali Test, Na_2O	Descroizilles Degrees
79.51	46.5	47.11	48.00	73.57
82.07	48.0	48.63	49.54	75.87
85.48	50.0	50.66	51.61	79.03
88.90	52.0	52.68	53.67	82.19
90.61	53.0	53.70	54.70	83.77
94.03	55.0	55.72	56.77	86.93
97.45	57.0	57.75	58.83	90.09
99.16	58.0	58.76	59.87	91.68
100.02	58.5	59.27	60.38	92.45

TANK WASTE

102. The residue that is left after the removal of the soluble constituents from the black ash consists mainly of the sulphide and carbonate of calcium, with small amounts of various other substances, and is generally called the **tank waste.** Practically all the sulphur that was contained in the sodium sulphate is left in this waste, and therefore, unless it can be recovered, it represents an enormous loss of money. In addition to that, this waste requires room for dumps, and, by weathering, it produces an almost intolerable nuisance, due to the escape of hydrogen sulphide and sulphur dioxide into the air. The weathering of the tank waste also causes the formation of polysulphides of sodium and calcium, forming the so-called *yellow liquors*, which run into streams and sewers and contaminate them and which also saturate the soil of the neighborhood, spoiling the wells and doing other damage.

Table IV gives an idea of the composition of tank waste from mechanical and hand furnaces.

TABLE IV

COMPOSITION OF TANK WASTE FROM MECHANICAL AND HAND FURNACES

Constituents	Mechanical Furnace Per Cent.	Hand Furnace Per Cent.
Sodium carbonate	2.9	2.5
Calcium carbonate	24.7	33.2
Calcium hydrate	1.0	9.0
Calcium sulphide	54.7	37.3
Calcium thiosulphate	.5	2.0
Calcium sulphite	trace	
Calcium sulphate	trace	.3
Calcium silicate	2.5	1.0
Carbon	8.4	6.4
Alumina	.8	.5
Ferrous sulphide	1.5	2.5
Sand	2.0	5.0

These analyses are made on the dry substance, so that in addition to the percentages given in the table, it is necessary to calculate about 30 per cent. of water in the composition of the waste.

103. The disposal of this waste material has been one of the important problems of the Le Blanc manufacturer ever since the industry became sufficiently important for the waste to be noticed, although the problem is now practically solved. However, this waste will still continue to trouble the manufacturer unless he adopts the process about to be described. If this process is not adopted, the waste is best disposed of, when the works are located near the seacoast, by loading it on scows, towing it out to sea, and dumping it. This, of course, wastes the sulphur, but it avoids the nuisance. Where the tank waste cannot be conveniently sent to sea and a recovery process cannot be profitably employed, the waste may be spread out evenly and then packed down to prevent, as far as possible, infiltration by the rain.

The processes that have been proposed for recovering the sulphur from the waste are numerous, but only one has proved permanently successful; and, strange as it may seem, so far only a part of the waste is worked for sulphur recovery.

104. Chance-Claus Process.—The only process that has ever been commercially successful and the only one that is in successful operation today for the recovery of the sulphur from tank waste, is the so-called **Chance-Claus process.** This process depends essentially on the decomposition of the waste by carbon dioxide, which was proposed by Gossage in 1836. Gossage believed in the process so thoroughly that he spent 30 years of his life and a fortune in money striving to perfect it, but without success. His principal difficulties were that he could not get the escaping gas rich enough in hydrogen sulphide and that its composition varied too much. The attainment of this result, together with a method for getting the sulphur from the hydrogen sulphide, comprise the achievements of Chance and Claus.

105. In carrying out the process, the tank waste is made into a slurry with water and then charged into a cylinder. A battery of seven cylinders is usually employed, and these are so arranged that the gas can be passed from one cylinder to any other. In operation, six cylinders are in use and one is being emptied and recharged. The gas used must be of regular composition and must contain not less than 30 per cent. of carbon dioxide. This is best obtained from lime kilns similar to those used in the ammonia-soda process. The gas is passed into the cylinder containing the most nearly exhausted material, where it sets free the hydrogen sulphide according to the reaction

$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S$$

This hydrogen sulphide passes into the following cylinders, where it is absorbed by the calcium sulphide

$$CaS + H_2S = Ca(SH)_2$$

Since the most recently charged cylinder is placed last, all the hydrogen sulphide is practically absorbed, and the escaping gas is almost completely free from it and might escape directly into the air. For the sake of safety, this gas is usually run through a purifier similar to those used to purify coal gas and containing either oxide of iron or lime. The plan most generally pursued, however, is to pass the gas through earthenware towers packed with coke, down which sufficient water trickles to absorb the hydrogen sulphide.

106. When the contents of the last two or three cylinders are nearly converted into calcium sulphydrate, the escaping gas begins to be stronger in hydrogen sulphide. At this point the back cylinders are tested to see if the gas will burn, for this is an indication that it contains 30 per cent. or more of hydrogen sulphide. As soon as the gas from one of the intermediate cylinders is found to be strong enough, it is put in connection with a gas holder and the gas collected until its composition falls below 30 per cent. of hydrogen sulphide. (The water lute of the gasometer is shut off from the air by a heavy layer of oil to prevent the escape of the gas into the air.) When the gas contains less than 30 per cent. of hydrogen sulphide, it is turned into freshly charged cylinders, and the first cylinder, the contents of which should be so free from sulphides by this time that they do not blacken lead paper, is emptied and recharged with fresh slurry. The water from this residue is so pure that it can be run directly into the streams, while the solid material, which contains over 85 per cent. of calcium carbonate, can be used either for fresh black-ash mix or for making cement.

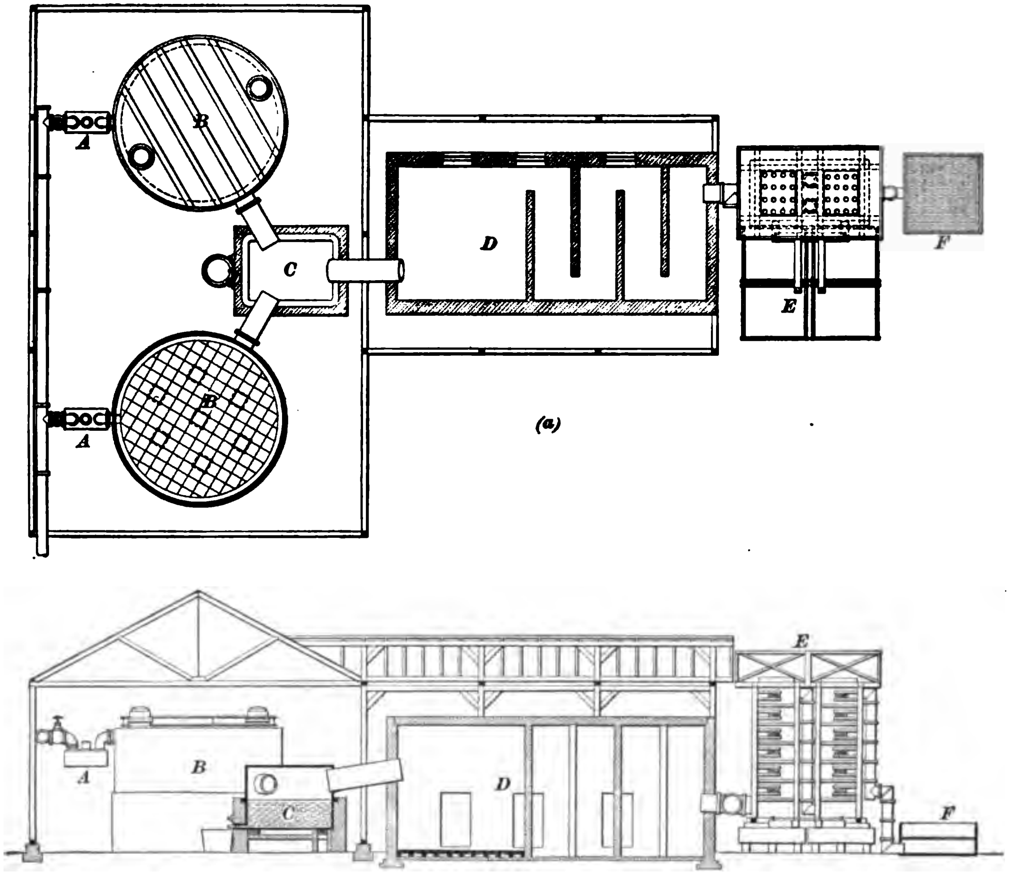
107. The hydrogen sulphide is so strong that it can be burned direct for the manufacture of sulphuric acid, and it yields an exceedingly pure acid free from arsenic. The greater part of the gas is converted into sulphur, however, for the sulphur is more valuable in the free condition than in sulphuric acid. What has probably done the most to make the Chance-Claus sulphur-recovery process commercially successful, is the method of converting the hydrogen-sulphide gas into sulphur. This consists in passing through iron oxide heated to dull redness a mixture of hydrogen sulphide and air in the proportions given by the equation

$$2H_2S + O_2 = 2H_2O + 2S$$

When the kiln is first started, it is necessary to heat the iron oxide to the proper temperature; but when once started, the reaction keeps the temperature of the oxide high enough to continue the reaction. The quality of the oxide of iron used as a catalytic agent in this process is highly important. The hematite obtained from the Cleveland district in England is found best adapted for this purpose.

108. Claus Kiln.—Fig. 17 shows the **Claus kiln,** as used at present in the Chance-Claus sulphur-recovery process. The gas is mixed in the gas holders with a proper amount of air for its decomposition, according to the equation in the preceding article.

The composition of this mixture must be very carefully determined by analyses, and the amount of air should be regulated so that there will be just sufficient oxygen to burn the hydrogen of the hydrogen sulphide, but no excess. By determining the amount of hydrogen sulphide in the gas in the holder, it is easy to calculate the amount of air necessary to add to make the proper mixture. From the equation,



(a)

(b)

FIG. 17

it is seen at once that each volume of hydrogen sulphide requires $\frac{1}{2}$ volume of oxygen. Then, if the gas in the holder is 32 per cent., by volume, hydrogen sulphide, each liter of the gas will contain .32 liter of hydrogen sulphide, which will require .16 liter of oxygen, but the air only contains 21 per cent. of oxygen, so that it becomes necessary to take $\frac{16}{21}$, or .76, liter of air; that is, 3 volumes of air must be mixed with every 4 volumes of the gas from the holder. Of course, when the gas from the holder has a different composition, the amount of air must be varied; thus it is very essential for the success of this process that the gas be of a very uniform composition, and that the work be constantly controlled by analyses. The gas mixture passes from the gas holder through its conduction pipe and the lute *A*, to prevent the flame from striking back and exploding the gas holder, into the top of the kiln proper *B*. This kiln is made of iron, is about 9 feet high, and, on an average, is 25 feet in diameter; it has a grate that bears a layer of broken bricks, on which is about 12 inches of ferric oxide. At first the gas was passed in at the bottom of the kiln, but it was found that here, as is generally the case where a gas must come in intimate contact with a solid, a better result is obtained by passing the gas mixture down through the oxide. In starting a kiln, a fire is built on the iron oxide and kept going until the oxide is red hot; the gas mixture is then turned in and the reaction between the oxygen of the air and the hydrogen sulphide takes place. The temperature of the oxide is kept up without any further outside heat. The best temperature is about 230° C., taken at the exit pipe of the kiln. The reaction is a reversible one, so that it will never be quite complete, and it is not possible to add an excess of oxygen to force it, for in that case sulphur dioxide in too large quantities would be formed.

From the kiln, the products pass into a small chamber *C*, where the molten sulphur deposits, while the gases and sulphur vapor pass into the larger chamber *D*, where the sulphur vapor deposits as flowers of sulphur and some of the steam is condensed. This chamber contains walls part way across, as shown in the figure. These walls serve as baffle plates and separate the fine sulphur, which would otherwise be carried into the washing tower and clog it, and at the same time be lost. From *D* the gases pass through the washing tower *E*, down which water is kept flowing to remove sulphur dioxide from the gas. It then passes through a purifier *F* containing lime or iron oxide, to remove the last of the hydrogen sulphide, so that the gas escaping into the air is practically pure nitrogen.

109. This process, when working well, recovers from 85 to 90 per cent. of the sulphur in the waste and entirely abates the nuisance otherwise due to the waste decomposing in the open air. The cost of the installation of the plant is small, and its operation is not expensive. The present price of sulphur, which is about $22.50 per ton of 2,240 pounds, fully warrants the investment. The cost of the recovery at the most is not over $10 per gross ton, including packages. In some large works, the cost is very much below that figure. The sulphur is 100 per cent. pure, and it can be molded into rolls or condensed as flowers of sulphur. Either of these forms brings a very much higher price than is obtained for crude brimstone.

In order to illustrate, it will be necessary to start with pyrites for the manufacture of sulphuric acid, which in turn is used for the manufacture of salt cake, which in turn is converted into soda ash with the recovery of the sulphur in part, originally present in the pyrites and existing in the tank waste.

One ton, 2,240 pounds, of 50 per cent. pyrites costs, say, $7.50, and is equivalent to	1,120 pounds of sulphur
Loss in converting into sulphuric acid and remaining in the ore, say 5 per cent., is	56 pounds of sulphur
Amount remaining	1,064 pounds of sulphur
This 1,064 pounds of sulphur is equivalent to	3,258 pounds of sulphuric acid
Loss in converting it into sodium sulphate, 4 per cent., is	130 pounds of sulphuric acid
Amount remaining	3,128 pounds of sulphuric acid

This 3,128 pounds of H_2SO_4 is equivalent to	4,532 pounds of sodium sulphate	
Say 82 per cent. of this sodium sulphate is utilized by conversion into soda ash, making	3,716 pounds of sodium sulphate	
The equivalent amount of sulphur present as sulphuric acid reconverted into sulphur is	837 pounds of sulphur	
Less 10-per-cent. loss in converting	83 pounds of sulphur	
Thus, the sulphur from the original 1,120 pounds present in the pyrites is	754 pounds of sulphur	
Value of 754 pounds of sulphur at $22.50 per gross ton is		$7.57
Cost of recovery at $10 per gross ton is		3.37
Difference		$4.20
But as this sulphur is 100 per cent. pure, it has a value of at least $1.50 per 100 pounds; hence, it is worth		$11.31
The cost of recovery at $10 per gross ton is		3.37
Difference		$7.94

Thus, it is evident that the entire cost of the sulphur originally present may be regained, and at the most, even if sold as crude brimstone, the original 1,120 pounds of sulphur present in 1 ton of pyrites will have cost the manufacturer only $3.30, or $6.60 per ton of sulphur present in the ore. Not this alone, but the intolerable nuisance of disposing of tank waste is entirely obviated.

110. The perfection of this process has given the Le Blanc process a new lease of life in England, and the manufacturers in that country are now competing successfully with the ammonia-soda process, wherein the chlorine is lost, but which, as will be shown later, is utilized in the Le Blanc process either as hydrochloric acid or as bleaching powder. Coupled with this improvement, the Le Blanc process should find a profitable use in the United States in utilizing the large quantities of niter cake or acid sulphate of sodium derived from the manufacture of nitric acid, by acting on the nitrate of sodium with an excess of sulphuric acid. In many works, large quantities of this valuable salt are exposed to the weather and allowed to waste away. In others, this salt is dumped into estuaries or water courses, resulting in their contamination.

111. Sodium Thiosulphate.—Since **sodium thiosulphate**, or what is more commonly known as *sodium hyposulphite*, or *hypo*, is made almost exclusively from tank waste, it deserves a few words here. It is made by blowing air through the waste suspended in water until all the sulphide is converted into calcium sulphite and thiosulphate, and then adding sodium sulphate or carbonate, which gives the insoluble calcium salt and leaves sodium thiosulphate in solution. This is boiled with sulphur to convert the sulphite into thiosulphate, and then crystallized out and purified by recrystallization.

Another method is to pass sulphur dioxide into the waste, thus converting the sulphide into thiosulphate according to the reaction

$$2CaS + 3SO_2 = 2CaS_2O_3 + S$$

and then converting it into the sodium salt as just stated. Sodium thiosulphate forms soluble salts with silver, thus dissolving silver iodide and chloride. For this reason it is used to a great extent in photography and in the metallurgy of silver. It is also used as an antichlor in paper making, in certain kinds of dyeing, and for various other purposes.

ALKALIES AND HYDROCHLORIC ACID

(PART 2)

CHEMICAL METHODS—(Continued)

SODIUM HYDRATE.

1. Historical.—The manufacture of **sodium hydrate** on a large scale does not date back nearly so far as the manufacture of soda ash. It is true that caustic soda has been used for soap making almost as long as soap has been known, but for a long time the soda was made at the soap manufactory and used in the form of solution. It was not until 1850 that the manufacture of caustic soda, as such, began, and then only on a small scale; and it was not until 1860 that the manufacture attained any considerable importance. From that time on, however, more and more caustic soda has been made, until now its manufacture is an important branch of the alkali industry.

2. Sodium Carbonate and Lime.—The most common process for the preparation of caustic soda is based on the reaction between sodium carbonate and slaked lime. This reaction is

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$$

Since the reaction is a reversible one, the sodium hydrate should not be made too strong, for the stronger the solution is in caustic soda, just so much more tendency is there for it to go toward the formation of calcium hydrate and sodium carbonate. On the other hand, although dilute solutions lead to a high percentage transformation of the sodium carbonate, they require large apparatus and much heat to drive off the water in the making of the solid caustic. It is necessary, therefore, to pursue a middle course. A solution of sodium carbonate of 1.1 specific gravity—that is, about 10 per cent.—is generally considered to be the most advantageous strength for conversion into the hydrate. With a solution of this strength, about 97 per cent. of the sodium carbonate used can be converted into caustic soda, which gives a fair strength of solution.

CRUDE MATERIALS

3. Soda Ash.—The soda from the Le Blanc process is well suited for making caustic soda, for it frequently contains considerable caustic that has been formed by the lixiviation of the black ash, and thus requires less lime than would otherwise be the case. By the addition of a large excess of limestone to the black-ash charge, practically all the sodium can be obtained as the hydrate; this method is sometimes employed. A suitable furnace charge to employ when the tank liquor is to be used for making caustic is 100 parts, by weight, of salt cake, 110 parts of limestone, and 65 parts of coal. Part of the limestone is frequently replaced by caustic mud (see Art. 10) in the proportion of about 20 parts of the mud to 12 parts of limestone. The red liquid (mother liquor from the black salt) from the La Blanc process, in which is concentrated much of the caustic originally in the black ash, is frequently utilized for making caustic soda.

At the ammonia-soda works, the sodium bicarbonate mixed with water is first boiled by steam in a closed apparatus, so that the ammonia and from 75 to 80 per cent. of the bicarbonate carbon dioxide are driven off and utilized in the carbonating towers, while the sodium-carbonate solution, which contains about 20 per cent. of the bicarbonate, is used for making caustic soda.

4\. **Lime.**—The lime used in making caustic must be of good quality, for a low percentage of CaO not only makes necessary the introduction of large amounts of impurity into the causticizing tank, but it also gives a caustic liquor that does not settle well and thus interferes with the work. A satisfactory lime should contain at least 85 per cent. of CaO.

DETAILS OF THE PROCESS

5\. **Causticizing the Sodium Carbonate.**—The causticizing of the sodium carbonate takes place in an iron cylinder that is placed horizontally and is provided with agitators *a*, as shown in Fig. 1. The charge is introduced at *b*, and when finished, is drawn off to a filter at *c*. During the process of causticizing, these openings are closed with plugs. Steam for heating the liquor may be blown in through the pipe *d*. There is also a rack *e* for holding the lime when it is used unslaked. In many works this rack is dispensed with, and the lime, before going to the causticizer as milk of lime, is slaked and passed through a screen so as to remove any lumps.

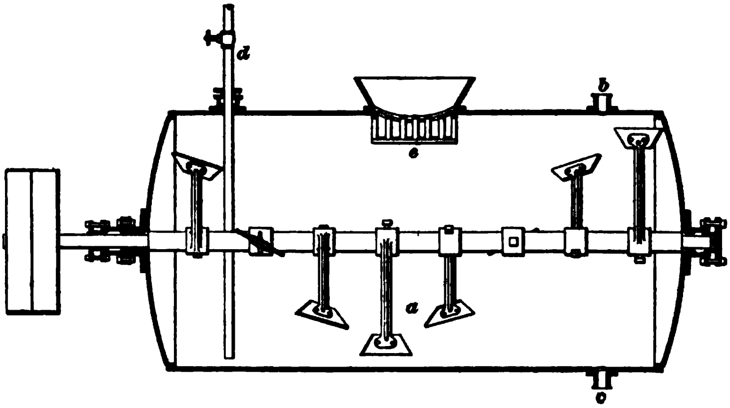


FIG. 1

For this operation, sufficient sodium carbonate of from 1.10 to 1.11 specific gravity is run in, so that when the lime is added the causticizer will be nearly filled. At the ammonia-soda works, the liquor comes hot from the decomposition of the bicarbonate; in other cases, it is better to heat the liquor. Sufficient lime is now added to complete the equation

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH$$

Theoretically, 106 grams of the sodium carbonate will require 56 grams of calcium oxide, or 62.2 grams of quicklime containing 90 per cent. of calcium oxide. Since the preceding reaction is a reversible one, it is advantageous to have an excess of lime present, so that about 10 per cent. in excess of that theoretically required is employed.

The mixture is now kept at a temperature of about 80° C. by blowing in steam, and is constantly stirred by the paddles for 2 or 3 hours, when about 92 per cent. of the sodium carbonate will be causticized.

6. Filtration.—The caustic liquor should now be separated from the calcium carbonate and other suspended material (caustic mud), and although this is done at some works by letting the liquor stand and settle, it is usually filtered. For this purpose, a filter like that shown in Fig. 2 is employed. This filter consists of an iron tank about 20 ft. × 20 ft. and 4 or 5 feet deep that is supported a little above the floor by brick piers, and is sloped so that the liquor drains toward the pipe *a*. On the bottom of the tank are placed strips *b*. These strips are cut out so that the liquor can circulate freely, and on top of them are placed cross-strips *c*. The cross-

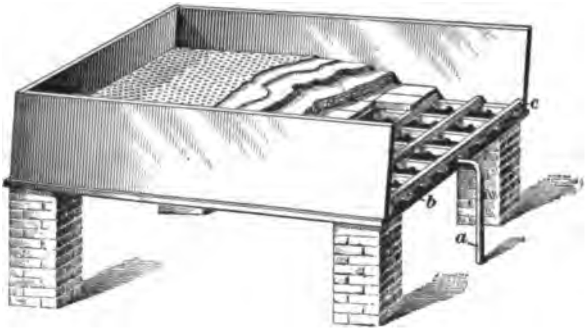


FIG. 2

strips support bricks laid close together, and on top of the bricks is placed a 6-inch layer of coke, about the size of hickory nuts, followed by a 3-inch layer of finer coke, and then a thin layer of clean sand. This is all covered with perforated iron plates so that the workmen can shovel off the caustic mud without disturbing the filter. The pipe *a* leads to the storage tanks, and, during the filtering, is under a vacuum. There is a tendency for the caustic mud to crack and let the liquid through unevenly; therefore, during the filtering and washing, workmen stir the mud occasionally with rakes. When the filtrate has drained off, the caustic mud is well washed, and the washings are collected in a separate tank. The washings are used to dilute liquor for causticizing.

7. **Evaporation.**—The filtrate, which is mainly a dilute solution of sodium hydrate, must now be evaporated, and in the most economical manner, for the evaporation of such dilute solutions is expensive at best. The proposition has been made and carried out in some places to carry on part of the evaporation in the steam boilers and then finally run the stronger liquor into pots to finish the evaporation.

The evaporation of the caustic liquor in steam boilers has several disadvantages and is for the most part abandoned. In a few works, the dilute caustic liquor is at once run into large iron pots that are heated by direct fire until all the water is driven off. In the more progressive works, the caustic liquors are brought up to about 1.3 specific gravity by means of the *Yaryan evaporator* and then run into iron pots that are heated by direct fire.

In the Yaryan evaporator, the same principle is applied as in the Pick evaporator for separating salt from brine. A battery of Yaryans consists of three or four elements that are exactly alike. Each following element, however, works under a lower pressure than the preceding one, so that, although the liquid in No. 2 element is more concentrated than in No. 1, it boils at a lower temperature and therefore can be boiled by steam from No. 1 element. In the same way, the steam from element No. 2 boils the caustic in element No. 3, and so on. Usually, only three elements are worked together in a battery on account of the difficulty of keeping the vacuum high enough in any more elements.

So far, the Yaryan apparatus resembles a large number of other arrangements for working multiple effects. It is in the construction of the elements, however, that the Yaryan is unique. Each element, Fig. 3, consists of an iron shell, inside of which is arranged a number of sets of small copper tubes—five or six tubes being in each set. The liquid to be evaporated enters at *e* and is distributed to the sets of tubes *a*. This liquid circulates back and forth through these tubes in the direction of the arrows, until it finally emerges against the baffle plates in the space *b*. Steam is meanwhile admitted through *f* to the space between the tubes and heats the contents to boiling. The admission of steam is so regulated that all of it practically condenses to water in the apparatus and finally flows away through *g*. This con-

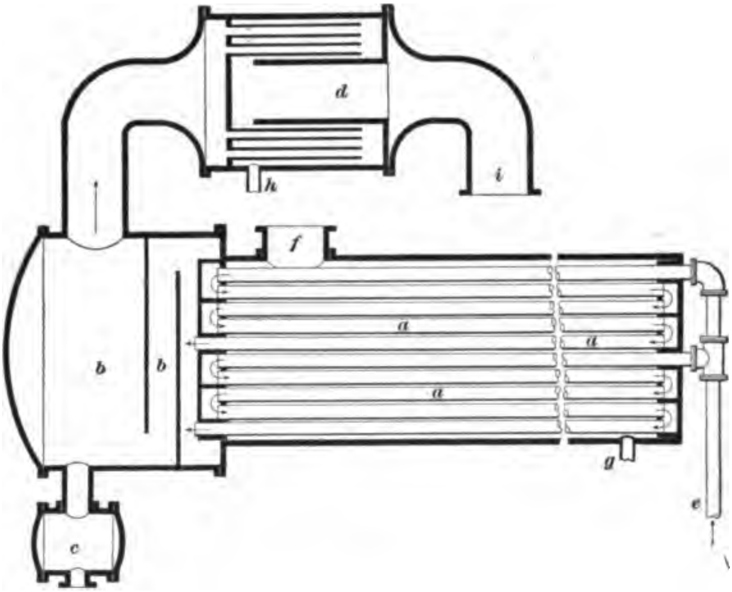


FIG. 3

densed steam can be used for boiler feedwater or similar purposes if desired. The liquid flowing through the tubes is in such a thin layer that, as it boils, it mixes with the steam and fairly foams, so that the liquid comes in contact with all parts of the tubes and gets the full benefit of the heat, thus evaporating rapidly. The foaming mixture of steam and solution issues from the tubes *a*, and by striking against the baffle plates in *b*, is separated. The solution settles and flows through *c* into the next element in the series, where it goes through the tubes in the same way. The steam passes upwards through the "catch-all" *d*, where the last of the particles of the solution, which are carried mechanically by the steam, are separated, and the solution flows through *h* into the next element. The steam then goes through *i*, which connects with *f* of the next element, into the next element, and there boils the solution that it has just left. This solution now passes through the tubes of the next element under a lower pressure than it had in the preceding case.

This system probably gives the most efficient evaporation of any style of evaporating arrangement and is very compact, as the elements can be placed one above the other. The inventor of this apparatus claims that from 23½ to 25 pounds of water can be evaporated with it in triple effect, and 30½ pounds in quadruple effect, per pound of coal, while in the ordinary vacuum pan only 8½ pounds of water is evaporated by the same amount of fuel. The apparatus has the further advantage that it is nearly automatic in its action, thus requiring but little attention, and since it contains only a small amount of liquid at one time, it can be easily stopped and started. The steam for the first element is generated in a boiler kept for that purpose, but for each following element it is supplied as just explained.

8. Caustic Pots.—The evaporation cannot be successfully carried beyond a specific gravity of 1.3 in the Yaryan, for at this point the dissolved salts, such as sodium carbonate, sodium sulphate, etc., begin to separate out. The solution is then run into iron pots, where the evaporation is finished. The salts that crystallize out are from time to time "fished" out, and the heating is continued until all of the water is expelled and fused caustic is left in the pot. The caustic pots are of cast iron and are similar in shape to the cast-iron pans used in making salt cake. They are ordinarily about 6 or 8 feet in diameter, from 3 to 5 feet deep in the deepest part, and are cast with a rim, so that they can be supported on brickwork over a grate. A coal fire is generally used for heating the pots, but since the fire must be allowed to die down when the pot is finished, it has been found very advantageous to use a gas fire for this purpose.

The caustic in the course of its evaporation attacks the metal apparatus with which it comes in contact, so that by the time the evaporation is finished the fused caustic contains copper, iron oxide, and various other substances in suspension, as well as aluminum, silicon, manganese, etc. in solution. As a rule, the substances in solution do not seriously affect the value of the caustic, although, frequently, the manganese is plainly shown by the green, manganate color. It is advisable, however, to remove as much of the suspended matter as possible, and for this purpose, after all the water has been driven off, the fires are cooled somewhat and the fused caustic allowed to stand. The fused caustic is then ladled into sheet-iron drums, which are sealed air-tight as soon as they become cold. In each pot there is a residue containing the settled impurities, which is called the *caustic bottom*. The caustic bottoms are put into drums and sold cheaply for making an inferior grade of soap. When this is not possible, they are left in the pots until they get too bad, when they are dissolved in water, filtered, and reconcentrated.

9. Removal of Sulphur.—In the case of caustic made from Le Blanc soda, the final removal of the sulphur takes place in the pots. The sulphide is best oxidized to thiosulphate, as already stated, by blowing in air. The final oxidation of the thiosulphate, however, is very slow, so that it is assisted by adding niter, a little at a time, until all the sulphide and the thiosulphate have been oxidized to sulphate. Sometimes, instead of oxidizing the sulphide and thus obtaining it in a comparatively valueless form, the sulphur is precipitated as zinc sulphide by using zinc oxide. The reaction is

$$Na_2S + H_2O + ZnO = 2NaOH + ZnS$$

The zinc sulphide is separated before evaporating the caustic liquor, and by calcination can be reconverted into the oxide. After the removal of the sulphur, the caustic is treated as in the preceding case. Owing to the comparatively high price of zinc oxide, this process has been abandoned.

10. Caustic Mud.—The material left on the filter in the filtration of caustic soda is known as **caustic mud,** and consists, especially when ammonia soda is used, principally of calcium carbonate. The composition of the caustic mud from the filter of a works making caustic soda from ammonia soda is as follows:

	PER CENT.
$CaCO_3$	72.05
$Ca(OH)_2$	15.39
$Mg(OH)_2$	5.61
SiO_2	2.80
$Fe_2O_3 + Al_2O_3$	1.70
$CaSO_4$	.29
$NaOH$	.48
H_2O	1.62
	99.94

Many suggestions have been offered for utilizing this material; for instance, to use it instead of limestone in the black-ash charge; to use it for making Portland cement; to use it for whiting; and to press it into form for crayon. Caustic mud has found some use in the still, instead of lime, to set ammonia free from its salts; probably, however, the greater part of this material is still run to waste.

11. Loewig's Process.—When sodium carbonate and ferric oxide are mixed and fused together, carbon dioxide is given off and sodium ferrite is formed according to the reaction

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2$$

For calcination, a revolving furnace is usually employed and the mass is heated to a dull red. After fusion, the sodium ferrite is allowed to cool and is then washed with cold water until all the soluble material is removed; then water of 80° to 90° C. is employed, and the sodium ferrite is decomposed into sodium hydrate and ferric oxide. The reaction is

$$2NaFeO_2 + H_2O = 2NaOH + Fe_2O_3$$

The lixiviation can be carried on so that a caustic liquor of 1.3 specific gravity is obtained direct. This is the strength at which the caustic leaves the Yaryan in the lime process, so that a considerable saving is made in apparatus and fuel, for this liquor can go direct to the pots. From that point the treatment of the liquor is the same as for caustic made from ammonia soda by the lime process. The iron oxide used in this process must be a high-grade natural ore, as free as possible from silica and other impurities, for these would lead to a loss of soda through the formation of insoluble compounds. The iron oxide obtained by igniting precipitated ferric hydrate is not suitable for this purpose, for, on account of its fineness, it gives a product hard to lixiviate and filter. On the other hand, the residue from the lixiviation of the sodium ferrite can be used repeatedly, and extra iron oxide is only needed to make up for the mechanical loss. The process is not especially valuable for making caustic from Le Blanc soda, for the tank liquor must be evaporated and might as well be causticized in solution and then evaporated; however, it seems very well suited for working the solid ammonia soda. Caustic soda of an excellent quality can be made by this process, but it is seldom followed.

12. Uses of Caustic.—Sodium hydrate is used principally in the manufacture of soap, in the making of wood pulp used for manufacturing paper, and in the purification of petroleum and other oils, although large quantities are employed in the purifying of phenol and other organic substances. It is also used extensively in the preparation of coal-tar dyes and in making sodium silicate and other sodium compounds.

SODIUM BICARBONATE

13. For some purposes, the **sodium carbonate** of the ammonia-soda process may be used just as it comes from the filters, but for most uses this is too impure. A few years ago, practically all sodium bicarbonate was made direct from the Le Blanc soda crystals by spreading them on racks and passing carbon dioxide over them. This process had the disadvantage of leaving all the impurities of the soda ash in the bicarbonate, but later the method was improved by dissolving the soda ash in water, or fusing it in its water of crystallization, and passing in carbon dioxide. The bicarbonate then crystallized out, and most of the impurities were left in solution. On account of its great purity, the soda from cryolite was especially valuable for making bicarbonate. The making of sodium bicarbonate from ammonia soda had the disadvantage for some time that it was difficult to free the bicarbonate from ammonia. That difficulty has been overcome, however, and at the present time practically all the best bicarbonate of soda is made from the crude bicarbonate of the ammonia-soda process. Two processes are in use for purifying the crude bicarbonate—the *wet* and the *dry*.

14. **Wet Process.**—The **wet process** consists in dissolving the crude bicarbonate in hot water and saturating the solution with carbon dioxide, and then allowing it to cool and the bicarbonate to crystallize out. The solution can be heated to 65° C. without more than atmospheric pressure, or to a higher temperature if a higher pressure is applied. By this method, nearly all of the salt and other impurities of the crude bicarbonate are left in solution. The recrystallized bicarbonate is filtered off by means of a centrifugal machine and is dried at a low temperature on traveling bands of cloth.

15. Dry Process.—The **dry process** consists in driving off ammonia and moisture by a hot current of carbon dioxide. This process is not so good as the other, for it only removes the volatile impurities from the bicarbonate.

16. Analysis of Bicarbonate.—No matter how it is made, the bicarbonate is ground fine before it is packed for shipment. The following analysis shows the high grade of purity attained by the bicarbonate prepared from the ammonia-soda crude bicarbonate. This sample was prepared by the wet method, which is the one most used.

	Per Cent.
$HNaCO_3$	99.400
Na_2CO_3	.380
$NaCl$	.023
SiO_2	.008
$Al_2O_3 + Fe_2O_3$	.009
Na_2SO_4	.007
$CaCO_3$	.021
$MgCO_3$	.011

HYDROCHLORIC ACID

PROCESS OF MANUFACTURE

17. The manufacture of **hydrochloric acid** is almost inseparably connected with the manufacture of salt cake, and really consists in the condensation of the acid set free in the salt-cake manufacture. In some modern works, salt is decomposed for the hydrochloric acid alone. In such places, the charge of salt is always in excess of the sulphuric acid. for the salt is much cheaper than the acid; also, the more expensive sulphuric acid is more completely utilized than it is in the ordinary salt-cake process. A purer hydrochloric acid is also obtained in this case. The apparatus and methods of working are, with the exception just mentioned, the same as in the making of salt cake. Therefore, merely the condensation of the hydrochloric acid that has been made in the salt-cake manufacture will be considered.

18. Condensation of Hydrochloric Acid.—During the early years of the manufacture of salt cake, the hydrochloric acid had very little value and was allowed to escape freely into the air. But the action of the gas was so bad on vegetation and—although it has not been proved that it has an injurious effect on animals and men—it became such a nuisance as the works increased in number that, in 1862, the Lord Derby Alkali Act was passed in England forbidding manufacturers to allow more than 5 per cent. of the hydrochloric acid to escape into the atmosphere. The present English Alkali Act only allows .2 grain of hydrochloric acid per cubic foot of chimney gas to escape into the atmosphere; this makes it necessary to absorb the acid in water. Formerly, the salt cake was a source of profit and the acid a troublesome by-product, but at present the acid is the chief source of profit. The problem that now confronts the manufacturer is how to get the most complete absorption of the hydrochloric acid in the cheapest manner, and at the same time make the strongest solution of the acid possible. Hydrochloric acid being a gas, its concentration in solution depends on the temperature and pressure. Under ordinary conditions, the strongest and purest acid is about 40 per cent., while in practice the best working gives about 36 per cent. in winter and 30 or 32 per cent. in summer.

19. Usually, the pan acid is absorbed separately from the roaster acid, for the pan gases contain a comparatively high percentage of hydrochloric-acid gas and can be more easily absorbed to a strong acid solution, while the roaster gases tend to give a much weaker and more impure acid. The gas from the pan is cool enough to be conducted away in glass or earthenware pipes; the gas from the roaster, however, is so hot that it would crack these pipes and either brick flues or iron pipes must be used. The brick flues are disadvantageous, because they do not permit rapid cooling, iron pipes are much better, for they permit very rapid cooling, but they cannot be used after the temperature of the gas gets below 200° C. After the roaster acid is fairly cool, it receives the same treatment as the pan acid, so that they will be considered together.

Cold hydrochloric acid absorbed in cold water will generate enough heat at a 16-per-cent. solution to boil water, and at a 20-per-cent. solution to boil hydrochloric acid of that strength; thus, if there is no outside cooling, 20 per cent. is the highest possible strength of the acid. The system should therefore be furnished with an efficient cooling arrangement, although it is now generally recognized that the best plan is to saturate the gas first with water vapor and then condense the mixture to as strong a solution as possible. The essential points to be borne in mind in condensing hydrochloric acid, therefore, are, to cool the gas thoroughly, to keep it cool throughout its condensation, and to bring it into intimate contact with the absorbing water.

20. Apparatus.—The kinds of apparatus used for the condensation of hydrochloric acid and the arrangement of the same have gone through several stages of development, until today the practice in this respect is quite varied. The following arrangement shows most of the various types of apparatus in their best forms, and it gives the most satisfactory condensing arrangement used at present.

Fig. 4 shows an elevation and ground plan of this system. The gas goes from the pan and roaster through pipes *A* and *A'*. The pipe *A* from the pan is made of earthenware tubes tapered so that the small end of one fits into the large end of the next, and so on. The pipe *A'* from the roaster is made of iron for one-half its length and of earthenware for the remainder. The conducting pipes are not made very long, as their function is to conduct the gas to the towers *B* and *B'* and not to cool it, although the gas is somewhat cooled in passing through them. The conducting pipes are sloped downwards to the bottom of *B* and *B'* so that any acid condensing in them will run to the bottom of these towers. The towers are made of stoneware, or preferably of sandstone slabs, as will be explained later on in tower *D*, Fig. 4, and are about 4 feet square and 12 feet high. The

lower half is empty, while the upper half is filled with fireclay cylinders set on end. Water is allowed to flow down these towers in such amounts that practically all is evaporated by the hot acid gas. This water serves the double purpose of washing the sulphuric acid from the gas and of cooling it. The fairly cool gas, saturated with water vapor, now enters the bombonnes *C* and *C'* where it meets a stream of water flowing in the opposite direction to the flow of the gas. This water and the tall connecting pipes of the bombonnes finally condense most of the hydrochloric-acid gas; a certain amount of the acid always escapes condensation here, however, and is removed by the coke tower *D*.

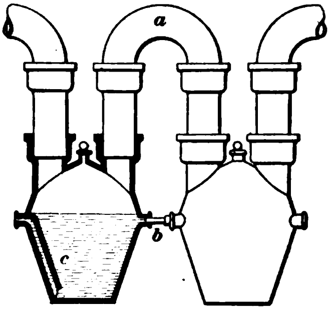


FIG. 5

21. The *bombonnes*, Fig. 5, are made of earthenware and are fitted with rather long earthenware pipes *a*, which serve to cool the gas, as well as to conduct it from one bombonne to the next. The bombonnes are also connected at *b* by ground joints or by a glass tube and rubber stoppers. On the inside of each bombonne there is a pipe *c* to conduct the incoming liquid to the bottom, and naturally the upper portion flows on to the next bombonne in order. From twenty to thirty of these bombonnes are used in series for each pan.

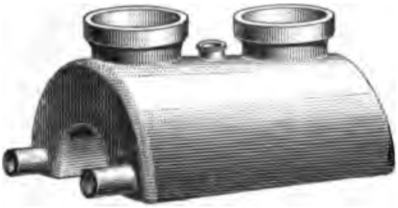


FIG. 6

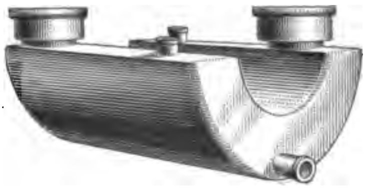


FIG. 7

22. Another form of earthenware receiver that is coming into use is illustrated in Figs. 6 and 7. This receiver possesses an advantage over the bombonnes just described in that it exposes a larger surface, with the result that the heat produced by the absorption of the acid gas by the water or weak acid is more rapidly radiated. In this receiver the connecting pipes are much longer than those shown at *a*, Fig. 5—extending up 10 or 12 feet—and thus offer greater assistance in cooling the gas. These receivers are connected with one another by inserting rubber corks and glass tubing in the tubulures shown.

23. The coke towers *D*, Fig. 4, are made of acid-proof stone slabs that are fastened together by iron bands that have been soaked in tar. These towers should be about 5 feet square and 30 or 40 feet high. Coke is generally employed as packing, but porous stone and other material have been used. The towers are best used in pairs; the acid gas entering at the bottom of one, and rising to its top, is carried by a pipe to the bottom of the next tower, and escapes at the top of this. Water constantly flowing down over the coke absorbs the acid. The packing of the tower requires attention; if it is too loose or the pieces of coke are too large, not enough surface is offered for the acid, while if the packing is too tight, there is not enough draft. The coke used in packing the towers should be the hardest oven coke of the Connellsville variety. In the bottom of the tower should be used the largest and longest pieces, then the smaller pieces in order, until, after an eighth of the way up, pieces 6 or 8 inches by 2 inches mixed with some smaller ones can be used. After one-third of the tower is carefully packed, the remaining space can be filled by dumping in coke that has been freed from all pieces under 2 inches by riddling.

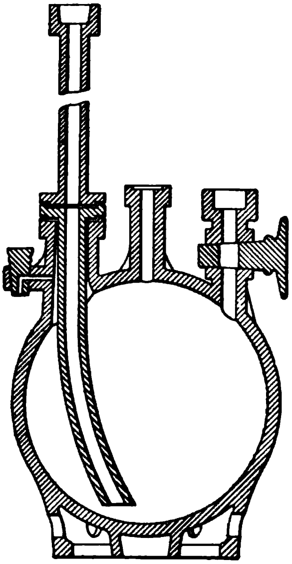


FIG. 8

24. A very necessary adjunct to the apparatus employed for manufacturing and handling hydrochloric acid is the device used for elevating and distributing the acid. Ordinary pumps cannot be used, and the old-style earthenware pumps are liable to break or get out of order. Such pumps have been displaced by the earthenware *monte-jus*, or *acid egg*, a common form of which is shown in Fig. 8. These devices are made with capacities ranging from 25 to 100 gallons, and they will withstand pressures of from 25 pounds per square inch for the larger size to 50 pounds per square inch for the smaller size. In operating, the acid egg is allowed to become full, when, by air pressure, the contents is forced into a large earthenware receiver situated at a higher level, say 35 feet above the acid egg. This device is also used to handle weak acid that has to be put through the system of receivers, or towers, in order to be strengthened.

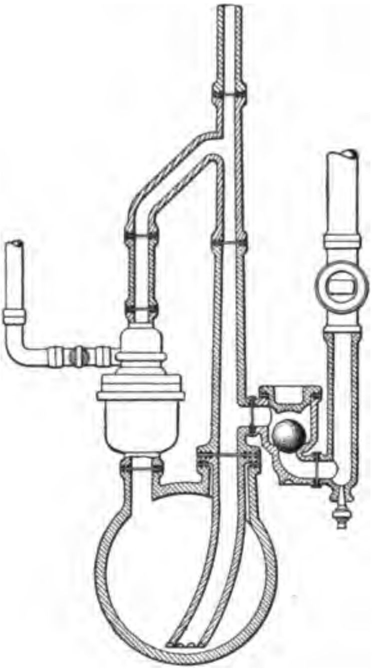


FIG. 9

25. Where large quantities of hydrochloric acid have to be handled, the apparatus shown in Fig. 9 is much better than the monte-jus just described. This apparatus is of earthenware, and is operated on the same principle as a pulsometer, but of course uses compressed air instead of steam. The capacity of this device may be as great as 150 gallons, but the larger the body of the apparatus the less pressure will it stand. The operation is automatic, and having determined the amount of air pressure necessary to elevate the acid to a given height, this pressure is constantly maintained. The acid is allowed to run into this device from a higher level than in the monte-jus, and when the vessel is filled, the supply is automatically cut off, and air is admitted by an earthenware ball acting as a valve. The contents of the acid egg is then driven up through a flanged earthenware pipe to the receiver, which is located at the necessary height above the acid egg for distribution.

This ingenious apparatus is in operation in nearly all large hydrochloric-acid works in Germany and in some works in the United States, and is rapidly gaining favor. It can be used for other acids besides hydrochloric. In using this apparatus, in which compressed air is the motive force, it is necessary to provide a splash egg on top of the receiver vessel so that the air may escape and that the entrained acid will not be splashed about.

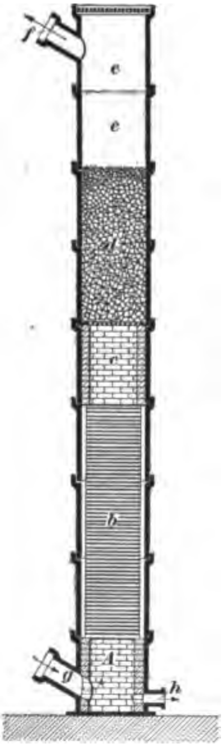


FIG. 10

26. Lunge Plate Tower. Another form of coke tower, or condenser, is obtained by using the **Lunge plates.** The plate tower, Fig. 10, not only occupies from one-tenth to one-twentieth the space required for coke towers, but is even more efficient in absorbing the gas. Of course, the size of the tower will vary with the work required of it, but for ordinary cases, the best tower consists of nine earthenware cylinders, each 3 feet in diameter and 3 feet 3 inches high, set together as indicated in the figures. The first cylinder *A* is left empty; the next three *b* are filled with sixty Lunge plates; the next one *c* is left empty; the next two *d* are filled with coke, and the last two *e* are empty. No matter what size of tower is used, this is the best distribution of the filling. The gas passes in at *g*, meets a descending stream of water or weak hydrochloric acid, which absorbs the hydrochloric acid, and flows out at *h* into the bombonnes. The waste gases pass out through the pipe *f*.

27. Hart System.—A system for the absorption of hydrochloric acid that has much to recommend it in compactness and simplicity has recently been patented by Hart, and although it has not been used long enough to warrant its being called an established method, it deserves some consideration. This system consists of a series of glass pipes *a*, Fig. 11, through which water runs. The water is fed in continuously at *b*, and flows from one pipe to the next until it finally runs into a tank *c* as strong acid. These pipes are cooled by running water over them, the water being supplied by a perforated pipe *d* and the excess being carried off by a drain *e*. The gas comes in at *f*, passes over the strong solution of acid in *c*, and then through the pipes to the flue *h*, where it goes to the chimney.

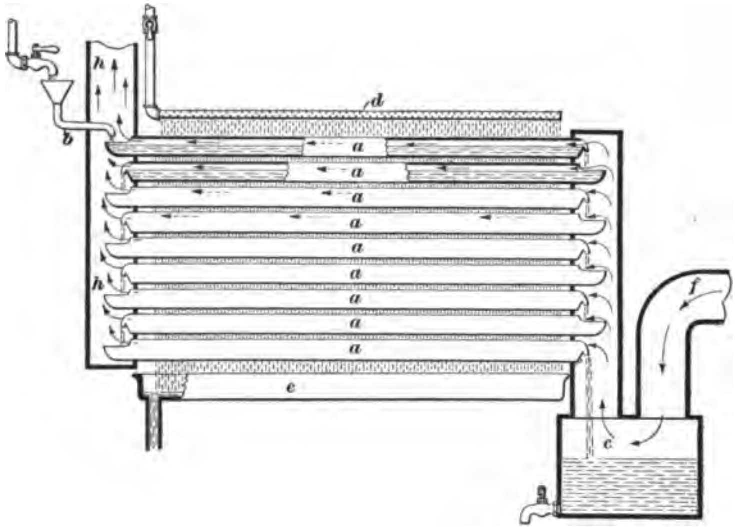


Fig. 11

28. Commercial Hydrochloric, or Muriatic, Acid. The commercial hydrochloric, or muriatic, acid is a yellow-colored solution of the gas in water, usually claiming a specific gravity of 1.2, but rarely containing over 30 or 35 per cent., by weight, of hydrochloric-acid gas, and seldom, if ever, reaching so high a concentration as 40 per cent. of the acid. The yellow color is due mainly to organic matter, for this acid seldom contains enough iron to affect its color seriously. The acid contains, as other impurities, sulphuric acid, chlorine, arsenic, and frequently lead and calcium chlorides.

29. Purification of Hydrochloric Acid.—For many purposes, the crude hydrochloric acid will answer very well, but for others, it must be as nearly chemically pure as possible. For this reason, a method of purification that is suitable in one case will be useless in another; and, furthermore, the question of cost must frequently be taken into consideration. An adoption of one of the following methods will usually meet every demand.

30. The cheapest and most effective method for purifying hydrochloric acid, especially from sulphuric acid, is the so-called **Hasenclever method.** This consists in treating the strong water solution with either concentrated sulphuric acid or calcium chloride, blowing air through the mixture, and heating. The hydrochloric acid is evolved free from practically all the impurities except the arsenic, and may be used in the gas form, as is sometimes done, or reabsorbed in water. In carrying out the Hasenclever method, 100 parts of the crude hydrochloric acid is run into a stone jar with 550 parts of sulphuric acid of 60.4° Baumé, and the mixture is stirred mechanically or by means of a current of air when there is no objection to having air mixed with the hydrochloric acid. The sulphuric acid is thus reduced to 55° Baumé, and is reconcentrated by surface heat after the expulsion of the hydrochloric-acid gas.

31. Sulphuric acid and sulphur dioxide may also be cheaply removed from hydrochloric-acid gas by passing it through towers containing solid sodium chloride. Where arsenic-free acid is needed, it is best to start with arsenic-free sulphuric acid, which is readily obtained by treating acid of 1.55 specific gravity with hydrogen sulphide, when the arsenic is precipitated as sulphide and removed by passing the acid through a sand filter. The acid is then concentrated in leaden pans to a specific gravity of 1.71, or the strength required. In the United States, such sulphuric acid is now almost invariably used when it is intended for sale purposes. If the hydrochloric acid is diluted to 1.12 specific gravity and barium sulphide is added, the arsenic will be precipitated as the sulphide and the sulphuric acid as barium sulphate. The hydrochloric-acid gas may then be distilled off and reabsorbed in water.

32. Another method consists in adding a solution of stannous chloride in concentrated hydrochloric acid to the strong hydrochloric acid. Arsenic separates out, the reaction probably being

$$2AsCl_3 + 3SnCl_2 = 2As + 3SnCl_4$$

This leaves stannic chloride in the acid unless it is redistilled.

Arsenic and chlorine may be removed by digesting the acid with scrap copper for several hours; the arsenic is precipitated and the chlorine combines with the copper. The acid is then redistilled.

33. A pure form of hydrochloric acid is now made at one of the electrochemical works at Niagara Falls. At this works, potassium chloride is decomposed electrolytically by means of a diaphragm cell, and the resulting potassium hydrate is concentrated to a strong solution and transported in tank cars to consumers, as, for instance, manufacturers of oxalic acid, liquid soaps, etc., or is evaporated to dryness, fused, and run into iron drums. The hydrogen given off at the cathode is very pure, as is also the chlorine given off at the anode, the cell being a closed one into which no air enters. In fact, the gases are under slight pressure.

It has been known for many years that when hydrogen is ignited in an atmosphere of chlorine it will burn to form hydrochloric acid; also, that mixtures of these two gases will explode with great violence, if brought in contact with a burning taper or fire of any kind, or even if an electric spark is passed through them, or if they are exposed to direct sunlight. Nevertheless, tons of this acid are made daily by conducting the hydrogen through a glass tube tipped with a platinum jet, igniting the gas, and then introducing it into an atmosphere of chlorine in a glass balloon. The combustion is kept up by surrounding the burning hydrogen with a secondary tube that supplies the chlorine in a pure or nearly pure state. The resulting hydrochloric acid is cooled in glass pipes by radiation, and the gas is absorbed in glass alembics and pots by distilled water. The only impurity resulting is a small amount of chlorine, which for most purposes does not affect the acid injuriously.

34. Uses of Hydrochloric Acid.—In Europe, about three-fourths of all the hydrochloric acid made is used in the preparation of chlorine, but in the United States practically none of it is used for this purpose, electrolytic chlorine being used almost exclusively for the manufacture of bleaching powder, etc. The remainder of the product in Europe is used for making the chlorides of various metals, gelatine, superphosphates, various acids, as carbonic, etc.; for purifying animal charcoal; in dyeing and bleaching; in the manufacture of dyestuffs; for the preparation of various food products; in various metallurgical operations; etc.

35. Table I, which shows the degrees Baumé, the specific gravity, the degrees Twaddell, and the corresponding percentage of hydrochloric acid, will be found useful. In using this table it will be well to remember that it is based on chemically pure acid, whereas the acid of commerce contains more or less impurities, running from $\frac{1}{4}$ to $\frac{1}{2}$ per cent. of sulphuric acid, and a slight amount of iron, alumina, salts, etc., which are derived from the receiver, the packing of the towers, or the luting material of the joints.

TABLE I

HYDROCHLORIC ACID

Baumé Degrees	Specific Gravity	Twaddell Degrees	Percentage of Hydrochloric Acid	Baumé Degrees	Specific Gravity	Twaddell Degrees	Percentage of Hydrochloric Acid
1.00	1.0069	1.38	1.40	13.00	1.0985	19.70	19.63
2.00	1.0140	2.80	2.82	13.25	1.1006	20.12	20.04
3.00	1.0211	4.22	4.25	13.50	1.1027	20.54	20.45
4.00	1.0284	5.68	5.69	13.75	1.1048	20.96	20.86
5.00	1.0357	7.14	7.15	14.00	1.1069	21.38	21.27
5.25	1.0375	7.50	7.52	14.25	1.1090	21.80	21.68
5.50	1.0394	7.88	7.89	14.50	1.1111	22.22	22.09
5.75	1.0413	8.26	8.26	14.75	1.1132	22.64	22.50
6.00	1.0432	8.64	8.64	15.00	1.1154	23.08	22.92
6.25	1.0450	9.00	9.02	15.25	1.1176	23.52	23.33
6.50	1.0469	9.38	9.40	15.50	1.1197	23.94	23.75
6.75	1.0488	9.76	9.78	15.75	1.1219	24.38	24.16
7.00	1.0507	10.14	10.17	16.00	1.1240	24.80	24.57
7.25	1.0526	10.52	10.55	16.10	1.1248	24.96	24.73
7.50	1.0545	10.90	10.94	16.20	1.1256	25.12	24.90
7.75	1.0564	11.28	11.32	16.30	1.1265	25.30	25.06
8.00	1.0584	11.68	11.71	16.40	1.1274	25.48	25.23
8.25	1.0603	12.06	12.09	16.50	1.1283	25.66	25.39
8.50	1.0623	12.46	12.48	16.60	1.1292	25.84	25.56
8.75	1.0642	12.84	12.87	16.70	1.1301	26.02	25.72
9.00	1.0662	13.24	13.26	16.80	1.1310	26.20	25.89
9.25	1.0681	13.62	13.65	16.90	1.1319	26.38	26.05
9.50	1.0701	14.02	14.04	17.00	1.1328	26.56	26.22
9.75	1.0721	14.42	14.43	17.10	1.1336	26.72	26.39
10.00	1.0741	14.82	14.83	17.20	1.1345	26.90	26.56
10.25	1.0761	15.22	15.22	17.30	1.1354	27.08	26.73
10.50	1.0781	15.62	15.62	17.40	1.1363	27.26	26.90
10.75	1.0801	16.02	16.01	17.50	1.1372	27.44	27.07
11.00	1.0821	16.42	16.41	17.60	1.1381	27.62	27.24
11.25	1.0841	16.82	16.81	17.70	1.1390	27.80	27.41
11.50	1.0861	17.22	17.21	17.80	1.1399	27.98	27.58
11.75	1.0881	17.62	17.61	17.90	1.1408	28.16	27.75
12.00	1.0902	18.04	18.01	18.00	1.1417	28.34	27.92
12.25	1.0922	18.44	18.41	18.10	1.1426	28.52	28.09
12.50	1.0943	18.86	18.82	18.20	1.1435	28.70	28.26
12.75	1.0964	19.28	19.22	18.30	1.1444	28.88	28.44

TABLE I—(*Continued*)

Baumé Degrees	Specific Gravity	Twaddell Degrees	Percentage of Hydrochloric Acid	Baumé Degrees	Specific Gravity	Twaddell Degrees	Percentage of Hydrochloric Acid
18.40	1.1453	29.06	28.61	22.00	1.1789	35.78	35.21
18.50	1.1462	29.24	28.78	22.10	1.1798	35.96	35.40
18.60	1.1471	29.42	28.95	22.20	1.1808	36.16	35.59
18.70	1.1480	29.60	29.13	22.30	1.1817	36.34	35.78
18.80	1.1489	29.78	29.30	22.40	1.1827	36.54	35.97
18.90	1.1498	29.96	29.48	22.50	1.1836	36.72	36.16
19.00	1.1508	30.16	29.65	22.60	1.1846	36.92	36.35
19.10	1.1517	30.34	29.83	22.70	1.1856	37.12	36.54
19.20	1.1526	30.52	30.00	22.80	1.1866	37.32	36.73
19.30	1.1535	30.70	30.18	22.90	1.1875	37.50	36.93
19.40	1.1544	30.88	30.35	23.00	1.1885	37.70	37.14
19.50	1.1554	31.08	30.53	23.10	1.1895	37.90	37.36
19.60	1.1563	31.26	30.71	23.20	1.1904	38.08	37.38
19.70	1.1572	31.44	30.90	23.30	1.1914	38.28	37.80
19.80	1.1581	31.62	31.08	23.40	1.1924	38.48	38.03
19.90	1.1590	31.80	31.27	23.50	1.1934	38.68	38.26
20.00	1.1600	32.00	31.45	23.60	1.1944	38.88	38.49
20.10	1.1609	32.18	31.64	23.70	1.1953	39.06	38.72
20.20	1.1619	32.38	31.82	23.80	1.1963	39.26	38.95
20.30	1.1628	32.56	32.01	23.90	1.1973	39.46	39.18
20.40	1.1637	32.74	32.19	24.00	1.1983	39.66	39.41
20.50	1.1647	32.94	32.38	24.10	1.1993	39.86	39.64
20.60	1.1656	33.12	32.56	24.20	1.2003	40.06	39.86
20.70	1.1666	33.32	32.75	24.30	1.2013	40.26	40.09
20.80	1.1675	33.50	32.93	24.40	1.2023	40.46	40.32
20.90	1.1684	33.78	33.12	24.50	1.2033	40.66	40.55
21.00	1.1694	33.88	33.31	24.60	1.2043	40.86	40.78
21.10	1.1703	34.06	33.50	24.70	1.2053	41.06	41.01
21.20	1.1713	34.26	33.69	24.80	1.2063	41.26	41.24
21.30	1.1722	34.44	33.88	24.90	1.2073	41.46	41.48
21.40	1.1732	34.64	34.07	25.00	1.2083	41.66	41.72
21.50	1.1741	34.82	34.26	25.10	1.2093	41.86	41.99
21.60	1.1751	35.02	34.45	25.20	1.2103	42.06	42.30
21.70	1.1760	35.20	34.64	25.30	1.2114	42.28	42.64
21.80	1.1770	35.40	34.83	25.40	1.2124	42.48	43.01
21.90	1.1779	35.58	35.02	25.50	1.2134	42.68	43.40

The specific-gravity determinations for Table I were made at 60° F. compared with water at 60° F. From the specific gravities, the corresponding degrees Baumé were calculated by the following formula:

$$\text{Baumé} = 145 - \frac{145}{\text{specific gravity}}$$

Baumé hydrometers for use with this table must be graduated by this formula, which should always be printed on the scale. The atomic weights are based on F. W. Clarke's table of 1906, O = 16.

CHLORINE

36. Historical.—About the time that soda ash was beginning to be made by the Le Blanc process, Scheele (1774) found that by certain reactions he could obtain a new substance from hydrochloric acid. He did not consider that this new gas was an element, but called it "dephlogisticated muriatic acid." Even after the phlogiston theory had been disproved, the idea still prevailed that an acid must contain oxygen, and that since this new gas was made by taking hydrogen away from muriatic acid, it must also contain oxygen. It was not until 1810 that Davy succeeded in proving the elementary character of chlorine, and this view was not accepted by Berzelius until 1821.

In 1785, Berthollet recognized the bleaching effect of chlorine on cloth and proposed its use on a commercial scale. He advised using chlorine water for this purpose. The chlorine water did not keep well, however, and its preparation on a large scale was not convenient; so in 1789 the plan of passing the chlorine into a solution of potash was originated at the Javel works, near Paris. In this manner, potassium hypochlorite, known as *Eau de Javel*, was made.

Early in 1798 Charles Tennant, an Englishman, tried to patent a process for absorbing chlorine in milk of lime, but the patent was not allowed on account of having been anticipated by some one. In April of the next year, however, Tennant patented the absorption of chlorine by dry, slaked lime, and thus established the method of making bleaching powder that is now followed. During 1799 he made 52 tons of bleach, which he sold at $700 a ton; this is in striking contrast to the large amount now turned out every year, and selling at an average of less than $28 a ton.

37. Source.—Just as sodium chloride is the substance from which practically all the sodium carbonate of commerce is made, so it is also the chief source of chlorine. Potassium chloride and magnesium chloride furnish a small supply, and calcium chloride and some other chlorine compounds have been proposed as suitable materials for the furnishing of chlorine, but the problem of getting the chlorine from these substances in a commercial way has not yet been solved.

38. Chlorine Direct From Salt.—In spite of the fact that the making of chlorine and sodium carbonate began to be important commercially at about the same time, and that the manufacture was frequently carried on by the same firm, and usually in the same locality, the chlorine was made direct from salt, and the hydrochloric acid from the salt-cake furnaces was allowed to go to waste and become a nuisance in the neighborhood.

The operation of making chlorine consisted in mixing salt and manganese dioxide and treating the whole with sulphuric acid. This brought about the reaction

$$2NaCl + MnO_2 + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + 2H_2O + Cl_2$$

and all the chlorine was obtained from the salt, but at the expense of large quantities of sulphuric acid. A portion of this sulphuric acid can be saved if the temperature is kept high enough to drive the reaction to the formation of the normal sodium sulphate. The reaction then becomes

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

This reaction is only obtained, however, at a temperature above 120° C., which is not easy to obtain with steam. Any other method of heating is almost out of the question, on account of the material necessarily used for decomposition vessels. This process is still sometimes carried out in the chemical laboratory and at a few places where chlorine is needed only in comparatively small quantities.

39. Chlorine From Hydrochloric Acid.—When the Le Blanc soda works began to increase in size and number, the escape of the hydrochloric acid into the air became such an unbearable nuisance that it had to be abated by absorbing the acid in water. This soon made hydrochloric acid abundant and cheap, so that it then came into use for making chlorine. The preparation of chlorine from hydrochloric acid consists essentially in the removal of the hydrogen from the acid by an oxidizing agent. In selecting the oxidizing substance, both its cheapness and its efficiency must be taken into account, as well as the ease in handling and the resulting products. Naturally, an oxidizing substance that can be easily and cheaply regenerated by means of the air is more preferable than one that must be thrown away when once used.

40. Oxidation by Oxides of Manganese.—Just as the oxides of manganese were used to act with salt and sulphuric acid for the preparation of chlorine, so they have been used more recently with hydrochloric acid for the same purpose, for they occur in nature in large quantities, but in varying states of oxidation. The oxides of manganese occurring in nature are manganosite, MnO, and pyrolusite, MnO_2, which represent the high and low degrees of oxidation, and the intermediate oxides braunite, Mn_2O_3, manganite, Mn_2O_3, H_2O, hausmannite, Mn_3O_4, wad, and psilomelane. The last two contain the manganese mostly in the form of manganese dioxide, but also contain varying quantities of other metals. The reactions that occur between the oxides of manganese and hydrochloric acid are as follows:

$$\begin{aligned}
MnO + 2HCl &= MnCl_2 + H_2O \\
MnO_2 + 4HCl &= MnCl_2 + 2H_2O + Cl_2 \\
Mn_2O_3 + 6HCl &= 2MnCl_2 + 3H_2O + Cl_2 \\
Mn_3O_4 + 8HCl &= 3MnCl_2 + 4H_2O + Cl_2
\end{aligned}$$

It will be readily seen that manganese dioxide yields the highest amount of chlorine for a given amount of hydrochloric acid, and that the presence of other oxides, as well as of iron, calcium, and other metals, is a disadvantage, as it lowers the oxidizing power of the ore and uses acid to no purpose. The manganese ore is usually bought according to its percentage of available oxygen, which is considered to represent the amount of manganese dioxide in the ore.

The hydrochloric acid is, of course, used in solution, and the stronger the solution, the better it is. At best, only 50 per cent. of the acid in the solution can be made to yield chlorine, as will be seen from the second reaction. The reaction does not continue after the strength of the acid has fallen to 5 per cent., and usually, under ordinary working conditions, 7 or 8 per cent. of the acid is left in the residual liquors. These latter percentages do not represent the acid originally present, but are the actual percentages of acid in the solution, so that it is easily seen that a far greater percentage of the acid is left unused when an acid of 10 per cent. original strength is used than when one of 35 per cent. is employed. Working under the best conditions, by this method rarely over 30 or 33 per cent. of the total chlorine of the acid is obtained in an available form, as in bleaching powder.

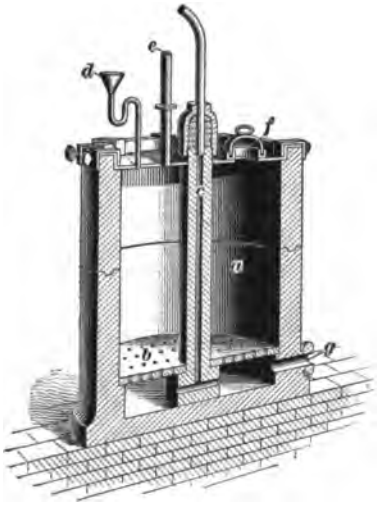


FIG. 12

41. **Apparatus.**—The stills for the decomposition of hydrochloric acid by means of manganese dioxide are made either of earthenware or of silicious sandstone that has been

boiled in tar to make it acid-proof. A small still used in works of limited capacity, and sometimes in larger establishments, is shown in Fig. 12. This still is made of sandstone and consists of two parts joined by a tongue and groove, being held together with rubber cement. Near the bottom of the still is a narrow ledge, on which rests the perforated section *b*. The manganese ore in small lumps is placed on *b*, and the hydrochloric acid is run in through *d*. The chlorine gas, as it is evolved, passes out through the pipe *e*, and as the action slackens, steam is run into the still through the pipe *c*, and, coming out under the false bottom, mixes and heats the contents of the still. At *f* is a manhole, which serves for introducing the manganese ore and for cleaning the still. The residual liquor is drawn off through the outlet *g*.

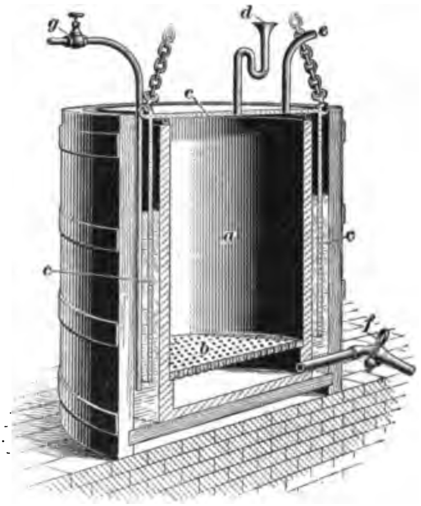


Fig. 13

42. In Fig. 13 is shown a form of still that will serve very well for the preparation of chlorine on a small scale, although it is hardly suitable for large works. This apparatus consists of a sandstone or earthenware still *a* that is provided with a false bottom *b*, as in Fig. 12. The still *a*, Fig. 13, is set in a wooden case, and is surrounded by a concentrated salt solution which serves as a lute for the bell *c*. This bell is suspended by chains on pulleys and is counterpoised by weights, so that it can be easily moved up and down as desired. The top of the bell is provided with a funnel tube *d* for the introduction of the acid, and an exit tube *e* for the chlorine. The spent liquor is drawn off through the pipe *f*. By blowing in steam through the pipe *g*, the salt solution can be warmed as desired and the contents of the still brought to the proper temperature without diluting the still liquor by blowing in steam.

43. Another form of still, which is shown in Fig. 14, is made of sandstone slabs that are grooved together and made tight by means of rubber cords that fill the connecting grooves. This type of still works on the same principle as those just described, but is much larger and more suitable for work on a large scale. In this apparatus, the lumps of manganese ore rest on the false bottom *a*, and the acid is run in through the tube *c*. The lower end of this tube dips into a cup, which is always full of hydrochloric acid, and thus forms a lute to prevent the chlorine from escaping through the tube. Steam is introduced through the pipe *b* when necessary, and the chlorine escapes through the pipe *d*. The waste liquor can be drawn off through the outlet *e* into a trough and allowed to run away.

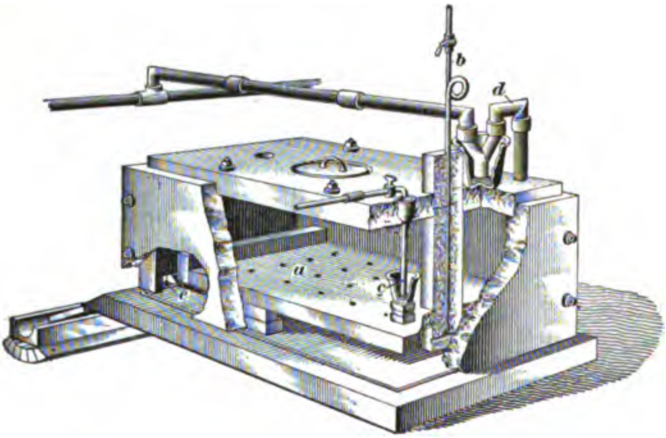


FIG. 14

44. Management of the Stills.—The operation of the stills consists in charging with manganese ore and then running in hydrochloric acid as rapidly as the reaction will permit. The evolution of chlorine is allowed to continue without heat for from 8 to 12 hours, when steam is blown in at intervals. Steam cannot be blown in continuously, for the temperature would become too high and too much hydrochloric acid and water would be carried over into the chlorine. The chlorine would also be likely to come off too rapidly. The pipes for conducting the chlorine are of either lead or earthenware, and the gas is often conducted from several stills into one large main pipe. In this case, when a still is stopped in order to be cleaned and refilled, it should be cut off from the main pipe. This cannot be accomplished by using valves or stop-cocks, but is brought about by a variety of means, two of which will be described.

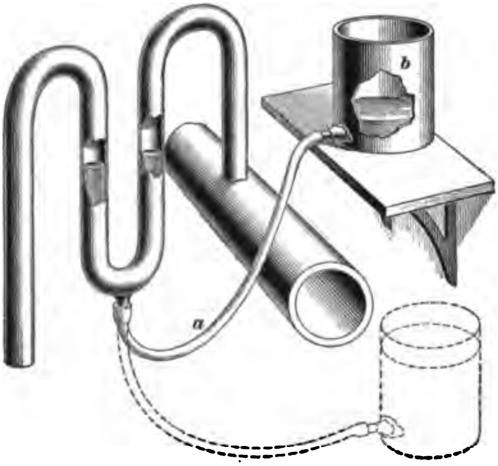


Fig. 15

45. One of these methods is shown at *d*, Fig. 14. The conducting tube is connected with a Y tube at a short distance from the still, and this Y tube, which is open at its lower end, sets in a jar, as shown. When it is desired to bring the tube into action, the liquid in the jar is lowered to below the branching point of the Y, but the lower end is left covered. The chlorine cannot escape to the outside, but can easily pass through the branches of the Y to the large conducting main. When the tube must be closed, it is easily done by filling the jar with water or a solution of salt. The branches of the **Y** will then be filled and the passage stopped. With this arrangement, it is necessary to empty or fill the jar each time a change is desired, which is inconvenient.

46. A much better arrangement consists in making a **U** bend in the tube, as shown in Fig. 15. At the lower end of the **U** a small tube is connected, to which may be fastened the flexible tube *a*. This tube is connected to the cup *b*, which contains a strong salt solution. When this cup is raised, the solution flows into the **U** tube and shuts off the flow of gas; when lowered, however, the solution flows out of the **U** tube into *b* and the passage is open for the gas.

47. Still Liquors.—The liquors from the stills contain, in the form of chlorides, all the manganese, aluminum, iron, calcium, etc. that were contained in the ore, together with considerable hydrochloric acid. Although the liquor varies considerably with the grade of manganese ore used and the strength of the hydrochloric acid, the following may be considered as a fairly representative analysis:

	Per Cent.
HCl	6.62
$AlCl_3$	.62
$MnCl_2$	10.57
$FeCl_3$	.46
H_2O	81.73

This liquor, on account of the large amount of acid that it contains, is hard to dispose of, for if given a chance, it will act on the mortar in the foundations of buildings and even on the stones themselves. If run into the streams, it kills the fish and acts in a generally disagreeable manner. No matter how the liquor is disposed of, when it is first run from the still it evolves a disagreeable odor of chlorine. In addition to all these bad qualities, the still liquor also carries away with it all the manganese, and as manganese ore began to be scarce and the price to increase, a method for treating these liquors became almost a necessity. Of the large number of processes proposed for this purpose only one will be described here.

48. Weldon's Process.—The facts that manganese hydrate can be precipitated by lime water and that it is somewhat oxidized by the oxygen of the air have long been known. All attempts to recover manganese by either of these methods, however, were for a long time futile, for the oxidation proceeded too slowly and could only be driven to the formation of Mn_3O_4, or, at best, Mn_2O_3. It was only when Weldon discovered that with an excess of calcium hydrate the oxidation went on more rapidly and to a greater degree that the process had any commercial possibilities. **Weldon's process** is now practically the only one used for the recovery of manganese, and it figures in the preparation of a large percentage of all the chlorine made.

49. The process consists in first neutralizing the still liquor with powdered chalk. An excess of chalk is to be avoided, as in settling it increases the precipitate and so increases the loss of manganese. When the liquor no longer gives an acid reaction with litmus paper, it is an indication that sufficient chalk has been added. The neutralized liquor is then run into settling tanks, where the excess of chalk and the iron and aluminum hydrates are allowed to deposit. The clear liquor is then run into the blowers, where it is heated to 55° C. and mixed with enough calcium hydrate to precipitate all the manganese as hydrate, and then from one-fifth to one-half more of the lime is added. The calcium hydrate used for this purpose should be as pure as possible, and must be especially free from magnesium compounds, for the magnesium chloride is not decomposed by the chalk in the neutralizing tank, but goes to the oxidizer, where it is precipated by the lime and goes on to use up hydrochloric acid at a later stage of the process. As soon as the manganese hydrate has been precipitated and a proper amount of lime in excess is present, air is forced through the mixture and the oxidation begins. The air is blown through the apparatus for from 2½ to 4 hours, depending on the apparatus, although at the same works the length of time for blowing is about the same for each batch. At the end of the first blow, a calcium manganite of practically the composition $CaO(MnO_2)_2$, together with other manganites, is formed. Then, without stopping the blowing, a suitable amount of manganese chloride (about one-fourth the amount originally taken) is run in, and the blowing is continued until this is oxidized as far as possible.

50. The oxidizing of the manganese hydrate requires considerable care and experience, for the blower must be started at exactly the right time and at the proper speed. If it is started too strongly before a sufficient excess of lime is added, the manganese is oxidized to Mn_3O_4, and after this is once formed, it is very difficult to force the oxidation any further. Such a result is called a *red*, or *foxy*, *batch* on account of its being a brownish-red color instead of black, as it should be. On the other hand, if the blower is not started quickly and strongly enough, the contents of the oxidizer becomes so thick that great difficulty is experienced in trying to force the air up through it; such a result is called a *stiff batch*. The only remedy is to start the blower at full strength and to carry the batch beyond this point, if possible. A stiff batch may also be caused by too high a temperature or by too little calcium chloride in the mixture. The best mixture contains about 3 gram molecules of calcium chloride to each gram molecule of manganese chloride. For the total oxidation, it is estimated that 300,000 cubic feet of air is required to recover the manganese for each ton of bleach made. At many works, the addition of the manganese chloride and the continuation of the oxidation is not practiced; that it is advisable, however, is shown by a consideration of the reactions taking place in the Weldon process.

51. Reactions.—If the neutralization of the still liquor, which is not really one of the parts of the process proper, is left out of consideration, the first reaction is the precipitation of the manganese hydrate. This, if represented for 100 gram molecules of manganese chloride, is

$$100MnCl_2 + 100Ca(OH)_2 = 100Mn(OH)_2 + 100CaCl_2$$

For oxidation, the extra lime is added, as already mentioned, and air blown in; the reaction then taking place, neglecting the nitrogen of the air, may be represented thus:

$$\begin{aligned} 100Mn(OH)_2 + 60Ca(OH)_2 + 43O_2 &= 48CaO \cdot MnO_2 \\ &+ 14MnO \cdot MnO_2 + 12CaO(MnO_2)_2 + 160H_2O \end{aligned}$$

This is, if the oxidizing and basic parts are considered separately, equal to $86MnO_2 + 74(CaO + MnO)$. Thus, out of 100 gram molecules of manganese chloride is obtained 86 gram molecules of MnO_2, or active material for oxidizing the hydrochloric acid; but there are also 74 gram molecules of substances that neutralize and thus destroy hydrochloric acid and yield no chlorine. Now, if an extra quantity of manganese chloride is added, a part of the above material reacts, and the following result is obtained:

$$\begin{aligned} 24H_2O + 48CaO \cdot MnO_2 + 24MnCl_2 &= 24CaO \cdot (MnO_2)_2 \\ &+ 24Mn(OH)_2 + 24CaCl_2 \end{aligned}$$

Then, by blowing, the manganese hydrate is oxidized according to the equation

$$24Mn(OH)_2 + 6O_2 = 12MnO \cdot MnO_2 + 24H_2O$$

By collecting the preceding equations and adding them algebraically, the results will be as follows:

$$\begin{aligned} 100MnCl_2 + 100Ca(OH)_2 &= 100Mn(OH)_2 + 100CaCl_2 \\ 100Mn(OH)_2 + 60Ca(OH)_2 + 43O_2 &= 48CaO \cdot MnO_2 + 14MnO \cdot MnO_2 \\ &+ 12CaO(MnO_2)_2 + 160H_2O \\ 24H_2O + 48CaO \cdot MnO_2 + 24MnCl_2 &= 24CaO \cdot (MnO_2)_2 + 24Mn(OH)_2 \\ &+ 24CaCl_2 \\ 24Mn(OH)_2 + 6O_2 &= 12MnO \cdot MnO_2 + 24H_2O \\ 124MnCl_2 + 160Ca(OH)_2 + 49O_2 &= 36CaO \cdot (MnO_2)_2 + 26MnO \cdot MnO_2 \\ &+ 124CaCl_2 + 160H_2O \end{aligned}$$

From this last equation it may be noted at once that at the end of the operations there is a mixture of $36CaO \cdot (MnO_2)_2$ and $26MnO \cdot MnO_2$, or $98MnO_2 + 36CaO + 26MnO$, from 124 gram molecules of manganese chloride. That is to say, there is 79 per cent. of the manganese in the form of the dioxide, as against 86 per cent. of the manganese in this condition before the last addition of manganese chloride. The present condition is much better, however, for although the percentage of the manganese converted to the dioxide is somewhat smaller than before, the amount of base present is much more reduced than the active manganese. Before the second addition of manganese chloride, there are 74 gram molecules of base to 86 gram molecules of manganese dioxide; that is, 53.75 per cent. of the total number of gram molecules that can react with hydrochloric acid is manganese dioxide. When the operation is completed, however, there are only 62 gram molecules of base to 98 gram molecules of the manganese dioxide, or 61.25 per cent. of the active gram molecules is manganese dioxide. It is obvious, then, that the second addition of manganese chloride and longer blowing are decided advantages.

52. Weldon Mud.—The mixture of calcium and manganese manganites obtained by the operations just mentioned is a black, shiny precipitate, which is in suspension in a solution of calcium chloride. This mixture is run from the oxidizers to the settling tanks, where it is allowed to stand for 3 or 4 hours. At the end of this time the precipitate will have settled into the lower half of the solution, and the clear calcium-chloride solution can be drawn off from the top; the shiny mass remaining is called **Weldon mud.**

The Weldon mud finds several uses besides the preparation of chlorine; it is used in gas purifiers, to remove iron from alum, to remove sulphides from caustic soda, and for several similar purposes. Weldon at one time recommended that this mud be used instead of chalk for neutralizing the still liquors, but later abandoned it for that purpose. At present, Weldon mud is used quite extensively in that way, for it not only saves the chalk, but also utilizes the acid of the liquor to neutralize the bases in the mud, and thus increases the efficiency of the mud as an oxidizing agent. The use of Weldon mud for neutralizing the still liquors has the disadvantage that all the impurities, such as calcium sulphate, iron, and aluminum, are left in the mud. This makes it necessary occasionally to neutralize a batch with chalk and allow the impurities to settle out. When this method is used, great care is taken to keep sulphuric acid out of the hydrochloric acid. Sometimes, calcium chlorine is added to precipitate the sulphuric acid before the hydrochloric acid is used.

CHLORINE BY THE WELDON PROCESS

53. Weldon mud is used chiefly in the generation of chlorine, and for this purpose it is much more active than manganese ore. The stills used are similar to those already described, but the method of working is somewhat different from that when manganese ore is used. In working with Weldon mud, the hydrochloric acid is run as hot as possible directly from the condensers into the stills, and the mud is then added slowly, so as to regulate the flow of chlorine until sufficient for the acid is present. Too much must not be added, especially if the still liquors are neutralized by chalk, for in that case the manganites that are unacted upon will settle with the mud from the neutralized liquors and be lost. When the color of the liquor in the still shows that enough mud has been added, steam is blown in and the chlorine is driven off as completely as possible. In this way, it is possible to leave only from ½ to 1 per cent. of free hydrochloric acid in the still liquor. This is equivalent to about 3 per cent., as counted on still liquor from manganese ore, for the water in the Weldon mud makes its still liquor more dilute than that from manganese ore. From 1½ to 3 per cent. of the manganese is lost in the cycle of operations, and this is supplied by continuously decomposing the necessary amount of manganese ore in a small still and adding its liquor to the general supply. Only about 30 per cent. of the chlorine in the hydrochloric acid is obtained in the bleaching powder. The remainder is, for the most part, run to waste as calcium chloride.

54. Apparatus.—The apparatus used in performing this cycle of operations is shown in Fig. 16, which represents a cross-section through part of it. Starting with the still liquor from the still *A*, the liquor runs into the neutralizing tank *B*, where it is mixed with either chalk or Weldon mud and thoroughly stirred. It is then pumped, by means of the pump *C*, through the pipe shown, to the settling tank *D*. If chalk is used for neutralizing, the mud obtained is valueless; if Weldon mud is used, however, the mud here obtained can be used in the chlorine still. From *D* the neutralized liquor goes to the oxidizers *E*, *E*. Meanwhile, lime is slaked in tanks *F*, *F*, and made to the proper consistency. This lime is then pumped, by the pump and pipe shown, to the reservoir *G*,

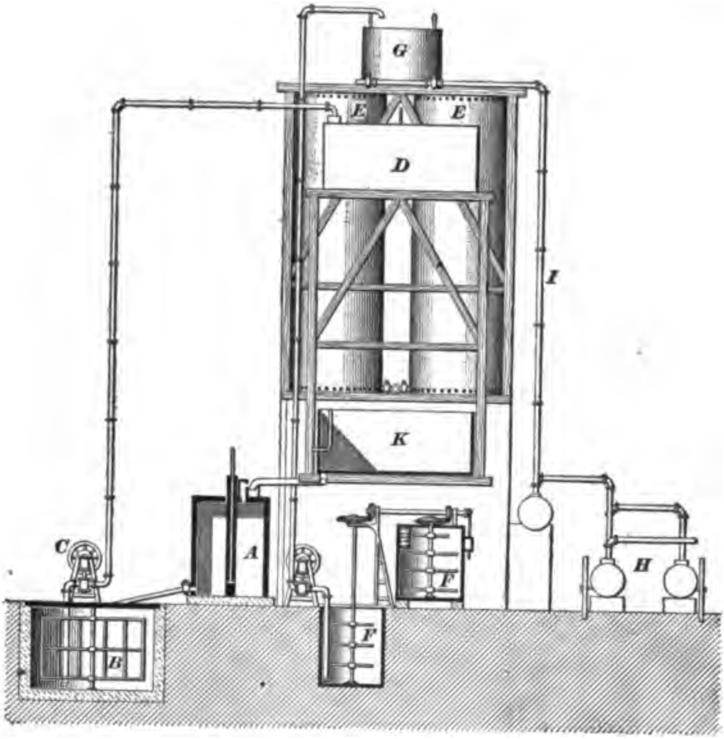


FIG. 16

from which place it is run in proper quantities into the oxidizers *E*, *E*. Air is forced into the mixture through the pipe *I*, which extends to the bottom of the oxidizers, by the blowers *H*. From the oxidizers, [illegible] batch is drawn off into the settling tanks *K*, from which [illegible] mud is again run as needed into the still *A*.

It will be noted that nearly all the materials are removed as solutions, or slimes, so that the work is almost entirely mechanical. The solutions, or slimes, are pumped to the highest point of the plant and then allowed to flow down through the various pieces of apparatus until they once more reach the lowest point. Practically the same number of men are required for a small plant as for a large one, so that on this account, the working of a large plant is more economical.

DEACON'S PROCESS FOR CHLORINE

55. In the process just described the manganese has acted simply as an oxidizing agent to remove the hydrogen from the chlorine and set the latter free. Although the steps are a little further removed, there is a direct analogy between this operation, when the Weldon manganese-recovery method is employed, and the making of sulphuric acid, where nitric oxide is used as a carrier of oxygen from the air. And, just as recently the problem of causing sulphur dioxide to combine directly with the oxygen of the air by passing a mixture of the two gases over platinized asbestos or ferric oxide has been solved in a practical manner, so, much earlier, it was found that when hydrochloric acid and air are passed over porous material saturated with salts of copper, lead, or manganese, the oxidation of the hydrogen of the hydrochloric acid into water takes place direct.

It was discovered and patented by Oxland, in 1845, that when a mixture of hydrochloric acid and air is passed through a tube filled with red-hot pumice, the following reaction takes place:

$$4HCl + O_2 = 2H_2O + 2Cl_2$$

This is a reversible reaction, however, and, under the conditions here stated, the decomposition of the hydrochloric acid is very incomplete. Ten years later, in 1855, Vogel found that when cupric chloride is heated it decomposes into cuprous chloride and chlorine, according to the reaction

$$2CuCl_2 = 2CuCl + Cl_2$$

Then by passing hydrochloric acid and air over the cuprous chloride, an oxychloride of the composition $CuCl_2 \cdot 3CuO \cdot 3H_2O$ is formed, which finally goes over into cupric chloride, the final reaction being

$$4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O$$

In practical working, however, it was found that only about one-third of the chlorine was obtained from the cupric chloride, instead of the theoretical one-half. There was also a loss of copper salts, and on account of these and other difficulties, the process was never successful.

56. The idea occurred to Deacon, however, to combine these two methods, and he took out his first patent to that effect in 1868. Various contact substances have been proposed and patented, but certain salts of copper are found to be the best. In general, the process as carried out now consists in passing a suitable mixture of hydrochloric acid and air through tubes containing clay balls saturated with a copper salt. Copper sulphate is generally used to saturate the balls, but it is claimed that this is soon converted into the chloride. The reactions taking place in the tube are generally considered to be

$$\begin{aligned} 2CuCl_2 &= 2CuCl + Cl_2 \\ 2CuCl + O_2 &= 2CuO + Cl_2 \\ 2CuO + 4HCl &= 2CuCl_2 + 2H_2O \end{aligned}$$

It is held by some, however, that the copper salt only acts catalytically, and that the reaction is direct between the hydrogen of the acid and the oxygen.

DETAILS OF THE DEACON PROCESS

57. Hydrochloric Acid.—The acid used for the Deacon process must be as uniform in composition as possible and free from dust, sulphuric acid, and arsenic compounds, for otherwise the contact substance will deteriorate very rapidly. Uniformity of composition is not hard to get when the acid is liberated from its solutions. When the acid goes to the decomposer direct from the salt-cake oven, however, it is not so easy to maintain uniformity, for the acid is given off rapidly at first and more slowly later. This difficulty is largely overcome, however, by connecting several furnaces to each decomposer, so that by charging the salt-cake furnaces in rotation, a nearly uniform flow of acid gas is obtained. Where the acid is used direct from the salt-cake ovens, only the pan acid is used, for this acid is much purer than that from the roaster, and the acid from the latter can be condensed and sold as acid or used in the Weldon process.

At the present time, the custom at many works is to condense all the hydrochloric acid produced and then liberate the gas from its solution by running it into hot, concentrated sulphuric acid, and blowing a current of air through the mixture; a very pure hydrochloric-acid gas is thus obtained. This method of purifying the hydrochloric acid was worked out by Hasenclever, and has done much to make the Deacon process a success; for this reason, the process is frequently referred to as the **Deacon-Hasenclever process.**

Calcium chloride has been proposed for setting hydrochloric acid free from its solutions. It possesses no advantage over sulphuric acid for this purpose, however, and the latter is more generally used.

58. The hydrochloric acid is mixed with about an equal volume of air, which furnishes the theoretical amount of oxygen necessary to decompose it. Since, however, even in the presence of the catalytic substance, the reaction is not complete, an excess of air will drive the decomposition of the hydrochloric acid further. The disadvantage, however, enters here, that the excess of air dilutes the already much diluted chlorine, so that it is better to allow a portion of the acid to escape decomposition than to produce such dilute chlorine. The mixture of air and hydrochloric acid must be as dry as possible—the drier the better—before going to the decomposer. It has been found in practical working, however, that very satisfactory results are obtained if the mixture is cooled to 37° C. Gas saturated with moisture at that temperature works in the hot decomposer nearly as well as perfectly dry gas, and the cost of drying is saved.

59. A portion of the reactions in the decomposer absorbs heat and a part evolves heat, but the sum total of these reactions is an evolution of several calories of heat for each gram molecule of hydrochloric acid oxidized. There is not enough of this heat, however, to make up for loss through radiation and also bring the gas mixture to the best temperature for the decomposition. The gas mixture should therefore be heated to about 450° C. before it goes to the decomposer, as this temperature has proved to be the best for decomposition.

60. The gas that issues from the decomposer consists of a mixture of hydrochloric acid, chlorine, oxygen, nitrogen, and water vapor. Both the hydrochloric acid and the water vapor must be removed if the chlorine is to be used for bleach making. The gases therefore pass through a cooling arrangement to condense the water as much as possible, and with it the acid. The gas is then washed with water, and is finally passed through towers, down which sulphuric acid is sprayed, to dry it completely.

61. Apparatus.—The apparatus for carrying out the Deacon process is shown in Fig 17. It consists of a cooling and condensing arrangement for the gases as they come from the salt-cake furnace or from the Hasenclever purifier. This cooling and condensing apparatus usually consists of a long, upright pipe *A* and a small coke, or plate, tower *B*. The gas mixture goes to the heater *C*, which consists of a

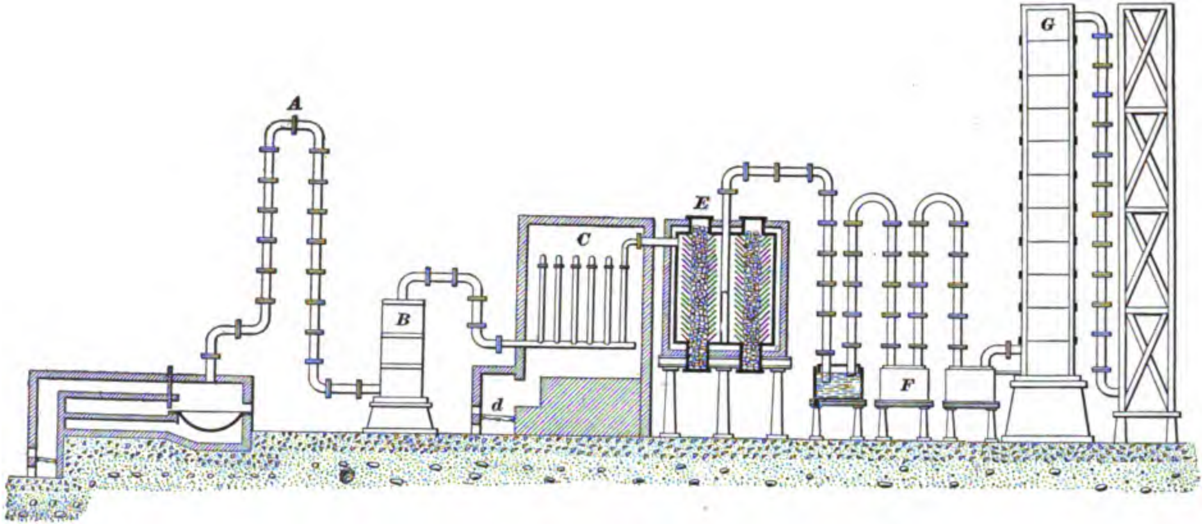


FIG. 17

series of pipes, up and down through which the gas must pass. The pipes are enclosed and heated by the gases from a fire in the grate *d*. Having been heated to about 450° C., the gases pass into the decomposer *E*. Several forms of this piece of apparatus have been proposed, but the one here illustrated is the most satisfactory. It consists of a large circular outer chamber, into which the mixture of air and acid passes from the heater. Arranged inside of this chamber, so that the gas must pass through them, are the cylinders containing the catalytic material. The walls of these cylinders are made similar to Venetian blinds, so that the gas must take a downward course on entering, and, after traversing the filling, must take an upward course on leaving. The gases from the whole system collect in the center, and are drawn off by a pipe to the purifying apparatus. Each cylinder is arranged so that it can be cut out of action when necessary for emptying and refilling, for the catalytic material deteriorates slowly by use and must be renewed about every 12 weeks. Frequently, in the style of decomposer shown here, all the cylinders are kept in continuous action, and when it is necessary to recharge them, the fresh material is charged at the top as rapidly as the old is withdrawn at the bottom. Many methods have been proposed for cooling and washing the gas that comes from the decomposer, but the one illustrated at *F* is probably the most efficient and at the same time the most simple. The apparatus for this method consists of upright pipes that end in troughs of water, the pipes serving to cool the gases and the water to wash out the hydrochloric acid. Finally, the gas is completely dried by sulphuric acid in the towers *G*. A suitable vacuum is maintained in the whole apparatus by means of a pump placed beyond *G*.

62. Comparison of the Weldon and the Deacon Processes.—It is difficult to say whether the Weldon or the Deacon process leads in the production of chlorine at the present time, and it is equally difficult to say which process is the better, as this depends on general conditions.

In the old manganese-dioxide method, theoretically 50 per cent. of the chlorine of the acid was obtained free, but in practice not over 30 to 33 per cent. was realized. In the Weldon process, only 40 per cent. of the chlorine of the acid is theoretically available, but about 30 to 33 per cent. is also obtained here and the manganese is recovered as well. In both cases a strong chlorine is made. In the Deacon process, 100 per cent. of the chlorine in the acid is theoretically obtainable, and in practice 50 to 80 per cent.; the rest is recovered as acid to be used over. The chlorine is much diluted, however, only averaging from 7 to 10 per cent. chlorine, so that it is not so suitable for as many purposes as the stronger gas obtained from the other methods.

NITRIC-ACID CHLORINE PROCESS

63. A number of processes have been proposed that involve the oxidation of hydrochloric acid by means of nitric acid, according to the reaction

$$3HCl + HNO_3 = 2H_2O + NOCl + Cl_2,$$

but these have never been put in practice.

Where chlorine is used in large quantities it is sometimes made on the spot, either directly from salt or from hydrochloric acid. The use of salt, however, is almost obsolete, and the carrying of the hydrochloric acid is inconvenient and somewhat dangerous. For this reason, it can rarely be economically made at any place far removed from alkali works. On the other hand, the chlorine gas is bulky and must be converted into some compact form for shipment.

64. Liquid Chlorine.—Chlorine is a gas that is comparatively easily liquefied, for it becomes liquid when cooled to −34° C. at the ordinary atmospheric pressure, or when subjected to a pressure of 6 atmospheres at the ordinary temperature. Liquid chlorine is such a corrosive substance, however, that until recently it was not considered possible to find pumps to work it, or tanks to hold it when it was compressed. The pumps used in compressing chlorine consist, for the most part, of a plunger that works in petroleum and forces the petroleum against a column of sulphuric acid. The chlorine collects over the acid, and when the acid is raised, the chlorine is forced into a tank and compressed.

Moist chlorine acts very strongly on iron at the ordinary temperature, but when perfectly dry, it has practically no action on this metal, and iron tanks can be safely used for storing and shipping it when in the liquid form. In Germany, chlorine is transported in iron or steel tanks. These tanks hold about 5,000 pounds each, and three or four of them are fastened to a railroad car. Chlorine is also largely sold in steel cylinders that hold from 50 to 200 pounds each. One volume of liquid chlorine is equal to 400 volumes of chlorine gas at ordinary conditions of temperature and pressure.

No matter from what source chlorine is derived, whether from hydrochloric acid, as previously described, or electrolytically, as will be described later, its principal use is in the manufacture of bleaching powder, and all the methods for that purpose are the same

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BLEACHING POWDER

65. When chlorine is passed over dry, slaked lime, a compound is formed that again gives up the chlorine when treated with an acid. This compound was at first supposed to be calcium hypochlorite, $Ca(OCl)_2$, and was called *chloride of lime;* it is now more commonly known as **bleaching powder.** Bleaching powder yields only 100 volumes of chlorine for each volume of the substance, and requires acid to set it free. It is, nevertheless, a most convenient means for the transportation and storing of chlorine and is almost universally used.

66. Lime.—The lime used for making bleaching powder should be very pure and well burned. Impurities are decidedly undesirable, for in addition to making it impossible to make a strong bleach if the lime does not contain a high percentage of calcium oxide, clay and similar substances cause the bleach solutions to settle badly. Iron and manganese cause a colored bleach, which does not sell readily; besides, these substances cause a more rapid decomposition of the bleach than would otherwise occur. Thus, a limestone of as great purity as possible having been selected, it is burned in such a manner as to avoid having the ashes of the fuel mix with the lime. A reverberatory furnace is frequently used for this purpose. The carefully burned quicklime is slaked by sprinkling with water; and as an excess of water cannot be used, the best plan is to let the lime lie for 2 or 3 days to allow it to slake well through before using. Perfectly dry slaked lime does not work well with chlorine, and, on the other hand, too great an excess of water must be avoided or the lime will cake together and not chlorinate through. Theoretically, calcium oxide requires 32 per cent. of its weight of water to convert it into the hydrate, and from 2 to 4 per cent. of water in addition to this, depending on the dehydration of the chlorine, is generally used. After slaking thoroughly, the lime is sifted through a sieve having from 12 to 25 holes to the linear inch. The finer the division of the lime, the better it absorbs the chlorine. It is now ready to spread in the *absorption chambers*.

67. Absorption Chambers.—The chambers for absorbing the chlorine are commonly large rooms made of brick or stone laid in asphalt cement; though they are sometimes made of lead, which is probably the best material and is not much more expensive than the others. The floors are either of asphalt or lead. The lime in the chambers must be turned over when the layer is thick, so that the chambers must be high enough for a man to stand upright while turning and removing the material. An ordinary chamber is about 100 feet long, 30 feet wide, and 6½ feet high. It is usually estimated that 200 square feet of floor space is required per ton of bleach per week. The slaked lime is spread on the floor in a layer from 2 to 4 inches thick, and is furrowed by a rake to give a large absorbing surface. The gas passes into the chamber at the top of one end and out of it at the top of the opposite end. The chlorine, being heavy, settles to the bottom of the chamber and is very rapidly absorbed at first and then more slowly, as the lime becomes more nearly saturated. In the case of single chambers, when the absorption becomes too slow, the gas is shut off and, after freeing the chamber of chlorine, men go in and turn and relevel the lime. In the more modern works, where three or more chambers are worked together, the turning can be avoided, for the strong gas goes into the most nearly finished chamber and then to fresher lime, so that the chlorine does not escape. When the layer of lime is not over 2 inches thick, the operation will usually be finished without turning the material; when the layer is more than 2 inches thick, the material usually has to be turned. A second passing of the gas will generally bring the available chlorine in the bleach to 36 to 38 per cent., and that is sufficient. If this percentage is not obtained, the material must be turned a second time and again treated with gas. If this treatment does not bring the bleach to the desired strength, it must be packed and sold for what it will bring, for further treatment with chlorine will only result in the decomposition of the bleach already formed.

68. Chlorine.—The chlorine must be free from carbon dioxide and hydrochloric acid, and as free from water as possible. The stronger the chlorine the better; very dilute chlorine, such as comes from the Deacon method, cannot be used in this form of apparatus. The chlorine must be introduced into the chamber very slowly, so as to avoid a rise in temperature, for if the temperature is too high, chlorates will form and the bleach will decompose, giving oxygen. On no account should the temperature go above 40° or 45° C., while a lower temperature is better.

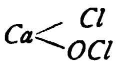
69. On opening the chamber to turn or remove the bleach, the chlorine escapes into the air and thus makes the task disagreeable. This is obviated somewhat by letting the chambers stand for some time before opening, or, better, by sprinkling a little fine dust of calcium hydrate in from the top. At best there is a great deal of hard, disagreeable work connected with the process, and the plant covers a large area. The attempt has been made to do away with these difficulties by stirring the lime mechanically while it is being chlorinated. By this means the lime is chlorinated rapidly and discharged into the barrels without much hand labor. This method is subject to a great disadvantage, since the rapid absorption of the chlorine causes the temperature to rise too high. This has been somewhat obviated lately by cooling the apparatus from the outside.

70. As already mentioned, the apparatus that is suitable for strong chlorine cannot be used for the more dilute chlorine obtained in the Deacon method, for the absorption is too slow with such weak gas. Deacon avoided this difficulty by using large stone chambers in which shelves were placed close together. On the shelves, the finely powdered slaked lime was spread in layers not over $\frac{5}{8}$ inch thick, and the chlorine passed downwards over these shelves. This arrangement works very well, but it requires very large chambers. For each ton of bleach produced in a week a shelf space of 1,373 square feet is necessary. With the dilute chlorine, the absorption is not so rapid, and a mechanical chlorinating apparatus can be used to good advantage.

71. The best of the mechanical chlorinating devices consist of cast- or wrought-iron cylinders that are 15 to 18 inches in diameter and about 20 feet long. These cylinders are fitted with a conveyer that operates on the principle of an Archimedean screw. A carefully regulated quantity of slaked lime passes continuously into the cylinder at one end and meets the chlorine, which is moving in the opposite direction. When using very dilute chlorine, as from 4 to 6 per cent., three of these cylinders are placed so that one is over the other, the top one fitting into the one below and the second into the third, from which the bleach is allowed to flow into a drum, or cask, in which it is packed.

The chlorine is prevented from escaping by luting all openings with lime or bleaching powder. Bleach made in this manner rarely contains over 35 per cent. of chlorine, which is the lowest standard when freshly made. These methods are patented, although the validity of the patents is open to question.

72. Properties of Bleaching Powder.—The chloride of lime should be either in the form of white powder or in lumps that will break easily. It is acted on by the carbon dioxide of the air, and will therefore lose strength if exposed; even when protected from the air, it gradually loses strength, especially when it is jarred, as in transportation. The bleach has a peculiar odor, which is probably due to chlorine. In order to exclude air and moisture, it is usually packed tightly in barrels, and these should be kept out of the sun as much as possible. The bleach loses about 1 per cent of chlorine in packing (probably chlorine that is held mechanically in the bleach), and then should have from 33 to 38 per cent. of available chlorine at the works. When bleach is imported into the United States, it rarely contains over 32 or 33 per cent. of available chlorine, the rest being lost in transportation.

73. Composition of Bleaching Powder.—When bleaching powder was first made, it was considered to be calcium hypochlorite, $Ca(OCl)_2$. It was then shown that this was improbable and that certain considerations seemed to lead to the view that the powder was a mixture of calcium chloride and hypochlorite, $CaCl_2 + Ca(OCl)_2$. There are, however, several reasons for assuming that this formula is incorrect. Among others, it might be mentioned that if it contained calcium chloride, it should be deliquescent, but bleach is not; calcium chloride is soluble in alcohol, but it cannot be extracted from bleach by this means. Lunge has proposed the formula  $Ca\begin{matrix} \diagup Cl \\ \diagdown OCl \end{matrix}$ for the substance, and has so well supported this view by experiment that it is generally accepted as correct. When bleach is dissolved in water, it breaks up into calcium chloride and hypochlorite.

74. Valuation of Bleach.—The only constituent of value that bleaching powder contains is the chlorine that can be utilized for bleaching purposes. The amount of the available chlorine is determined by analysis, and in most countries, outside of France, the value of the bleaching powder is expressed in terms of the percentage of the available chlorine contained, as shown by analysis. For example, a 32-per-cent. bleach means that the bleach under consideration contains 32 per cent. of chlorine that is available for bleaching purposes. In France, and to some extent outside of that country, the strength of the bleach is expressed in Gay-Lussac degrees; that is, the number of cubic centimeters of chlorine gas, reduced to the standard conditions of 0° C. temperature and 760 millimeters of mercury pressure, that 1 gram of the bleaching powder will yield. If it is remembered that 1 gram of chlorine under standard conditions occupies 314.7 cubic centimeters, it is easy to calculate the Gay-Lussac degrees from the percentage in the composition. For example, if there is 32 per cent. of available chlorine in a sample of bleach, each gram of the bleach will contain .32 gram of available chlorine and will yield $314.7 \times .32 = 100.7$ cubic centimeter of chlorine under standard conditions, or it is 100.7° Gay-Lussac, strong. These are sometimes called *French degrees*, and the percentage of available chlorine in the bleach is frequently called *English degrees*. Table II shows at once the relation between the Gay-Lussac degrees and the English degrees.

TABLE II

RELATION BETWEEN GAY-LUSSAC AND ENGLISH DEGREES

Gay-Lussac Degrees	English Degrees	Gay-Lussac Degrees	English Degrees	Gay-Lussac Degrees	English Degrees
63	20.02	85	27.01	107	34.00
64	20.34	86	27.33	108	34.32
65	20.65	87	27.65	109	34.64
66	20.97	88	27.96	110	34.95
67	21.29	89	28.28	111	35.27
68	21.61	90	28.60	112	35.59
69	21.93	91	28.92	113	35.91
70	22.24	92	29.23	114	36.22
71	22.56	93	29.55	115	36.54
72	22.88	94	29.87	116	36.86
73	23.20	95	30.19	117	37.18
74	23.51	96	30.41	118	37.50
75	23.83	97	30.82	119	37.81
76	24.15	98	31.14	120	38.13
77	24.47	99	31.46	121	38.45
78	24.79	100	31.78	122	38.77
79	25.10	101	32.09	123	39.08
80	25.42	102	32.41	124	39.40
81	25.74	103	32.73	125	39.72
82	26.06	104	33.05	126	40.04
83	26.37	105	33.36	127	40.36
84	26.69	106	33.68	128	40.67

75. Uses.—Bleaching powder is used mostly for bleaching vegetable fibers. The fiber to be bleached is first saturated with the bleach in clear solution; it is then "soured" by passing it through dilute acid and is finally washed. Since the bleaching powder must be dissolved, it would seem that it might better be made direct in solution, as was done in the early days of the industry. The solution of bleaching powder does not keep well, however, and the large amount of water makes it inconvenient and expensive to transport. Liquid bleach therefore is made only in a few cases where the bleaching establishment is near an alkali works. In making liquid bleach, the chlorine is not passed through the milk of lime, for this operation would put too much pressure on the chlorine stills, but goes over the surface of the liquid and is thus absorbed.

76. Eau de Javel.—The first bleach manufactured was prepared by passing chlorine into a solution of potassium carbonate (crude potash). As the works were situated at Javel, near Paris, the bleach took its name from that place. A little later, sodium carbonate was substituted for the potash, and the solution made from this substance became known as *Eau de Labarraque*. This latter substance is still sometimes made and used for certain purposes. When the chlorine is passed over a sodium-carbonate solution, the first action is to convert the carbonate into the bicarbonate and form hypochlorous acid, according to the reaction

$$Na_2CO_3 + Cl_2 + H_2O = NaCl + HNaCO_3 + HClO$$

If the chlorine is passed long enough, the bicarbonate is decomposed and the carbon dioxide is evolved. The reaction is

$$NaHCO_3 + Cl_2 = NaCl + CO_2 + HClO$$

In this case, however, chlorate is likely to be formed. Another class of liquor, which is more stable than the preceding, is made by passing chlorine over caustic soda. The solution must be left slightly alkaline and kept cool to prevent the formation of the chlorate. The reaction then is

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O$$

By this means, a fairly stable solution of bleaching material is obtained. Until recently it was not considered possible to make this bleach solution stronger than 15 per cent. of available chlorine, and that strength did not keep well. It has been found, however, that this instability is caused by the presence of sodium ferrate, which acts catalytically and causes the solution to decompose. When the sodium hydrate is carefully purified from iron, solutions of the hypochlorite containing as high as 50 per cent. of available chlorine can be made, and solutions with 35 per cent. of available chlorine are quite stable. Solutions with 20 per cent. of available chlorine can be kept for weeks with practically no change. The solution must be kept slightly alkaline, however, or the hypochlorite will change over into the chlorate.

77. With the aid of the bleach liquors so far spoken of, acid must be used to get the bleach effect, and then it is necessary to wash thoroughly. Sometimes this is disadvantageous, and other hypochlorites are made that decompose more readily on the fiber and thus do not need acid. Practically all of these hypochlorites are made from the calcium hypochlorite. The aluminum bleach is the most important of these, and its method of preparation is typical of the method used in the preparation of all the others.

The aluminum bleach consists of a solution of a mixture of aluminum chloride and hypochlorite that is made by treating a solution of calcium bleach with aluminum sulphate; the calcium sulphate separates out, and the aluminum compounds are left in solution. The aluminum hypochlorite is very unstable and is made only as needed; it is so unstable that it decomposes on the fiber without the use of acid. The aluminum compound left is antiseptic, so that it not only does not need to be washed out, but in many cases it is a decided advantage to leave this compound on the bleached material. For example, when used to bleach paper stock, the aluminum chloride prevents fermentation when the stock is stored.

POTASSIUM CHLORATE

78. There are at present two general methods for making **potassium chlorate,** the *electrolytic,* which will be discussed in its proper place, and the *chemical.*

The chemical process most generally used consists in making calcium chlorate and then converting this into potassium chlorate by adding potassium chloride and allowing the less soluble potassium chlorate to crystallize out. The calcium chlorate is made by absorbing chlorine in milk of lime; so that probably calcium hypochlorite is first formed and then transformed into the chlorate. The reactions taking place are doubtless

$$\begin{aligned} & 2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O \\ \text{and} \quad & 3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2 \\ \text{or} \quad & 6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O \\ \text{and} \quad & Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3 \end{aligned}$$

A greater saving is made in this way than would be possible by starting with caustic potash instead of caustic lime.

RAW MATERIALS

79. Lime.—The lime used in this process should be the very best, and as free from impurities as possible. It is usually burned in a reverberatory furnace. The thoroughly burned lime is slaked, made into milk of lime, and strained before it goes to the absorbers. It should then be used without delay, as otherwise calcium carbonate will form and thus lead to a loss of chlorine.

80. Chlorine.—Chlorine made by either the Weldon or the Deacon process can be used, and generally no attempt is made to remove the water and carbon dioxide. The hydrochloric acid is removed only when it occurs in such large quantities as in the Deacon process. Chlorine made by Weldon's process is preferable, as it is stronger and gives better absorption.

81. Potassium Chloride.—Nearly all the potassium chloride used is imported from Germany, and it contains from 90 to 93 per cent. of potassium chloride. The other constituents are mostly soluble and are practically harmless. The following analysis gives a fair idea of the average composition of commercial potassium chloride, so-called *muriates:*

	PER CENT.
H_2O	4.50
Organic	.05
Insol. and Fe_2O_3	.15
Al_2O_3	.47
$Al_2(SO_4)_3$	.20
Na_2SO_4	.30
$CaCl_2$	.25
$MgCl_2$	.50
$NaCl$	2.25
KCl	92.00

82. Water.—The water, especially that used for crystallization, must be pure. Suspended matter tends to prevent the formation of crystals and leaves them impure when formed. The presence of sulphides leads to the formation of lead sulphide, for there is usually lead in the final liquor from the lead crystallization pans. Sulphates are liable to be reduced by organic matter and thus lead to the presence of sulphides; they should therefore be excluded, as the lead sulphide will make the crystals dark colored and spoil their sale. Iron and carbonates are also objectionable.

APPARATUS AND PROCESS

83. Absorbers.—In making the calcium chlorate, the chlorine must be passed over the surface of the milk of lime. The absorption of the chlorine by this material takes place in large, flat, quadrangular tanks, which are built of slabs of sandstone. Where the sandstone slabs come together, they are grooved out, and a thick rubber cord is introduced. The whole is then tightly fastened together by means of iron tie-rods that are placed around the outside. In order that the absorption may take place more readily, each tank is fitted with an agitator that stirs and splashes the milk of lime so that an intimate mixture of it and the chlorine takes place. These agitators pass into the tanks through hydraulic lutes; the manholes in the tanks are also provided with hydraulic lutes, so that the tanks are closed tightly when in operation.

The absorbers are usually set up in series of from three to five, so that the liquor can flow from one to the next, while the chlorine enters the absorber that is most nearly finished and leaves the one newly charged. The gas that leaves the last absorber is nearly free from chlorine, but is finally run through a tower, down which milk of lime is flowing, in order to remove the last trace of chlorine before escaping into the air.

84. In carrying out the operation, the lowest absorber is emptied when the absorption is complete, and the contents of each absorber is run into the next lower one. The upper absorber is then charged with milk of lime of 1.085 or 1.100 specific gravity (that is, about 113 grams of CaO per liter). The absorber should not be charged over two-thirds full, for there is danger that it will foam over at some stage of the absorption. Chlorine is now passed into the lowest absorber, and this operation is continued until all the lime is converted into calcium chloride and calcium chlorate. As the chlorine is absorbed, the temperature of the absorbing liquid gradually rises and must therefore be carefully watched. The temperature should not be allowed to exceed 55° C., or the yield of chlorate will decrease. The temperature can be very easily regulated by adjusting the flow of chlorine. The charge requires from 12 to 30 hours from the time it is first run in until it is finished. The time depends on the size of the absorbers and the strength of the chlorine gas and the milk of lime. Slow absorption, using weak solutions, gives the best results from a chemical point of view; but, on the other hand, more concentrated solutions and quick absorption save time and fuel, so that a balance must be struck for each locality, depending on the price of coal.

The end of the reaction in the absorber is shown by the appearance of a pink color, which is due to the formation of calcium manganate from manganese in the lime or carried over with the chlorine. Another rapid test consists in filtering off a little of the solution and adding dilute hydrochloric acid to it. An effervescence, or evolution of chlorine, shows that the solution still contains calcium hypochlorite and that the operation is incomplete.

85. Settling Pans.—When the absorption is completed, the finished liquor is run into large iron pans, where it is left for from 3 to 10 hours for the insoluble matter, such as sand, calcium carbonate, etc., to settle out. The capacity of the settling pans must at least equal the capacity of the absorbers, for, on account of the sand, etc. that settles in these pans, their actual capacity is frequently much less than their nominal. When the liquor has settled thoroughly, it is pumped by means of force pumps having gun-metal barrels to a higher level, in order that it may then run by gravity through the rest of the operations. The best suction pipe for the pump is a short, rubber hose that can be moved so as to suck the liquor close to the mud without getting part of the latter into the concentrating pots. The mud is allowed to accumulate in the pans until they are nearly half full; it is then washed two or three times. The wash water is used in making milk of lime, while the mud is thrown out.

86. Concentrating Pots.—The liquor from the settling pans is carefully gauged, and a sample is sent to the laboratory for analysis. Meanwhile, the liquor goes to the concentrating pans, which are best made of cast iron and are similar in size and shape to those used in making caustic soda, and is here warmed. By this time the analysis of the liquor should be made, and the amount of potassium chloride necessary to convert the calcium chlorate into potassium chlorate is calculated. This amount, plus about 1½ per cent., is then added, and the whole is concentrated to about 1.31 specific gravity (taken hot). In winter, a slightly lower specific gravity will answer.

87. First Crystallizing Pans.—The concentrated liquor is now baled into the crystallizing pans. These are generally U-shaped, and are set into brickwork so as to be a slight distance above the floor. These pans are made of iron, and should be of such a size that the contents of a pot just fills a certain number of them. The room in which these pans are set should have a cement floor that slopes toward a catch basin. The pans are allowed to stand for from 9 to 14 days, depending on the time of year, to crystallize the liquor.

The crystals are filtered off by means of a centrifugal machine, thoroughly washed with water to remove the calcium chloride and iron, and then recrystallized.

The mother liquor, which is mainly calcium chloride, contains from 10 to 35 grams of potassium chlorate per liter, and is cooled to −10° C. by artificial means. In this way, the amount of potassium chlorate is reduced to about 3 grams per liter.

88. Recrystallization.—The crystals obtained by the first recrystallization always contain a large amount of impurities, and are therefore placed in a large, lead-lined, iron cylinder. Water is added and steam blown in until the solution has a strength of 1.10 to 1.11 specific gravity (taken hot). This apparatus is placed high enough so that the solution can be drawn direct to the crystallizing pans through 3-inch, steam-heated, steel pipes. These operations are carried out in a separate building and with all possible cleanliness. The crystallizing vats are usually of iron and are lead-lined; a convenient size is 5 feet by 4 feet, and 3 feet deep. These vats should be raised a little above the cement floor, so that leaks can be detected, and the floor should slope to a catch basin, to avoid loss of the liquor accidentally spilled. From 7 to 10 days are allowed for the crystals to separate out; they are then filtered off in a centrifugal machine and washed until not over .05 per cent. of chlorides is shown by testing.

The mother liquor is used for dissolving fresh crystals until it reaches a specific gravity of about 1.08; it is then too impure and is stored until enough is obtained, when it is boiled down and crystallized for crude crystals. The mother liquor from these crystals is run into the ordinary concentrating pots.

89. Drying the Crystals.—The thin, transparent crystals are thoroughly drained and then put on the drying table. This table is made of boiler iron, has an upturned rim, and is covered with lead. It is heated by steam.

90. Grinding the Crystals.—For many purposes, the dry crystals can be marketed direct; but for others, they must be ground to a fine powder. This is a very dangerous operation and must be performed with the greatest care. The engine for driving the mill is situated outside of the building, and all inflammable material is excluded so far as possible. The crystals are ground between two small stones (about 26 inches in diameter), of which only the top one revolves. The crystals are fed in at the center of the top stone through a hopper, and are best ground warm from the drying table, as in this way the mill clogs less. The ground crystals are then sifted through mechanically rocked sieves, and the fine powder is packed.

OTHER CHLORATES

91. Sodium chlorate is more soluble than the potassium salt, and for this reason is more suitable for many purposes; it is, however, for the same reason, not so easy to make, as it cannot be readily separated from the other substances in solution. Sodium chlorate can be made from the calcium-chlorate solution by evaporating it to 1.5 specific gravity, and then cooling to 10° or 12° C. The calcium chloride is crystallized out until there is only 1.2 molecules of calcium chloride to 1 molecule of calcium chlorate. By then adding sodium sulphate and a little sodium carbonate, all the calcium is precipitated and sodium chloride and chlorate are left in solution; then by boiling down, the salt is separated out and the chlorate alone is left in solution. The solution is then run off and cooled, when most of the sodium-chlorate crystallizes out free from salt.

92. Hargreaves makes sodium chlorate by the direct action of chlorine on crystalline sodium carbonate and systematic leaching, so as to dissolve out the soluble chlorate and leave the less soluble salt behind. He places the crystallized sodium carbonate in the tower *b*, Fig. 18, which is supported on the grate *c c*; the chlorine enters at *d* and, passing upwards, is absorbed. Liquor from the tank *e* slowly trickles down over the charge and is run off through pipe *f*. From this point the liquor goes into the sieve, which holds back any solid material, and then runs through into the cistern, from which it is pumped back again to the tank *e* until it is saturated with sodium chlorate. The liquor is then run off into pans and crystallized.

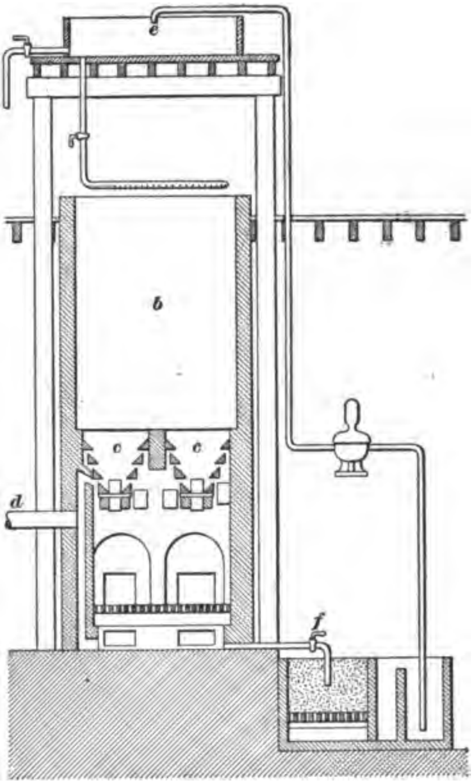


Fig. 18

93. Barium chlorate as well as any other metallic chlorates can be made from sodium chlorate by mixing the chloride of the metal whose chlorate is wanted, evaporating the mixture down, and fishing out the sodium chloride. The metallic chlorate then separates out in cooling. These chlorates may also be made in a similar manner to the methods just given for the making of sodium chlorate.

94. Chlorates, especially the potassium salt, are coming into extensive use in the manufacture of explosives for tunnel work, as the gases resulting from explosives of this type are less injurious than those from dynamite; they are also safer, as their constituents are transported separately and mixed on the spot. Nitrobenzal and nitrotuluol mixed with the chlorate are frequently used for this purpose.

ALKALIES AND HYDROCHLORIC ACID

(PART 3)

ELECTROLYTIC METHODS

GENERAL PRINCIPLES

THE ELECTRIC CURRENT

1. Sources of Current.—There are three sources from which a continuous flow of electricity may be obtained, namely, the *voltaic cell* in some one of its various forms, the *dynamo*, and the *thermopile*. Of these, the voltaic cell is too expensive to be used as a source of electricity for electrolytic work on a commercial scale, because its action depends on the dissolving of expensive materials. In the thermopile a flow of electricity is obtained by heating the junction of two metals and thus converting heat directly into electricity. This method, however, wastes heat, and is also too expensive for commercial use. The dynamo depends for its action on the rotation of a coil of wire in the field of force of a magnet, and as the coil can be rotated by means of a steam engine, or, better still, by water-power, it furnishes the most economical source of electricity at present known. The dynamo current is generally used direct from the machine, but it may be stored for future use by means of a special form of battery, called a *storage battery.*

The storage battery also has the advantages that it can be transported and that it will yield a uniform current. Any voltaic cell that, after being used, can be returned to its original condition by the passage of an electric current in the opposite direction is, in the perfect sense of the word, a storage battery. Only one form of battery, however, has proved itself useful for practical purposes. This consists of a plate of lead coated on both sides with lead peroxide and a plate of spongy lead dipped in a solution of sulphuric acid. If this battery has been charged and the two lead plates are joined by a wire, the lead becomes transformed into lead sulphate and hydrogen separates at the lead-peroxide plate. Here the hydrogen is oxidized to water, and the lead peroxide is reduced to lead oxide, which also goes over into lead sulphate. If a current is now passed into the cell for the purpose of recharging it, the reverse operations go on, and the cell is returned to its original condition.

For convenience, in this Section, the storage battery will be referred to as the source of current, although it should be borne in mind that all statements made will hold equally well for the current from any other source, at least so long as it is not an alternating current.

2. Analogies.—When two unconnected dishes of water are placed on different levels, there is a latent power in the water in the higher dish, by virtue of its position, that gives the water a tendency to flow into the lower one, which it will do if they are connected by an open tube. In a similar manner, the electric energy accumulated in the plates of the storage battery is latent so long as they are not connected; but as soon as they are joined by a wire, a current flows through the wire from the plate that corresponds to the higher dish of water into the plate that corresponds to the lower one. In the case of the water, it is said to have a "head" of a certain amount, measured by the difference of level of the two dishes; in the case of the electricity, the term head is synonymous with *difference of potential*, and this is measured in a unit called a *volt*. This difference of potential of the plates of a cell is called the *electromotive force* of the cell. The water in flowing through the tube is retarded by the friction of the tube, and therefore does not reach the lower level with as much force as would otherwise be the case. The flow of electricity is resisted by the conductor, and this resistance is measured in *ohms*. The quantity of electricity corresponding to the quantity of water is measured in *coulombs*, and its rate of flow is measured in *amperes*.

Since electricity is a manifestation of energy, perhaps its analogy to heat is a better one than that just given. In this case, the difference of potential, or electromotive force, corresponds to the difference of temperature of two points, the resistance of the conductor corresponds to the non-conductivity of the connecting medium for heat, and the quantity of current corresponds to the quantity of heat, in calories, that passes from the point of higher to that of lower temperature.

3. Units of Measurement.—Just as in measuring distance, a certain unit, as the foot or the meter, is arbitrarily selected to express the distance, or as in measuring differences of temperature, some definite unit, as a degree, is selected to express the difference of temperature, so, in electrical measurements, certain units have been selected carefully to express the various values that are dealt with.

The unit of resistance, the **ohm**, is the resistance at 0° C. of a column of mercury 1 square millimeter in section and 1.0626 meters long. The unit quantity of electricity, the **coulomb**, is the quantity of electricity that will deposit 1.118 milligrams of silver from the solution of a silver salt under suitable conditions. The unit of difference of potential, or electromotive force, the **volt**, is the difference of potential that will send 1 coulomb per second through a resistance of 1 ohm. The unit of the rate of flow of a current, the **ampere**, is the rate of flow that will carry 1 coulomb past a point on the conductor each second. The unit of electrical power, the **watt,** is the product of the volt and ampere, and is equivalent to $\frac{1}{746}$ horsepower; or, in other words, 746 watts equals 1 horsepower. The unit of electrical energy, the **volt coulomb,** or **joule,** is the product of the volt and coulomb, and is equivalent to .24 calory. The current density is measured by the number of amperes entering or leaving the solution per unit surface of the electrodes; it is usually expressed in *amperes per square decimeter*, although other units of surface are sometimes used, as the square meter, square foot, etc.

MEASUREMENTS

4. Resistance.—Electrical resistance may be measured by an apparatus called a **Wheatstone bridge.** A bridge when completed, ready for taking measurements, consists of three main parts: (1) An adjustable resistance box containing a number of coils, the exact resistance of each coil being known; (2) a galvanometer for detecting small currents; and (3) a battery of several cells. The coils of the resistance box are divided into three groups; two of these are called *proportional*, or *balance*, *arms*, and the third is known as the *adjustable arm*. Each proportional arm is composed of three and sometimes four coils with resistances of 1, 10, 100, and 1,000 ohms, respectively. The adjustable arm contains a large number of coils ranging from .1 ohm to 10,000 ohms.

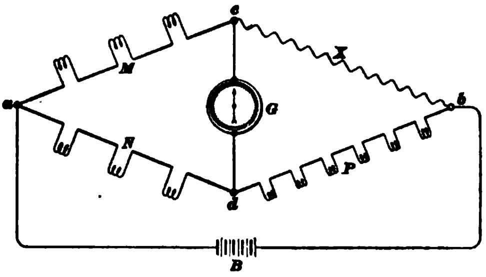


Fig. 1

The operation of the bridge depends on the principle of the relative difference of potential between two points in a divided circuit of two branches. The electrical connections of the bridge are shown in Fig. 1. *M* represents the resistance of one of the balance arms, which, for convenience, will be termed the upper balance arm; N, the resistance of the other balance arm, which will be termed the lower balance arm; P, the resistance of the adjustable arm; and X, an unknown resistance, the value of which is to be determined. One terminal of the detecting galvanometer G is connected at c, the junction of the upper balance arm and the unknown resistance; the other terminal is connected at d, the junction of the lower balance arm and the adjustable arm. One pole of the battery is connected at a, the junction of the two balance arms; the other pole at b, the junction of the adjustable resistance and the unknown resistance. The current from the battery divides at a, part of it flowing through resistances M and X, and the rest through N and P. When the resistances M, N, P, and X fulfil the proportion $\frac{M}{N} = \frac{X}{P}$, then the two points c and d will have the same potential, and no current will flow through the galvanometer G. Since the resistances of M, N, and P are known, the resistance of X may be found by the fundamental equation $X = \frac{M}{N} \times P$, provided the arms are so adjusted as to cause no deflection of the galvanometer. For example, suppose that the two ends of a copper wire are connected to the terminals b and c, and after adjusting the resistance in the arm so that the galvanometer shows no deflection, the resistances of the different arms read as follows: $M = 1$ ohm, $N = 100$ ohms, and $P = 112$ ohms. Then, by substituting these values in the fundamental equation,

$$X = \frac{M}{N} \times P = \frac{1}{100} \times 112 = 1.12 \text{ ohms}$$

5. The coils of resistance can be bought already put up in boxes and standardized, so that it is frequently more convenient to buy them that way than to make them. They are called **resistance boxes.** In these resistance boxes, as shown in Fig. 2, the ends of the wire of each spool are fastened to metal pieces a, which are so arranged that they can be connected by a metal pin b. When the pin is in place, the current can flow from one plate to the next through the pin, and there is practically no resistance. When the pin is removed, however, the current must flow through the wire, and a resistance is thus introduced.

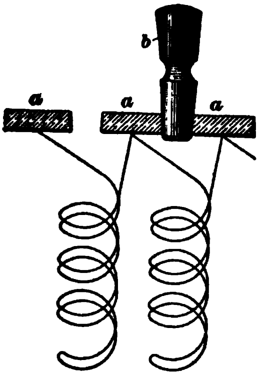


FIG. 2

Just as a certain resistance is found when an attempt is made to pass an electric current through a wire, so is a resistance met when a solution is used as a conductor. The determination of the amount of this resistance is a matter of importance.

6. Conductivity of Solutions. Although it is customary to speak of the resistance of a wire, sometimes the *conductivity* is spoken of, and in the case of solutions, it is much more common to speak of the conductivity than of the resistance. The unit of conductivity, which has no special name, is the conductivity of a body that, for 1 centimeter length and 1 square centimeter base, has a resistance of 1 ohm. The specific conductivity of a solution is the conductivity of a centimeter cube of the solution. The conductivity of solutions, however, is expressed as the equivalent conductivity of the solution; this is the specific conductivity multiplied by the number of equivalent weights in grams of the dissolved substance in 1 cubic centimeter of the solution. By the term *equivalent weight* is meant the molecular weight divided by the number of valences represented in the metal part of the salt; or, in the case of acids, by the the number of acid-hydrogen atoms. For example, $\frac{H_2SO_4}{2}$, HNO_3, CH_3COOH, $\frac{K_2SO_4}{2}$, $\frac{CaCl_2}{2}$, etc., if the formulas are expressed in terms of the atomic weights, are equivalent weights.

7. Effect of Temperature.—The conductivity of solutions increases very rapidly with a rise of temperature. The amount of the increase varies for different solutions, but it averages about 2 per cent. of the conductivity for each degree rise of temperature; of course, a fall of temperature gives the reverse effect. It is therefore very necessary to keep the solution at a definite temperature while making the conductivity measurements. For this reason, the vessel containing the solution is kept in a constant-temperature bath during the whole time of the measurement.

8. Constant-Temperature Bath.—A suitable **constant-temperature bath** for technical work may be made by wrapping a wooden pail in felt, as by this means water at nearly the same temperature as the room can be kept at a constant temperature for a long time. (Most determinations are made at either 18° or 25° C.) With an arrangement of this kind, the desired temperature can be obtained by mixing hot and cold water, the temperature being determined by a thermometer hanging in the water. When higher temperatures are to be used or several determinations are to be made at one time, more elaborate apparatus, with stirrers and automatic temperature regulators, can be arranged.

9. Conductivity Vessel.—The **conductivity vessels** vary in form, according to the conductivity of the solution. For solutions of low conductivity, as the organic acids, ammonia, etc., a resistance vessel with broad electrodes placed close together is necessary; for better conducting solutions, as inorganic acids, salts, and caustic alkalies, a small surface of electrodes with a rather long and small connecting tube is more suitable.

For the first class of solutions, a vessel like the one shown in Fig. 3 is the most suitable. This vessel *S*, which is cylindrical, is made of glass and is fitted with a hard-rubber cap *b* having three holes. One of these holes is for a pipette, when it is necessary to introduce or remove liquid, and the other two are for the electrodes. The electrodes consist of two

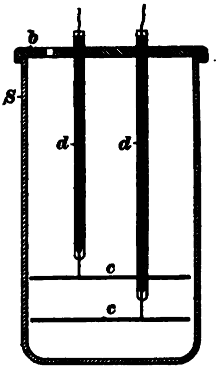


FIG. 3

circular platinum disks *c*, *c* that are fastened to capillary glass tubes *d*, *d* by means of heavy platinum wire. The capillary tubes are filled with mercury, which makes a connection between the ends of the platinum wires from *c*, *c* and the copper wires that lead to the other connections. The glass tubes *d*, *d* are securely fastened into the cover *b* by means of sealing wax, so that the platinum disks *c*, *c* always hold their relative positions.

For the better conducting solutions, a vessel of the form shown in Fig. 4 is very suitable. It consists of a glass

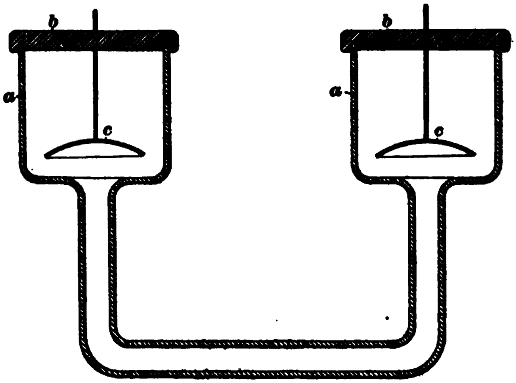


FIG. 4

vessel *a*, each arm of which is provided with a hard-rubber cap *b* bearing a curved platinum electrode *c*.

10. Platinizing the Electrodes.—The electrodes in either vessel should be coated with a good layer of platinum black. This is best obtained by introducing the clean platinum electrodes into a 3-per-cent. solution of platinum chloride containing $\frac{1}{40}$ per cent. of lead acetate, passing the current from four Daniell cells for 5 or 10 minutes, and then reversing the current and passing it for an equal length of time in the reverse direction. The electrodes must be thoroughly washed before they are ready for use.

11. Determination of the Conductivity of Solutions.—In determining the **conductivity of solutions,**

use is made of the apparatus described in Art. **4**, except that, on account of the polarization (see Art. **26**) by the passage of the current, it is not possible to use a direct current. Instead of the direct current, it is necessary to have a current that flows in one direction at one instant and in the opposite direction at the next instant. By this means, polarization can be largely avoided. The alternation of the current can be produced by means of an induction coil that is introduced between the battery *B*, Fig. 1, and the Wheatstone bridge. The difficulty then arises that the galvanometer cannot be used, for the rapidly alternating current will simply cause the needle of the galvanometer to vibrate. Therefore, in place of the galvanometer *G*, a telephone is used. This instrument gives a buzzing sound as long as a current flows through it, and thus shows when the branches of the bridge are equal.

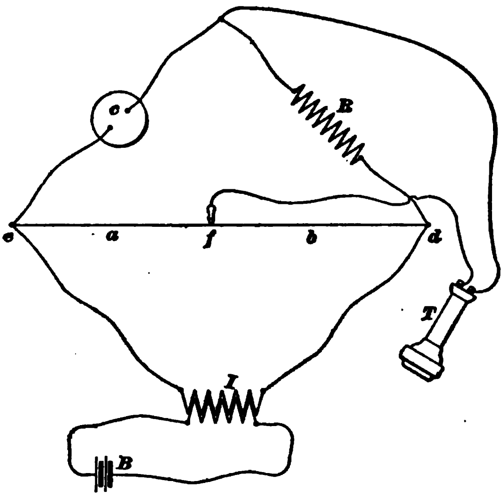


FIG. 5

This arrangement is shown in Fig. 5. The battery *B* furnishes the current to the induction coil *I*, where it is made to alternate rapidly. The conductivity vessel is represented by *c*, and a known resistance by *R*. *R* and *c* make up two sides of the Wheatstone bridge and the wire *e a b d*, which is stretched over a graduated scale and has a sliding contact f, makes up the other two sides. In making a determination, the solution is placed in the conductivity vessel c, and this vessel is put in a constant-temperature bath. The resistance R is selected so as to be nearly equal to the unknown resistance (or conductivity). (If the resistance of the solution in c is totally unknown, a preliminary determination will show the approximate value of c, when R can be suitably selected.) The induction coil I is then started, and the contact f is slid until the noise in the telephone T ceases. By then reading the length of a and b on the scale, the ratios $\frac{a}{b} = \frac{c}{R}$ will be known. That is, a, b, and R are known, and since $R \times \frac{a}{b} = c$, c is easily found, and the conductivity equals $\frac{1}{c}$. To get the specific conductivity, which is the conductivity of a cube of the solution with 1 centimeter edge, it is necessary to know the surface measurements of the electrodes and their distance apart. This is not easily determined, however, so that use is generally made of what is called the *resistance capacity* of the vessel.

12. Resistance Capacity.—In order to determine the **resistance capacity**, use must be made of some compound that can be obtained in a pure state, of which a solution of definite strength can be prepared and whose specific conductivity is already known. In order, however, to obtain accurate results, the resistance capacity of the vessel in which the determination is to be made must be ascertained.

Calling the specific conductivity of a certain solution l, that of the same solution in the vessel used L, and the desired resistance capacity of the vessel K, the following formula is obtained:

$$K = \frac{l}{L}$$

In all further determinations with the same vessel, the value K can be used, as it represents a constant so long as the electrodes keep their relative positions. From this it follows that, having determined the conductivity of any other solution in the same vessel, the specific conductivity of any such solution may be obtained by the formula

$$l = KL$$

13. Solutions for Resistance Capacity.—The following solutions may be used in determining the resistance capacity of a vessel:

A sulphuric-acid solution, 30 per cent. H_2SO_4, has a specific gravity of 1.223 at 18° C. Ordinary chemically pure sulphuric acid is suitable for making the solution. The specific conductivity at 18° C. is $l = .7398$. A ± error of .005 in the specific-gravity determination causes a ± error of .004 in the conductivity value.

A magnesium-sulphate solution has a specific gravity of 1.19, at 18° C. Commercial chemically pure magnesium sulphate is good enough for use. The specific conductivity at 18° C. is $l = .04922$. An error of .003 in the specific gravity corresponds to an error of .00001 in the specific conductivity.

Other solutions are sometimes used, but these will usually meet the needs of the worker in the electro-alkali industry.

14. Quantity of Electricity.—The **quantity of electricity** is measured by determining the amount of silver deposited by the current; or, since there is a direct relation (see Art. **23**) between the amount of silver and any other metal that may be separated, copper and, sometimes, hydrogen are separated instead of silver. A suitable arrangement for carrying out this measurement consists of a copper plate or wire gauze that can be accurately weighed and two other copper plates. In measuring the quantity of electricity, the weighed plate is hung, between the other two copper plates, in a solution of 15 grams of copper sulphate, 5 grams of sulphuric acid, and 5 grams of alcohol in 100 cubic centimeters of water. When the current passes, the copper is dissolved from the outside plates and deposited on the weighed one; thus, by weighing the middle plate at the end of the process, the amount of current that has passed can be readily calculated. Each coulomb deposits .329 milligram of copper;

therefore, the total weight, in milligrams, of copper deposited divided by .329 gives at once the number of coulombs of electricity that has passed through the voltmeter.

In another style of apparatus for this purpose, platinum electrodes are used. The current is passed through a solution of sulphuric acid, and the gas evolved is measured.

The arrangement first mentioned can also be used for measuring amperes; thus, by noting the time required for copper to deposit on the plate, all the information necessary for the calculation is obtained. The number of coulombs divided by the number of seconds required for them to pass gives the number of amperes. For example, if the voltmeter shows 40 coulombs in 40 seconds, then the number of amperes is 1.

15. Ammeters.—Although the preceding arrangement is the most exact for measuring the quantity of the current of electricity, there are instruments, known as **ammeters**, that have a sufficient degree of accuracy for most technical work, and, on account of their great convenience in handling, they are extensively used. These instruments are made in many forms, but probably the most convenient and accurate is that shown in Fig. 6, which is known as the *Weston ammeter*.

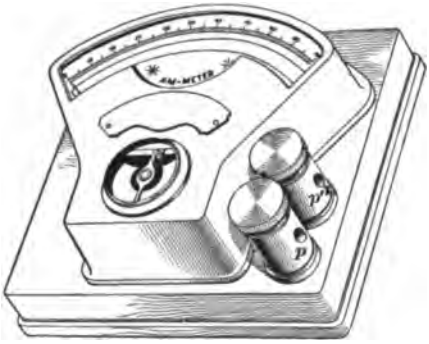


FIG. 6

The Weston instrument depends for its operation on the fact that if a coil, free to move, is pivoted in a magnetic field, it will swing around its axis when a current is passed through it. In these instruments, a rectangular coil is delicately pivoted between the poles of a permanent magnet, and when a current flows through the coil, it is deflected, carrying with it a pointer that swings over the scale shown in the figure. The movements of the coil are counterbalanced by small spiral springs; the greater the current, the greater is the deflection of the coil. The ammeter is inserted in the circuit so that all the current will pass through.

16. Measurement of Electromotive Force.—The electromotive force is measured most exactly by using a standard cell of known electromotive force and comparing the unknown electromotive force with it. The best known standard element is Clark's, which consists of a rod of zinc in a saturated solution of zinc and mercury sulphates, and has mercury for the other pole. Such an element, when carefully made, has an electromotive force of 1.4336 volts at 15° C. This cell varies considerably with the temperature, on account of the varying solubility of the zinc sulphate with varying temperature. The high temperature coefficient is a decided disadvantage, so that the Weston cell, which has a comparatively small temperature coefficient, is gaining favor. The Weston cell consists of a cadmium amalgam in a saturated solution of cadmium and mercury sulphates, with mercury for the other pole.

A very suitable form of the Clark element, and one that can be conveniently made in any laboratory, is shown in Fig. 7. This element consists of a small glass cylinder *a* set in a wooden block *b*. The cylinder contains mercury *c* in the

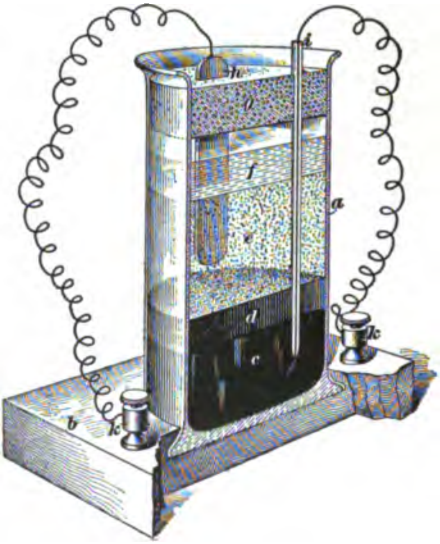


FIG. 7

bottom, then a layer of mercurous sulphate *d*, which is covered with a mixture of zinc-sulphate crystals *e* and a saturated zinc-sulphate solution *f*. A cork *g* is then soaked in melted paraffin, and a zinc stick *h* and a glass rod *i*, in which a platinum wire is fused, are fastened into the cork and the whole inserted in the cylinder. A layer of wax is then placed over the stopper, and wires lead from the platinum wire and the zinc stick to the binding screws *k*, *k*.

17. It is not advisable to compare a number of cells direct with a standard element, because this operation taxes the capacity of the element too much. The capacity of a constant element can be checked up against the standard and then used for comparison. The determination depends on the fact that if a constant cell is closed with a resistance, the fall of potential will be uniform over the whole length of the resistance. Furthermore, if a cell is connected with another cell of equal but opposed electromotive force, no current will flow.

The operation consists in closing the cell *E*, Fig. 8, with a resistance *a b*. The fall of potential is uniform then for each portion of *a b*. The wires connecting *E* with *a* and *b* are so large that they have practically no resistance compared with *a b*. From *a* a wire leads through the galvanometer *G* and the unknown cell *x* to the slide contact *c*. At intervals, to check the constancy of *E*, the standard cell is introduced at *x*, and *c* is moved until no current flows. Then *a c* represents the fraction of the electromotive force of *E* that is equal to the electromotive force *Y* of the standard cell. The standard cell is then replaced by the one to

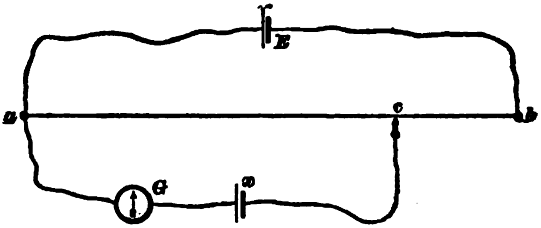


FIG. 8

be measured, and the point c, at which no current flows, is again established. Calling this resistance ac', then the electromotive force of the cell that is being measured is equal to $Y \times \frac{ac'}{ac}$. If a Clark standard cell is being used, $Y = 1.4336$ and $1.4336 \times \frac{ac'}{ac}$ is the unknown electromotive force.

A small storage battery is a very suitable cell for E, and the distance ac need only be determined twice a day.

18. The Voltmeter.—For a great many purposes, an instrument called a **voltmeter** is sufficiently accurate and much more convenient for measuring electromotive forces than the method just described. This instrument is really an ammeter having a *high* resistance and provided with a scale calibrated to read volts instead of amperes. By calling the current c, the electromotive force e, and the resistance R, then $e = cR$ (see Art. **20**). Then, if the resistance of the instrument is infinitely large compared with the resistance of the rest of the current, the instrument having been calibrated to read volts can be used to read direct. A voltmeter is connected across the circuit, so that the entire current does not flow through it.

19. Shunt Circuit.—When a wire leads continuously from one side of a battery, or other source of current, to the other side, it is called a **circuit**. If, however, two points of the circuit are connected by a wire, it is called a **shunt circuit**. For example, in Fig 9, the wire acb forms a circuit from the battery E. When a wire is brought across from a to b, a shunt circuit, or *shunt*, is formed. If the wire ab has a small resistance compared with acb, then most of the current will pass across ab, and in the reverse case, the opposite is true. If the wires are of equal resistance, the current will be equally

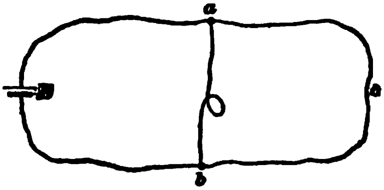


FIG. 9

divided. If it is desired to obtain the difference of potential between the points a and b, a high-resistance voltmeter is inserted in the shunt ab and the difference of potential is read direct.

20. **Ohm's Law.**—The relation existing between the current, the electromotive force, and the resistance of a system is known as **Ohm's law.** According to this law, the current is directly proportional to the electromotive force and inversely proportional to the resistance, or, expressed as an equation,

$$\text{current} = \frac{\text{electromotive force}}{\text{resistance}}$$

21. **Electric Conductors.**—When an electric current passes through a wire, the wire may become hot or suffer other physical changes, but it remains essentially the same as before. On the other hand, if the current passes through a solution, it decomposes the dissolved substance, and its products collect at the points where the current enters and leaves the solution. This leads to a division of electric conductors into two classes. All electric conductors that are not decomposed by the electricity passing through them are called conductors of the *first class;* all conductors that are decomposed by the electricity passing through them are called conductors of the *second class*, or *electrolytic conductors.*

There is an indefinite number of conductors of the second class, most of which may, however, be comprehended in the general title of solutions. Comparatively few pure substances other than the metals conduct electrolytically. Such substances as hydrochloric, nitric, and sulphuric acids, which are comparatively good conductors in water solution, do not conduct at all when in the pure, dry condition. By the pure, dry state is meant hydrochloric-acid gas condensed to a liquid; the same applies to nitric acid and sulphuric acid. Water is also a very poor conductor. Fused salts, however, conduct quite well, and some few, as lead and silver chlorides, conduct somewhat in the solid condition when not too far from their melting point.

ELECTROLYSIS

22. As just stated, sulphuric acid, although a non-conductor when pure and dry, is a good conductor when mixed with water, and the solution is an electrolyte. Solutions in general that conduct are called **electrolytes,** although the term electrolyte is frequently applied to the dissolved substance. For instance, in this case it is customary to speak of sulphuric acid as an electrolyte, meaning that its water solution is a good conductor.

The current enters and leaves the solution by wires, and these, where they dip into the solution, are called **electrodes.** When a current is passed through a sulphuric-acid solution, oxygen separates at one electrode and hydrogen at the other. The electrode at which oxygen, or, in general, the acid radical, separates is called the *positive electrode,* or **anode;** and the one at which hydrogen, or, in general, the metallic radical, separates is the *negative electrode,* or **cathode.** Since by the passing of an electric current through an electrolyte, matter separates out at the electrodes, the electrolyte must be decomposed and matter must be carried with the current, as the concentration about the electrodes soon differs from the rest of the solution.

The matter that travels with the current is called an *ion.* Ions are divided into two classes. The ions that travel toward the anode are called *anions,* and those which travel toward the cathode are called *cations.* The ions are perfectly definite substances, but frequently they are not the substances that separate at the electrodes, because, at the instant they are set free, they may react with the solvent to form new substances. For example, the ions from sulphuric acid are hydrogen and SO_4, the hydrogen separates as such, but the SO_4 breaks down and gives oxygen and sulphuric acid once more. In the electrolysis of sodium sulphate, the ions are sodium and SO_4, but the sodium reacts with the water to give hydrogen and sodium hydrate, and the SO_4 acts as in the preceding case, giving oxygen and sulphuric acid.

23. Faraday's Law.—When a certain amount of electricity passes through a solution of sulphuric acid, a definite amount of hydrogen is liberated. It does not matter how quickly this amount of electricity passes through the solution, because the same amount of hydrogen is sure to be liberated. Neither do the concentration of the solution and the temperature have any effect. Each gram of hydrogen liberated by an electric current requires the passage of 96,540 coulombs. It makes no difference what substance is electrolyzed to give hydrogen, so long as only hydrogen is liberated at the cathode, 1 gram will be freed when 96,540 coulombs of electricity have passed. If, therefore, an electric current is passed successively through solutions of hydrochloric acid, sulphuric acid, phosphoric acid, etc., exactly the same amount of hydrogen will be liberated.

What has been stated for hydrogen holds true for other elements and combinations of elements. If, in electrolyzing a solution of sulphuric acid, the hydrogen given off at the cathode and the oxygen at the anode (having waited until secondary reactions, which appear at the beginning of the electrolysis, have stopped) are measured, it will be found that the volume of the hydrogen is twice that of the oxygen; that is, the gases are liberated in the proportions in which they combine. *Equivalent weights of the substances are liberated.* Furthermore, if an electric current is passed successively through solutions of sulphuric acid, copper sulphate, silver nitrate, ferrous sulphate, and ferric sulphate, provided the solutions are suitably prepared to avoid secondary actions at the electrodes, there will result, when 1 gram of hydrogen is liberated, 31.5 grams copper, 108 grams silver, 28 grams iron from the ferrous solution, and 18.7 grams iron from the ferric solution. If the atomic weights of these elements are noticed, it will be found that the values just mentioned are in each case the atomic weight of the element, expressed in grams, divided by its valence. This relation was first noticed by Faraday and is known as **Faraday's law.**

Briefly stated, this means that chemically equivalent quantities of substances are separated by the same amount of an electric current, and for every 96,540 coulombs of current that pass, if no side reactions enter in, 1 gram equivalent each of the cation and of the anion is obtained.

24. Electrolytic Dissociation.—The way in which the current is carried in an electrolyte has long been a subject for speculation. It is now possible, however, to account for the quantitative phenomena of electrolysis by assuming that the dissolved substance is dissociated before the passage of the current. For example, when sodium chloride is dissolved in water, it is dissociated to a greater or smaller extent into sodium ions and chlorine ions, each of which bears a charge of electricity. That substances are dissociated is also made very probable by measurements of the boiling and freezing points of solutions of electrolytes. Now, when the current passes through the solution, for every 96,540 coulombs of electricity passed, a gram equivalent of the cation and of the anion separates out, gives off its charge at the proper electrode, and becomes an ordinary substance again.

Substances are usually not entirely dissociated in solution, but consist of a mixture of undissociated and dissociated molecules. In water solution, most of the salts and the stronger acids and bases are quite highly dissociated at moderate dilution, and the dissociation ranges from this to zero dissociation for non-conductors.

Since the electricity is carried by the ions, its conductivity by a solution must depend on the number of free ions in solution and the speed with which they move. An increase in the concentration of a solution increases the number of free ions and its conductivity, but this conductivity is not proportional to the increase in concentration, for the more concentrated a solution is, the less is it dissociated.

25. Migration Velocity.—The speed with which the ions move, generally known as **migration velocity**, depends on the viscosity of the solvent and the individual kind of ion. The speed with which some ions travel at 18° C. in water solution, with a difference of potential between the electrodes of 1 volt, is given in Table I.

It will be seen that the velocity with which ions move through water varies considerably, hydrogen and hydroxyl far exceeding all others. Hydrogen moves about five times as rapidly as chlorine, so that in the electrolysis of hydrochloric acid, there is a tendency for the concentration of the acid to decrease rapidly at the anode and to increase at the cathode.

TABLE I

SPEED OF IONS IN WATER SOLUTION

Cations	Centimeters per Hour	Anions	Centimeters per Hour
H	10.80	OH	5.60
K	2.05	Cl	2.12
NH_4	1.98	I	2.19
Na	1.26	NO_3	1.91
Ag	1.66	$C_2H_3O_2$	1.04

26. Polarization.—When a suitable electric current is passed between copper electrodes through a zinc-sulphate solution, the copper dissolves from the anode to form copper sulphate, and the zinc is deposited at the cathode. If, after the current has been passing for some time, the source of current is cut out and the copper plates are connected by a wire, a current will flow in the opposite direction from the first one. This phenomena is known as **polarization.** If the electromotive force of the cell is measured, it will be found to be about 1.1 volts. That is, a Daniell cell has been formed, and the condition very soon after the direct current begins to pass is the same as if a current were running against a Daniell cell. Therefore, it will not be possible to keep up the passage of electricity through a cell of this kind unless the original current has an electromotive force greater than the electromotive force of polarization.

The passage of a current through copper electrodes in a solution of copper sulphate simply dissolves copper from the anode and deposits it at the cathode, so that in this case there is no polarization, and a current of the smallest electromotive force will flow continuously.

Nearly all cases of electrolysis give polarization, and the passage of the current can only be continued when the electromotive force of the source of the current is greater than the electromotive force of polarization of the solution. This electromotive force of polarization can be measured directly, or it can be calculated from the heat of the reaction that would cause the polarization.

27. Calculation of the Electromotive Force of Polarization From the Heat of Reaction.—When a metal reacts in an electric cell, there is a certain amount of energy set free that may be evolved as heat or as electrical energy, as circumstances may favor the one or the other. If, therefore, the heat of the chemical reaction is known, the electromotive force of the cell can be calculated. This however, will, not give the exact value for the cell, because a temperature coefficient, which varies with the kind of cell, also enters into the calculation. Since the electromotive force of polarization is only the current tendency set up by the separated product, it can also be calculated in the same way as the direct electromotive force.

If the electromotive force of polarization is called e, and the valence of the ion is represented by n, then, when 1 gram ion has separated out, or if the gram ion is formed from the electrode and going into solution, the electrical energy is $ne\ 96{,}540$ volt coulombs. This, in calories, is $ne\ 96{,}540 \times .24 = ne\ 23{,}170$ calories. If the heat energy is represented by Q, then $Q = ne\ 23{,}170$, and $e = \frac{Q}{n\ 23{,}170}$ volts.

From this can be calculated very nearly the minimum electromotive force necessary to electrolyze a solution, assuming that no secondary reactions enter in. For example, if a solution of hydrochloric acid is electrolyzed, hydrogen separates at one pole and chlorine at the other. These, from their tendency to combine, will give an electromotive force opposed to the decomposing current, which can be calculated by the preceding formula. The heat of formation of a gram molecule of hydrochloric acid in dilute solution is 39,300 calories, and the valence of hydrogen is 1; therefore, $e = \frac{39,300}{23,170} = 1.69$ volts, and it will require a current of at least that electromotive force to pass continuously through such a solution.

28. Summary.—The electrolysis of a solution according to the preceding explanations may be summarized as follows:

1. Every electrolyte is, by the passage of the current, decomposed into two parts—the cation and the anion. These are in certain cases the positive and negative elements of the compounds. In other cases they are combinations of elements, as in potassium ferrocyanide, where the cation is potassium and the anion is the ferrocyanide radical.
2. The metal of a compound usually separates at the cathode, but in certain cases, as in ferrocyanides, one metal goes to the anode.
3. Water solutions of salts of the metals that decompose water naturally do not give the metal at the cathode, because as soon as the metal is separated it decomposes the water and forms a hydrate. Very strong solutions of the hydrates may be exceptions to this; also, when a mercury cathode is used, the metal dissolves in the electrode and is protected from decomposition.
4. The liberated ion appears only at the surface of the electrode.
5. There is a certain minimum electromotive force required for the electrolysis of a solution, and this is determined by the heat of reaction of the liberated ions. If less than this minimum electromotive force is supplied, the current will pass until enough of the ions are liberated to set up the electromotive force of polarization, when the current will stop. In the case of the electrolysis of a solution between electrodes of the same metal as the positive ion, there will be no polarization, and the weaker current will flow continuously.

6. The chemical work done is proportional to the minimum electromotive force of polarization, and if a greater electromotive force than the minimum is required, it will not appear as chemical work in separating more ions, but as heat energy.

7. Various secondary reactions may take place as: (*a*) The decomposition of one or both of the ions (usually the negative one, however); for example, SO_4 may decompose into SO_3 and O. (*b*) The ions may react on the electrodes, as in the electrolysis of dilute sulphuric acid between zinc electrodes, in which case the SO_4 acts on the anode, giving $ZnSO_4$, and only hydrogen is set free. (*c*) Abnormal ions may be liberated, as the frequent formation of ozone, O_3, the deposition of a black porous deposit of copper, and the deposition of lead or manganese dioxide on the anode.

ELECTROLYTIC PREPARATION OF ALKALI AND CHLORINE

INTRODUCTION

29. Historical.—The fact that solutions are decomposed by the electric current has been known since the beginning of the 19th century, and a process was patented for the electrolysis of salt solutions during the first half of that century. It was not until the dynamo was perfected, however, that the commercial electrolysis of salt solutions could even be considered. About 1880 an interest in the subject began to be shown by applications being made for patents; but even in 1888 many leading men in the alkali industry considered the electrolysis of salt in a commercial way impractical. At the present time, however, there are several processes that are considered commercially successful for the making of alkali and bleach from salt by electrolysis, and much more than half of all the chlorate of the world is made by this method.

30. Electrolysis of Salt.—The electrolysis of salt involves first the separating of the ions—sodium at the cathode and chlorine at the anode. Then, if fused sodium chloride is being electrolyzed, the chlorine is evolved and collected, and the sodium separates as metal; if the temperature is kept suitably high, the sodium can be drawn off and cast into bars. This process might be used for the preparation of metallic sodium, but the metal can be produced more cheaply and easily by the electrolysis of the fused hydrate. If a solution of salt is used for electrolysis, the chlorine will be evolved as before, but the sodium acts on the water as soon as set free and forms sodium hydrate and hydrogen. As soon as formed, the caustic-soda solution begins to conduct a portion of the current and to be decomposed, liberating oxygen at the anode and wasting the current. There is also a possibility that a portion of the chlorine will get mixed with the caustic liquor and thus form sodium hypochloric, which may in turn be converted into sodium chlorate, or be reduced by the hydrogen to sodium chloride. These various processes may be represented by the equations

$$\begin{aligned} 2NaCl &= Na_2 + Cl_2 \\ Na_2 + 2H_2O &= 2NaOH + H_2 \\ 2NaOH + Cl_2 &= NaCl + NaClO + H_2O \\ 3NaClO &= 2NaCl + NaClO_3 \\ NaClO + H_2 &= NaCl + H_2O \end{aligned}$$

In addition to the loss of alkali and chlorine by its reversion to salt, it should be remembered that, as was pointed out with the sodium hydroxide, all of these substances conduct and waste current.

31. Conditions Favoring Electrolysis.—The ideal conditions to be sought in selecting a process for the electrolysis of salt, for the formation of sodium hydrate and chlorine, may be summarized as follows:

1. The process must work at as low voltage as possible, in order to give the maximum decomposition per electrical horsepower.

2. The combination of the caustic soda and the chlorine to form sodium hypochlorite must be avoided, in order to prevent a loss of current and to avoid great wear and tear on the electrodes. The accumulation of the sodium hypochlorite also prevents the continuous use of the electrolyte.

3. The products of the electrolysis must not be allowed to accumulate in the decomposition cell.

4. Strong and pure solutions of sodium hydrate must be obtained, in order to avoid the expense of concentrating the solutions and that the product may be salable.

5. The apparatus must be simple and need but little attention and repairs.

32. Electrodes.—The cathodes in the electrolysis of salt solutions cause very little trouble, as it is comparatively easy to find materials that are resistant to the action of caustic soda. With the anode, however, it is much different, for here is set free the very active chlorine, and, by secondary actions, the still more active oxygen and oxides of chlorine. The obtaining of anodes that would be sufficiently resistant, and at the same time not too expensive, was one of the most difficult problems to solve in the early days of this work.

The two conditions that a successful electrode must fulfil are that it shall be a good conductor and at the same time resistant toward the products of electrolysis. The only substances that satisfactorily meet these conditions are carbon and the platinum metals, with their alloys. Carbon, in the form of coke, is not badly acted on by chlorine, but oxygen and the oxides of chlorine act on it considerably and cause it to disintegrate. The overcoming of this difficulty was at one time almost despaired of, and recourse was had to making the electrodes as cheaply as possible from slabs of gas coke and frequently renewing them. At the present time, however, carbon electrodes are made by mixing finely ground coke with tar and some suitable metal or metallic oxide, pressing the mixture into shape, and heating it to drive off the more volatile substances. The electrodes are then subjected to the highest temperature of the electric furnace. By this means, carbides of the metal are formed; but these are immediately decomposed, liberating the metal and leaving carbon behind in a fine graphite form. Carbon electrodes made by this or a similar method are now very generally used in the production of caustic soda and chlorine by electrolysis.

The other possible composition for anodes is an alloy of 90 per cent. of platinum and 10 per cent. of iridium, which is for more resistant toward the products of electrolysis than platinum alone. These electrodes are expensive, however, and are not so much used in the preparation of chlorine and caustic soda as the carbon electrodes. On the other hand, in the preparation of chlorates, the platinum-iridium alloy is almost exclusively used, as the use of carbon is practically out of the question on account of the oxidizing substances that form in large amounts.

FUSED ELECTROLYTE

33. The use of fused salt as an electrolyte offers certain difficulties that do not occur with the solution, and inventors have largely turned their attention to the perfecting of those processes which use solutions of salt in water. Three of the processes that use fused salt as an electrolyte and have been patented deserve mention; they are *Vautin's*, *Hulin's*, and *Acker's*. Of these processes, Vautin's proved impractical and has apparently been abandoned, but the other two processes are in apparently successful operation.

HULIN'S PROCESS

34. Hulin's process consists in the electrolysis of a fused mixture of sodium and lead chlorides, using a lead cathode. One difficulty that is experienced ordinarily in the electrolysis of fused salt is, that both the sodium and the chlorine rise to the top of the material and it is very hard to prevent loss by their reuniting. In this method, however, the lead cathode is fused; but this occurs at the bottom of the electrolyte, so that the chloride is evolved and carried away from the top of the apparatus and the sodium remains as an alloy with the lead at the bottom. Vautin employed a similar arrangement, but attempted to electrolyze sodium chloride alone. This led to the formation of a crust of the lead-sodium alloy on the surface of the cathode, with a subsequent high electromotive force and loss of sodium. Hulin avoids this difficulty by using an electrolyte of a mixture of sodium and lead chlorides, so that lead is continuously deposited with the sodium and an alloy of the proper composition is built up. By this method, the mixture of chlorides must continuously become poorer in lead chloride unless more of the substance is continuously added. This addition of lead chloride is best made, or rather the lead for the cathode is best supplied (for it consists in a simple transfer of lead from the anode to the cathode), by employing two anodes—one of carbon and the other of lead.

By allowing any desired fraction of the total current to pass through the lead anode, as much of it as is needed is dissolved in the electrolyte. It is found in practice that the best results are obtained by allowing 12 per cent. of the total current to pass through the lead anode and the remainder through the carbon anode. The electrolysis takes place in cast-iron crucibles, which are surrounded by poor heat-conducting material and lined with an insulator. The heat of formation of salt from sodium and chlorine is 97,600 calories, and therefore, according to the formula $\left(e = \frac{Q}{n\,23{,}170}\right)$, the electromotive force theoretically necessary to decompose fused sodium chloride is about 4.2 volts, because this value is calculated by using the heat of formation of solid sodium chloride; that for the fused chloride will be diminished by a value equal to the heat of fusion, and its electromotive force of polarization will also be less. In practice, each crucible employs a current density of 700 amperes per square foot of electrode surface and an electromotive force of 7 volts. By the use of such high current density it is possible to get a large amount of decomposition of the electrolyte per unit of electrode surface, and thus to employ a small plant.

The yield per electrical horsepower-hour is 81 grams of chlorine and 54 grams of sodium. The chlorine is converted into bleaching powder by the usual method. The lead alloy, which contains from 23 to 25 per cent. of sodium, may be sold directly for many uses where metallic sodium is required. This alloy, however, is usually treated with water, and by suitable working, a strong solution of caustic soda of a high degree of purity is obtained. This caustic requires very little fuel for its evaporation, and for this reason is much better than the more dilute caustic obtained by many processes. The lead is left by this operation as a spongy mass, and, together with considerable lead peroxide that is also formed, it makes a valuable by-product.

This process was considered so promising in 1899, that a company with a capital of over $500,000 was formed, and works, that are still in successful operation, were erected at Clavaux, France, for carrying out this method.

ACKER'S PROCESS

35. The **Acker electrolytic process**, which was operated at Niagara Falls, New York, until some years ago, when the works were destroyed by fire, differs from the Hulin process in that it uses fused lead as the cathode and continuously removes the sodium from the sodium-lead alloy, so that the lead can be used continuously. The apparatus for carrying out this process is shown in Fig. 10. It consists of an iron base *a* embedded in brick work *b*, which rests on brick pillars *c*. Sometimes, however, the apparatus rests on the ground and has places excavated for the parts projecting below the surface. The upper part consists of slabs *d* that are made of acid-resisting slate or of fireclay. These slabs are carefully luted into the iron shoulders, as shown, by fireclay. Through the top cover project three graphite anodes *e*, while at *f* is provided a charging hole for fresh salt. At *g* is molten salt, and at *h* an alloy of molten lead and sodium. At *i* is a pipe for conducting away the chlorine. At *j* is a pipe for blowing in steam; *k* serves for conducting away the hydrogen; and *l* conducts the fused caustic soda *o* to the shipping tin *m*. The extension *p* serves for drawing away the fused contents of the cell, when it is necessary to empty it for repairs, and *q* shows the cathode connection. At *s* is an iron plate that serves to separate the molten salt, which is the cathode proper, from the alloy below. The top is covered with a non-conducting material *t*, as asbestos wool.

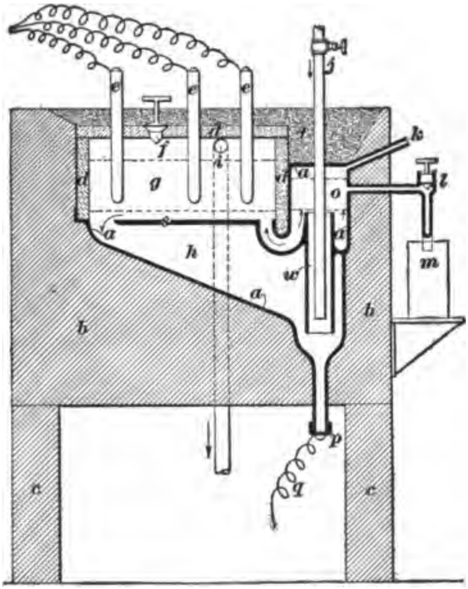


FIG. 10

36. To start the operation, the interior of the cell is heated by hydrogen flames until it is thoroughly hot; then molten lead and molten salt are run in, the covers and electrodes put in place, and the current started. The chlorine is given off at the anodes, rises to the surface, and is conducted away through the pipes *i*. The sodium separates on the surface of the fused lead, which acts as the cathode and alloys with it. Meanwhile, superheated steam is blown in through pipe *j* and thus causes the lead to rise in *w*, overflow, and circulate as shown by the arrows. As soon as the cell is in working order, the sodium alloy is decomposed in *w* by the steam, and the fused caustic soda rises to the surface of the lead in *o* and runs off through pipe *l* into the shipping can *m*. Pipe *l* contains a plunger valve, so that the flow of caustic can be stopped if desired. The lead flows in the direction of the arrows, displaces the sodium alloy just formed, and thus forms a system of circulation. The hydrogen, which is formed by the action of the steam on the sodium in the alloy, escapes through the pipe *k*, and can be collected and burned over the salt, in the form of an oxyhydrogen flame, to keep up the temperature of the cell. Since the cell is well insulated, the heat from the steam and the heat of the reaction

$$Na + H_2O = NaOH + H$$

nearly suffice to keep the temperature of the cell at the proper point.

DISSOLVED ELECTROLYTE

37. The so-called wet processes, or those in which the sodium chloride is in solution as an electrolyte, comprise the most important methods for obtaining the products of electrolysis. A serious difficulty is encountered in working these processes, however, because the materials formed at the electrodes tend to mix and form compounds that are not wanted. There are three methods by which the products formed about the electrode may be kept separate: (1) by a difference in the density of the liquids; (2) by diaphragms; (3) by using a mercury cathode.

DIFFERENCE IN DENSITY

38. In the processes that depend on the difference between the specific gravity of the sodium hydrate formed and the rest of the solution to keep the products of the reaction separate, the anode is placed at the top of the decomposition vessel, so that the chlorine is set free without traversing more than a small portion of the liquid. On the other hand, the cathode is placed at the bottom of the cell, and the caustic solution, being heavy, stays at the bottom and can be drawn off. Theoretically, this is a good arrangement, but practically, it is almost impossible to prevent the diffusion and mixing of the chlorine and caustic soda. This difficulty is also increased by the hydrogen, which is set free at the cathode, rising through the electrolyte and mixing it.

The *Richardson-and-Holland process* avoids the difficulty with the hydrogen by using a copper cathode covered with a coating of copper oxide. The copper oxide oxidizes the hydrogen as rapidly as it is formed. When necessary, the electrodes are removed and the copper oxide is regenerated by heating in the air. By this method a fairly good separation of the caustic soda and the chlorine can be maintained; this process was tried on a manufacturing scale, but it has been abandoned.

PROCESSES USING DIAPHRAGMS

39. The use of a diaphragm is a favorite method for keeping the solutions around the cathode and anode separate, but it is very difficult to find a diaphragm that will meet all the requirements. To be satisfactory, a diaphragm must resist the action of the contents of the bath, must keep the anode liquor well separated from that of the cathode, and must not offer great resistance to the passage of the current. Many diaphragms have been proposed, but none of them has proved very satisfactory until recently. Only a few of the various forms of apparatus using diaphragms for electrolysis of a salt solution, however, will be mentioned.

40. The Townsend Process.—Among the large number of diaphragm cells, the one invented by E. P. Townsend can be considered as one of the best and most efficient at the present time. A longitudinal section of this cell is shown in Fig. 11.

This cell is rectangular in shape and is about 9 feet 6 inches long, 3 feet high, and the upper part is 12 inches wide, while the lower part is 18 inches wide. The foundation *H* is made of a good concrete and extends the whole length of the cell. To this foundation is fastened a plate *D*, made of either hard rubber, earthenware, hardened asbestos, or some similar non-conductive material.

This plate is perforated and simply serves as a support for a diaphragm. Next to this perforated plate is placed the diaphragm *S* of woven asbestos cloth, the inequalities, or interstices, of which are filled with a paint made of ground asbestos fiber, oxide of iron, and hydrated oxide of iron in a colloidal condition. The object of this coating is to protect the asbestos cloth and to make it equally pervious to the brine. A sheet of metal or wire gauze, which acts as the cathode, is fastened as shown, so that there is first the perforated plate *D*, then the diaphragm *S*, and finally the metal or wire-gauze cathode. The reservoirs *I*, formed of bulging wire plates and generally known as the *cathode compartments*, are filled with some liquid hydrocarbon compound that is immiscible with and inert toward the cathode product, which, in this case, is sodium hydrate. The hydrocarbon compound best adapted for the purpose, is refined petroleum, or kerosene. On top of each of the cathode compartments is an outlet *R* for the escape of the liberated hydrogen, and at the bottom of each is another outlet *P* for the withdrawal of the cathode liquid, which is sodium-hydrate solution, as pre-

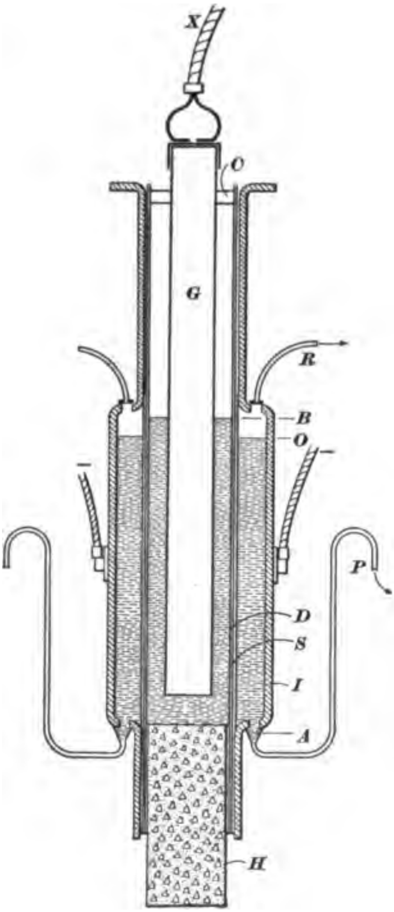


FIG. 11

viously stated. The level at which the sodium-hydrate solution is kept is indicated at *A*, and above this is the column of kerosene oil, the upper level of which is marked *O*. At *G* is shown the anode, or anodes, of Acheson graphite connected with the current conductors *X*, and the current connection to the cathodes is shown at the side of the cathode reservoir. The upper part of the anode chamber is closed with a perforated layer *C* of some inert substance, such as concrete. These perforations serve to conduct away the chlorine gas evolved.

The brine flows through the anode compartment in the center of the cell, and on its passage becomes weaker and weaker, owing to the transmission and transformation of the salt through the diaphragm and the cathode. This weakened brine, which also contains small amounts of sodium hypochlorite, sodium chlorate, caustic soda, and chlorine, is conducted to a reservoir, where it is again strengthened with salt, the hypochlorite decomposed, and the solution neutralized with a suitable amount of hydrochloric acid. The decomposition of the sodium hypochlorite and the neutralization of the brine are of considerable importance, owing to the fact that the accumulated hypochlorite acts on the anodes and rapidly disintegrates them. With little care, however, the formation of sodium hypochlorite can be avoided; in fact, the presence of this compound in more than comparatively minute quantities is an indication of a lack of care in the adjustment of the current and general management of the cells.

41. The most notable feature of the Townsend cell is the use of a non-conducting liquid, such as kerosene, in the cathode chamber. When this cell is in operation, the globule of the caustic-soda solution is forced through the perforated cathode plates by hydrostatic pressure and is surrounded by the kerosene, which is not only indifferent to the action of the caustic soda, but also to that of the electric current. The globule of caustic-soda solution, being thus removed from the field of activity, drops to the bottom of the cathode compartments from which it is drawn off. By increasing or decreasing the height of the salt solution in the anode chamber, its flow through the diaphragms and cathode plates should be regulated to conform to the decomposing potentiality of the current and the decomposition of the sodium hydrate into metallic sodium and subsequent reoxidation thus avoided. At present, a saturated solution of salt is used that circulates continually into and out of the cell through passages molded in the concrete for that purpose. The brine leaving the cell contains about .02 gram of sodium hypochlorite per liter, is decidedly alkaline, and is practically saturated with chlorine.

The chlorine leaving the anode chamber at *C* can be obtained about 97 per cent. pure, but it is considered better practice to draw it off 90 per cent. pure, owing to the fact that this gas is used in the manufacture of bleaching powder; also, in order to prevent a too rapid combination with the slaked lime employed in this process and a subsequent decomposition due to the heat of formation, the chlorine gas, especially during the warm weather, would have to be diluted with air anyhow.

In practice, it is found that with a current of 4.5 volts and 4,000 amperes 460 pounds of sodium chloride can be decomposed in 24 hours in the Townsend cell. The efficiency of the cell is 96 per cent. of the theoretical output, and even if pressed to its highest output, it is never lower than 90 per cent., as will be seen from an average yield, which consists of 270 pounds of chlorine and 300 pounds of sodium hydrate, calculated to 100 per cent. $NaOH$. More economical work, but with a decreased output, may be done by reducing the voltage to 3.3.

The solution of caustic soda as it leaves the cathode chamber contains about 20 per cent. of sodium hydrate, but it is more economical to reduce this percentage, at least so far as the current utilization is concerned.

42. As has been previously stated, the solution of caustic soda is saturated with salt, which is crystallized out by evaporation. Triple-effect evaporators are used for this purpose, and by means of this kind of apparatus the specific gravity of the caustic-soda liquid can be brought up to 1.5, although in practice it is advisable to keep it much lower, owing to the fact that by bringing up the specific gravity as high as 1.5, too much salt is crystallized out and deposited in the vacuum chambers. After the caustic solution leaves the evaporators it is further concentrated in open iron kettles by direct heat. Finally, the solution is ladled from these open iron kettles into a finishing pot, where it is fused and then run into the usual form of sheet-iron drums. During the process of evaporation in the iron kettles, most of the salt is deposited and fished out. The finished caustic tests 76 per cent. sodium oxide, Na_2O. Although, as has been previously stated, it would be more economical theoretically to use a voltage of 3.3 in this cell and a strength of caustic-soda solution leaving the cathode chamber of 9 per cent. sodium hydrate, in practice it is better to run the cell at the higher voltage with the stronger solution of caustic, this, of course, at the expense of the increased current.

43. Le Sueur Process.—The **Le Sueur process** is a combination of the density and diaphragm methods of separation, for while it uses a diaphragm, the electrodes are so placed that the gravity separation will be as effective as possible. The electrolyzing vessel *a*, Fig. 12, is made of ¼-inch boiler steel, and is about 9 feet long, 5 feet wide, and 1½ feet deep. The anode compartment is made by building common bricks *b* in Portland cement to a height somewhat greater than the electrolyzing vessel and then covering the compart-

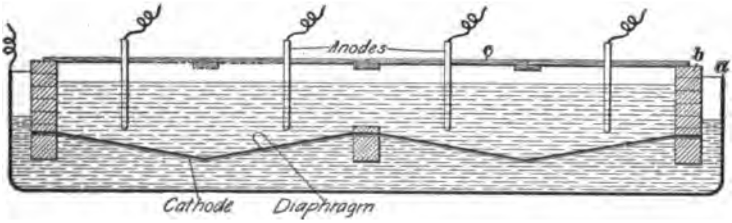


FIG. 12

ment with spruce planks *c*. Carbon has been discarded as an anode substance in favor of the 10-per-cent. iridium-platinum alloy already referred to.

The anodes are made according to a method devised by Le Sueur. This consists in rolling 4-inch pieces of the platinum-iridium wire very thin, except at one end; the unrolled ends are then bunched together and fastened in a glass tube so that they just extend into the interior, and the flat ends are spread out. When the anodes are in place through the spruce cover to the anode compartment, connection is made with the main conductor by means of a drop of mercury in each glass tube, an iron wire reaching to the top of each tube. These electrodes cost about 73 cents each, and enough to make 200 tons of bleach per month will cost about $5,000.

44. The anode compartment is separated from the cathode compartment by an asbestos diaphragm supported on a wire gauze, which at the same time serves as the cathode. By thus bringing the diaphragm close to the cathode, the resistance of the cell is diminished; also, by making use of the gravity system, the caustic soda is kept quite well separated from the chlorine. It is nevertheless impossible to prevent some diffusion and the formation of sodium hypochlorite, which not only causes loss of current, but also acts on the electrodes. This is avoided in the anode compartment by keeping the solution slightly acid with hydrochloric acid, which decomposes the hypochlorite and gives chlorine. The sodium hypochlorite that collects in the cathode compartment is converted into sodium chlorate and recovered. The diaphragm and cathode are arranged as shown, being sloped to one end of the cell, so that the hydrogen will pass to the higher parts and then out of the cell. On an average, the diaphragms last 7 weeks, but some have been known to last as long as 24 consecutive weeks. The anodes and the cell itself are practically indestructible. Instead of the theoretical 2 volts, the process uses 6½ volts and 1,000 amperes per cell. A solution containing from 10 to 15 per cent. of sodium hydrate can be separated by this process, but it will also contain considerable salt. This liquor is concentrated under diminished pressure, the salt separated by centrifugal machines, and the evaporation completed in iron pots.

The efficiency of the Le Sueur process is about 87 per cent. of the theoretical amount of chlorine and somewhat less of sodium hydrate. The process is in successful operation on a commercial scale at Berlin Falls, New Hampshire, where the caustic is used in making wood pulp and the chlorine is used to bleach the pulp.

45. Hargreaves-and-Bird Process. — The **Hargreaves-and-Bird process** can be best classed under the head of diaphragm processes, although, strictly, the diaphragm does not divide the cell. The process is distinctive in that the walls of the cell are composed of the diaphragm and the cathode. The diaphragm is composed of a layer of paper or some other suitable material, as a copper-wire gauze, covered with a layer of Portland cement, which in turn is covered with a layer of asbestos. This is impermeable to the salt solution, but allows the sodium ion to pass. The cell is put together with a copper-wire gauze, which serves as the cathode, on the outside, and the whole is set into an enclosing jacket. The carbon anodes are hung in the anode compartment, and the brine to be electrolyzed slowly flows in at the bottom of the cell and passes out at the top through the same pipes as the chlorine. During electrolysis, the sodium ions migrate to the top cathode and are there, as rapidly as set free, converted into caustic soda by blowing in steam; or into soda crystals, by steam and carbon dioxide.

The diaphragm and cathodes are made 10 feet long and 5 feet high, and as one is on each side of the cell this construction gives 100 square feet of cathode surface. A cell of this size decomposes on an average 237 pounds of salt every 24 hours, and gives 365 pounds of 37-per-cent. bleach and 213 pounds of soda ash by the use of 2,300 amperes and 3.9 volts per cell. This represents an efficiency of about 97 per cent. of the electrical energy used. The brine is best obtained direct from the wells; in passing through the cell, 75 per cent. of it is decomposed. The dilute brine can be returned to the well to be resaturated. The chlorine can be converted directly into bleach, and the caustic is strong and pure. In the manufacture of sodium carbonate, for which this process is well suited, the solution is so concentrated that the carbonate crystallizes out without concentration. The sodium carbonate made in this manner is very pure, averaging, when dehydrated, 97.9 per cent. of Na_2CO_3, 1.53 per cent. of $NaCl$, and .53 per cent. of Na_2SO_4, etc. The sulphate is probably due to sulphur dioxide in the furnace gases that are used for carbonating.

The apparatus is simple and requires very little attention. The only part that suffers great wear is the diaphragm, and that is quite cheap. This process has been running satisfactorily in a small way for several years, but a large plant has been erected recently in England.

46. A considerable amount of money has been spent in recent years in the purchase of many of these cells, with the right to use them, by paper makers that consume large quantities of bleaching powder, and also by those who employ the soda-pulp process for the manufacture of wood pulp. The main reason for making bleaching powder and caustic soda at paper mills is to reduce the cost of these products. It will readily be seen that the freight on the product is often the largest single item of cost, especially where mills that use from 10 to 15 tons of bleach per day are located a great distance from the chemical manufactory. Then, again, paper mills generally locate where water-power can be obtained, and thus have plenty of cheap power to operate the electrical apparatus. Even where soda wood pulp is not made, but where the sulphite process is in operation, a bleaching liquor is made by using the caustic soda as a base and saturating it with chlorine. This liquor is much more efficacious than bleaching powder. Then, too, owing to competition, mined salt of great purity is now sold much cheaper than lime.

PROCESSES USING A MERCURY CATHODE

47. Many processes for the electrolysis of salt in which a mercury cathode is used have been proposed. These have the advantage that the sodium separates with the mercury as an amalgam and can be converted into hydrate outside of the cell. By this means a solution of caustic soda of high concentration and practically free from salt can be made. The process suffers from the disadvantage that only dilute amalgams can be made, for otherwise there is a loss of current, and the mercury must therefore be frequently changed. There is also a chance of a large loss of mercury, because when the sodium is acted on by the water, mercury is mechanically carried away by the hydrogen; also, considerable mercury is carried off in the form of vapor, even at ordinary temperatures.

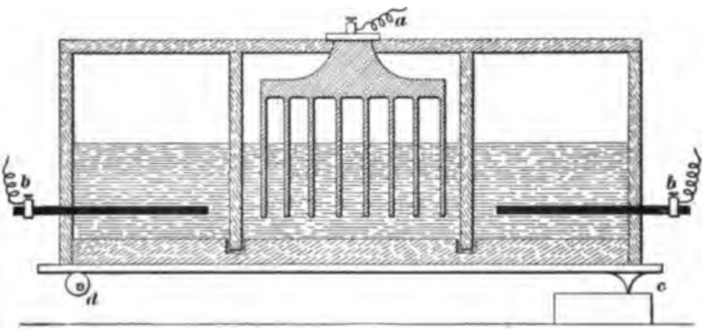


FIG. 13

48. Castner-Kellner Process.—The **Castner-Kellner process** is the most satisfactory and successful process of this character; in fact, it has proved to be the most satisfactory of all processes for the electrolytic decomposition of salt.

As shown in Fig. 13, the cell is divided into three compartments, the center one of which contains the iron cathode *a* and serves for the decomposition of the sodium amalgam. The two end divisions serve as anode compartments and contain the carbon anodes *b*, *b*. One end of the cell rests on a knife edge *c*, and the other is supported on an eccentric *d*, which revolves and thus slowly raises and lowers the end of the cell. Brine fills the two end compartments and is renewed, as necessary, by fresh brine flowing in; the exhausted brine is always resaturated. A thin layer of mercury covers the bottom of the apparatus, and is so regulated in amount that all of it practically flows alternately from the end compartments into the middle, as the cell rocks.

Strictly speaking, the ends of the cell are not anode compartments, but are alternately complete cells in which the salt is decomposed, the chlorine separating on the carbon anode and passing off, and the sodium dissolving in the mercury cathode to form an amalgam. Then, as the cell tips, the amalgam flows into the center compartment, where it forms the anode of a primary battery, and the iron electrode here becomes the cathode of this battery. This arrangement has the advantage that the hydrogen, instead of coming from the surface of the mercury and thus carrying that metal with it, comes from the iron cathode, and the sodium simply goes into solution from the mercury as caustic soda. There is also an advantage in that the current from this battery aids in the electrolysis in the end cells. Owing to the frequent removal of the sodium amalgam from the anode cell, it rarely contains over .02 per cent. of sodium, and as a consequence the cell gives a high degree of efficiency, being from 88 to 90 per cent. of the theoretical.

49. Since no caustic soda is formed in the anode compartment, there is no formation of sodium hypochlorite, and therefore the anodes have practically no wear. Also, since the electrolyte contains no hypochlorite, it can be used continuously by being conducted through a supply of salt so as to be resaturated. The resistance in the cell is very low, so that a current of 4 volts and 550 amperes per cell will decompose 56½ pounds of salt every 24 hours and will yield 38½ pounds of caustic soda and 34½ pounds of chlorine. The caustic solution can be made of nearly any desired concentration, and is practically made about 20 per cent. sodium hydrate. This solution can be concentrated by simple evaporation and yields a caustic 99½ per cent. pure. The chlorine obtained is from 95 to 97 per cent. pure, and for the rest contains a small amount of hydrogen. The cells are very simple and require only little attention, the work being almost automatic. Repairs are seldom needed, but when necessary any cell can be cut out of action without disturbing the work of the others. This process has been operating successfully for several years in England, on the Continent, and in America. The English company has been able to declare 8-per-cent. annual dividends on a capital of over 1½ million dollars, and the American company is doing much better.

CONCLUSIONS

50. From the foregoing, the following conclusions may be formed:

1. In the fusion processes, fused salt is a good conductor of electricity, and very high current densities can therefore be used, which means that a large output can be obtained from a small plant. Concentrated solutions of caustic soda, or, as in the Acker process, even fused caustic soda, can be made. On the other hand, the wear and tear on the cell, especially if heated from without, is very great, and the cost of keeping the material fused must be considered. The hot chlorine is not so easy to handle as the cold chlorine from the other processes and is also much more dilute.

2. The process using gravity for separating the products has very few good points.

3. In the diaphragm processes, the cells are cheap and the wear and tear on the cell is not great. They require very little skilled labor. They suffer, on the other hand, considerable loss of caustic soda and chlorine through their recombination and by reduction at the cathode, and have high resistance in the cell. This, however, is nearly proportional to the power of the diaphragm to stop diffusion, so that the higher the resistance, the smaller is the loss of the

products through mixing, and the reverse. Except in the Townsend process, the diaphragm processes furnish a low strength of caustic, the concentration and purification of which is expensive.

The Hargreaves-and-Bird process cannot be included in this general statement, as it is not strictly a diaphragm process.

4. The mercury-cathode cell has very little loss through the recombination of the products of the reaction. The cells are quite free from wear and tear. A highly concentrated caustic-soda solution can be made if desired, but it is usually cheaper to concentrate the solution after it has attained a strength of about 20 per cent. than to overcome too great a resistance of the solution. The initial cost of the cells is high, and a large amount of mercury is constantly in use. About 7 tons of mercury is required for each ton of caustic soda produced in a day. The power to move the cell is small, but must be considered in estimating the cost of working the plant; it also adds to the complication of the plant.

Various estimates of the cost of bleach and caustic by the electrolytic process have been made, and practically all of them show that these products cost more by this method than by the older processes. Nevertheless, the electrolytic processes are able to continue and pay dividends, so that, apparently, something is wrong with the calculations. The truth of the matter is that sodium hydrate can be made more cheaply by the ammonia-soda process than by any other, but this process cannot produce chlorine. The electrolytic process can produce chlorine more cheaply than the Le Blanc process, so that the electrolytic processes must be considered essentially as processes for the production of chlorine, and the caustic soda as a valuable by-product.

5. It may be well to discuss here the best method to adopt for the manufacture of caustic soda and bleaching powder, whether the Le Blanc, the ammonia-soda, or the electrolytic process.

In England, using Spanish pyrites, and in fact in any country where pyrites carries copper and where the utilization of the sulphur is of secondary importance, but where its oxidation products have to be condensed in order to prevent the insufferable nuisance caused by letting the sulphurous acid arising from the burning of the pyrites escape into the air, the Le Blanc process, coupled with the recovery of the sulphur, bids fair to hold its own. These conditions, however, do not prevail in the United States at present, and but few plants exist here where this process is practicable. With increased demand for copper and the enactment of laws compelling the condensation of sulphurous acid resulting from the roasting of its ores, the number of plants employing the Le Blanc process may be increased.

In the United States, the ammonia-soda process is the method principally used for the production of carbonate and caustic soda; but, unfortunately, as has been shown, the chlorine is lost in combination with calcium as calcium chloride, which finds only few large uses. In England, one use for calcium chloride is to add it to water used for sprinkling the roads, and, from reports, this plan has met with good results. Where good brine can be obtained from salt wells or strata for the pumping, and where limestone is cheap and coal can be had at a low price, these advantages far outweigh the loss of the chlorine.

The electrolytic processes have made great strides in late years—utilizing, as they do, both of the constituents of salt, and that directly without the intervention of complicated methods, as in the Le Blanc process—and leave nothing to be desired, provided electric power can be obtained cheaply, and, as in the Hargreaves process, carbonate can be quite easily made by introducing carbon dioxide into the cathode compartment of the cell. To illustrate, say that 1 electrical horsepower produced by means of water-power costs from \$18 to \$20 per annum. At the same point, using the most economical type of steam boiler and a turbine engine, it will cost from \$37 to \$38 per annum; with producer gas and a gas engine, \$40 to \$42; and with a reciprocating steam engine, \$42 to \$45. But it must be borne in mind that the electric power has to be paid for whether used or not. If 7,000 horsepower is to be contracted for, and, through the exigencies of supply and demand, the manufacturer's production should be curtailed one-half and only 3,500 horepower used, he would still have to pay for the 7,000 horsepower. Again, there are localities where good bituminous coal can be had for from 80 cents to $1 per ton at the mines, and if works could be located advantageously in such places, it would bring the cost of electric energy very close to that derived from water-power, considering the enormous investment necessary for installing the latter.

ELECTROLYTIC BLEACH

51. One of the main things to overcome so far has been the formation of hypochlorite in solution; however, when a bleaching solution is wanted, the hypochlorites are just what are needed. As early as 1883 Hermite patented a process and advocated the use of electrolytic bleach. He proposed to electrolyze solutions of calcium chloride, magnesium chloride, or a mixture of one or both of these with salt in such a way as to obtain hypochlorites in solution. This is easily accomplished by placing the cathode over the anode, so that the chlorine in arising, must pass through the caustic formed; and if the electrolyte is kept circulating through the bleach vat, the apparatus lasts well and the process is satisfactory.

52. A very satisfactory apparatus for carrying out an electrolysis of this character has been invented by Kellner. Fig. 14 shows an apparatus of this character in vertical section and ground plan. It consists of a cell *c* with a cover *d*. The side walls, which act as insulators, carry electrode plates *e*, *e'*, etc. and *f*, *f'*, etc. of carbon, or metal with platinum on one side. These extend alternately into the cell, so that the electrolyte is forced to zigzag between them in passing from one end of the cell to the other. The first and last plates extend through the cover and serve for connecting with the current. This arrangement makes it possible to electrolyze the solution in a small space, and also enables the operator to use a current of high voltage, as is frequently available from electric-light plants. By regulating the number of intervening plates, the current can be reduced in voltage for each section of the cell, in the same manner as if a series of the same number of cells was used.

In operating, the electrolyte enters *a* and flows in the direction of the current, finally leaving at *b*. The circulation of the brine is so regulated that about .05 per cent. of active chlorine is formed during each passage of the brine through the apparatus. When the brine has 1 per cent. of active chlorine, it is used for bleaching. The composition of the electrolyzed brine depends on the voltage, amperage, temperature, and the amount of sodium chloride present. The bleaching solution is clear, has an apple-like odor, and

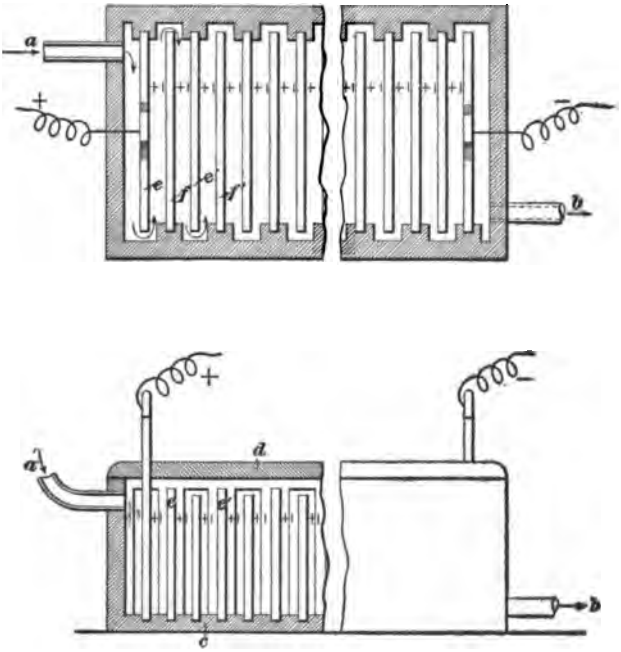


FIG. 14

keeps better than a solution of bleaching powder having the same amount of available chlorine.

53. The question as to whether it will pay to use this method is one that every user of bleach must decide from the conditions prevailing at his factory. In most cases, it is probably better and cheaper to allow the brine to be electrolyzed at some central plant, where the sodium can be saved as hydrate, and there to convert the chlorine into bleach, to be shipped to the place where it is needed. In some places, where large quantities of bleaching liquors are used, however, it will undoubtedly pay to make it on the spot, thus saving the carriage of large amounts of inert material in order to get the necessary chlorine.

POTASSIUM CHLORATE

54. It has been shown that if the products of electrolysis of an alkaline chloride are allowed to combine, the result is the formation of the hypochlorite. If, now, the conditions are suitable, the hypochlorite changes to the chlorate. The total result of the electrolysis of potassium chloride, when the solution is kept cool and the current density low, is represented by the equations

$$2KCl + 2H_2O = 2KOH + Cl_2 + H_2$$
$$2KOH + Cl_2 = KCl + KClO + H_2O$$

If the solution is allowed to heat up, however, the potassium hypochlorite goes over into potassium chlorate and chloride, according to the reaction

$$3KClO = 2KCl + KClO_3$$

If the intermediate reaction is omitted, the reaction for the formation of potassium chlorate from potassium hydrate and chlorine is

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$$

Finally, neglecting all intermediate steps, the reaction representing the final result of electrolyzing a solution of potassium chloride in such a manner as to give potassium chlorate, is written

$$KCl + 3H_2O = KClO_3 + 3H_2$$

A glance at this reaction, recalling Faraday's law, will show that it takes at least six times as much electricity to make 1 molecule of potassium chlorate as is required to decompose a molecule of potassium chloride; or, 6 molecules of potassium chloride is decomposed in order to get 1 molecule of potassium chlorate. It will thus seem that there is a great waste of current in this process; but if it is considered that by the older chemical methods 6 atoms of chlorine is required to make 1 molecule of potassium chlorate, it will be seen that as much loss occurs in the older methods as in the electrolytic process. The greatest argument in favor of the electrolytic method, however, is that it has been running for several years and at a profit. Apparently, therefore, potassium chlorate can be made at least as cheaply by the electrolytic method as by the old methods.

That it is possible to make chlorates by electrolysis, was probably first noted by Stadion in 1816. The process was patented in England by Charles Watt, in 1851, and the methods in use at present differ only in the details of the process and in the apparatus.

55. Gall-and-Montlaur Process.—The oldest process by which potassium chlorate has been successfully manufactured electrolytically is the **Gall-and-Montlaur process.** It uses lead-lined, rectangular tanks of about 11,000 gallons capacity that are insulated from the floor by means of oil cups. The same means are used for insulating the whole building. The anodes are an alloy of 90 per cent. platinum and 10 per cent. iridium, while the cathodes consist of a nickel-iron alloy. Large quantities of hydrogen (about 19,000 cubic feet for each ton of potassium chlorate) are set free in the process, and if this hydrogen comes in contact with chlorate or hypochlorite, either of the latter will be reduced and thus cause loss. To avoid the action of the hydrogen, the cathodes are enclosed in asbestos bags, which aid in carrying off the hydrogen. About a 25-per-cent. solution of potassium chloride is used in the electrolysis. This solution must be as pure as possible, for the presence of metallic oxides causes very rapid decomposition of the potassium hypochlorite first formed into potassium chloride and oxygen. An electromotive force of 5 volts and a current density sufficiently high to keep the temperature at 50° to 60° C. are employed in the electrolysis. The relative sizes of the cathode and the anode are so arranged that there is a high current density at the cathode and a low one at the anode. By this method of working, it is possible to obtain a current efficiency of over 50 per cent. The process is in use at several places.

56. Corbin Process.—The **Corbin process** is quite similar to the Gall-and-Montlaur process in that it produces the complete action in the cell. It makes use of secondary electrodes, however, and causes the electrolyte to circulate between them. The apparatus consists of cement cells with primary electrodes at the ends and a large number of platinum plates that act as secondary electrodes. These plates are set in ebonite frames and are placed from 12 to 15 millimeters apart.

When the current passes, one side of the secondary electrode acts as the cathode and the other as the anode, and since the plates are so close together, the reaction between the caustic potash and chlorine takes place readily, and by a high-density current the temperature is kept high enough, so that the chlorate forms at once. The process is in operation at Chedde, Savoy, but no details as to its success are available.

57. Blumenberg Process.—In the **Blumenberg process**, an attempt is made to avoid the secondary decompositions, the high density, and the reduction by hydrogen. This is done by first making caustic potash and chlorine, collecting them separately, and combining them outside of the cell. The potassium chloride is dissolved, filtered, and run into storage tanks *A*, Fig. 15, from which it can run directly into the electrolysis cell. This consists of a simple cell *B*, which is divided into anode *c* and cathode *d* compartments by a simple diaphragm *e*. During electrolysis, the potassium hydrate collects in the cathode compartment and the chlorine is saved in the gas holder *F*. When the electrolysis has continued long enough to give considerable caustic, the contents of both compartments *c* and *d* are allowed to mix in the pan *G*, and the chlorine is run in from the gas holder *F* to form the chlorate. Both the electrolysis cell and the pan *G* are arranged so that they can be heated by means of steam pipes when necessary. From the pan *G* the chlorate is run down into concentration and crystallization tanks. High efficiency is claimed for this process.

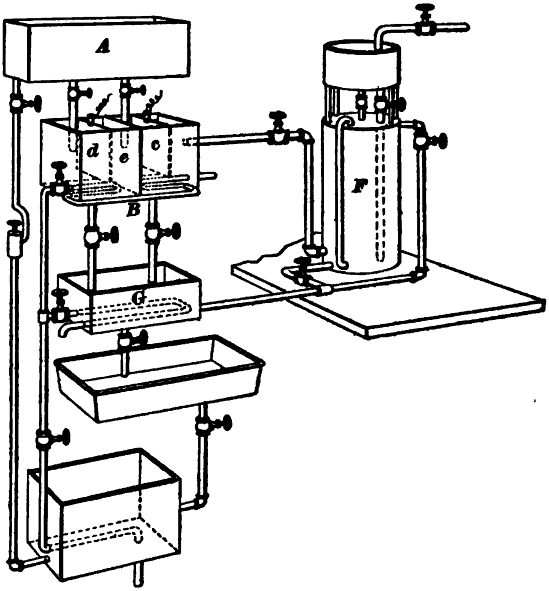


FIG. 15

58. Gibbs Process.—The fact that during the formation of potassium chlorate by electrolysis large quantities of hydrogen are formed, has already been mentioned. In order to avoid the reducing action of this gas, Gibbs makes use of cathodes of copper oxide, so that the hydrogen is oxidized as rapidly as it is set free. This also reduces the polarization at the electrodes. In other respects, the Gibbs method has little that is peculiar to it, and the feature just mentioned seems to be adapted from the Richardson-and-Holland process for caustic and chlorine. In the cell, the cathode is placed above, the anode below, and the temperature is kept at 80° or 90° C. When one-half of the potassium chloride in the cell has been converted into chlorate, the liquor is drawn off and the chlorate crystallizes out. The cathodes are then renewed, and those just used are reoxidized by heating in the air. This process is at present in successful operation at Niagara Falls.

59. Cell Solutions.—It has recently been shown that the presence of alkaline carbonates or the alkaline-earth hydrates in the cell greatly increases the yield of the chlorate, and probably all of the factories use one of these substances or calcium chloride as a constituent of the cell solution. In just what way these materials act is at present unknown, although several theories have been advanced.

ALKALIES AND HYDROCHLORIC ACID

(PART 4)

ANALYTICAL METHODS

AMMONIA SODA

CRUDE MATERIALS

1. Brine. — 1. The *specific gravity* is determined by means of a hydrometer or specific-gravity spindle; the amount of salt in the brine can then be stated with a fair degree of accuracy by reference to a table. This test is so rapidly made that it is used frequently for checking the brine as to its salt content when it comes to the works. Table I gives the percentage of sodium chloride corresponding to each specific gravity from 1 per cent. of salt to a saturated solution.

For convenience, special hydrometers are frequently used which are so graduated that percentage of salt is read direct, or the point where it stands in a saturated salt solution is marked 100 and the stem between this point and that which pure water gives is divided into 100 parts, so that the observer reads the percentage of the saturation of the brine.

To obtain the number of grams of salt in a liter of its brine, we move the decimal point in the specific-gravity value one point to the right and multiply by the percentage of salt at the specific gravity observed. For example, if the specific gravity is 1.204, then $12.04 \times 26.39 = 317.74$ grams per liter.

TABLE I

Specific Gravity	Per cent. *NaCl*	Specific Gravity	Per cent. *NaCl*	Specific Gravity	Per cent. *NaCl*
1.00725	1	1.07335	10	1.14315	19.000
1.01450	2	1.08097	11	1.15107	20.000
1.02174	3	1.08859	12	1.15931	21.000
1.02899	4	1.09622	13	1.16755	22.000
1.03624	5	1.10384	14	1.17580	23.000
1.04366	6	1.11146	15	1.18404	24.000
1.05108	7	1.11938	16	1.19228	25.000
1.05851	8	1.12730	17	1.20098	26.000
1.06593	9	1.13523	18	1.20433	26.395

2. *Inorganic sediment* is determined by filtering 500 cubic centimeters of the brine through a filter of known ash, igniting, and weighing. After subtracting the ash and multiplying the remainder by 2, the result is grams of inorganic sediment per liter of brine.

3. *Ferric Oxide and Alumina.*—200 cubic centimeters of filtered brine is acidified with a few cubic centimeters of nitric acid and heated for 10 minutes in order to oxidize any possible ferrous compounds, made slightly alkaline with ammonium hydrate, warmed 10 minutes, and filtered. The precipitate is redissolved in hydrochloric acid and the ferric oxide and alumina determined as usual. The number of grams of Fe_2O_3 and $Al_2O_3 \times 5 =$ grams of Fe_2O_3 and Al_2O_3 per liter of brine.

4. *Calcium oxide* is determined in the filtrate from the iron and alumina. One-half gram of ammonium chloride is added, and to the hot ammoniacal solution sufficient ammonium oxalate added to precipitate all the calcium. The calcium oxalate is filtered off, strongly ignited over a blast, and weighed as CaO. This weight, after subtracting the filter ash and multiplying by 5, gives the grams of CaO per liter of brine.

5. *Magnesia* is determined in the filtrate from the calcium precipitate by adding ammonium phosphate and strong ammonia solution, equal to one-third of the total volume of the solution, allowing to stand 24 hours, filtering, washing with dilute ammonia water, igniting at red heat, and weighing. The precipitate, after subtracting the filter ash, is magnesium pyrophosphate $Mg_2P_2O_7$. Wt. $Mg_2P_2O_7 \times .36036 \times 5 =$ grams MgO per liter of brine.

6. *Sulphur Trioxide.*—50 cubic centimeters of the filtered brine is acidified with a few drops of hydrochloric acid, diluted with an equal volume of distilled water, and heated to boiling. Boiling hot barium chloride is slowly added in slight excess and the whole allowed to stand until the precipitate completely settles. The barium sulphate is then filtered off and washed with hot water, first by decantation and then on the filter until free from chlorides. The precipitate is then ignited and weighed as usual. The weight of barium sulphate $BaSO_4 \times .34335 \times 20 =$ grams SO_3 per liter of brine.

7. *Sodium Chloride.*—The amount of salt in the brine is usually determined with sufficient accuracy by means of the hydrometer. If a more accurate determination is wanted, 10 cubic centimeters of the clear brine is diluted to 1,000 cubic centimeters and 10 cubic centimeters of this dilute solution is titrated with $\frac{1}{10}$ normal solution of silver nitrate, using potassium chromate as indicator. The number of cubic centimeters of $\frac{1}{10}$ normal solution of silver nitrate $\times .00355 \times 10{,}000 =$ grams of chlorine per liter.

Or, without a very great error, we may state, number cubic centimeters $\frac{1}{10}$ normal $AgNO_3$ solution × .00585 × 10,000 = grams salt per liter.

2. Grouping of Substances Determined. — The most rational method of procedure is to report each substance as found, but it is a very common requirement that the results shall be reported grouped together so as to form salts. In this case, this result is obtained by combining the SO_3 and CaO to form $CaSO_4$, any excess of calcium and the magnesium are then combined with chlorine and the excess of chlorine is then calculated as salt. Ferric oxide and alumina are usually reported as such.

3. Limestone.—For the analysis of an average sample of the limestone used through the month, and, in general, for a careful control of the materials used, the method of analysis given for limestone in *Quantitative Analysis* should be used. It frequently happens, however, that it is necessary to analyze one or more samples of the rock each day as it comes from the quarries. In that case the following more brief method is preferable.

1. *Insoluble.*—1 gram of the limestone is treated with an excess of dilute hydrochloric acid, warmed, filtered, washed, ignited, and weighed. In case the limestone contains a large amount of organic matter, this may be determined by filtering through a filter paper that has been heated to 100° C., cooled in a desiccator, and weighed. In this case the insoluble matter is dried at 100° C., cooled, and weighed before ignition. The difference between the weight of the insoluble matter before and after ignition gives the amount of organic insoluble matter.

2. *Lime.* — Dissolve 1 gram of the sample in 25 cubic centimeters of normal hydrochloric acid and titrate back to the neutral point with normal soda solution, using methyl orange as indicator. The difference between the number of cubic centimeters of acid and alkali used gives the number

of cubic centimeters of acid neutralized by the limestone. The number of cubic centimeters of acid used × 2.8 = percentage of CaO; or number of cubic centimeters of acid used × 5 = percentage of $CaCO_3$. By this method the magnesium carbonate in the limestone is reported as a calcium compound, but for most limestone used in the ammonia-soda industry this can be overlooked.

3. *Magnesia.* — In case the amount of magnesia is required, dissolve 2 grams of limestone in hydrochloric acid and precipitate the calcium directly by the addition of ammonium hydrate and ammonium oxalate to the hot solution. Allow to stand 10 minutes at a gentle heat, then filter and wash. Determine the magnesium in the filtrate by precipitating with ammonium phosphate. Make the solution strongly ammoniacal and let stand 2 hours with frequent, thorough stirring. The precipitate may then be filtered off, ignited, and weighed as $Mg_2P_2O_7$. $Mg_2P_2O_7 \times 18.018$ = percentage of MgO in the limestone; $Mg_2P_2O_7 \times 37.868$ = percentage of $MgCO_3$ in the limestone.

We can now correct the value obtained for lime. The molecular weight of $MgO = 40$ and of $CaO = 56$, therefore CaO is $\frac{56}{40}$, or 1.4 times heavier than MgO; therefore the percentage of $MgO \times 1.4$ = percentage of CaO that this percentage of magnesia would give as lime. In the same way we find that the percentage of $MgCO_3 \times 1.19$ = percentage of $CaCO_3$. It is now possible to report the percentage of lime or calcium carbonate in the limestone with a fair degree of accuracy. For example, if it is found that the limestone apparently contains 95 per cent. of $CaCO_3$ and then find 2 per cent. of $MgCO_3$, the true percentage of $CaCO_3$ is 95 − (2 × 1.19) = 92.62 per cent.

4. **Quicklime.**—The analysis of the monthly average and the careful check determinations should be carried out in the same manner as is described for limestone in *Quantitative Analysis.* In reporting the result of the analysis, the carbon dioxide and sulphur trioxide are combined with the lime, and the remainder of the calcium and the magnesium

reported as oxides. Where less accurate results will answer, the following method is preferred.

1. *Insoluble.*—The amount of insoluble matter is determined as in Art. **3.**

2. *Free Calcium Oxide.*—Weigh out 50 grams of an average sample of the lime, and after carefully slaking it, bring the mass into a 1,000-cubic-centimeter measuring flask, fill to the mark, and thoroughly mix. Pipette out, without allowing the suspended matter to settle, 100 cubic centimeters and dilute to 500 cubic centimeters, shake thoroughly and pipette out 100 cubic centimeters for titration with normal hydrochloric acid, using phenol phthalein as indicator. The number of cubic centimeters of acid required to just discharge the pink color multiplied by 2.8, gives the percentage of CaO.

3. *Calcium Carbonate.*—Titrate 1 gram of the sample, using methyl orange as indicator, as under Art. **3.** By subtracting the number of cubic centimeters of normal acid required above from the number of cubic centimeters required here, the number of cubic centimeters of normal acid required for the calcium carbonate is obtained. This value multiplied by 5 gives the percentage of calcium carbonate.

4. *Magnesia.*—Determine as under Art. **3.**

5. Ammonia Liquor.—The crude ammonia liquor as it comes to the works from the gas manufacturer frequently, especially in cold weather, contains crystals. The liquor is measured and the crystals weighed before sending them to the storage tanks, and a sample of each is sent to the laboratory for analysis.

1. *Specific Gravity.*—The specific gravity of the gas liquor is taken with a hydrometer. This determination is, however, of very secondary importance to the direct determination of the ammonia.

2. *Ammonia* is determined, both in the crystals and in the gas liquor, according to the volumetric method described in *Quantitative Analysis.*

6. Coal and Coke.—These are analyzed by the method described in *Quantitative Analysis.*

INTERMEDIATE PRODUCTS

7. Ammoniacal Brine.—The determinations ordinarily made are free and combined ammonia and salt.

1. *Free and Combined Ammonia.*—Dilute 10 cubic centimeters of the ammoniacal brine with distilled water to about 100 cubic centimeters, introduce it into a distilling flask (see *Quantitative Analysis*), and boil until all the ammonia and ammonium carbonate are driven off. The ammonia and ammonium carbonate are collected in normal sulphuric acid and determined as usual. The result is free ammonia.

A new receiver containing normal sulphuric acid is then attached and ammonia-free sodium-hydrate solution is introduced into the distilling flask. The combined ammonia is then driven over by the boiling and is determined by titrating the acid in the receiver.

2. *Salt.*—On account of the free alkali present in this brine the common method of titrating with silver nitrate cannot be used, unless the ammonia is exactly neutralized with nitric acid; even then the results lack exactness. The so-called Volhard method, which possesses the advantage that it can be used in a nitric-acid solution, is therefore used. This method is described in *Quantitative Analysis.*

8. Lime-Kiln Gases. — Carbon dioxide, carbon monoxide, and oxygen must be determined in the gases coming from the lime kiln. These determinations may be made with the Orsat-Muenke apparatus, described in *Quantitative Analysis*, under "Gas Analysis," or, on account of its cheapness, by means of the Bunte burette.

9. Bunte Burette.—The apparatus shown at *e*, Fig. 1, consists of a simple glass tube a little over 100 cubic centimeters capacity and closed at each end by well-fitting stop-cocks *g* and *f*. The stop-cock at *g* is the ordinary two-way style; the one at *f* is a three-way stop-cock, so that the tube can be put in connection with the source of gas through the end of the cock and the rubber tube *m*, or it can be connected with the cup-shaped receptacle *l*, which is made above *f*. The tube *e* is graduated in $\frac{1}{10}$ cubic centimeters for 100 cubic centimeters down from *f*. Frequently the burette is surrounded by a water-jacket to prevent variations of temperature. This is, however, an unnecessary accessory and seriously interferes with the manipulation of the burette.

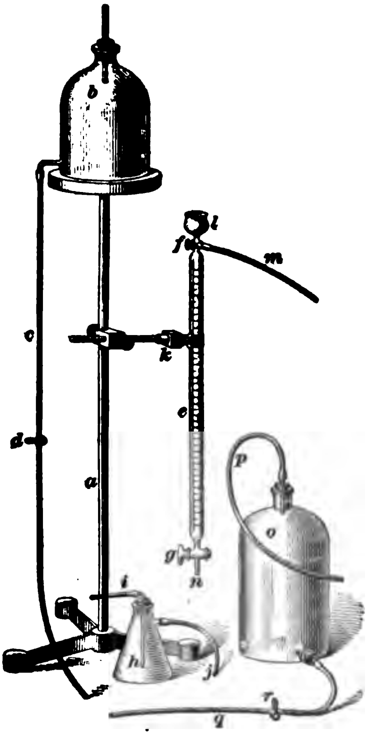


FIG. 1

10. Manipulation of the Bunte Burette.—The burette is first filled with gas to be analyzed.

(*a*) If only a limited amount of gas is available for analysis, the burette is first filled with water from the reservoir *b*, Fig. 1. For this purpose the rubber tube *c* is attached to the tip of the burette *n*, the stop-cock *g* is opened, and *f* is turned so as to connect the burette with *m*. Then by releasing the pinch cock *d* water flows from *b* to fill the whole apparatus. The stop-cocks are then closed, *c* is removed from *n*, and *m* is attached to the gas supply. By then again opening the stop-cocks *f* and *g* the water flows out at *n* and the burette fills with gas, which is then secured by closing the stop-cocks.

(*b*) When gas is abundant and under pressure, the tube *m* is attached to the source, *f* and *g* are opened, and 2 or 3 liters of gas allowed to flow through the burette, thus sweeping out the air and leaving a good sample of gas. By closing *f* and *g* the gas is enclosed.

(*c*) When the gas is abundant, but not under pressure, as happens in taking samples between the lime kilns and the pumps, it is necessary to attach an aspirator at *n* to draw the gas through the burette. A suitable arrangement for aspirating in this case consists of a large bottle *o*. This bottle is filled with water, the rubber tube *p* attached at *n*, the pinch cock *r* opened, and then the stop-cocks *g* and *f* opened. After 2 or 3 liters of gas have been drawn through the burette, first *g* and then *f* is closed, *p* is disconnected from *n*, and the sample is ready for analysis.

Having the burette filled with the sample of gas, the cup *l* is filled with water to a mark that is 1 centimeter above the stop-cock *f*, *c* is then attached to *n*, and *d* and *g* opened. Water thus flows into the burette and compresses the gas. When the water reaches the 100-cubic-centimeter mark, *g* is closed and *f* is turned to connect the burette with *l*. Gas will escape until the gas in the burette is under the atmospheric pressure, plus the pressure of 1 centimeter of water. *f* is then closed and the volume of gas read (it should be exactly 100 cubic centimeters). The rubber tube *i* of the suction flask *h* is then attached at *n*, *g* is opened, and, by sucking on *j*, the water is almost completely removed from the burette, leaving a partial vacuum; *g* is then closed, and *i* removed from *n*.

For the determination of carbon dioxide, a small beaker containing a suitable solution of caustic potash is brought under *n*, and *g* turned so that the alkali solution rises in the burette; *g* is then closed. The burette is then grasped at *l*, loosened from the clamp *k* (the ends of the burette are grasped between the first and second fingers of each hand beyond the stop-cocks to avoid heating the gas by the hands), and after the water is emptied from *l*, the burette is thoroughly shaken, so that the gas is well mixed with the caustic potash. The burette is then replaced in the clamp *k*, *n* is brought under caustic-potash solution, and *g* again opened. The alkali will rise in the tube, and when it has filled as much as it will, *g* is once more closed and the burette shaken as before. This is repeated as long as the alkali solution continues to rise in the burette. Water is then filled to the 1-centimeter mark in *l*, *f* is opened to insure equal pressure, then closed, and the volume of gas read. The difference between this reading and 100 gives the volume percentage of the carbon dioxide in the gas mixture.

For the determination of oxygen, the caustic potash is removed as far as possible by means of the suction flask *h*, and alkaline pyrogallol allowed to rise in the burette in its place. The same operations as for carbon dioxide are performed until all the oxygen is absorbed. The volume of gas is then read. The difference between this volume and 100 gives the volume percentage of carbon dioxide and oxygen, and deducting the volume percentage of carbon dioxide leaves the volume percentage of oxygen in the gas.

In each of the above cases the gas is read over strongly alkaline liquids that tend to adhere to the burette and render the results inaccurate. This can be avoided by sucking out the alkaline liquid, allowing water to enter, rinsing the burette two or three times, each time sucking out the water, and then measuring the gas over nearly pure water.

The carbon monoxide is determined by sucking out the alkaline pyrogallol or water after measuring the oxygen, replacing it with a hydrochloric-acid solution of cuprous chloride, and proceeding as in the preceding cases. After the carbon monoxide has been completely absorbed, as shown by the absorbing liquid no longer rising in the burette, the absorbing liquid is sucked out as completely as possible and the gas washed two or three times with water to completely remove the hydrochloric acid. This diminution in volume of the gas gives the volume percentage of carbon monoxide in the gas; the remainder of the gas is the volume percentage of nitrogen in the gas.

11. Reagents for the Bunte Burette.—The caustic potash is made by dissolving 100 grams solid potassium hydrate in 200 cubic centimeters of water.

The alkaline pyrogallol is made by dissolving 32 grams potassium hydrate in 200 cubic centimeters of water and 40 grams of pyrogallic acid in 200 cubic centimeters of water. The two solutions are thoroughly mixed and kept carefully guarded from the air in a rubber-stoppered bottle. It is even better to keep the two solutions separate and only mix them when needed for use.

The cuprous-chloride solution is made by dissolving 200 grams of cupric chloride in 500 cubic centimeters of water and 500 cubic centimeters of concentrated hydrochloric acid, and allowing the solution to stand tightly stoppered in a bottle containing copper turnings or strips of sheet copper until it becomes clear and colorless.

12. Liquor From Carbonators.—The free and combined ammonia are determined as described in Art. **7.** These are the only determinations usually made.

13. Bicarbonate From the Filters.—1. *Total alkali* is determined by titrating 4.2 grams of the sample with normal sulphuric acid, using methyl orange as indicator. Each cubic centimeter of normal acid used corresponds to .738 per cent. of Na_2O in the sample.

2. *Sodium Bicarbonate.*—The determination of sodium bicarbonate in the presence of sodium carbonate depends on the reaction

$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O$$

Silver nitrate is used as indicator, for it gives a white precipitate with sodium carbonate, but as soon as a single drop of caustic-soda solution is present in excess the silver carbonate precipitate turns brown, owing to the formation of silver oxide.

Normal sodium-hydrate solution is prepared by dissolving 50 grams of pure sodium hydrate in 1 liter of water and adding sufficient barium hydrate to more than precipitate all the carbon dioxide. The solution is then standardized as usual by titrating with normal sulphuric acid, using phenol phthalein as indicator, and then corrected to exactly normal strength This solution must after standardization be carefully guarded from the carbon dioxide of the air.

FIG. 2

A convenient arrangement for the solution and burette is shown in Fig. 2. The burette *a* is closed at the top with a stopper, through which passes a glass tube connecting with a sugar funnel *b*, which is filled with pieces of soda lime and so removes the carbon dioxide from the air that enters the burette. At the lower end of the burette a tube is blown on which connects, by means of the glass tube *d* and two short pieces of rubber tube, with the bottle *e* containing the standard solution. The bottle *e* is closed with a two-holed rubber stopper, through one hole of which leads the tube *d* to the burette, and through the other a glass tube to the sugar funnel *f* that contains the soda lime. The liquid can be started first by blowing on the end of *f* after the stop-cock *c* has been opened. After the apparatus is once in operation the burette can be repeatedly filled, by merely opening the stop-cock *c*, without exposing the solution to the air at any point.

The determination is made by weighing out in a beaker 4.2 grams of the sample, adding 100 cubic centimeters of water (not warmer than 20° C.), and running in the caustic-soda solution until within about 1 cubic centimeter of the end reaction. The solution is then thoroughly stirred and the standard solution run in, at first .2, and then .1 cubic centimeter at a time, until a drop taken out and brought in contact with a 25-per-cent. silver-nitrate solution on a white plate shows a brown color at once. Even before the end point, the drops turn brown on standing. If the composition of the sample is not approximately known at first, it must be approximately determined by weighing out a portion of the sample and running in the standard caustic 2 or 3 cubic centimeters at a time and testing until the end point is passed. Then, for the final determination, somewhat less than this amount of the standard solution is taken as above. The number of cubic centimeters of the normal alkali used multiplied by 2 gives the percentage of sodium bicarbonate in the sample.

3. The percentage of *sodium carbonate* in the sample is given by multiplying the difference between the number of cubic centimeters of normal acid required for the total alkali and the number of cubic centimeters of normal caustic alkali required for sodium bicarbonate by $\frac{53}{42}$. For example, if it takes 39 cubic centimeters of normal acid to neutralize a sample and 35 cubic centimeters of normal alkali to convert the bicarbonate into the carbonate, then $39 \times .738 = 28.79$ per cent. of Na_2O; $35 \times 2 = 70$ per cent. of sodium bicarbonate; and $(39 - 35) \times \frac{53}{42} = 5.05$ per cent. of sodium carbonate.

4. *Ammonia* is determined according to the volumetric method given in *Quantitative Analysis.*

5. *Moisture* is determined by weighing out 10 grams of the sample in a small platinum or porcelain evaporating dish and heating, at first carefully on a sheet of asbestos, and finally to from 300° to 400° C. The loss in weight, after deducting the carbon dioxide corresponding to the sodium bicarbonate, gives the moisture.

14. Mother Liquor.—The mother liquor from the filtration of the liquors from the carbonators is tested for free and combined ammonia and salt.

1. *Free and combined ammonia* are determined as under Art. 7.

2. *Salt* is determined by evaporating 10 cubic centimeters of the liquor to dryness in a platinum dish, heating the residue until the ammonium chloride is volatilized, then cooling and weighing.

15. Milk of Lime.—1. The determination of the *specific gravity* usually is sufficient for controlling the milk of lime. If the milk of lime is thin, it is thoroughly mixed and the reading on the hydrometer is quickly taken. If the milk of lime is thick, a rather broad cylinder is selected, the milk of lime thoroughly mixed, the hydrometer inserted, and the cylinder jarred on the table until the hydrometer will sink no lower, when it is read. A hydrometer called the *Baumé hydrometer*, with the spindle arbitrarily divided into so-called degrees, is frequently used for this purpose. Table II shows the degrees Baumé and grams per liter of calcium oxide corresponding to a considerable range of specific gravities.

2. *Complete Analysis.*—At intervals a complete analysis of the milk of lime is required. For this purpose the sample is thoroughly mixed, and 250 cubic centimeters measured out and filtered. The residue on the filter is taken without washing, dried at 100° C., and weighed. This weight multiplied by 4 gives the undissolved portion per liter.

The undissolved portion and the filtrate are then separately analyzed, exactly as under "Quicklime."

16. Waste From Ammonia Stills.—1. *Excess of lime* is the constituent of this waste, concerning which it is most important for us to have information—that is, the lime that is still available for liberating ammonia from its salts. For its determination, boil 100 cubic centimeters of the waste until no more ammonia is given off, then add ammonium sulphate in excess, boil again, and collect the ammonia evolved this time in normal acid (see the volumetric determination of ammonia, *Quantitative Analysis*). By titrating, the necessary information for finding the amount of ammonia evolved is obtained, and from this it is a simple matter to calculate the amount of free lime in the waste.

$$(NH_4)_2SO_4 + \underbrace{Ca(OH)_2}_{74} = CaSO_4 + \underbrace{2NH_3}_{34} + H_2O$$

$$34 : 74 = \text{wt. } NH_3 \text{ found} : x$$

$x \times 10 =$ the amount of available lime per liter of the waste.

TABLE II

Specific Gravity	Degrees Baumé	Grams CaO in Liters	Specific Gravity	Degrees Baumé	Grams CaO in Liters
1.007	1	7.5	1.125	16	159
1.014	2	16.5	1.134	17	170
1.022	3	26.0	1.142	18	181
1.029	4	36.0	1.152	19	193
1.037	5	46.0	1.162	20	206
1.045	6	56.0	1.171	21	218
1.052	7	65.0	1.180	22	229
1.060	8	75.0	1.190	23	242
1.067	9	84.0	1.200	24	255
1.075	10	94.0	1.210	25	268
1.083	11	104.0	1.220	26	281
1.091	12	115.0	1.231	27	295
1.100	13	126.0	1.241	28	309
1.108	14	137.0	1.252	29	324
1.116	15	148.0	1.263	30	339

2. *Complete Analysis.*—Determine the specific gravity, the amount of undissolved material, and analyze the insoluble portion as in Art. **15.** In the soluble portion:

(*a*) Titrate 50 cubic centimeters with normal sulphuric acid, using phenol phthalein as indicator, and calculate the result as $Ca(OH)_2$.

(*b*) Determine the calcium in 25 cubic centimeters, as usual, by precipitating with ammonia and ammonium oxalate, filtering, and titrating the precipitate with potassium permanganate. Deduct the calcium corresponding to the amount of calcium hydrate found under (*a*) and calculate the remainder as calcium chloride in grams per liter.

(*c*) Determine the sulphur trioxide in 50 cubic centimeters by precipitating with barium chloride, and calculate the result as sodium sulphate in grams per liter.

(*d*) Determine the chlorine in 5 cubic centimeters by Volhard's method. Deduct the chlorine corresponding to the calcium chloride found under (*b*) and calculate the remainder as sodium chloride in grams per liter.

THE FINISHED PRODUCT

17. Soda Ash.—For the complete analysis of soda ash, the following determinations are usually made :

1. *Sodium Carbonate.*—Weigh out 2.65 grams of the dry substance, dissolve in about 150 cubic centimeters of water, and titrate with normal sulphuric acid, using methyl orange as indicator. The number of cubic centimeters of acid used multiplied by 2 gives the percentage of sodium carbonate.

2. *Sodium Bicarbonate.*—This substance rarely occurs in large amounts in soda ash, and its determination may usually be omitted. If there is a reason for determining it, use the method given under Art. **13.**

3. *Sodium Chloride.*—Dissolve 5 grams of the sample in water and titrate by Volhard's method.

4. *Silica.* — Dissolve 50 grams of the sample in about 150 cubic centimeters of water and acidify with concentrated hydrochloric acid, evaporate to dryness on the water bath, take up with water and a little hydrochloric acid, filter, ignite, and weigh. Calculate as silica; of course it consists of everything insoluble in hydrochloric acid.

5. *Ferric Oxide and Alumina.* — Determine the ferric oxide and alumina in the filtrate from the silica by precipitating with ammonia as usual.

6. *Calcium Carbonate.* — Divide the filtrate from the above determination into two equal parts, and in one half

determine the calcium, as usual, with ammonia and ammonium oxalate, and calculate as calcium carbonate.

7. *Magnesium Carbonate.*—Determine the magnesium in the filtrate from the calcium determination, as usual, with ammonium phosphate, and calculate as magnesium carbonate.

8. *Sodium Sulphate.*—Determine the sulphur trioxide in the other half of the filtrate from the ferric oxide and alumina determination by means of barium chloride, as usual, and calculate as sodium sulphate.

A complete analysis of this character is necessary from time to time, usually each month, of an average of the soda ash made. For the daily control of the output, however, a determination of the sodium carbonate and the sodium chloride is generally sufficient.

SALT-CAKE PROCESS

CRUDE MATERIALS

18. Salt. — The usual determinations are as follows: 1. *Sodium Chloride.*—Weigh out 4 grams of the sample, dissolve in water, and dilute to 1,000 cubic centimeters. Take 50 cubic centimeters of this solution and titrate with $\frac{1}{10}$ normal silver nitrate, using about $\frac{1}{2}$ cubic centimeter of potassium chromate as indicator. This gives the total chlorine, and when no other substances are determined, this is all calculated as sodium chloride. When magnesium and other substances present as chlorides are determined, the chlorine of these is first subtracted from the total before calculating it as sodium chloride.

2. *Water.*—The determination of water in salt offers some difficulties on account of its tendency to decrepitate and so fly out of the dish in which one is heating it. The most satisfactory method of making the determination is to select a tall Erlenmeyer flask of Jena glass, of about 250 cubic centimeters capacity, and weigh it with a small

funnel in its mouth. About 5 grams of salt are then introduced and its weight exactly established by weighing flask, funnel, and salt. The funnel is then removed and the flask is heated for 3 or 4 hours on a suitable sand bath, which has a temperature of about 150° C. The funnel is then replaced in the mouth of the flask and the whole allowed to cool and then weighed. The funnel serves the purpose of preventing the air from circulating in the flask, so it can be cooled out of a desiccator. This determination gives all the water in the salt except part of that which is chemically combined with impurities. For most purposes the combined water can be neglected, but when it is necessary to determine it, this can be done by heating the flask to 300° or 400° C. with the funnel in its mouth, cooling and weighing.

3. *Sulphur Trioxide.* — Dissolve 10 grams of salt in about 300 cubic centimeters of water, acidify with hydrochloric acid, and digest at 70° or 80° C. for an hour to dissolve all the calcium sulphate present. Make this to 500 cubic centimeters, filter through a dry filter, and take 250 cubic centimeters for analysis. Determine the sulphur trioxide by precipitating, as usual, with barium chloride in a hot solution. Unless there are reasons for doing otherwise, the sulphur trioxide is calculated as calcium sulphate.

4. *Other Determinations.* — These determinations are sufficient for the daily work, unless salt happens to come in from a new source, when it must be analyzed like the average sample below. The daily samples are saved, however, and at the end of each month an average sample is prepared and, in addition to the above determinations, insoluble in acids, ferric oxide and alumina, calcium, and magnesium are determined. For this purpose 50 grams of the sample are dissolved in water and hydrochloric acid and the determinations are carried out as under Art. **1.**

The magnesium is calculated as chloride, and the calcium in excess of the sulphur trioxide is calculated as calcium chloride. Conversely, any sulphur trioxide in excess of the calcium is calculated as sodium sulphate.

FINISHED PRODUCT

19. Salt Cake.—The determinations usually made are as follows:

1. *Free Acid.*—Dissolve 20 grams of the salt cake in water and dilute to 250 cubic centimeters. Take 50 cubic centimeters and titrate with normal sodium-hydrate solution, using methyl orange as indicator. The acidity is calculated as sulphur trioxide, although it may be due to hydrochloric acid and salts of the heavy metals, as well as acid sodium sulphate. If the salt cake contains large amounts of iron and aluminum salts, and it is desired to exclude the acidity due to these salts, the titration may be carried on without an indicator and the end point taken when flakes of the precipitate of the hydrates begin to appear. Each cubic centimeter of sodium-hydrate solution used corresponds to 1 per cent. of sulphur trioxide.

2. *Salt.*—Take 50 cubic centimeters of the solution prepared as above and determine the chlorine according to Volhard's method, using $\frac{1}{20}$ normal silver nitrate. Calculate all the chlorine to sodium chloride. Each cubic centimeter of silver-nitrate solution used corresponds to .0731 per cent. of salt.

For the daily determinations, these two substances are all that are necessary, except when the salt cake is being made especially free from iron for use in glass manufacture, when this must also be determined in each batch. For the monthly average sample and for certain cases for shipment, it is also necessary to make the following determinations:

3. *Insoluble in Acids.*—Determine in 50 grams of sample, as under "Silica," Art. **17.**

4. *Ferric Oxide.*—Weigh out 20 grams of the sample, reduce with zinc and sulphuric acid, and titrate with permanganate, as directed in *Quantitative Analysis.*

5. *Alumina.*—Dissolve 20 grams of the sample in about 150 cubic centimeters of water, add hydrochloric acid, and

precipitate with ammonia as usual. After weighing the combined oxides, deduct the ferric oxide found above and calculate the remainder to the percentage of alumina.

6. *Lime.*—Determine, as usual, in the filtrate from the alumina determination.

7. *Magnesia.*—Determine, as usual, in the filtrate from the lime determination.

8. *Sodium Sulphate.*—The determination of the sodium sulphate in this case is a rather difficult matter and it is frequently taken as the difference between the total percentage of the other substances found and 100. Perhaps the most satisfactory method of procedure is to dissolve 2 grams of the sample in as little hot water as possible, make alkaline with ammonia, and precipitate so far as possible with ammonium carbonate. Filter and redissolve the precipitate in as little hydrochloric acid as possible and reprecipitate with ammonia and ammonium carbonate. Filter and unite the two filtrates in a platinum dish and evaporate to dryness, moisten the residue with sulphuric acid to be certain that the salt present is all converted into sulphate, heat to drive off the excess of acid, and weigh. Calculate the salt found by Volhard's method to sulphate, deduct this weight from that found above, and the remainder is sodium sulphate.

LE BLANC PROCESS

CRUDE MATERIALS

20. **Salt cake** is analyzed according to Art. **19.**

21. **Limestone** is analyzed according to Art. **3.**

22. **Coal** is analyzed according to the method given in *Quantitative Analysis.* In addition, determine the nitrogen by Kjeldahl's method, which also is described in *Quantitative Analysis.*

INTERMEDIATE PRODUCTS

23. Black Ash. — The obtaining of a representative sample presents perhaps more difficulties than are usually the case, for the charges as drawn from the furnace are hard and very non-homogeneous, so that great care must be exercised in selecting the sample to get it as representative as possible, for even at best it is imperfect. After the sample has been carefully selected, it is rapidly crushed and mixed so that 50 grams of an average of the sample can be weighed out. These 50 grams are rapidly but thoroughly ground in a mortar and then brought into a 500-cubic-centimeter flask, the mortar rinsed down with water, which has been boiled to expel carbon dioxide, and then cooled to about 35° C. The rinsings of the mortar are poured into the flask and the flask filled nearly to the 500-cubic-centimeter mark with the same warm water. During the pouring of the rinsings and water on the black ash, it must be thoroughly shaken to prevent its caking together on the bottom of the flask. The flask is then allowed to stand about 2 hours with frequent shaking. A preferable arrangement, and one that saves much work, is to use one of the many stirrers that run by a turbine or an electric motor. They may be obtained from any dealer in chemical apparatus. After standing 2 hours the flask is filled to the mark and the solution is ready for use.

1. *Free Lime.*—Thoroughly mix the contents of the flask and pipette out 25 cubic centimeters of its contents into a porcelain dish. The outside of the pipette should be rinsed off before running out its contents and then the inside should be rinsed into the porcelain dish. Add an excess of a 10-per-cent. barium-chloride solution and titrate with normal hydrochloric acid, using phenol phthalein as indicator. Each cubic centimeter of acid solution equals 1.12 per cent. of CaO.

2. *Total Lime.*—Pipette out, as above, 25 cubic centimeters from the supply flask into a small flask, make acid with concentrated hydrochloric acid, and boil to expel all

the carbon dioxide. Add a few drops of methyl orange and then sodium carbonate to exactly neutralize. Add 40 cubic centimeters of a normal sodium-carbonate solution and boil to precipitate all the calcium (together with magnesium, etc., which, however, can be neglected) as the granular carbonate. Make up to 250 cubic centimeters and filter through a dry filter. Take 125 cubic centimeters and titrate back to neutral with normal hydrochloric acid, using methyl orange as indicator. Each cubic centimeter of the sodium carbonate used in excess of the acid required to titrate back is equal to 2.24 per cent. of CaO. Neither of the above methods is very exact, but they answer for factory control. The supply flask is now tightly stoppered and allowed to stand until the liquor has become completely clear.

3. *Total alkali* comprises all the sodium present as carbonate, sulphide, and hydrate. Pipette out 20 cubic centimeters of the clear liquid from above and titrate, as usual, with normal hydrochloric acid, using methyl orange as indicator. Each cubic centimeter of acid corresponds to 1.55 per cent. of Na_2O.

4. *Sodium Sulphide.*—Pipette out 10 cubic centimeters of the clear liquor from the supply flask, dilute to about 200 cubic centimeters, acidify with acetic acid, and titrate with $\frac{1}{10}$ normal iodine solution, using starch paste as indicator. Each cubic centimeter of iodine solution used equals .39 per cent. of sodium sulphide, and is equivalent to .1 cubic centimeter of normal acid.

5. *Caustic Soda.*—Pipette out 40 cubic centimeters of the clear liquid from the supply flask into a 100-cubic-centimeter measuring flask, add 20 cubic centimeters of a 10-per-cent. barium-chloride solution, and fill to the mark with water. Thoroughly shake and allow to settle. Pipette out 50 cubic centimeters and titrate with normal hydrochloric acid, using methyl orange as indicator. This titration gives both sodium hydrate and sodium sulphide. To determine the hydrate alone, multiply the number of cubic centimeters of iodine solution used above by 20 and

subtract the product from the number of cubic centimeters of normal acid used here. The remainder gives the number of cubic centimeters of normal acid used for the caustic soda, and each cubic centimeter equals 2 per cent. of $NaOH$.

6. *Sodium Carbonate.* — Subtract the total amount of hydrochloric acid used for the sodium hydrate and the sodium sulphide above from the amount used for the total alkali, and the difference gives the number of cubic centimeters of normal acid used for the sodium carbonate. Each cubic centimeter of normal acid equals 2.65 per cent. of sodium carbonate.

7. *Salt.*—Pipette out 10 cubic centimeters of the clear liquid from the supply flask and titrate according to Volhard's method for chlorine. All the chlorine is calculated as salt, and each cubic centimeter of the $\frac{1}{10}$ normal silver nitrate solution used equals .58 per cent. of salt.

8. *Sodium Sulphate.*—Pipette out 20 cubic centimeters of the clear liquid from the supply flask and add hydrochloric acid in slight excess. Boil to expel carbon dioxide and precipitate hot, as usual, with barium chloride. The weight of barium sulphate multiplied by .3047 gives the percentage of sodium sulphate.

24. Lye From Extraction of Black Ash.—The following determinations are made :

1. *Specific Gravity.*—Determine the specific gravity of the warm lye by means of the Baumé hydrometer.

2. *Total Alkali.*—Determine the total alkali in 2 cubic centimeters of the lye, as under Art. **23.**

3. *Sodium Sulphide.*—Determine the sodium sulphide in 2 cubic centimeters of the lye, as under Art. **23.**

4. *Caustic Soda.*—Determine the caustic soda in 2 cubic centimeters of the lye, as under Art. **23.**

5. *Sodium Carbonate.*—Determine the sodium carbonate, as under Art. **23.**

6. *Salt.*—Determine the salt in 2 cubic centimeters by Volhard's method, described in *Quantitative Analysis.*

7. *Sodium Sulphate.*—Determine the sodium sulphate in 5 cubic centimeters, as under Art. **23.**

8. *Total Sulphur.*—Treat 5 cubic centimeters of the lye with an excess of bleaching powder and hydrochloric acid (the chlorine must smell strongly). Boil off the chlorine, filter from insoluble matter, and precipitate with barium chloride, as usual.

9. *Sodium Ferrocyanide.*—Acidify 30 cubic centimeters of the lye with hydrochloric acid and add, with constant stirring, a strong solution of bleaching powder from a burette, until a drop taken out shows no blue color with a ferric-chloride solution. The ferric chloride must be free from ferrous salts, and the end point must be quite accurately reached, although a drop or two in excess does no harm. This oxidizes the sodium ferrocyanide completely to sodium ferricyanide. Add to the oxidized solution $\frac{1}{10}$ normal copper sulphate from a burette, until a drop of the solution no longer gives a blue color with ferrous sulphate, but shows a red color. This indicates that no more sodium ferricyanide is present in the solution, and that the ferrous sulphate is reducing the yellowish copper ferricyanide to the reddish copper ferrocyanide. The first decided red color must be taken as the end point, even if it disappears after a time.

The copper-sulphate solution is made by dissolving 12.457 grams of crystallized copper sulphate in 1,000 cubic centimeters of water and standardizing it against pure non-effloresced potassium ferrocyanide.

10. *Silica, Ferric Oxide, and Alumina.*—Acidify 100 cubic centimeters of the lye with hydrochloric acid, heat to boiling, add about 1 gram of ammonium chloride, and precipitate with ammonia. Heat until the ammonia odor is very faint, filter, ignite, and weigh as usual.

25. Carbonated Lye.—The determinations are made as above, but in addition the sodium bicarbonate is determined.

Sodium Bicarbonate.—The method given in Art. **13** cannot be satisfactorily used here, for the sulphide that may be present will interfere with the test. The following method, however, gives good results when carefully carried out. A standard solution of caustic soda free from carbon dioxide is required and is best prepared by dissolving 50 grams of the best caustic soda in 1 liter of water and adding barium chloride to precipitate all the carbon dioxide. The solution is then standardized by acid as usual, made to normal, and preserved as under Art. **13.** For the analysis, take 50 cubic centimeters of the carbonated lye and add 30 cubic centimeters of the caustic-soda solution, then an excess of a 10-per-cent. barium-chloride solution, and finally titrate with normal hydrochloric acid, using phenol-phthalein solution as indicator. The difference between the amount of caustic-soda solution taken and the normal acid required gives the number of cubic centimeters of normal caustic soda required for the bicarbonate present, and each cubic centimeter equals .084 gram of sodium bicarbonate.

For example, if 25 cubic centimeters of normal acid is required to titrate back, then $30 - 25 = 5$ cubic centimeters of caustic soda required for the bicarbonate present. Therefore, $.084 \times 5 = .42$, and $.42 \times 20 = 8.4$ grams of sodium bicarbonate per liter of lye.

26. Red Liquors.—The red liquor may be analyzed the same as the crude lye, except that in the case of crude lye all the oxidizable sulphur compounds are assumed to be sulphides. In the case of a red liquor, however, through oxidation and other changes the sulphite and thiosulphate become prominent and must be determined, especially when the red liquor is used for the manufacture of caustic soda.

1. *Sodium Sulphide, Sulphite, Thiosulphate, and Sulphate.* (*a*) Determine the total alkalinity by titrating 25 cubic centimeters of the liquor with normal acid, using methyl orange as indicator. This gives sodium carbonate, sodium hydrate, sodium sulphide, and one-half of the sodium sulphite (Na_2SO_3 is alkaline to methyl orange, while $HNaSO_3$ is neutral).

(*b*) Acidify 25 cubic centimeters of the liquor with dilute acetic acid and titrate with $\frac{1}{10}$ normal iodine solution. This gives sodium sulphide, sodium sulphite, and sodium thiosulphate.

(*c*) Take 50 cubic centimeters of the liquor and precipitate it with an alkaline-zinc solution, make to 200 cubic centimeters, and take 100 cubic centimeters. Acidify this with dilute acetic acid and titrate with $\frac{1}{10}$ normal iodine solution. This gives sodium sulphite and sodium thiosulphate.

(*d*) Take 100 cubic centimeters of the liquor and add an excess of a 10-per-cent. barium-chloride solution to precipitate the sulphite, make up to 200 cubic centimeters, cork tight, and allow to settle clear (or filter); then take 50-cubic-centimeter portions of the clear liquid for titration. (1) Titrate a 50-cubic-centimeter portion with normal hydrochloric acid, using methyl orange as indicator. This gives sodium hydrate and sodium sulphide. (2) Acidify a second 50-cubic-centimeter portion with dilute acetic acid and titrate with $\frac{1}{10}$ normal iodine solution. This gives sodium sulphide and sodium thiosulphate.

2. *The Calculation.*— $b - d\,(2) = A$ cubic centimeters $\frac{1}{10}$ normal iodine solution corresponding to sodium sulphite.

$b - c = B$ cubic centimeters $\frac{1}{10}$ normal iodine solution corresponding to sodium sulphide.

$d\,(2) - B = C$ cubic centimeters $\frac{1}{10}$ normal iodine solution corresponding to sodium thiosulphate.

$d\,(1) - \frac{1}{10}\,B = D$ cubic centimeters normal acid solution corresponding to sodium hydrate.

$1 - [d\,(1) + \frac{1}{20}\,A] = E$ cubic centimeters normal acid solution corresponding to sodium carbonate.

Each cubic centimeter of $\frac{1}{10}$ normal iodine solution equals .0039 gram of Na_2S, .0063 gram of Na_2SO_3, or .0158 gram of $Na_2S_2O_3$.

Each cubic centimeter of normal acid equals .04 gram of $NaOH$, or .053 gram of Na_2CO_3.

27. Tank Waste.—Samples are collected in wide-mouth glass-stoppered bottles and kept closed until analyzed. The determinations are made on the moist substance, as any attempt to dry it inevitably leads to oxidation, and so to a change of composition.

1. *Alkaline Sodium Compounds.*—Stir 20 grams of tank waste thoroughly together with about 175 cubic centimeters of warm water, let stand 1 hour to thoroughly settle, and pour off the clear liquid. Pass carbon dioxide for 5 minutes, and boil to about one-half of the original volume, to decompose calcium bicarbonate and precipitate calcium carbonate. Filter and titrate the filtrate with normal acid, using methyl orange as indicator. Each cubic centimeter of normal acid equals .031 gram of Na_2O.

2. *Total Sodium Compounds.*—Heat 17.7 grams of the waste in a porcelain dish with sulphuric acid of 50° Baumé until the waste is completely decomposed, heat to drive off all the free acid, add hot water, and bring into a 250-cubic-centimeter measuring flask. Add milk of lime (made by slaking lime, shaking up with water, pouring off one portion to remove alkalies and then shaking up with water and filtering) to remove any free acid and magnesia, fill to the mark, let settle, and pipette off 50 cubic centimeters. To this 50 cubic centimeters add 10 cubic centimeters of a saturated barium-hydrate solution and filter through a dry filter. Take 50 cubic centimeters of the filtrate and precipitate all the barium by carbon dioxide and boiling. Filter and titrate the filtrate with normal hydrochloric acid, using methyl orange as indicator. When the above amount of substance is taken and allowance is made for the precipitates in the volumes, each cubic centimeter of normal acid used equals 1 per cent. of Na_2O.

FINISHED PRODUCTS

28. Soda Ash.—The determination of silica, sodium sulphate, sodium chloride, ferric oxide and alumina, calcium carbonate, and magnesium carbonate is carried out as under Art. **17.** In addition to these substances, it is necessary to determine in Le Blanc soda, total alkali, sodium carbonate, caustic soda, sodium sulphide, and sodium sulphite.

1. *Total Alkali.*—Dissolve 3.1 grams of the soda ash in about 150 cubic centimeters of distilled water and titrate with normal sulphuric acid, using methyl orange as indicator. Each cubic centimeter of the acid used equals 1 per cent. of Na_2O.

2. *Sodium Carbonate.*—Calculate from determinations 3 and 4 (below) the equivalent percentages of Na_2O and deduct the sum of these results from the percentage of Na_2O found in 1. The remainder is the alkali equivalent of the sodium carbonate, and this remainder multiplied by 1.71 gives the percentage of sodium carbonate in the soda ash. For example, if 58 cubic centimeters of normal acid is used in 1, 10 cubic centimeters of $\frac{1}{10}$ normal acid in 3, and 5 cubic centimeters of silver nitrate in 4; according to 1, we have 58 per cent. of Na_2O, according to 3, .31 per cent. of Na_2O as $NaOH$, and according to 4, .39 per cent. of Na_2O as Na_2S; or $.31 + .39 = .7$ per cent. of Na_2O in the substance in other forms than sodium carbonate and $58 - .7 = 57.3$ per cent. of Na_2O as sodium carbonate. Then $57.3 \times 1.71 = 97.98$ per cent. of sodium carbonate in the soda ash.

3. *Caustic Soda.*—Dissolve 10 grams of the soda ash in about 75 cubic centimeters of water, add an excess of a 10-per-cent. barium-chloride solution, and titrate with $\frac{1}{10}$ normal hydrochloric acid, using phenol phthalein as indicator. Each cubic centimeter of acid used equals .04 per cent. of $NaOH$ and is equivalent to .031 per cent. of Na_2O.

4. *Sodium Sulphide.*—Dissolve 5 grams of the soda ash in about 100 cubic centimeters of water, heat nearly to boiling, and make strongly alkaline with ammonia. Titrate with an ammoniacal silver-nitrate solution until no more silver sulphide forms. Near the end it is advisable to filter off a little and test to make sure of the end point.

To make the standard silver solution, dissolve 13.845 grams pure silver in pure nitric acid, add 250 cubic centimeters of strong ammonia water, and dilute to 1 liter. Each cubic centimeter of the silver solution equals .1 per cent. of sodium sulphide, and is equivalent to .0795 per cent. of Na_2O.

5. *Sodium Sulphite.*—Dissolve 5 grams of the soda ash in about 50 cubic centimeters of water, acidify with acetic acid, and titrate with $\frac{1}{10}$ normal iodine solution. Each cubic centimeter of iodine solution equals .126 per cent. of sodium sulphite.

29. Crystal Soda.—This substance is analyzed in the same manner as the above, except that on account of the large amount of water of crystallization, about double the amount must be taken for analysis.

CHANCE-CLAUS SULPHUR RECOVERY

30. Available Sulphur in Tank Waste.—In this determination the sulphide sulphur is set free by hydrochloric acid, collected in sodium-hydrate solution, and after acidifying, titrated with iodine solution. The details of the process are as follows: Weigh out in a 500-cubic-centimeter flask 2 grams of the tank waste, insert a two-holed rubber stopper through one hole of which is passed a funnel tube with a stop-cock, and through the other a tube bent to connect, by means of a tight rubber tube, a suitable absorption apparatus. The apparatus described for the determination of sulphur in iron by evolution, in *Quantitative Analysis*, is suitable for this purpose. Two of the absorption tubes should be partially filled with sodium-hydrate solution and connected to the evolution flask. Slowly run hydrochloric acid (1 part of acid to 1 part of water) through the funnel tube on to the waste until the decomposition is completed. Boil the flask, to drive out all the hydrogen sulphide, and when the first absorption tube has become warm on account of the steam condensed in it, open the stop-cock of the funnel tube and allow the apparatus to cool. Empty the absorption tubes into a 500-cubic-centimeter measuring flask, fill to the mark with well-boiled water, and take 50 cubic centimeters for titration. Dilute this to

200 cubic centimeters with well-boiled water, acidify with acetic acid, and titrate with $\frac{1}{10}$ normal iodine solution. Each cubic centimeter of the iodine solution equals .0017 gram H_2S or .0016 gram S.

31. Lime-Kiln Gases. — Determine carbon dioxide, oxygen, and carbon monoxide as under Art. **8.**

32. Gas From the Gasometer.—Determine hydrogen sulphide and carbon dioxide together by absorbing them in caustic-potash solution in the same manner as carbon dioxide is determined in Art. **8.**

Determine hydrogen sulphide alone by fitting a flask of exactly known content (about 500 cubic centimeters) with a two-holed rubber stopper, through one hole of which passes a funnel tube with a glass stop-cock; the stem of the funnel tube should end just below the stopper. Through the other hole in the stopper passes a tube, which leads to the bottom of the flask and is fitted with a stop-cock. For making the determination, allow gas from the gasometer to pass through the apparatus until the air is completely displaced, close both stop-cocks, disconnect from the gasometer, and empty the gas from the tubes outside of the stop-cocks. Run in through the funnel tube about 25 cubic centimeters of a normal sodium-hydrate solution and shake thoroughly until all the gas is absorbed. Wash out into a 250-cubic-centimeter flask with air-free water and make to the mark on the flask. Take 50 cubic centimeters, dilute to about 250 cubic centimeters with air-free water, acidify with acetic acid, and titrate with standard iodine solution. The standard iodine solution should contain 11.43 grams of iodine per liter, when each cubic centimeter equals 1 cubic centimeter of hydrogen-sulphide gas at 0° C. and 760 millimeters of mercury pressure.

To reduce the gas employed to normal conditions use the formula given for this purpose in *Quantitative Analysis.*

If necessary to calibrate the flask, it can be done with sufficient accuracy by weighing it empty, then filling with water to the stop-cocks, and weighing again. The difference between the two weights gives the weight of water in the flask, and, therefore, the volume in cubic centimeters. If greater accuracy is desired, the temperature of the water may be taken and the expansion of the water above 4° C. allowed for. Furthermore, the volume of air in the flask at its first weighing is approximately given by the weight of water; the weight of the air can be deducted from the weight of the flask plus air, thus giving the weight of the empty flask. For example, the flask plus air weighs 300 grams, the flask plus water at 18° C. weighs 795 grams; then $795 - 300 = 495$ grams of water at 18° C., which equals, approximately, 495 cubic centimeters as the capacity of the flask.

Correcting, 1 liter of air under standard conditions weighs 1.293 grams; and if the barometer stands at 750 millimeters of mercury pressure, the weight of 495 cubic centimeters of air can be calculated (see *Quantitative Analysis*). For $v = \frac{750 \times 495 \times 273}{760 \times 291} = 458$ cubic centimeters at standard conditions $= .458$ liter. Therefore, $1.293 \times .458 = .6$ gram, the weight of air in the flask. The real weight of the flask is, therefore, less by this amount than the apparent weight and the weight of water becomes 495.6 grams. But 1 gram of water at 18° C. equals 1.001373 cubic centimeters, and therefore the corrected volume of the flask is 496.3 cubic centimeters.

33. Waste Gas From Claus Kiln.—The important substances to determine in this gas are sulphur dioxide and hydrogen sulphide. These are best determined by conducting 5 liters of the gas through a suitable absorption apparatus containing caustic-soda solution. The gases are absorbed, giving sodium sulphide and sodium sulphite. The caustic solution is then made to 250 cubic centimeters with air-free water and 50 cubic centimeters taken, acidified with acetic acid, and titrated with $\frac{1}{10}$ normal iodine. This gives both the hydrogen sulphide and sulphur dioxide. 100 cubic centimeters of the original solution is then taken, the sulphide precipitated with an alkaline-zinc solution, one-half filtered off, acidified with acetic acid, and titrated with $\frac{1}{10}$ normal iodine solution; this gives the sulphur dioxide. 1 cubic centimeter of $\frac{1}{10}$ normal iodine solution equals .0017 gram of H_2S or .0032 gram of SO_2, and equals 1.12 cubic centimeters of either gas at 0° C. and 760 millimeters of mercury pressure.

SODIUM BICARBONATE

34. The crude materials for sodium bicarbonate manufacture are the soda crystals from Le Blanc soda or the ammonia-soda ash, and lime-kiln gas. For the analysis of these substances, see Arts. **8**, **17**, and **29.**

FINISHED PRODUCT

35. Sodium Bicarbonate.—Analyze the same as soda ash, Art. **17.** The daily tests consist in the determination of total alkali, sodium carbonate, sodium bicarbonate, and sodium chloride.

CAUSTIC SODA

CRUDE MATERIALS

36. The crude materials for the manufacture of caustic soda differ, depending on whether the substance is made at a Le Blanc or at an ammonia-soda works. The methods for all of them, however, will be described, and the student can select those that apply to the work that he is doing.

1. *Red Liquor.*—Analyze as under Art. **26.**
2. *Soda Ash.*—Analyze as under Art. **17** or **28.**
3. *Milk of Lime.*—Analyze as under Art. **15.**

INTERMEDIATE PRODUCTS

37. While some of the following may be very properly considered as finished products, or otherwise classified, for the sake of simplicity they are given under this head.

38. Caustic Liquor.—The following determinations are made:

1. *Specific Gravity.*—The specific gravity is taken of the liquor at different stages of the evaporation, and although other substances affect the results, a fair idea of the run of the liquor can be obtained by this determination alone. Table III gives the percentage of caustic soda corresponding to the different specific gravities at 15° C.

TABLE III

Specific Gravity	Grams of $NaOH$ Per Liter	Specific Gravity	Grams of $NaOH$ Per Liter	Specific Gravity	Grams of $NaOH$ Per Liter
1.007	6	1.142	144	1.320	381
1.014	12	1.152	156	1.332	399
1.022	21	1.162	167	1.345	420
1.029	28	1.171	177	1.357	441
1.036	35	1.180	188	1.370	462
1.045	42	1.190	200	1.383	483
1.052	49	1.200	212	1.397	506
1.060	56	1.210	225	1.410	528
1.067	63	1.220	239	1.424	553
1.075	70	1.231	253	1.438	575
1.083	79	1.241	266	1.453	602
1.091	87	1.252	283	1.468	629
1.100	74	1.263	299	1.483	658
1.108	104	1.274	316	1.498	691
1.116	112	1.285	332	1.514	721
1.125	123	1.297	348	1.530	750
1.134	134	1.308	364		

2. *Total Alkali and Sodium Carbonate.*—These two values are determined according to Art. **23.**

3. *Salt.*—In caustic from ammonia soda, it is frequently necessary to determine the amount of salt. Proceed according to Volhard's method, described in *Quantitative Analysis.*

4. It is only necessary to determine *sulphur compounds* when the caustic is made from red liquor or crude Le Blanc soda. Sodium sulphate is sometimes determined in liquor from ammonia soda. Make the determinations according to Art. **26.**

39. Fished Salts.—For analysis dissolve 25 grams of the salts in 500 cubic centimeters of water.

1. *Total Alkali.*—Titrate 25 cubic centimeters, as usual, with normal acid, using methyl orange as indicator.

2. *Salt.*—Titrate 25 cubic centimeters with silver nitrate by Volhard's method, described in *Quantitative Analysis.*

3. *Sodium Sulphate.*—Determine in 25 cubic centimeters, by acidifying with hydrochloric acid and precipitating hot with barium chloride, as usual.

4. *Oxidizable Sulphur Compounds.*—Treat 25 cubic centimeters of the solution with bromine water until it is colored, acidify with hydrochloric acid, boil off the excess of bromine, and precipitate as sulphate with barium chloride as usual. The difference between the amount of sulphate found here and that found above gives the oxidizable sulphur. This determination is, of course, unnecessary when the caustic is made from ammonia soda.

40. Caustic Bottoms.—This sample sometimes comes to the laboratory in fairly large lumps in a stoppered bottle that has the stopper covered with sealing wax. This wax should not be broken until the sample is wanted for analysis. Then several pieces are taken, wrapped quickly in several thicknesses of heavy brown paper, and crushed on an anvil by means of a hammer; 20 grams are then weighed off and dissolved in water. It is necessary to work quickly until the caustic is weighed, to prevent its absorbing water from the air.

1. *Insoluble.*—When the above 20 grams are dissolved, filter, and wash thoroughly. Collect the filtrate and washings in a 500-cubic-centimeter measuring flask, make to the mark, and save. The filter and contents are ignited and weighed.

2. *Total Alkali.*—Take 50 cubic centimeters of the above filtrate, add a little lacmoid for an indicator, and add normal acid to more than neutralize. Heat to boiling, to expel the carbon dioxide, and titrate back with normal alkali. The difference between the acid and alkali used gives the acid required for neutralizing the total alkali. Each cubic centimeter of normal acid equals .031 gram of Na_2O.

3. *Sodium carbonate* is determined according to Art. **23.**

4. *Salt* is determined according to Art. **23.**

41. Caustic Mud.—The determinations are as follows:

1. *Total Alkali.*—Extract 25 grams of the sample by shaking it with several small portions of hot water, finally filter, wash, and unite the filtrates and washings, pass carbon dioxide for 10 minutes, boil to decompose bicarbonates, refilter, if necessary, and titrate with normal acid, using methyl orange as indicator. Each cubic centimeter equals .031 gram of Na_2O.

2. *Caustic Lime.*—Shake about 25 grams of the waste with a little water and titrate with normal acid and phenol phthalein. The sodium above was present as hydrate and carbonate, but a fair average will be reached if we deduct one-half of the number of cubic centimeters of acid required for total alkali, from the amount taken above, and call the remainder of the acid used by the waste, caustic lime. Each cubic centimeter of acid equals .037 gram of $Ca(OH)_2$.

3. *Calcium Carbonate.*—Titrate 1 gram of the sample with normal hydrochloric acid, using methyl orange as indicator, and deduct the acid required for caustic lime. Each cubic centimeter of acid equals .05 gram of $CaCO_3$.

FINISHED PRODUCTS

42. Caustic Soda. — The method for preparing the sample for analysis given under Art. **40** can be used to advantage here. For analysis weigh out 50 grams, dissolve in water, and make to 1,000 cubic centimeters.

1. *Total Alkali.*—Titrate as usual, using normal hydrochloric acid and methyl orange.
2. *Caustic soda* is determined as under Art. **23.**
3. *Sodium carbonate* is determined as under Art. **23.**
4. *Salt* is determined as under Art. **23.**
5. *Sodium sulphate* is determined as under Art. **39.**
6. *Other constituents* are determined as under Art. **17.**

HYDROCHLORIC ACID

RAW MATERIALS AND INTERMEDIATE PRODUCTS

43. Hydrochloric acid is almost without exception obtained from salt by the action of sulphuric acid. For its crude materials and intermediate products, see under the heading "Salt Cake."

The absorption of the gas in the bombonnes and towers is watched by means of specific-gravity tests. These are best made by arranging a cylinder and hydrometer in such a way that a portion of the acid is being continuously collected in the cylinder in which the hydrometer floats. By this means it is possible to see the specific gravity at a glance, and the delay and trouble of collecting the sample is avoided.

Table IV gives the specific gravity and composition of solutions of hydrochloric acid at 15° C.

44. Waste Gases. — The gas that escapes from the absorption towers must not contain much hydrochloric acid, for it is injurious to vegetation. The sample is taken by inserting a glass tube to the center of the chimney through which the gas passes to the outside air. To the outer end of the tube is attached a double-acting rubber suction bulb, and this, in turn, is connected to an absorption apparatus similar to that mentioned in Art. **30.** The absorption apparatus is fitted with large test tubes, or small flasks, so that two pieces will hold 150 or 200 cubic centimeters of water. It is then filled with water and is connected in

TABLE IV

Specific Gravity	Per Cent. HCl	Grams HCl per Liter	Specific Gravity	Per Cent. HCl	Grams HCl per Liter
1.000	.16	1.6	1.1150	22.86	255
1.005	1.15	12.0	1.1200	23.82	267
1.010	2.14	22.0	1.1250	24.78	278
1.015	3.12	32.0	1.1300	25.75	291
1.020	4.13	42.0	1.1350	26.70	303
1.025	5.15	53.0	1.1400	27.66	315
1.030	6.15	64.0	1.1425	28.14	322
1.035	7.15	74.0	1.1450	28.81	328
1.040	8.16	85.0	1.1500	29.57	340
1.045	9.16	96.0	1.1520	29.95	345
1.050	10.17	107.0	1.1550	30.55	353
1.055	11.18	118.0	1.1600	31.52	366
1.060	12.19	129.0	1.1630	32.10	373
1.065	13.19	141.0	1.1650	32.49	379
1.070	14.17	152.0	1.1700	33.46	392
1.075	15.16	163.0	1.1710	33.65	394
1.080	16.15	174.0	1.1750	34.42	404
1.085	17.13	186.0	1.1800	35.39	418
1.090	18.11	197.0	1.1850	36.31	430
1.095	19.06	209.0	1.1900	37.23	443
1.100	20.01	220.0	1.1950	38.16	456
1.105	20.97	232.0	1.2000	39.11	469
1.110	21.92	243.0			

position. The bulb is then compressed a sufficient number of times to force the desired amount of chimney gas through the absorption apparatus. By careful work the amount of gas used can be quite accurately estimated by this method; if greater accuracy is wished, the gas after passing through the absorbing apparatus may be run into a gasometer and measured. The liquid from the absorption apparatus is washed into a flask and titrated by Volhard's method, which is described in *Quantitative Analysis.*

FIG. 3

Another very simple and very effective form of absorption apparatus that can be used has been recommended by the English alkali inspectors; it is shown in Fig. 3. The gas enters at *a*, passes out through the holes at the lower end of the tube, and passes up through a number of thin ends cut from a small rubber tube, which breaks the gas into fine bubbles, then out through the holes, in the direction of the arrows, into the bottle, and finally escapes through the tube *b*. This tube is filled below with pieces of rubber tube and above with glass wool. By moistening the contents of *b* with water and adding a little indicator, as methyl orange, any failure on the part of the apparatus to absorb the acid is shown in *b* by the change in the indicator.

FINISHED PRODUCT

45. Hydrochloric Acid.—The analysis of hydrochloric acid varies according to the purpose for which the acid is to be used. For many purposes a simple determination of the specific gravity is sufficient, while for other purposes a more extended examination is necessary. In the following, the methods of analysis are given for all cases, except the so-called chemically pure acid, the examination of which is practically never required in the ordinary chemical works.

1. *Sulphuric Acid.*—Take 50 cubic centimeters of the acid to be tested, almost neutralize with pure sodium carbonate, heat to boiling, and precipitate with barium chloride, as usual. Each gram of barium sulphate found corresponds to .34335 gram of SO_3.

Another method, which gives quite accurate results and, on account of its rapidity, is very suitable where several determinations must be made each day, is as follows: Prepare a glass tube 6 millimeters broad and 250 millimeters long closed at the lower end, while the upper end expands into a tube 15 millimeters broad. Provide a rubber stopper for the broad tube. By mixing acids of known composition make a series of acids containing from .2 or .6 up to 3 per cent. of sulphuric acid. Take 10 cubic centimeters of the first of these acids, heat to boiling, pour into the above tube, nearly neutralize with ammonia, and precipitate with 5 cubic centimeters of a boiling hot, saturated, barium-chloride solution. Insert the rubber stopper, place in a centrifugal machine, and whirl for 5 minutes. Mark the height of the precipitate, empty, and repeat with the next stronger sample. In this way graduate the tube and use it for the determination in the same way, using 10 cubic centimeters of the sample, instead of the known solution, and reading off the percentage of sulphuric acid on the tube.

2. *Sulphurous Acid.*—Add bromine to 50 cubic centimeters of the acid to color it and boil until color disappears. Proceed as for sulphuric acid. For rapid work, use 10 cubic centimeters of the sample and use the rapid method given above. In either case, deduct the barium sulphate found above from the total and each gram of barium sulphate in excess corresponds to .27468 gram of SO_2.

3. *Arsenic.*—The detection and determination of arsenic in hydrochloric acid that is to be used in the preparation of

foodstuffs is very important. A very large number of methods for both its qualitative and quantitative determination have been proposed and are in use. The following, however, seem to be the most convenient and exact.

(*a*) *Qualitative Tests.*—Take 10 cubic centimeters of the sample in a test tube, dilute with 10 cubic centimeters of distilled water, carefully pour on the top of the acid 5 cubic centimeters of a freshly prepared hydrogen-sulphide solution, and allow to stand for 1 hour. Prepare a second tube in exactly the same manner and allow to stand for 1 hour in a water bath at from 70° to 80° C. If no precipitate, or yellow ring, appears between the two layers in either case, arsenic is absent. By this method the presence of $\frac{1}{20}$ milligram of arsenic in the 10 cubic centimeters of acid can be detected.

For the most accurate detection of arsenic take 5 liters of the acid, add about $\frac{1}{4}$ gram of potassium chlorate, to prevent the arsenic volatilizing as $AsCl_3$ during evaporation, and dilute with water until the specific gravity does not exceed 1.1. Evaporate to dryness in a well-enameled porcelain evaporator, take up the residue in a little water, and test the solution in a Marsh apparatus, which is described in *Qualitative Analysis.*

(*b*) *Quantitative Determination.*—When very small amounts of arsenic are to be determined, take 5 liters of the acid, and concentrate to small bulk as above, using potassium chlorate to prevent loss of arsenic by volatilization, then proceed as follows: If fairly large amounts are known to be present or are shown by the qualitative test, take 50 cubic centimeters, partly neutralize with sodium carbonate, dilute to 150 cubic centimeters, and precipitate as sulphide, following the directions given in *Quantitative Analysis.* Remember here that the arsenic may be present as arsenic acid and that, under those circumstances, heat and considerable time (from 12 to 20 hours) are necessary to completely precipitate all the arsenic.

4. *Selenium.*—Test with stannous chloride as described in *Qualitative Analysis.*

5. *Hydrochloric Acid.* —Take 10 cubic centimeters of the sample in an accurate pipette, dilute to 250 cubic centimeters, and take 25 cubic centimeters for titration. Titrate with normal caustic-soda solution, using methyl orange as indicator. Deduct the amount of caustic corresponding to the SO_3 already found from the total and the rest corresponds to HCl. Each cubic centimeter of alkali equals .0365 gram of HCl.

For example, if 10 cubic centimeters of normal alkali is required for 1 cubic centimeter of the sample and .004 gram of SO_3 has been found in the previous determination, then .1 cubic centimeter of the alkali was used by the sulphuric acid, and the amount used by the hydrochloric acid is 9.9 cubic centimeters, which equals .36135 gram of HCl in 1 cubic centimeter of the sample, or 361.35 grams per liter.

It is customary to report results of this kind in grams per liter; but if the percentage is wanted, determine the specific gravity and divide the grams per liter by 10 times the specific gravity, the result will be the percentage of HCl.

When the amount of hydrochloric acid alone is to be determined in a sample, it is simpler to titrate 10 cubic centimeters of the diluted sample with $\frac{1}{10}$ normal silver nitrate, using Volhard's method, which is described in *Quantitative Analysis*. Each cubic centimeter of the silver-nitrate solution equals .00365 gram of HCl.

CHLORINE, BLEACHING COMPOUNDS, CHLORATES

CRUDE MATERIALS

46. Manganese Ore.—The ordinary determinations are as follows:

1. *Moisture.*—Spread 2 grams of the finely powdered ore thinly on a watch glass and dry at 100° or 110° C. until the weight remains constant.

2. *Available Oxygen.*—For this determination are needed a ½ normal potassium-permanganate solution and a ferrous-sulphate solution made by dissolving 100 grams of ferrous sulphate and 100 grams of sulphuric acid in 1 liter of water. For the determination, weigh out 1.0875 grams of the dried ore (preferably that used for the moisture determination) into a 200-cubic-centimeter flask provided with a tube leading to the bottom of a second flask containing sodium-bicarbonate solution. The arrangement of the flasks is shown in Fig. 4. Measure exactly 75 cubic centimeters of the ferrous sulphate into the flask with the manganese ore, insert the stopper with the tube leading into the sodium-bicarbonate solution, and heat until a dark-colored residue is no more apparent. Allow the solution to cool, wash into a 500-cubic-centimeter beaker, dilute to about 200 cubic centimeters, and titrate with ½ normal potassium-permanganate solution until the color stays permanent for about ½ minute.

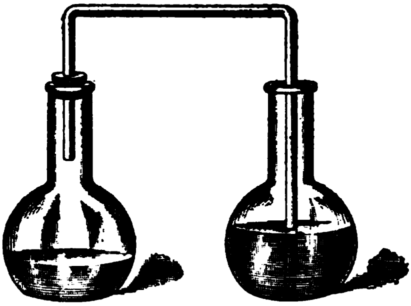


FIG. 4

The ferrous-sulphate solution must be standardized each day by measuring out 75 cubic centimeters, using the same pipette as above, and titrating it with the ½ normal potassium-permanganate solution.

The difference between the amount of potassium-permanganate solution used to titrate the ferrous-sulphate solution and that used with the ore gives the available oxygen, or rather the manganese present in the ore as MnO_2. If the above amount of ore is weighed out, each cubic centimeter of ½ normal potassium-permanganate solution corresponds to 2 per cent. of MnO_2.

Another very exact and rapid method that can be used direct, or as a check on the above method, is given in *Quantitative Analysis*, under the description of the nitrometer.

3. *Carbon Dioxide.*—Determine according to the absorption method given in *Quantitative Analysis.*

4. *Acid Necessary to Decompose Ore.*—Bring 1 gram of the ore into a flask containing 10 cubic centimeters of the hydrochloric acid being used in the chlorine manufacture and whose titration strength has been previously determined. Insert a stopper, with a return condenser, in the flask and heat until the ore is dissolved. Allow to cool and titrate with normal caustic-soda solution until the brown flakes of iron hydrate no longer dissolve by shaking. The difference between the caustic soda used here and that required for the titration of 10 cubic centimeters of the original acid gives the acid used in decomposing the ore.

47. Limestone.—Analyze according to Art. **3.**

48. Quicklime.—Analyze according to Art. **4.**

49. Slaked Lime.—Water, carbon dioxide, and calcium hydrate are usually determined.

1. *Water.* — Weigh out from a well-closed weighing tube 1 gram of the sample into a weighed platinum crucible and heat, at first gradually and then to the strongest temperature of the blast lamp; cool; and weigh. The loss of weight equals carbon dioxide and water.

2. *Carbon Dioxide.*—Determine according to the absorption method given in *Quantitative Analysis* and deduct the result from the carbon dioxide and water previously determined.

3. *Milk of Lime.*—See Art. **15.**

INTERMEDIATE PRODUCTS

50. Free Acid in Still Liquor.—Titrate 25 cubic centimeters of the still liquor with normal sodium-hydrate solution until the brown flakes of ferric hydrate no longer dissolve by thorough shaking. Each cubic centimeter of caustic-soda solution used equals .0365 gram of free hydrochloric acid.

51. Calcium Chloride in Clear Liquor.—Acidify 25 cubic centimeters of the clear liquor with acetic acid, add ammonium oxalate in excess, allow to stand 3 hours to insure complete precipitation of the calcium oxalate, and filter on an asbestos filter, using a Gooch crucible. Bring the crucible containing the precipitate of calcium oxalate into a 300-cubic-centimeter beaker, add 100 cubic centimeters of distilled water and 10 cubic centimeters of concentrated sulphuric acid. (Use care in adding the acid, that the contents of the beaker do not spatter out.) Now titrate the oxalic acid obtained from the above operations with $\frac{1}{10}$ normal potassium-permanganate solution. Each cubic centimeter of the $\frac{1}{10}$ normal potassium-permanganate solution is equal to .0028 gram of calcium oxide, or .00555 gram of calcium chloride.

52. Weldon Mud.—The following determinations are required:

1. *Manganese Dioxide.*—See Art. **46.**

2. *Total Manganese.*—Weigh out 10 grams of the mud, acidify with concentrated hydrochloric acid, boil to drive off all the chlorine, and then neutralize the excess of acid with precipitated chalk. Acidify with acetic acid, add bromine, heat, and continue the addition until the solution retains the odor of bromine. Add alcohol slowly until the red color disappears and filter on a Gooch filter. Test the filtrate, to see if it turns brown, with the addition of a drop of bromine water; if so, precipitate the rest of the manganese and add it to the precipitate already obtained. All the manganese is now on the filter as manganese dioxide. Introduce filter and all into a flask and proceed to determine the manganese dioxide according to Art. **46.**

3. *Total Base.*—This indicates the base present that neutralizes the hydrochloric acid without producing chlorine. Dilute 25 cubic centimeters of normal oxalic-acid solution to about 100 cubic centimeters, warm to 75° C., and add 10 grams of the mud. Shake until the precipitate is pure white, dilute to 202 cubic centimeters, filter through a

dry filter, take 100 cubic centimeters of the filtrate and titrate back with normal caustic-soda solution. (The extra 2 cubic centimeters is to allow for the precipitate.) If we call the caustic-soda solution used x, the oxalic acid used is $25 - 2x$. Of this, part is used to neutralize the base, and part to reduce the manganese dioxide to manganese monoxide and then neutralize that. We have just found the amount of manganese dioxide in 10 grams of the mud and can calculate its equivalent in oxalic acid from the equation

$$MnO_2 + 2(COOH)_2 = Mn(CO_2)_2 + 2CO_2 + 2H_2O$$

Calling this amount of oxalic acid expressed in cubic centimeters of normal solution y, then the amount of normal acid used by the base is $25 - (2x + y) = z$. Since the base consists of a mixture of lime, magnesia, manganese hydrate, and iron hydrate, it is customary to report the result here in cubic centimeters of oxalic acid used.

53. Gas From Sulphate Pan.—The hydrochloric-acid gas from the "pan" must be mixed with the proper amount of air as it goes to the "decomposer," and this mixture is controlled by analysis. The analysis is carried out by sucking the gas, by means of an aspirator, through a standard solution of caustic soda containing methyl orange. The instant the color changes, the flow of the gas is stopped and the volume of gas in the aspirator is determined by measuring the amount of water that has run out of the aspirator. A suitable piece of apparatus for this determination is shown in Fig. 5. The lower end of the tube leading into the absorption bottle is blown out and arranged with a number of small holes to

FIG. 5

break up the gas into small bubbles and so assist the absorption.

By using the same amount of normal alkali each time, the amount of hydrochloric acid absorbed is constant; and by measuring the air carried through, the composition of the mixed gas can be easily calculated. As, for example, if we use 100 cubic centimeters of normal alkali that is equal to 3.65 grams hydrochloric acid, which is equal to 2.24 liters of hydrochloric-acid gas under 0° C., and 760 millimeters of mercury pressure. If the gas collected measures 3 liters after correcting for temperature and pressure, then the total gas used is 5.24 liters, of which 57.3 volume per cent. is air and the remainder hydrochloric acid.

54. Gas From Decomposer.—Arrange three absorption bottles, similar to that shown in Fig. 5, in a series as close to the decomposer as possible, and divide 250 cubic centimeters of caustic soda of 1.075 sp. gr. between the three bottles. The aspirator is so regulated that it continues during the working off of a pan charge. Five liters of the gas are sucked through the absorption bottles, then the contents of all three flasks are united and diluted to exactly 500 cubic centimeters.

(*a*) Pipette off 100 cubic centimeters of the above solution, add 25 cubic centimeters of standard ferrous-sulphate solution, and proceed as for available oxygen in Art. **46,** titrating at the end with $\frac{1}{2}$ normal potassium-permanganate solution. Deducting the amount of potassium permanganate required here from the amount required for 25 cubic centimeters of the ferrous-sulphate solution gives the amount of the permanganate equivalent to the chlorine in 1 liter of the gas. The number of cubic centimeters of $\frac{1}{2}$ normal potassium permanganate times .01775 equals the number of grams of chlorine per liter of gas.

(*b*) Pipette off 25 cubic centimeters of the original solution and add somewhat of an excess of sodium-sulphite solution (approximately the amount of sodium sulphite needed can be estimated from the preceding determination).

Add sulphuric acid until the solution is acid, when it should smell strongly of sulphur dioxide, thus showing that more sulphur dioxide is present than is needed to reduce the sodium hypochlorite to sodium chloride. Heat to boiling, cool, and, if necessary, add potassium-permanganate solution until the color fades out very slowly. Titrate with $\frac{1}{10}$ normal silver-nitrate solution, using the Volhard method.

If the number of cubic centimeters of $\frac{1}{2}$ normal potassium-permanganate solution required for the chlorine under (*a*) is called x, and the number of cubic centimeters of $\frac{1}{10}$ normal silver-nitrate solution, y, $\frac{2x}{y}$ equals the percentage decomposition of the hydrochloric acid.

55. Bleaching-Powder Chambers.—Whenever it is necessary to open the chamber in which bleaching powder is being made, the gas in the chamber must be tested in some way, in order that too much chlorine will not be allowed to escape into the surrounding atmosphere. A very simple apparatus, and the one in most common use for this purpose, is shown in Fig. 6. The cylinder *d* contains 25 cubic centimeters of a solution made as follows: .495 gram of arsenic trioxide is dissolved in sodium-carbonate solution and neutralized by sulphuric acid; then 25 grams of potassium iodide, 5 grams of precipitated chalk, and from 8 to 10 drops of ammonium-hydrate solution are added, and the whole made up to 1 liter with distilled water. A little starch paste is added to each 25 cubic centimeters just before it is used. The cylinder *d* is fitted with a two-holed rubber stopper *c*; through one hole passes the tube *e*, which is drawn out at the lower end to a hole about the size of a knitting needle; through the other hole passes

FIG. 6

a glass tube *f*, the lower end of which projects a short distance into the cylinder, while to the upper end is attached the rubber bulb *a* of about 100 cubic centimeters capacity.

The tube *f* is also provided with the small hole *b*. To test the gas in a bleach chamber, the tube *e* is inserted through an opening in the chamber about 2 feet above the floor. The bulb *a* is then compressed, *b* is closed by the finger, and *a* allowed to expand. By doing this the gas from the chamber is drawn through the test solution in *d*. By counting the number of bulbs full of the gas necessary to color the test solution by separated iodine, the chlorine in the gas can be calculated; for 25 cubic centimeters of the above solution is equivalent to 9.135 milligrams of chlorine. That is, if it takes 10 bulbs full to bring a color, then the gas contains 9.135 milligrams of chlorine per liter of the gas.

56. Bleach Liquors.—When liquid bleach is made direct from the base, or carbonate, and chlorine, the manufacture requires a careful attention to the course of the absorption.

1. *Available chlorine* is determined in 5 cubic centimeters of the liquid by Penot's method, which is described in *Quantitative Analysis*, under "Bleaching Powder."

2. *Chlorides*.—Take the solution from the determination of available chlorine and which now contains arsenates, nearly neutralize with nitric acid, but still leave a slight excess of alkali, and titrate with $\frac{1}{10}$ normal silver-nitrate solution. The formation of the red silver arsenate when the chlorine is all precipitated shows the end point.

3. *Chlorates*.—Bring 5 cubic centimeters of the bleach solution into a flask arranged as shown in Fig. 4; add 50 cubic centimeters of the solution of ferrous sulphate described in Art. **46**, and the strength of which against $\frac{1}{2}$ normal potassium-permanganate solution is known, boil the mixed solution, and after allowing to cool, titrate back with potassium-permanganate solution. If the number of cubic centimeters of $\frac{1}{2}$ normal potassium-permanganate

solution used for 50 cubic centimeters of the original ferrous-sulphate solution is called *a*, and the number of cubic centimeters of $\frac{1}{2}$ normal potassium-permanganate solution used by 50 cubic centimeters of the ferrous-sulphate solution after oxidation with the bleach liquor *b*, then $a - b$ gives oxidizing equivalent of the bleach liquors in terms of $\frac{1}{2}$ normal potassium-permanganate solution. The oxidizing action is due to the available chlorine and the chlorates. The available chlorine has been determined, and 5 cubic centimeters of the $\frac{1}{10}$ normal arsenite solution is equivalent to 1 cubic centimeter of the $\frac{1}{2}$ normal potassium-permanganate solution. If the number of cubic centimeters of $\frac{1}{10}$ arsenite solution used for available chlorine is called *c*, then $(a - b) - \frac{c}{5}$ equals the number of cubic centimeters of $\frac{1}{2}$ normal potassium-permanganate solution equivalent to the chlorate in the solution. Each cubic centimeter of $\frac{1}{2}$ normal potassium-permanganate solution is equivalent to .01021 gram potassium chlorate, .00888 gram of sodium chlorate, or .00862 gram of calcium chlorate. This gives the amount of the chlorate in 5 cubic centimeters of the solution, which result multiplied by 200 gives the number of grams per liter.

4. *Caustic Alkali.*—Take 10 cubic centimeters of bleach liquor and dilute with 150 cubic centimeters of distilled water, add a few drops of a phenol-phthalein solution, and titrate with a normal acid solution until the red color disappears. Add a few more drops of the indicator, and if the color again disappears after about 5 seconds shaking, the result is taken as equivalent to the caustic alkali present.

5. *Carbonates.*—Take 10 cubic centimeters of the bleach liquor and add ammonia (in a well-covered beaker to avoid loss by the gas evolved) until the evolution of nitrogen ceases and the liquid smells of ammonia. Then heat until the ammonia odor disappears, dilute to 150 cubic centimeters, and titrate with normal acid, using methyl orange as indicator. The difference between this result and that for the caustic gives the carbonate in the solution.

57. Chlorates.—The methods of control here are practically the same as those described for bleach liquors under Art. **56.** The usual determinations made are chlorates, chlorides, and sometimes available chlorine (chlorine and hypochlorites). The chlorate is reported as potassium chlorate, and for calculating the amount of potassium chloride necessary to convert the calcium chlorate into potassium chlorate, we can multiply the number of cubic centimeters of ½ normal potassium permanganate used by 3.105. That is, in Art. **56** $\left[(a - b) - \frac{c}{5}\right] \times 3.105 =$ number of grams of potassium chloride required per liter of the chlorate liquor to convert the calcium chlorate into potassium chlorate.

FINISHED PRODUCTS

58. Bleaching Powder.—The only determination that it is necessary to make with bleaching powder is the determination of the available chlorine. A large number of methods have been proposed for this determination, but the only one of importance for this country is the Penot method, which is described in *Quantitative Analysis.* A somewhat similar method, using a hydrochloric-acid solution of arsenic trioxide, was introduced into France in 1835 by Gay-Lussac and is still largely used in that country. It is far inferior, however, to the Penot method.

59. Bleach Liquors.—Analyze as given under the methods for factory control, in Art. **56.**

60. Potassium Chlorate.—Potassium chlorate as a finished product is so nearly chemically pure that seldom more than a qualitative analysis is necessary, or at most a quantitative determination of the chloride present.

1. *Potassium Chloride.*—Dissolve 50 grams of the sample in as little distilled water as possible, precipitate the chlorine with silver nitrate, shake to collect the precipitate together; filter on a Gooch filter, wash thoroughly, dry at 125° C., and

weigh. Each gram of silver chloride is equivalent to .5192 gram of potassium chloride, or $\frac{\textit{weight of } AgCl \times .5192 \times 100}{50}$ = percentage of KCl in substance.

2. *Qualitative Tests.* — The solution should be water white, free from sediment, and should not color or precipitate by the addition of ammonium sulphide or carbonate.

61. Electrolysis.—The analyses required in the control of electrolytic processes for the preparation of alkali, chlorine, and potassium chlorate are so similar to those already treated that no more than a reference to them is required.

1. *Brine.*—Analyze according to Art. **1.**

2. *Caustic liquor* may contain sodium chloride, sodium hypochlorite (possibly sodium chlorate), sodium hydrate, and more or less sodium carbonate. Analyze according to Art. **56.**

3. *Bleaching Powder Chambers.*—See Art. **55.**

4. *Bleach Liquor.*—See Art. **56.**

5. *Potassium-chlorate liquor* may contain potassium chloride, potassium hypochlorite, potassium chlorate, and hypochlorous acid. Analyze according to Art. **56.**

MANUFACTURE OF PAPER

(PART 1)

INTRODUCTION

DEVELOPMENT OF PAPER MANUFACTURE

1. The exact time when paper was first used is not recorded. According to history, the Egyptians made a kind of paper from the papyrus plant (from which the word *paper* is derived) as early as 2400 B. C., and the Chinese made paper from cotton in the 2d century B. C. The process employed in making cotton paper was unknown to the rest of the world, however, until the Arabs made it in 704 A. D.

The manufacture of paper was begun in Spain in the 11th century, and paper was made in France as early as 1189, but the industry did not progress rapidly in the latter country. The first paper manufactory was established in Germany in 1390, but the industry did not appear in England until 1490. In America, the first paper mill was established in 1690 at Germantown, near Philadelphia, by William Rittenhouse. Since that time the industry has advanced rapidly, and at present there are more than fourteen hundred pulp and paper mills in the United States and Canada.

2. The rapid progress of the paper industry is largely due to the application of chemistry. The influence that this branch of science has had on the advancement of the paper industry cannot be overrated.

It was a discovery made by a chemist that led to the isolation of the large group of celluloses that enter into different grades of paper. The manufacture of soda, the discovery of the bleaching action of chlorine, and the subsequent manufacture of bleaching powder, together with the discovery and application of the coal-tar dyes, were great steps in the advancement of this industry. Many other cases might be cited in which chemistry has played an important part. It is now necessary for a good paper maker to have a considerable knowledge of chemistry, in order that he may understand the changes going on and be able to regulate conditions so as to obtain the best results. It is the aim to give a practical idea of the paper industry, and at the same time to show the chemical changes that take place and to set forth methods for testing and keeping a check on the ingredients used.

PAPER-MAKING MATERIALS

CELLULOSE

3. Paper is now made from the fiber of many varieties of plants and from materials that were themselves made from vegetable fibers. In a treatise of this kind it is almost impossible to enumerate and describe all the different materials that could be used. Suffice it to say that everything in the vegetable kingdom, could, under proper treatment be reduced to a pulp. Wood, straw, and other vegetable structures are composed of innumerable small fibers that are cemented together by a resinous or gummy non-cellular substance. These fibers have a cellular structure and are composed mainly of a chemical compound called **cellulose**, $C_6H_{10}O_5$, which is known to paper makers as the available paper-making material, and constitutes the essential basis of all manufactured paper. The cellulose is obtained by depriving the vegetable fiber of all incrusting and cementing resinous and gummy matters. This is accomplished in several ways, all of which depend on the conversion of the non-cellular constituents into soluble derivatives, the soda and the sulphite processes being the most noted.

4. **Chemical Properties of Cellulose.**—Cellulose that has been treated with a solution of bleaching powder at a very high temperature or exposed to this action at ordinary temperature for a long period, becomes oxidized, forming oxycellulose, $C_6H_{10}O_6$. This treatment, which is known as *chlorination of the fiber*, results in a loss of the fiber, and no antichlor will restore it to its original condition. This action is very marked in the treatment of straw and esparto.

5. **Schweitzer's Reagent.**—The only solution in which cellulose can be dissolved without undergoing chemical change is **Schweitzer's reagent.** This reagent is made by dissolving cupric hydrate in ammonium hydrate (.9 specific gravity) until saturated. When cellulose is treated with this reagent, it dissolves, forming a thick, sirupy solution. The cupric hydrate used can be prepared by precipitation from a solution of copper sulphate with caustic-soda solution.

PRINCIPAL MATERIALS FOR PAPER MAKING

6. The materials brought into most general use in the manufacture of paper are *cotton*, *linen*, *straw*, *esparto*, *wood* from various kind of trees, and *jute*, all of which, under proper treatment, will produce good fibrous stock that can be readily used.

7. **Cotton and Linen.**—For some time **cotton** and **linen**, were the only materials used in the manufacture of paper by machinery, and they are still extensively used in the manufacture of the better class of writing paper. Cotton is the purest form of cellulose and possesses the quality of durability, being remarkable for its resistance to the action of caustic soda. Linen is cellulose isolated from flax by treatment with caustic soda. Müller gives the following analyses of cotton and linen:

COTTON	PER CENT.
Water	7.00
Cellulose	91.35
Fat	.40
Aqueous extract	.50
Ash	.12
Cuticular substance	.63
Total	100.00

LINEN	PER CENT.
Water	8.60
Cellulose	81.99
Fat and wax	2.37
Aqueous extract	3.62
Pectous substance	2.72
Ash	.70
Total	100.00

8. Straw and Esparto Grass.—In the manufacture of cheap grades of paper, **straw** and **esparto grass** are used extensively. Straw is not so valuable as esparto, for the reason that it has to undergo a more severe treatment, which greatly reduces the yield of pulp. The cellulose extracted from these materials is considered as *oxycellulose*, because it oxidizes very readily when exposed to air at 100° C. The following are analyses of straw and esparto according to Müller:

STRAW (RYE)	PER CENT.
Cellulose	47.69
Fat and wax	1.93
Aqueous extract	9.05
Non-cellulose	26.75
Water	11.38
Ash	3.20
Total	100.00

ESPARTO (SPANISH)	PER CENT.
Cellulose	48.25
Fat and wax	2.07
Aqueous extract	10.19
Pectous substance	26.39
Water	9.38
Ash	3.72
Total	100.00

9. Wood.—Owing to the large amount of wood available, the fiber of this material now holds the most important position in the manufacture of paper. A great variety of wood is used for this purpose, and the fiber of the wood is freed from the intercellular substances by either the soda or the sulphite process, which will be described later. For cheap grades of paper, the wood is ground up and pulped without removing the intercellular substances. The chief woods used, together with the yield of pulp per cord and the process by which the fiber is isolated, are given in Table I. In addition to those mentioned in the table, the following woods are used extensively: Cypress, chestnut, birch, sweet gum, larch, locust, and linden.

TABLE I

YIELD OF PAPER PULP FROM VARIOUS KINDS OF WOOD

Wood Used	Yield of Pulp per Cord, in Pounds		
	Soda Process	Sulphite Process	Mechanical Process
Poplar	1,000–1,500		1,400–2,000
Spruce		900–1,300	1,600–2,200
White pine			1,600–2,000
Aspen			1,600
Cottonwood			2,000
Basswood	900–1,000		
Hemlock		700–800	700–900
Jack pine			
Spruce and poplar	1,000	900–1,000	1,600–2,000
Spruce, poplar, and pine			1,000–1,200
Poplar and pine			2,000
Spruce and hemlock		1,100	
Spruce, bass, and hemlock		1,000	
Spruce and pine			1,400–2,000
Poplar, bass, and pine	900–1,000		
Poplar, bass, pine, and maple	700–1,200		
Hemlock, pine, beech, and bass	1,000		
Spruce, buckeye, and maple			1,800
Cottonwood and bass			1,700
Poplar, bass, pine, and spruce	1,000		
Bass and poplar			1,100–1,400
Aspen, poplar, and cottonwood			1,000
Poplar, pine, spruce, balsam, and tamarack			1,700
Aspen, pine, poplar, spruce, and bass			1,400
Tamarack and fir			1,700
Bass and maple	900–1,200		

NOTE.—Where two values are given, the lower ones are for "rough" wood, and the higher ones for "prepared" wood. The yield is also affected by the severity of the cook. When stock is cooked hard in order to cut bleach figure, there is a greater loss of fiber and hence a smaller yield.

10. Jute.—The material known as jute, which is cultivated in Bengal, consists of the bast, or fibrous inner bark, of Corchorus. It is used to a great extent in the manufacture of paper. This fiber cannot be bleached white in the ordinary way, as the action of bleaching powder will chlorinate it. Jute is therefore used mostly in the manufacture of strong wrapping paper, etc., the strength of which is of more importance than the appearance. The composition of jute is shown by the following analysis:

	Per Cent.
Water	10.92
Aqueous extract	1.43
Fat and wax	.41
Cellulose	62.96
Non-cellulose	23.53
Ash	.75
Total	100.00

11. Miscellaneous Fibers.—Flax, hemp waste, manila, waste paper, bamboo, and the inner bark of the paper mulberry are also used to some extent in the manufacture of paper. Woolen rags are used to a moderate extent, but as it is almost impossible to bleach them, they are only mixed with other materials in the manufacture of coarse papers and wrappers.

MANUFACTURE OF PULP

12. Before wood, rags, and other material can be made into paper, they must undergo some treatment by which the fibers are separated from one another, reduced to a certain degree of fineness, and, for the better qualities of paper, all resinous and other foreign matter removed. This is accomplished in various ways, the product being known as **pulp.** The methods of treatment of different substances in the manufacture of pulp will here be discussed separately.

RAG PULP

13. Sorting of Rags.—Rags as they are received at the factory are unfit for immediate use. They must first undergo a preliminary treatment of sorting, cutting, and dusting before they are ready to be made into pulp.

The rags are taken from the bales and sorted as to condition of wear, color, the nature of the fiber, that is, whether linen, cotton, etc., the better qualities being used in the preparation of pulp for the better class of paper. At this point of the process, buttons and other materials mixed with the rags are removed.

The usual grades of rags are: (1) New white linen cuttings, and (2) new white cotton cuttings, from textile factories; (3) fine whites (domestic rags); (4) seconds (grade next to "fines"); (5) thirds (dirty, well-used rags); (6) colored rags (all grade of colors); (7) canvas; (8) manila and hemp rope; and (9) bags and jute.

14. Cutting and Boiling of Rags.—After the rags are sorted they are cut into pieces about 4 inches square by means of machinery. The *guillotine rag cutter*, which is adopted by quite a number of mills, will cut about 1 ton of rags per hour. The rags pass from the cutter to the dusting

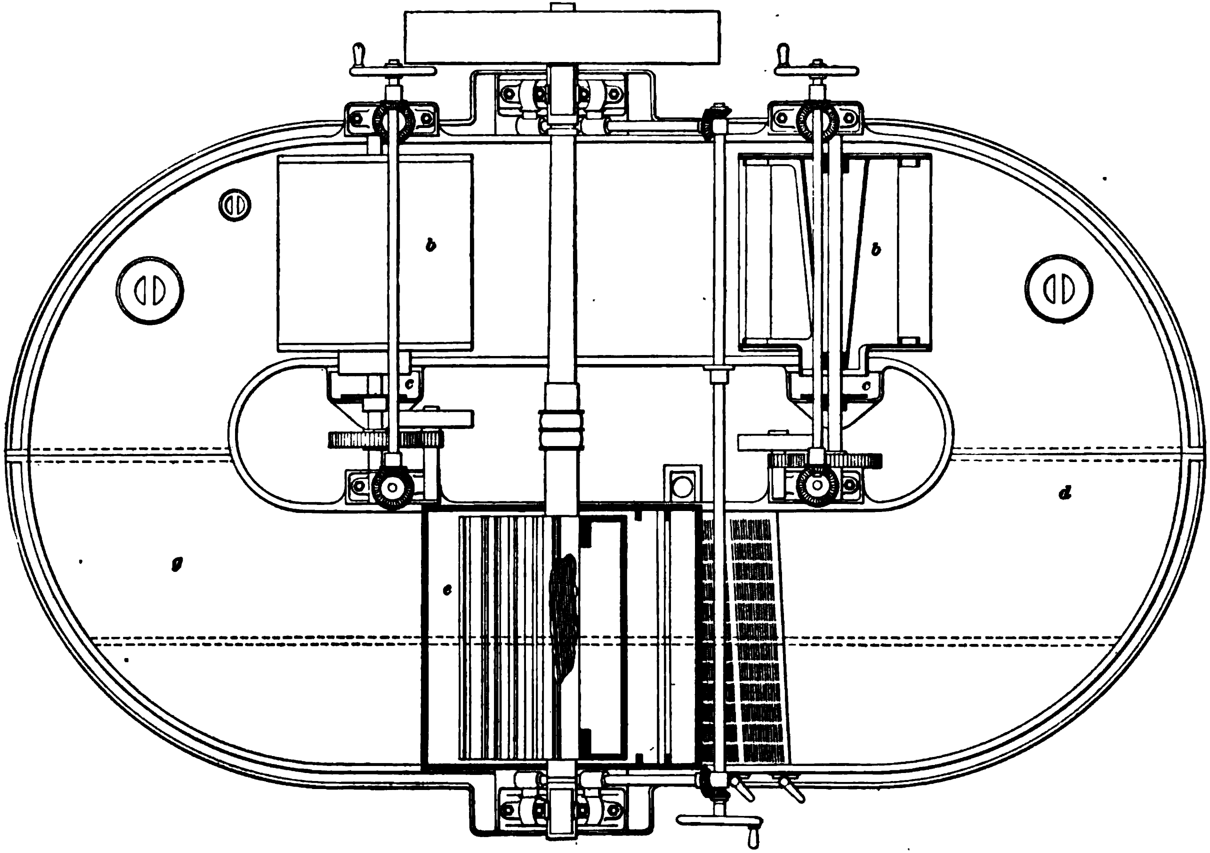


Fig. 1

machine, which is usually some form of inclined, revolving cylinder, the interior skeleton of which is provided with arms, or spikes, that revolve in the opposite direction. The cylinder being perforated, the dust passes through it freely, while the rags are removed at the lower end. The rags pass from the duster to the boiler, which is either cylindrical or spherical, and is either rotary or stationary. A solution of caustic soda is used in the boiler. This solution insures the removal of all incrusting substances and renders the rags much more susceptible to the subsequent bleaching action; it also has the effect of softening the fibers and rendering them more flexible. The amount of caustic soda used varies, with rags treated, from 5 to 10 pounds per 100 pounds of rags. Some paper makers use lime instead of caustic soda, but more lime is required than is absolutely necessary to reduce the stock, and at the same time more dirt is introduced than with caustic soda, thus rendering the use of lime less desirable for the better class of papers. For fine grades of cotton and linen rags, stationary boilers are generally used, while for dirty, coarse stock, it is customary to use rotary boilers.

15. Bertam Boiler.—A convenient form of boiler for boiling rags is the **Bertam.** This boiler is spherical, is from 8 to 9 feet in diameter, and is made to revolve. Steam enters through the hollow journals in one side of the boiler, the steam line being provided with a cock that is kept closed until the boiler is charged. On each side of the boiler is a door through which the boiler is charged with rags, and discharged when the boiling is complete. The liquor line, which enters through another journal, is also provided with a cock.

When the boiler is charged with rags, the caustic liquor is run in, the cock closed, and steam turned on. The boiling is carried on under a pressure of from 35 to 45 pounds per square inch, depending on the treatment desired, and the time of boiling varies from 2 to 6 hours. After the boiling is complete, the pressure is blown off and the spent liquor is

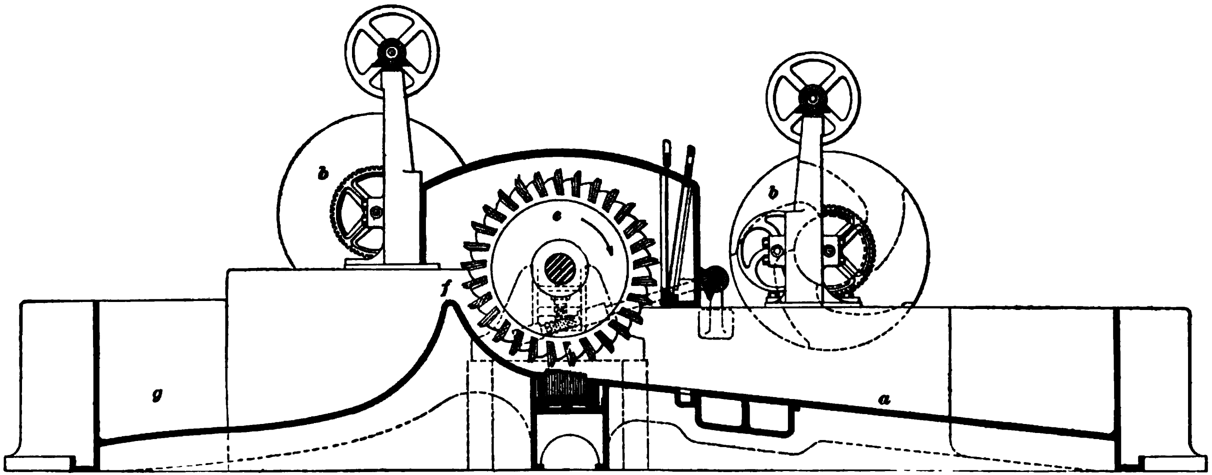


FIG. 2

discharged by means of a cock at the bottom of the boiler. The rags are usually given a preliminary washing in the boiler.

16. Washing and Breaking.—After the rags are boiled, they are taken to the rag engine, where they undergo the process called **washing and breaking.** In this engine, the rags undergo a thorough washing and the breaking up of the fibrous matter is accomplished.

17. Rag Engine.—The ordinary **rag engine,** which is illustrated in Figs. 1 and 2, consists of an oval tank divided in the center longitudinally by a partition called the *midfeather*. In one side is situated a roll *e* bearing knives around its circumference. Immediately under this roll, in the bedplate, are knives set with their cutting edges in the opposite direction. The distance between the knives on the roll and those in the bedplate can be varied at will so as to regulate the degree of fineness to which the rags are cut. The floor *a* of this side of the tank is inclined and has a raised portion *f* that keeps the rags well under the roll. On the opposite side of the tank are placed the drum washers *b*. These washers are either cylindrical or octagonal drums of wire cloth, the ends of which are made of wood. This construction permits the water to flow through the washers and pass out at *c*, but the pulp is held back by the wire cloth.

When washing, the tank is partly filled with water and the boiled rags are fed in at *d*. The roll *e*, revolving in the direction shown by the arrow, carries the rags between the knives of the roll and those on the bedplate, where they are cut. The cut rags pass over the raised portion *f* into *g*, from which place they pass on to the drum washers, and the dirty water passes out. The supply of fresh water is such that a constant level is maintained. The washing is continued until the wash water passes out clear. The supply of water is then shut off and the washer kept in motion, being lowered as the level falls, until completely drained. The bleaching is sometimes done in the washer itself, but generally in what are called *potchers*. The bleaching of rags will be taken up later.

ESPARTO PULP

18. Esparto grass is received in bales and undergoes a treatment somewhat similar to rags. The bales are undone, and the small bundles are put into the hopper of a machine called a *willow*. This machine usually consists of several revolving cylinders with projecting teeth that agitate the grass violently and thereby remove the dirt, which falls below the machine, where it is removed by means of a fan. The esparto is then taken to the boilers, which are usually upright and hold about 3 or 4 tons of grass each. The grass is boiled in caustic soda, the strength of which is about 9½° Baumé, under a pressure of about 20 pounds, the time required for boiling being about 3 hours at full pressure. The pressure is then blown off, and, after running off the spent liquor, the grass is again boiled with water for about ½ hour, after which it is well drained and removed, by means of a door at the bottom of the boiler, to the washing engine.

The amount of caustic soda used, the pressure at which the esparto is boiled, and the time required, all vary with the character of the boiler used and the sort of grass treated. The range is from 8 to 12 pounds of 70-per-cent. caustic soda for each 100 pounds of grass; from 20 to 45 pounds of pressure; and from 3 to 4 hours of boiling. In this boiling action, the fatty and resinous bodies are converted into soluble soaps, the silica of the grass is partly dissolved as silicate of soda, and the complex cellulose is split up into cellulose on one hand and soluble derivatives on the other.

19. Washing of Esparto Pulp.—The washing of esparto pulp is first carried on in engines, similar to the rag engine; after this the drum is allowed to run until there is room for the bleach liquor, when it is added, and the bleaching conducted in this engine, as will be described later.

As quite a large proportion of the fiber is lost by using the washer just mentioned, many paper makers object to this machine. Very good results have been obtained by using a series of tanks, arranged one above the other. In this method, fresh water enters the bottom of the upper tank, and overflowing from the top of this tank, enters the bottom of the next lower tank, and so on, the motion of the water being very slow, so that the finer particles are not carried away.

The yield of esparto fiber depends, of course, as in the case of wood, on the strength of the liquors used, the time of cooking, and the quality of the grass.

PULP FROM STRAW, JUTE, AND OTHER MATERIALS

20. Straw requires a more severe treatment than esparto or rags, as the knots in the straw must be reduced, and this, of course, necessitates the use of an excessive amount of soda. By this treatment, the finer fibers are liable to be carried away with the wash water, and the yield has been as much as 10 per cent. less than that of esparto. Wheat, oat, rye, and barley straws are generally used for making straw pulp, wheat and oat straws forming the bulk of the material used in the United States. From 10 to 20 pounds of caustic soda for each 100 pounds of straw is required to boil the straw thoroughly.

The straw is first cut into short lengths by means of a cutter similar to the rag cutter. The cut straw is then conveyed through a wire cylinder to remove any dust, after which it is sent to the boiler. The boiler is usually of a cylindrical, rotary form, although some paper makers prefer to use a stationary boiler. On account of the straw being so bulky, the boiler is first partly filled with the caustic liquor. The straw is then added until the full amount has been put in, the balance of the liquor is run on, and the head of the boiler is screwed into place. The straw is cooked from 3½ to 8 hours at a pressure of from 29 to 40 pounds. The strength of the liquor varies from 6° to 10½° Baumé. When the boiling is complete, the boiler is allowed to cool and the charge is run through a pipe to the drainer tanks. These are large tanks provided with perforated bottoms that permit the liquor to be drained out and the stock washed to some extent. The straw pulp is then usually transferred to a breaking engine where the washing is completed, after which it is pumped over sand traps, which are long, shallow trays containing boards stretched from side to side, sloping at an angle, and nailed to the bottom of the trays. The dilute pulp flows over the trays leaving the heavy particles, knots, etc. behind the sloping boards. It then passes through steamers and is conveyed to the bleachers.

21. A low-grade pulp, suitable for the manufacture of the coarser grades of paper, such as wrapping paper, is made from such materials as jute, flax, manila, and hemp waste. The materials are prepared by cutting and boiling by processes very similar to those used in the treatment of esparto and straw. Jute is boiled with a solution of lime instead of caustic soda.

The materials just mentioned do not require such careful treatment as is necessary in the manufacture of better grades of pulp.

WOOD PULP

22. By far the greater quantity of paper used at present is made from **wood pulp,** wood being an abundant and cheap raw material. There are three processes in common use for the manufacture of wood pulp: the *mechanical*, the *soda*, and the *sulphite*. The last two mentioned are chemical processes in which the intercellular substances are dissolved and removed by the aid of certain solvents. In the mechanical process the intercellular substances are not removed, and as a consequence the paper made from this pulp is of a poorer grade.

MECHANICAL PROCESS

23. Grinding the Wood.—Wood made into pulp by mechanical means alone is called *mechanical pulp*, or *ground wood*. Mechanical pulp plays a very important part in the manufacture of the cheaper grades of paper. The quality of such pulp depends largely on the manner in which it is ground and screened. Although these processes are not chemical, yet ground wood is of such importance in the manufacture of paper that a description of the mechanical operations will not be out of place. Spruce is used almost exclusively for making mechanical pulp, although other soft woods are employed to a limited extent. Hardwoods, however, are never used.

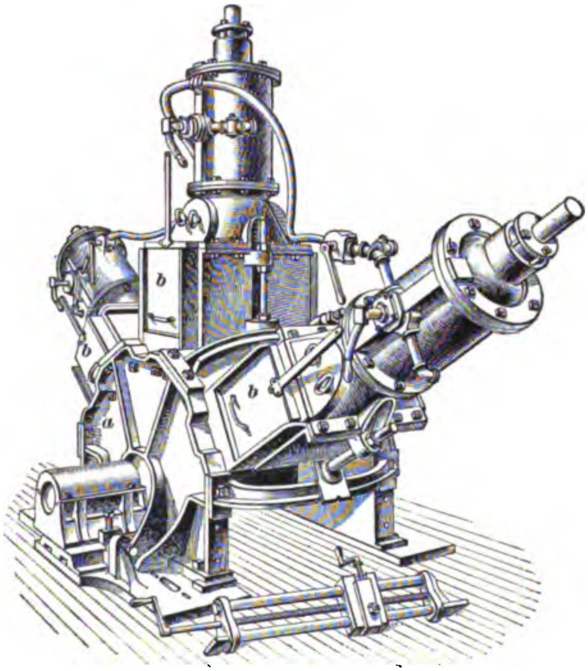


Fig. 8

As from 200 to 400 horsepower is required to drive a pulp grinder, it is almost universal practice to make use of the water turbine as a source of power, the grinders being directly connected to the shaft of the turbine. It is evident therefore that cheap and abundant power is absolutely essential to the economical production of ground wood, and for this reason ground-wood mills are located on rivers where good water-power is available. Water-power is also used for running screens, beating engines, etc.

24. A pulp grinder is shown in Fig. 3. There are several forms of grinders, but they are all constructed on the same general principle, namely, a grindstone enclosed in a case *a* with pockets *b*, into which the wood is placed and pressed on the stone by hydraulic pressure. The grindstone is made of sandstone of suitable quality, Ohio, English, and Canadian sandstones being most extensively used. The size of the stone generally employed is 54 inches in diameter and 27 inches wide. The wood to be ground is first cut into lengths to suit the width of the stone—for instance, 24 inches for a 27-inch stone. The bark is removed by means of a *barker*, which consists of a revolving disk with knives set in it, similar to the chipper shown in Fig. 5. The wood treated in this manner is known as *prepared*, or *rossed*, *wood*.

This wood is then put into the pockets of the grinder at the openings *b*, after which it is pressed against the face of the stone by means of the hydraulic presses, shown above *b*. This is done in such a manner that the grains of sand of which the stone is made up strike the fibers of the wood at a right angle to their length, thus tearing them off in shreds instead of grinding them to powder. Water is kept running on the stone, and serves to wash away the fibers ground off the wood as well as to reduce the heat generated by the friction of the wood against the stone. In this manner, the wood is prevented from being burned and darkened in color.

25. Much depends on the sharpness of the stone. If the stone is made too sharp or too rough, the pulp will be too coarse; if permitted to become too dull or too smooth, the stone will not produce enough pulp and the fibers will not be long enough. A stone can be sharpened while revolving by pressing a *burr*, or *jigger*, made of hardened steel against its face. This same device is used to grind a stone that has worn uneven.

As the grain and sharpness of a stone have a most decided influence on the quality of the pulp produced, constant attention should be given to the condition of the stone in order to get the maximum quantity of pulp of the best quality. The character of the pulp produced also depends on the speed of revolution of the stone, the pressure of the wood against the stone, and the temperature produced by the friction of the wood against the stone. No fixed rules can be given for producing the best results at all times and under various conditions; this can be learned only by practical experience.

26. Screening the Pulp.—The ground wood comes from the grinder in the form of a mush, and is thinned with water so that it will flow freely. This pulp is passed through either coarse gratings or perforated plates, in order to remove pieces of unground wood, after which it is passed through screens or perforated plates having somewhat finer openings, which remove the coarser portions. This screened pulp is now run through screens similar to those shown in Figs. 7, 8, and 9, which will be described later, and finally must pass through screen plates with slots about $\frac{1}{100}$ inch in width. These screen plates permit only the finest fibers to pass, and the coarser fibers and slivers pass on to second screens provided with plates with somewhat longer slots. The material that goes through the second screens is returned to the first screens and rescreened. Practice differs somewhat in regard to screening, but the preceding method is the one in most general use.

The coarse fibers and slivers that are separated by the screens are sometimes reground by special appliances, but they are generally disposed of by simply washing them into a river. This method of disposal causes an unnecessary waste of material, and there is room for improvement along the line of utilizing this wood.

27. The fine, well-screened, ground-wood pulp that comes from the screens is a very thin liquid composed largely of water. In order to remove the bulk of the water and to obtain the pulp in a compact form suitable for handling and shipping, it is taken off in the form of thick sheets by means of a specially constructed machine, known as a *wet machine*, which will be described later. These sheets are then folded and made into bundles. Instead of taking off the pulp in the form of thick sheets by means of a wet machine, it is sometimes scraped off in thin sheets, called *leaf pulp*, which will also be described later.

At mills where both a ground-wood plant and a paper mill are operated together, the ground-wood pulp is concentrated to a thick consistency and then pumped through pipes to the beating engines in the paper mill. Such thick liquid pulp is called *soft pulp*.

When ground wood is shipped to some point located a great distance from where it is made, the freight on the water it contains amounts to a considerable sum. Therefore, in order to reduce this expense, the bundles of moist pulp are sometimes submitted to hydraulic pressure, which removes a large amount of water. Pulp treated this way, however, is difficult to disintegrate in the beating engine.

28. Color of Ground Wood.—The color of ground spruce wood is yellow, but of a lighter shade than the original wood. To bleach ground spruce to pure white is practically impossible, although it can be whitened to some extent by treating it with sodium bisulphite. In the manufacture of paper from ground-wood pulp, the yellow color is neutralized by means of aniline blue. This produces a fairly white effect, but it is neither so bright nor so white as can be obtained from bleached stock.

Wood is sometimes steamed or boiled before grinding. This process softens the wood and gives a longer and stronger fiber, but, unfortunately, the color is so darkened that the ground wood cannot be used in the manufacture of white or light-colored paper. Practically all the pulp made from steamed wood is employed in the manufacture of box boards.

SODA PROCESS

29. In the **soda process** the acid compounds making up the intercellular substances of the wood are brought into solution as salts of soda, which result is accomplished by treating the wood with caustic soda. On account of the strong solvent power of the caustic liquor, it is not necessary to remove knots or rotten portions of the wood.

30. Chipping the Wood.—For the soda process, either the bark is peeled from the wood, which is then cut into pieces about 4 feet long, or the wood is cut into 2-foot lengths and prepared on a barker in the same manner as it is prepared for grinding. The pieces of wood are conducted to the chipper, which is shown in Figs. 4 and 5, and consists of a trough, or hopper, *a* and a large revolving cast-iron disk that has three knives *b* bolted to it in a slanting position. These knives are spaced equal distances apart and are set so that the blades project. The size of the chip, which ranges from $\frac{1}{4}$ to $\frac{3}{4}$ inch, is regulated by the setting of the knives.

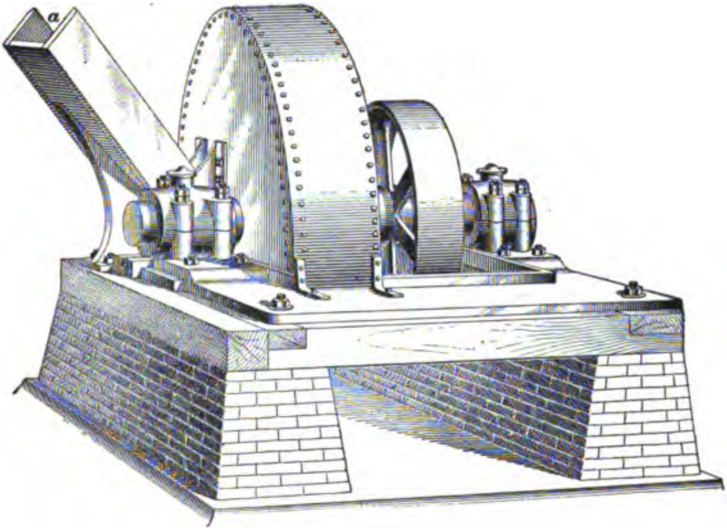


FIG. 4

The large sticks of wood are introduced through the trough *a*, which is set in a slanting position, so that each stick will move forwards by means of its own weight. The disk revolves at a speed of about 200 revolutions per minute, and the sticks are cut into chips across the grain. The chips are caught and conveyed to a bin above the digesters by means of an endless chain of buckets. Here the chips pass through a mechanical screen, which removes the dirt and fine particles, and they then pass on to the digesters. From 10 to 15 minutes is required to chip 1 cord of wood.

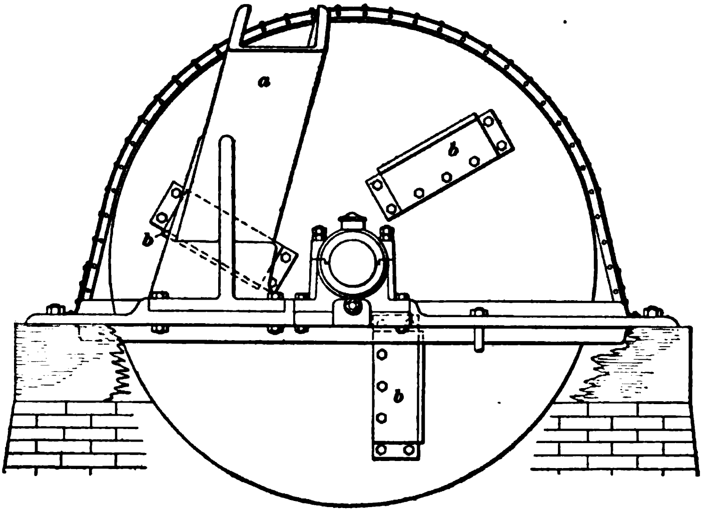


Fig. 5

31. Digesters.—The digesters are either rotary or stationary, and either cylindrical or spherical. There seems to be a question as to which form is the most common, it being almost equally divided between the upright cylindrical stationary and the horizontal cylindrical rotary. Spherical digesters are usually 9 or 10 feet in diameter. The rotary form is heated by coils that are supplied with steam through the trunnions. The upright digesters are heated by live steam, by direct fire, or by means of a steam jacket, the greater number being heated by live steam.

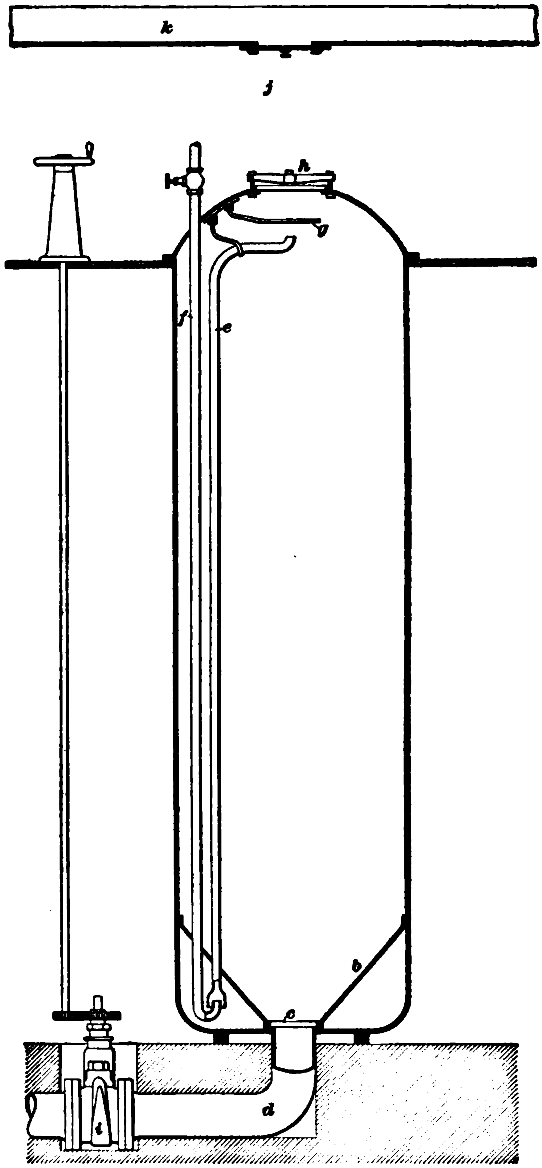


FIG. 6

Good results are obtained by the use of an upright cylindrical digester that is 27 feet high by 7 feet in diameter, and has a top that is dome-shaped and contains an opening through which the chips and liquor can be charged. This digester is heated by live steam. The steam line enters the top and extends to the bottom, where it discharges through a steam ejector so constructed as to keep the liquor in constant circulation through an arrangement for that purpose. At the bottom of the digester there is a perforated plate, or cone, that surrounds the outlet but does not cover it. The liquor passing through this plate is conveyed by the circulating pipe to the top of the digester and again discharged over the wood. This circulation is kept up continuously throughout the entire cooking operation.

32. A digester of this type is shown in cross-section in Fig. 6, in which *b* is the perforated cone that extends from the side of the digester to the ring *c* and surrounds the outlet into the dump line *d*. This plate holds back the stock, but allows the liquor to pass through to be conveyed by means of the circulating line *e* and steam line *f* to the top of the digester, where it is discharged against a plate *g*, which sprays it over the wood. The plate *g* and the top of the circulating line *e* are held by brackets, but can be moved to one side while the digester is being filled. The digester is charged through the manhole *h* by opening a slide *j* in the conveyer box *k*, which extends over all the digesters. The pipe through which the liquor is run into the digester can be swung to one side when the required amount of liquor has been added.

After the digester is charged with chips and liquor, the manhole cover is bolted down securely and the steam is turned on. In order to insure good results, it is necessary to keep up a continuous circulation during the process of cooking, which is accomplished as described in Art. **31.** The gate valve *i* in the discharge, or dump line, can be opened or closed conveniently from the top floor of the digester room.

33. Digesting, or Cooking.—One of the digesters just described holds about 4½ cords of wood. The liquor used is caustic soda having a strength of from 10° to 15° Baumé at 60° F. and a causticity of from 92 to 95 per cent. From 4,000 to 5,000 gallons of this liquor is required, depending on the kind of wood used, the condition of the wood, and the strength of the liquor employed. The time required for each cook is from 5½ to 10 hours at full pressure, depending on the conditions just mentioned. It is customary to cook at a pressure of from 100 to 120 pounds per square inch, and 2½ to 3 hours is required to get up pressure. When the cooking is complete, the pressure is blown down to about 75 pounds per square inch, after which the gate valve is opened at the bottom of the digester and the pulp forced up through the discharge line into the blow tank, where it strikes with great force against a dash plate, which separates the fibers. This operation is known as *blowing the digester.* When blowing down pressure, the steam is also discharged into this tank, which is generally situated on top of the building in which the stock is washed. There is usually a funnel-shaped arrangement at the top of the blow tank through which the steam has to pass, and, by this means, some stock that would otherwise be lost is saved. The yield per digester depends on the wood used, as given in Table I. After cooking, the pulp is of a light brown color, while the liquor is dark brown, verging on black. This liquor, which contains about all the alkali combined with the acid products of the wood, is termed *spent liquor.*

34. Washing the Pulp.—The next step in the process is the washing of the stock, which is usually accomplished in large wash pans that holds one digesterful of stock. This type of pan has a perforated false bottom through which the liquor and wash water pass freely, while the stock is held back. The stock to be washed is dumped into the pan from the blow tank and leveled with a long rake. The spent liquor is then allowed to drain off, after which the stock is washed for a short time with weak spent liquor, and finally with hot water. The liquor and washings are caught in tanks below and the soda recovered from them, as will be discussed later. When the wash water comes through reasonably clear, the stock may be considered washed, after which it is ready to pass through the screens and over the wet machines, or through the washers to the bleachers. The object of washing first with weak liquor is to use as little water as possible, as all the water added to the liquor must be removed again in the soda-recovery process.

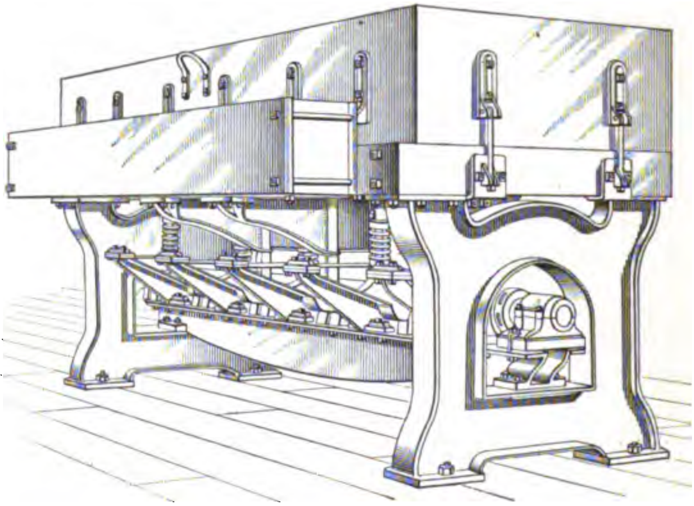


Fig. 7

The liquor and the washings are run into what is termed the *strong tank* until they become too weak to be used economically in the recovery department, after which they are run into the weak-liquor tank to be pumped up and used for preliminary washings of other pans. After the stock has been washed thoroughly, the plug at the bottom of the pan is removed by means of a screw arrangement at the top of the pan. The stock is then washed into the dump line by means of a rubber hose throwing a strong stream of water. From the dump line the stock is pumped up into the screens where all coarse material that has not been acted on in the process of cooking is removed. As described later, this coarse material is worked up and used in the manufacture of coarse wrapping paper, etc.

In some mills the washed pulp is first passed through *sand traps*, which are long, wide, shallow boxes having slanting baffle boards to retain knots and large pieces of uncooked wood, after which the pulp is sent to the screens:

35. Screens.—The screens used are of various makes, but all have about the same form and accomplish the same purpose. In Figs. 7, 8, 9, and 10, which show the **Success screen**, the general idea is plainly set forth. Fig. 7 shows a general exterior view of the screen box, together with the flow box. Fig. 8 shows the screen box open, exposing the wooden diaphragm top plates *a*, the rubber diaphragm *b*, and the apertures *c* through which the stock passes in going to the flow box *d*. Fig. 9 shows the diaphragm top plate *a*, the rubber diaphragm *b*, the wooden diaphragm *c*, the iron diaphragm *d*, the wooden pitman *e*, the spiral spring *f*, the spring plank *g*, the cam oil box *h*, the wooden shoe *i*, the pitman head *j*, the shoe clamp *k*, the bridge tree *l*, the cam *m*,

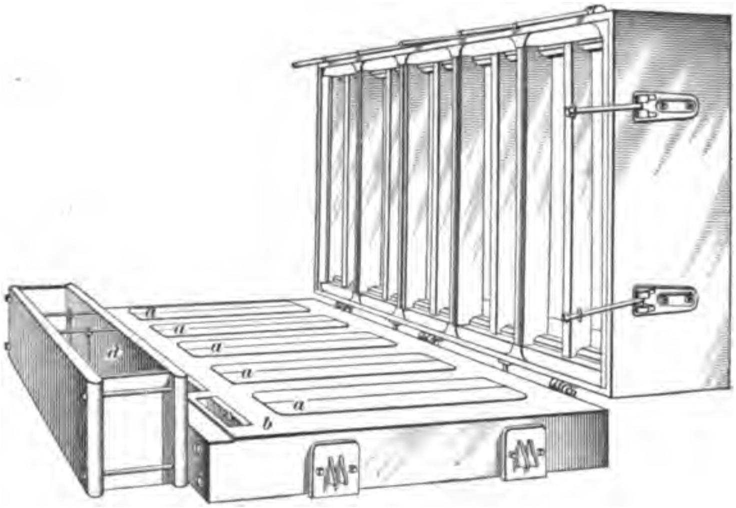


FIG. 8

the journal *n*, the ring oiling pillow-block *o*, and the screen shaft *p*.

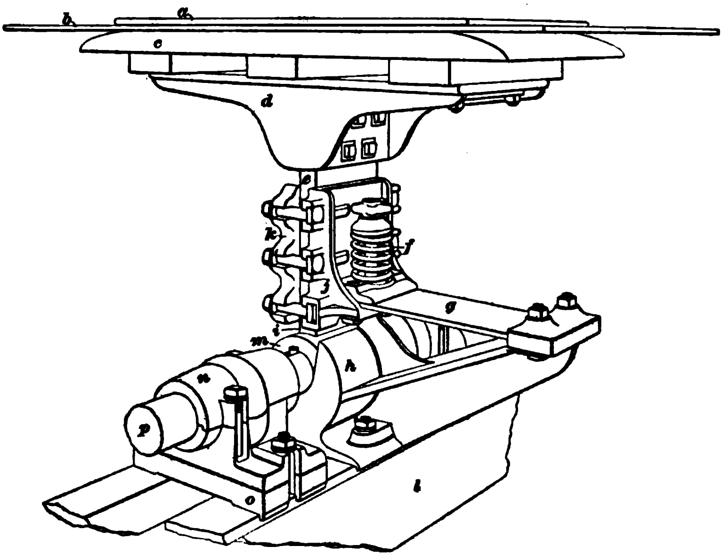


Fig. 9

Fig. 10 shows one of the brass screen plates. The slits in this plate are made very fine so as to permit the passage of only well-cooked fiber, to hold back material that has not been acted on, etc. These screen plates should be watched very carefully, and when there are any openings large enough to allow this slivery substance to pass through, the plate should be changed. Screen plates that have thus become worn and removed are generally used as *second*

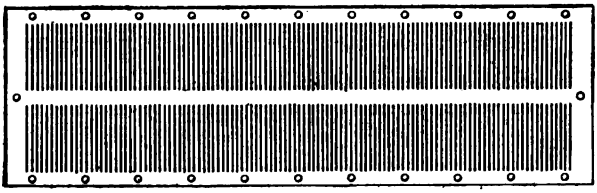


Fig. 10

screens. The slots in these plates can be closed up and recut once or twice.

36. In the screening operation, the pulp is pumped upon the screens in a thin, watery suspension containing about one-half of 1 per cent. of pulp, when it is carried through the screens as follows: The screen shaft *p* is perfectly round, but the cam is made square with the corners rounded off; thus, for every revolution of the shaft there are four upward and four downward movements of the shoe. These movements are communicated to the rubber diaphragms, which give the screen its suction. When the shaft is running at full speed, it makes from 165 to 175 revolutions per minute, which causes from 660 to 700 vibrations of the diaphragm per minute. There is a space of 4 inches between the screen plate and the top diaphragms, so that at each downward stroke the pulp is sucked through the screen plate into this space; from here it runs through the apertures at the side of the diaphragms and out through the flow box. The flow box is provided with a partition that causes the outflowing stock to stand at such a level that the apertures in the diaphragms are always covered; otherwise the screen would lose its suction, by air coming back through the flow box, and refuse to act. In case the screen refuses to act and flows over, the stock is shut off and, after raising the partition, water is turned into the flow box until it rises to the screen plates in the screen. This operation will drive out all the air, and the screening can then be continued as before. Good results are obtained by the use of the Success screen.

37. The **Gotham screen** is built somewhat similar to the Success screen. The advantage claimed for the Gotham over other makes lies mainly in the simplicity of its construction. The rod that at one end carries the wooden shoe that runs on the surface of the cam and is attached to the iron diaphragm on the other end, comes as near to being a solid casting as is possible. This rod has a taper-fit joint at each end. When the shaft is running up to its proper speed of 175 revolutions per minute, the rod and all parts of the screen attached to it are vibrating at the rate of 700 times per minute. Having this shaft practically in one piece is of great advantage, as it eliminates the use of bolts and nuts, which have a tendency to work loose on account of the rapid vibration. The cam on this screen is so adjusted that the upward stroke is quick and of shorter duration than the downward stroke; and if slivers, etc. are sucked into the slits of the screen, the quick upward stroke will almost invariably clean the plates of such obstructions. The stock is taken away through apertures arranged along the side of the diaphragms. These apertures discharge into spouts, which run crosswise to the screens underneath the frame and connect with the flow box. By this arrangement there is ample room for the stock to get away from the diaphragms; and since the stock is taken down to the level of the spouts underneath the frame, the suction on the screens is much assisted. The Gotham screen is used extensively by paper makers and produces good results.

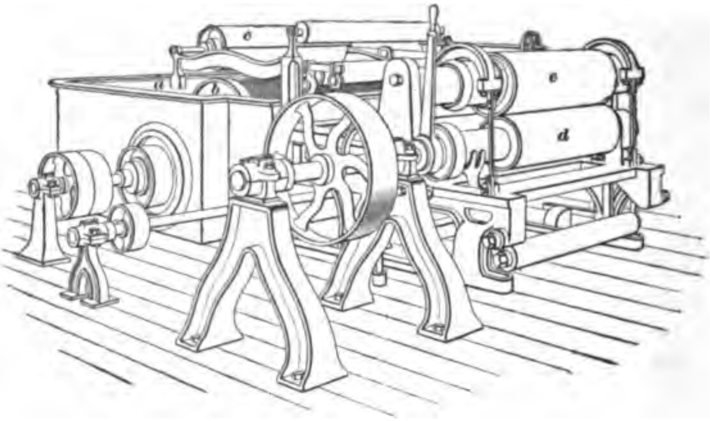


FIG. 11

38. In addition to the flat, or diaphragm, screens just mentioned, there are rotary and centrifugal screens, such as the *Moore rotary screen* and the *Baker and Schevlin centrifugal screen*. Such screens are coming into extensive use.

39. Wet Machine.—From the screens, the stock passes to the wet machines, Fig. 11, in which it is separated from much of the water. When the wet machine is in operation, the stock from the flow box of the screen passes into the vat *a*, in which a roll *b* covered with wire cloth is revolving. This roll takes up the stock and transfers it to an endless felt, which runs over the couch roll *c*. The stock is carried by the felt between the rolls *e* and *d*, the felt passing around the roll *d* and back to the couch roll, while the stock clings to roll *e*. In some mills the stock is allowed to collect until it reaches the required thickness, when it is cut from the roll, folded, and transferred to the bleachers or shipped as unbleached fiber. This stock, however, is generally removed from the roll as fast as it forms, the operation being carried on by means of a mechanical arrangement that rubs against the full length of the roll *e*, cutting the pulp off and allowing it to drop upon a slanting board. This board guides the stock to an alley belt, which conveys it to the bleachers. As it is taken off of the wet machine, the pulp usually contains about 60 per cent. of water.

40. In case the water is removed by means of washers, the process is as follows: The pulp is run directly from the flow box to a long washer box that has a number of octagonal drum washers situated at short intervals along the whole length of it. All these washers are rotated by means of an endless chain and take up the water, which passes out at the axis of the drum and is conveyed away by means of a small trough located along the side of the washer box. When the pulp reaches the outlet end of the washer box it is very thick and can then be conveyed to the bleachers.

41. Liquor for the Soda Process.—The liquor for digesting the wood in the soda process is made up in pans that are usually about 10½ ft. × 10½ ft. These pans are provided with agitators that extend to the bottom and are worked by means of a friction clutch and gearing at the top; also, with siphon pipes that can be raised or lowered and with steam lines running to the bottom. At the bottom of each pan is an opening through which the sludge is washed into the sewer. When making liquor, this opening is closed with a tight-fitting plug. A water-line, a weak-liquor line, and a line from the leachers empty into each pan, and each of these lines is provided with a cock.

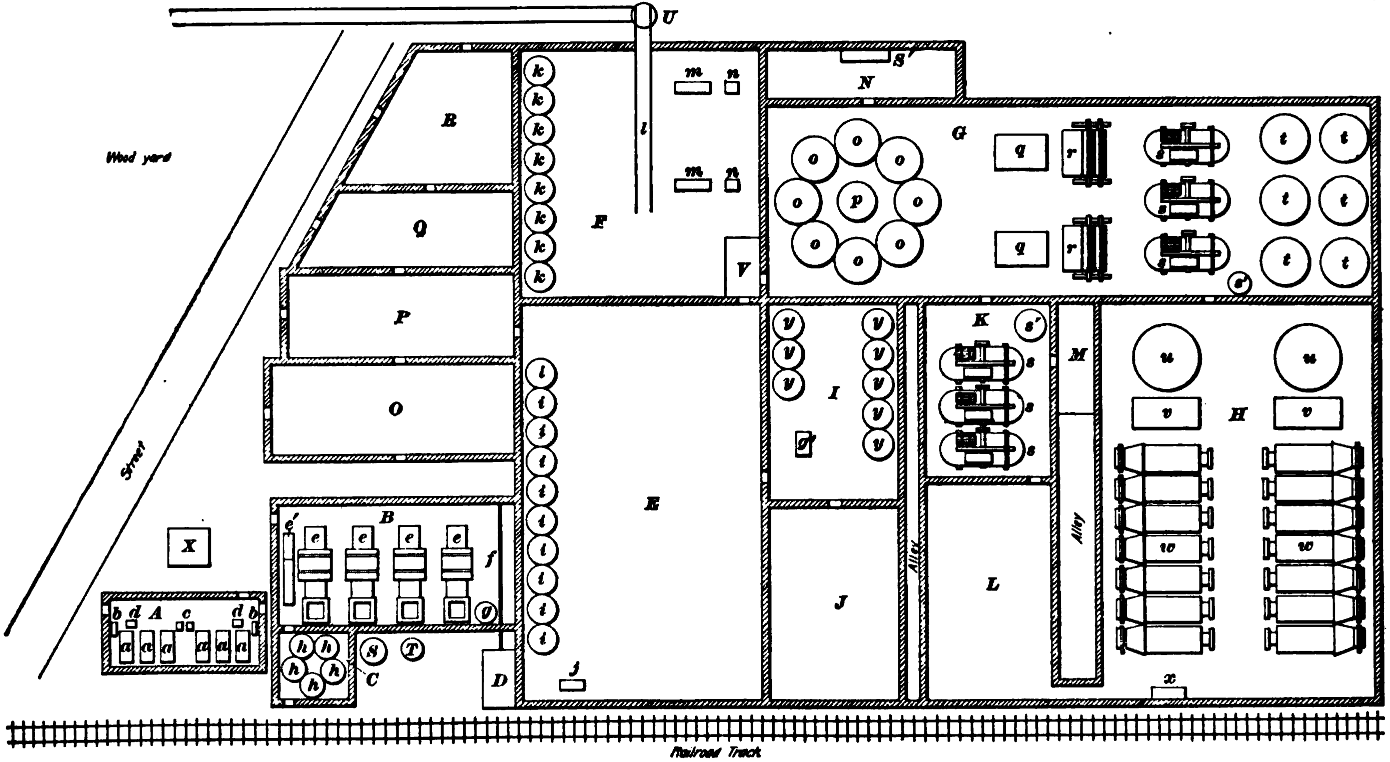
42. When making up a pan of liquor, the leacher-line cock is opened (the leaching system is explained under the heading Recovery of Soda), the recovered liquor allowed to flow in, and the agitator started. The liquor maker tests the liquor with a Baumé hydrometer from time to time, while it is coming up, to ascertain its density. If he finds that the liquor is getting too strong, the weak-liquor pump is started and the cock of that line is opened. By practice, the liquor maker is enabled to regulate the supply of the liquors so that there will not be a difference of more than ¼° Baumé in the finished pans. If, when a pan is filled up to a certain mark, the liquor does not come up to the desired strength, fresh soda is added to accomplish this end. When using caustic liquor from an electric-bleach plant, as is the case in many of the present mills, this liquor contains a certain amount of salt, which should be allowed for in making up the required strength of the liquor. For each per cent. of salt there should be an allowance of 1° Baumé, so that, for instance, in making up a 14½° caustic liquor, the strength should be 15½° if the bleach contains 1 per cent. of salt. When aiming at a certain strength of caustic liquor, the carbonate liquor should be made about 2½° Baumé stronger than the strength of caustic liquor required. A liquor of good strength is made from carbonate liquor testing 16¾° to 17° Baumé, which, when causticized produces a caustic liquor testing about 14½° Baumé. If a carbonate liquor is made stronger than 17° Baumé, it is very hard to causticize. To convert the sodium carbonate to the hydrate, the liquor is causticized by the addition of lime, which is generally put into an iron cage hanging down into the liquor. The lime must be added carefully to avoid boiling over. When the required amount of lime has been added, the steam is turned on gradually and the pan allowed to boil for about ½ hour, agitating the liquor continuously. After about ½ hour, the agitator is stopped and the sludge is allowed to settle. The conversion of sodium carbonate into caustic soda by the addition of lime takes place according to the following equation:

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$$

The lime sludge settles to the bottom of the pan, leaving the liquor perfectly clear, provided the recovered ash was well burned. About 8,000 pounds black ash or 48 per cent. Na_2O is used to make a 10½′ × 10½′ pan of strong liquor. In practice, from 625 to 650 pounds of good caustic lime is required to causticize 1,000 pounds of soda ash.

43. It is customary to have two tanks in the cellar under the alkali room—one for storing the strong liquor for the digester room, and the other for storing weak liquor for the second and third washes. This weak liquor is also used in making up the first wash, if necessary, and when crowded it is pumped through the leachers in place of water. In some mills each wash is kept in a separate tank and is used in making up the wash preceding it in the next tank.

The washes are made as follows: When the pan of strong liquor has settled sufficiently, the siphon pipe is lowered and the liquor is siphoned into the strong-liquor tank in the cellar. (It is customary to run a pan of strong liquor and the first wash of another pan at the same time, in order that they will mix in the right proportions in the strong-liquor tank in the cellar.) When the liquor is all out of the strong-liquor pan and the siphon pipe is down to the sludge, the pipe is raised, the agitator started, and the pan pumped up with weak liquor by means of a centrifugal pump in the cellar. (It might be well to note here that the centrifugal, or fan, pump is made use of in almost every department.) It is the aim of the liquor maker to make as large a first wash as will be carried by a full, strong-liquor pan, and to produce liquor of the required strength for the digesters. The second and third washes are made similar to the first, and are run down into the weak-liquor tank, to be used as stated. The plug is


U
Wood yard
Street
Railroad Track
A
B
C
D
E
F
G
H
I
J
K
L
M
N
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P
Q
R
S
S'
T
V
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FIG. 12

then withdrawn, and the sludge is washed either out into the sewer or over to the lime reclaimer, where it is well drained and burned back to caustic lime so that it can be used again. It is customary in most mills to keep samples of the strong liquor and each of the washes made; these are tested morning and evening by the chemist in charge for Baumé strength, causticity, and per cent. of salt.

44. Ground Plan of a Typical Soda Pulp Mill. Fig. 12 shows the relative position of rooms and machinery in a typical soda pulp mill.

A is the Yaryan room, which contains the Yaryan evaporators *a*, the vacuum pumps *b*, the lead pumps *c*, and the tail-pumps *d*.

B is the rotary room, which contains the rotary furnaces *e* with fireboxes and flues, the line shaft *f*, the fan blower *g*, and the ash conveyer *e'*.

C is the leacher room, which contains the battery of leaching pans *h*. The black-ash tank is located over the battery, the ash being carried into this tank by the conveyer just mentioned.

D is the lime shed, under which is situated as a rule the rotary engine.

E is the alkali room, which contains the causticizing pans *i* and the scales *j*. The balance of the room is generally kept filled with a stock of soda ash in bags of convenient size to handle. The storage tanks are in the cellar under this room.

F is the digester and chipper room in which are the digesters *k*, the track *l* for hauling wood to the chippers, the chippers *m*, and the conveyers *n*. The chippers are on the ground floor, and the room is all opened up to the top floor of the digester room, there being a platform *V* to get from the alkali room to the wet-machine room.

G is the wet-machine room, which contains the wash pans *o*, the blow tank *p*, which is above the wash pans, the screens *q*, the wet machines *r*, the bleachers *s*, the drainers *t*, and the tank *s'* of bleach liquor for bleachers. Strong- and weak-liquor tanks are located under the wash pans.

H is the machine room, which contains the chests *u* of bleached and drained stock for the machines, the screens *v*, the pulp machines *w*, and the scales *x*.

I is the bleach room, which contains the bleach mixers *y*, and the stairs *g'*, leading to the cellar, where the bleach liquor is stored.

J is the bleach storeroom.

K is a room in which there is another set of bleachers *s*.

L is the pulp storeroom.

M is the pulp-machine engine room.

N is the chipper and conveyer engine room, in which are stairs *S'*, leading to top floor of the digester room.

O is the boiler room; *P*, the engine room; *Q*, the supply room; and *R*, the iron storeroom.

X is the blacksmith shop.

S is the weak-liquor tank for the Yaryans.

T is the strong-liquor tank for the rotaries.

There is an alley between rooms *I*, *J*, and *K*, *L*, and also one between rooms *K*, *L*, and *H*. These alleys furnish light to these rooms.

The laboratory and wood yard are situated across the street. The wood is conveyed to the chippers in cars, the turntable *U* being used to turn the cars entering and leaving the mill.

RECOVERY OF SODA

45. Evaporation of the Liquor.—In Fig. 13 are shown several views of a Yaryan evaporator into which the strong liquor from the wash pans is pumped, (*a*) being the pan, (*b*) a front elevation, (*c*) a side elevation, and (*d*) a longitudinal section showing the circulation. The operation of evaporating the liquor is as follows:

Steam, which may be exhaust steam from the engine or live steam direct from the boilers, is led into the cylindrical chamber surrounding the coils in the first effect by the pipe *s*. The liquor to be concentrated, which should test from 8° to 10° Baumé at 60° F., is fed into the first tube *c* of the return-bend coils of the first effect in a small but continuous

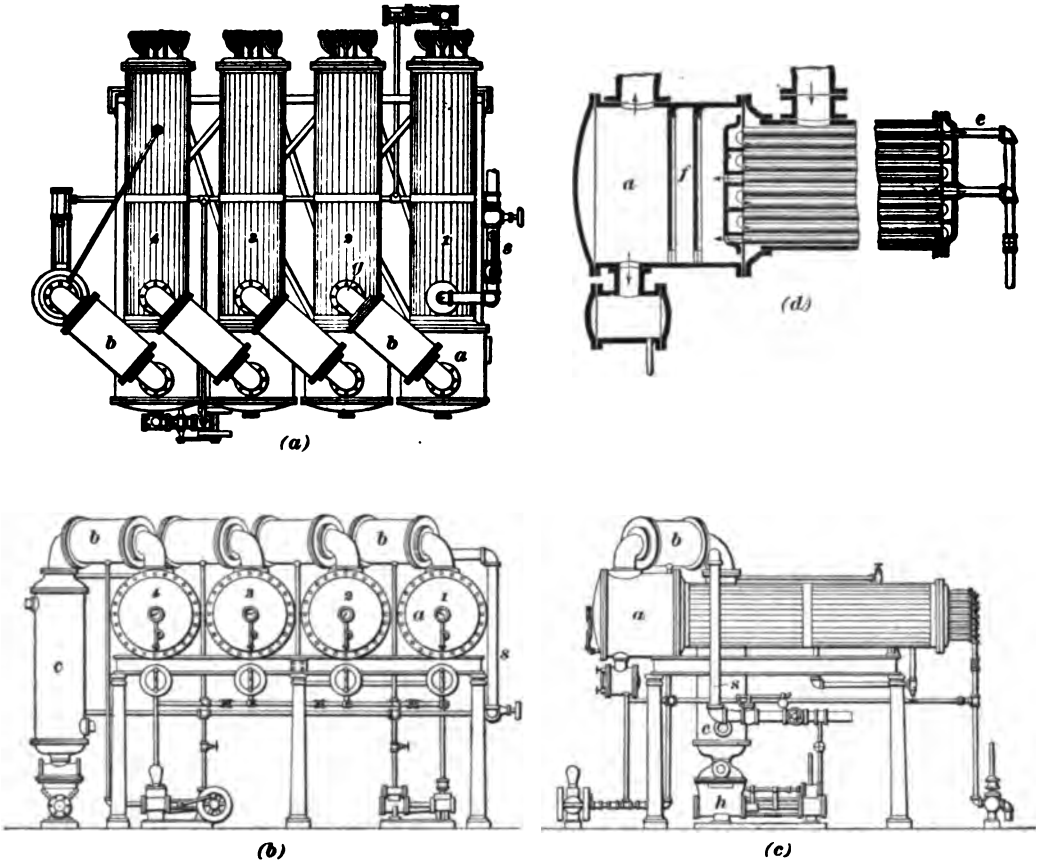


FIG. 18

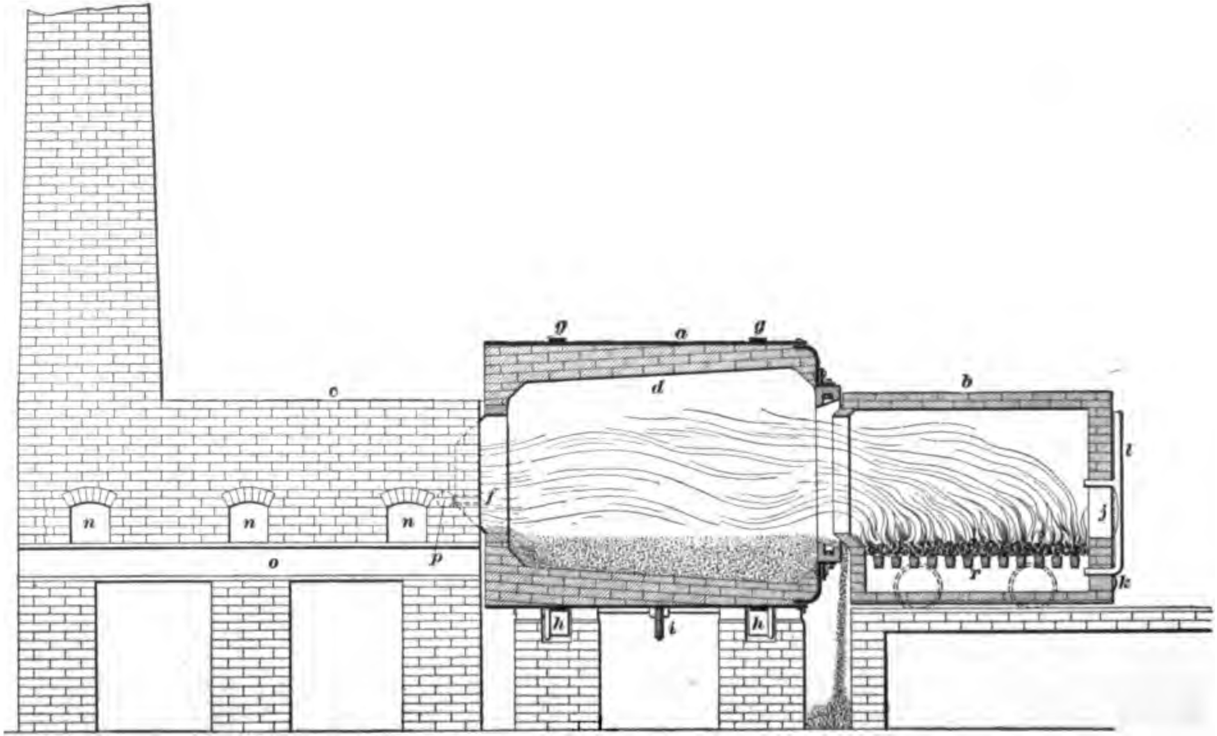


Fig. 14

stream. This liquor immediately begins to boil violently, becoming a mass of spray, containing, as it advances through the heated coils, a constantly increasing proportion of steam. The inlet end of the coil being closed to the atmosphere, and steam being continually formed, the contents is propelled through the tubes at a high velocity, finally escaping from the last tube of the coil into the separator *a*. Here, the steam, or vapor of evaporation, and liquor carried with it are discharged with great force against the baffle plates *f*. These plates separate the liquor from the steam, causing the liquor to fall to the bottom of the effect and allowing the steam to pass off through the ingeniously contrived catch-all *b*, as shown by the arrows in (*d*). This operation effectually removes any liquor still remaining in the steam and conveys it into the liquor line coming from the first effect. The liquor from the first effect is led to the back of the second effect, where it enters the coils, and the same operation is performed as in the first effect. This operation is carried on through the entire system, the liquor being constantly reduced in volume. The steam from the liquor in the first effect passes into the second effect at *g*, and surrounds its coils. The steam from the final effect goes to the condenser *c* and vacuum pump *h*, a high vacuum being maintained in the separating chamber and, consequently, in the coils. Hence, the boiling point of the liquid in each effect is always lower than the temperature of the surrounding steam, and by the condensation of steam from the previous effect on the cooler pipes in this effect, a vacuum of a less degree is maintained in the next succeeding effect. This relative reduction in pressure, and consequently in boiling temperature, automatically adjusts itself, no matter how many effects are used, thus accomplishing the boiling of the liquor by the steam produced by its own evaporation in the previous effect. The only steam required to be supplied is that of the first effect, and that varies in different mills from 20 to 40 pounds pressure per square inch. The liquor entering at about 8° or 10° Baumé at 60° F. is condensed in the Yaryan to a gravity of from 38° to 42° Baumé at 60° F.

The evaporated liquor is conducted to a tank, from which it is supplied to the rotary furnaces, where it is dried and calcined.

46. Rotary Drying Furnaces.—In Fig. 14 is shown a typical rotary furnace with a movable firebox and also a flue, the rotary *a* and the firebox *b* being shown in cross-section, and the flue *c* in elevation.

The rotary, which is 16 feet long and 8 feet in diameter, is lined with firebrick *d*, so as to form a conical interior requiring about 10,000 bricks, which are held firmly in place by face irons. Surrounding the rotary are bands, or rings, *g*. These run on flanged rollers *h*, and, since the flanges are on the opposite sides of the two rollers, they hold the rotary firm. The rollers, and consequently the rotary, are made to rotate by a sprocket *i* that connects by means of an endless chain with a sprocket on the line shaft. The liquor line passes through the wall of the flue at *p*, and thence into the back of the rotary at *f*, the rotary revolving around the line. The concentrated liquor entering through this opening in the back of the rotary passes on through, becomes thicker and thicker, and finally ignites. By the time the liquor reaches the front of the rotary, all the resins, etc. taken from the wood have been burned. Each rotary will burn about 20,000 pounds of black ash, or 48 per cent. of soda, in 24 hours.

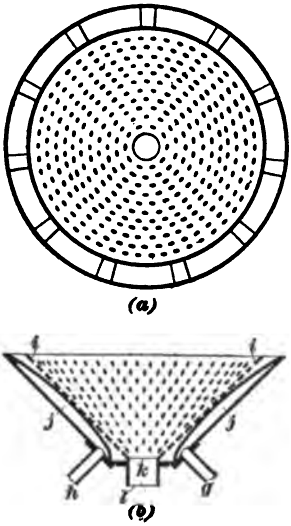
Fuel is passed into the firebox through the door *j*, and the ashes are removed at *k*. The grate bars *r* can be removed from time to time and cleaned. The blowpipe *l*, which delivers air from the fan blower, enters the furnace above the door and also under the grate bars, and thus drives the fire back into the rotary. The firebox is mounted on wheels and can be moved back when repairing the rotary.

The flue is built of brick and is mounted on iron supports *o*, which are in turn mounted on brick pillars. This flue is so arranged that much of the ash carried back into it by the draft can be removed through doors *n* along its side. The back end of the rotary is conical and projects into the flue.

47. In some cases as much as 8 per cent. of the soda ash used in the recovery system is lost by permitting it to escape in the form of a fine dust through the flue of the drying furnace, and to prevent this loss, some of the more important mills have recently devised a dust catcher to recover the ash. This device consists of an iron stack that is about 50 feet high and 8 feet in diameter, and is fitted at intervals, from the top to the bottom, with projecting baffle plates; extending to the top of the stack, there is also a pipe to the end of which is attached a bell sprayer. To save the soda ash, the smoke from all the rotaries is passed through large flues to the iron stack and weak spent liquor is pumped to the top of the stack and then sprayed, by means of the bell sprayer, down the stack, thus meeting the ascending smoke. In order not to destroy the draft, the stack is augmented by an induced draft from a fan blower, which draws the smoke from the rotaries and forces it up the stack. The liquor, which descends over the baffle plates, is caught in a tank at the bottom of the stack. It is then pumped up again, and circulation is thus continued until the liquor, by absorbing the gaseous smoke and by dissolving the floating particles of solid matter, reaches the desired density. In addition to working the soda out of the smoke that passes up the stack, this process helps to evaporate and concentrate the weak liquor by utilizing the heat of the stack. As the liquor contains considerable carbonaceous matter absorbed from the smoke, it originally gave more or less trouble by plugging the flues, etc. when sent directly to the Yaryans to be evaporated. This trouble has been overcome, however, by passing the liquor through filter presses before sending it to the evaporators.

48. The method of conveying the ash from the rotaries differs in different mills. Some convey the ash by means of an endless chain to a tank over the leachers, while others allow it to drop into a car placed below and at the end of a chain running along the front of the rotaries. When full, the car is conveyed to the leachers and replaced by another one.

49. Leaching.—The black ash may be leached by several different methods. In most mills, the ash is spread out in large, shallow pans having perforated false bottoms, and it is then thoroughly washed with hot water, by which the carbonate of soda is leached out and conveyed to the causticizing pans. Some mills employ a leaching battery consisting of a series of iron shells with perforated false bottoms that surround but do not cover the outlet at the bottom, as shown in Fig. 15. The shells are so connected by means of necessary piping that the water used in leaching passes into the top of the weakest shell, from the bottom of this shell into the top of the next stronger, and so on until it reaches the last shell to be filled, after which it passes into the causticizing pans. Any one of the shells can be turned into the line going to the causticizing pans or can be cut out.



(a)
(b)
FIG. 15

50. In some mills the leaching shells are connected in a circle, in which case the ash is carried by an endless chain to the tank over the center of the leaching battery, from which it can be dumped, by means of a pipe, into any one of the shells. In other mills these shells are piped up in a row. The ash is then taken up in cars, which are run on a track located over the leachers and dumped into any one of them.

Fig. 15 shows two views of the bottom of a leacher, (*a*) being a section looking down upon it and (*b*) a vertical cross-section through the center. In the figure, at *h* is shown the circulating line; at *g*, the line leading to the alkali room; at *i*, the perforated false bottom; at *j*, the space between the false bottom and side of the shell; at *k*, the ring in which a plug fits; and at *l*, the dump line.

The pressure caused by the water gas formed in the leachers when the water comes in contact with the hot ash has at times caused some of the weaker shells to blow up, particularly when the workmen have neglected to watch the pressure gauge. It is advisable first to wet the ash with the shell open; then, after thoroughly wetting the ash, the cover may be adjusted and leaching carried on as described.

51. When filling a shell, a plug is securely placed in the bottom of the ring *k*, Fig. 15, and the ash dumped in until the shell is about three-fourths full, when the cap is placed on the manhole at the top and screwed down tightly. Hot water is now pumped into the weakest shell until a pressure of from 45 to 60 pounds is reached in the battery, when the cock in the line leading from the last shell filled to the causticizing pans is opened. The leaching is then continued, as already suggested, until the pan is up, or liquor coming from the last shell tests only about 1½° Baumé. After this the weakest shell is cut out, dumped, filled with fresh ash, and the leaching continued as before.

52. Calculation of Recovery.—Recovered black ash contains from 43 to 48 per cent. of Na_2O. When figuring recovery, in some mills the black ash made is weighed and the recovery calculated from the amounts of each ash used in making up the liquor. The recovery is usually calculated by multiplying the amount of 48-per-cent. soda necessary for one digester by the number of digesters put on, subtracting the amount of soda used in the alkali room (after calculating the latter to 48-per-cent. Na_2O), and dividing the remainder by the total amount used, as just calculated. The amount of black ash recovered varies from 75 to 90 per cent. in the different mills.

The sources of loss of soda through the mill are: (1) retention in the dump of lime sludge from causticizing pans; (2) blowing of the digester; (3) imperfect washing of stock in the wash pans; (4) dust carried up the chimneys of the rotaries; (5) formation of silicate of soda due to silica present in the lime; and (6) leaching the black ash, under which source will also come loss due to imperfect burning, as this is very frequently the cause of a considerable loss of soda.

The caustic liquor used in boiling straw and esparto is also recovered by a process similar to the one just described.

SULPHITE PROCESS

53. The **sulphite process,** which from its present use should be properly termed **bisulphite process,** was first worked on a practical scale in 1872, when Eckman and his associates first put the present Eckman process into operation. The sulphite process was introduced into England in 1884, and since then it has developed very rapidly, the work of Mitscherlich in Germany and Partington in America having had much to do in this direction.

In the sulphite process, the lignin in the wood is decomposed by the bisulphites of calcium and magnesium into sugar and calcium and magnesium salts of the dibasic lignin-sulphonic acid. Coniferin is decomposed in an analogous manner into coniferin-sulphonic acid. If there is not sufficient lime present to neutralize the lignin-sulphonic acid formed, the lignin glycide suffers polymerization and is converted into a dark-brown resin that is insoluble in sulphurous acid.

54. Bisulphite Liquor.—At the present time a solution of bisulphite of lime and magnesia, with excess of SO_2, is almost exclusively used in the sulphite process, although a solution of bisulphite of soda is used to some extent. The latter solution produces a soft, white pulp. This liquor is prepared by several different methods, a few of which will be described.

55. Sulphurous-acid gas, or sulphur dioxide, is generally prepared directly from sulphur. The operation is carried on in a set of sulphur burners, similar to the one shown in Fig. 16. The sulphur is shoveled into the burner at the doorway *a* and is spread out in a thin layer over the floor of the burner, after which it is ignited. Sulphur burns readily, and just enough air should be admitted to burn it properly to sulphur dioxide SO_2; that is, theoretically, 53.86 cubic feet of air per pound of sulphur should be used. The amount of draft is regulated by means of a sliding door *b*. This door is suspended on a chain *c*, which runs over a pulley *d* and has a weight *e* attached to the other end, by which means the door can be easily moved up or down. The burner is kept cool by water running on the top of it from a pipe *f* and escaping at *h*, there being about an inch of water on the top continually. The SO_2 gas formed according to the reaction $S + O_2 = SO_2$ is conducted through the pipe *g* to the coolers. The burner should be made air-tight all over, except where the air supply is regulated, and there should be an opening under the burner, extending its full length, in order to keep it as cool as possible. If too much air gets into the burner, there is a tendency to form sulphur trioxide and also to overheating, and, consequently, to sublimation of sulphur. Too little air also causes sublimation of sulphur; therefore, in order to obtain the desired results, the air supply should be regulated so that neither too much nor too little air will be supplied.

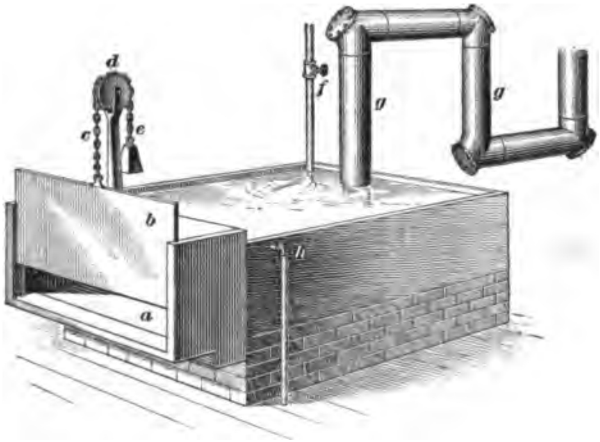


FIG. 16

The flat stationary type of sulphur burner has been replaced in a great many mills by either the ***rotary cylinder burner*** or by the ***J. C. Wise sulphur burner.*** Both of the burners are claimed to be efficient and economical.

56. If copper or iron pyrites are used as a source of sulphur, which is the case in some foreign mills and in a few mills in the United States, the mineral is crushed and roasted on the grate bars of some form of pyrite burner and the gas is conducted to the cooler in the same manner as in the preceding case. The chief objection to the use of pyrites is the difficulty encountered in removing the fine dust, which is carried along with the burner gas and eventually finds its way into the bisulphide liquor.

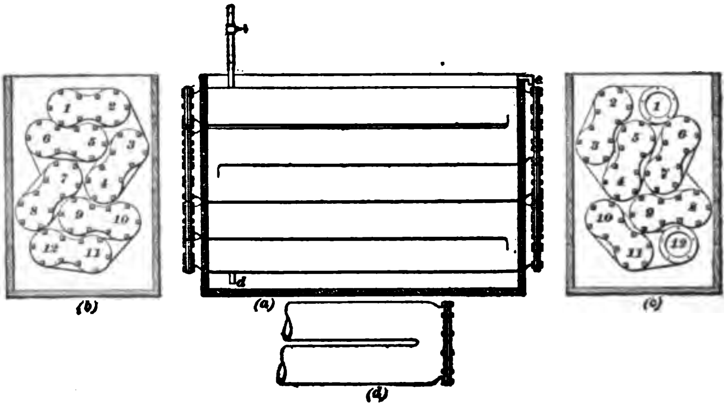


FIG. 17

It is always best to pass the gas through a series of large pipes that extend up and down, as shown at *g*, Fig. 16. These pipes should not have any abrupt turns in them. They may be made of iron, and where it is necessary to turn, crosses should be used. These crosses are provided with removable caps, so that the sublimed sulphur can be removed from time to time. The object of this piping is to catch any sublimed sulphur that comes from the burner, and thus prevent it from entering and clogging up the cooler.

The gas coming from these pipes is then passed through some form of cooler, of which there are several.

57. In Fig. 17 is shown a cooler that consists of a coil of lead piping encased in a wooden tank. This tank is filled with water and has a continuous stream of cold water entering and leaving it. A side view of the interior lead piping is shown at (*a*). The water flows in at the bottom of the box through the pipe *d*, and leaves it through the pipe *e* at the top. The two end views (*b*) and (*c*) show how the pipes are arranged in the cooler. The gas entering from the up-and-down pipes leading from the burners passes in through *1*, returns through *2*, passes back again through *3*, returns through *4*, etc., and finally passes out through *12*. Caps are bolted over the ends of the pipes, as shown at (*d*), so that they can be removed if the pipes become stopped up and require cleaning.

One of these coolers is provided for each sulphur burner, but the exit pipes of two coolers unite in one main for each set of absorption tanks. After leaving the cooler, the gas passes to the absorption tanks, or towers, where the bisulphite liquor is formed.

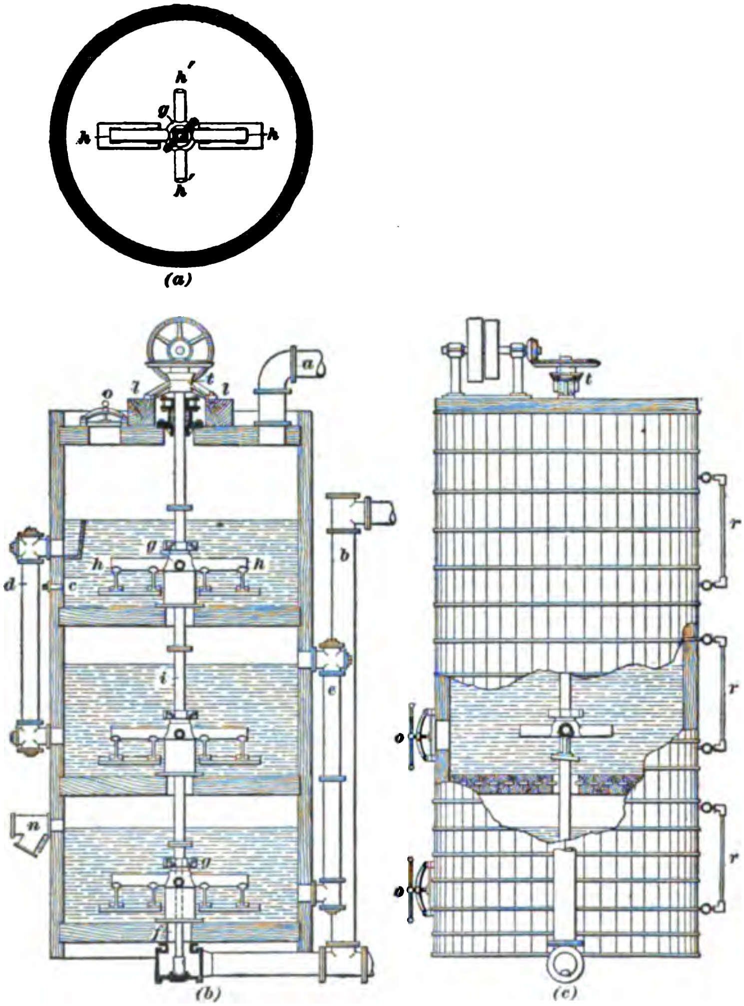
58. Methods of Absorbing Sulphur Dioxide.—There are a number of forms of absorption apparatus, some of which adhere to the old form of a limestone tower, in which the stone is placed in lumps and the gas drawn up through the tower, while water is sprinkled down over the limestone. The solution drawn off at the bottom is the bisulphite liquor. Scrap marble is the best stone to use in towers. Milk of lime is most commonly used at the present time for the formation of bisulphite liquors.

59. McDougald Absorption Apparatus.—The **McDougald absorption apparatus** consists of three tight tanks fitted with agitators. The tanks are nearly filled with milk of lime. The gas from the cooler enters the first tank near the bottom, passes up through the milk of lime and out at the top, thence to the bottom of the second tank, and so on through the series. The tanks are all so connected that the milk of lime can be transferred from one to the other. When the first tank has been brought up to strength and drawn off into the settling tank, the valves between the tanks are opened, and fresh milk of lime is run into the last tank until the liquid in all is at the same level. The valves are then closed. In the McDougald process, the sulphur is burned under pressure and the gas is thereby forced through the cooler, tanks, etc. This is called the *pressure and dumping system.*

60. A modification of the McDougald apparatus that furnishes good results is one in which the tanks are placed one above the other and the gas carried through the series by means of a vacuum pump attached to the top tank. All of the tanks are provided with agitators and are air-tight. The milk of lime is pumped into a tank located above the series of absorption tanks, where it is kept mixed by means of an agitator. This lime water is run into the top absorption tank through an inlet located near the bottom, and flows from an outlet near the top, entering the next lower tank near the bottom, and so on. At the same time the gas is being drawn up through the tanks, the pipe for this purpose entering at the top of the bottom tank, but discharging the gas at the bottom. The gas then passes up through the milk of lime, and is conducted by a pipe from the top of the bottom tank into the top of the next higher tank, discharging at the bottom, and so on through the series. By this arrangement there is a continual flow of liquor through the apparatus. Fresh milk of lime is continually entering the top tank, while a corresponding amount of finished liquor is being drawn from the bottom tank. This is called the *vacuum* and *continuous system.*

The pressure system can also be run continuous, and the vacuum system can be run on the dumping plan.

61. Burgess Absorption Apparatus.—A very effective absorption apparatus for the manufacture of bisulphite liquor is the **Burgess triple acid-absorption tank,** shown in Fig. 18. In this figure, (*a*) is a section through the top compartment, showing the hollow arms *h*, *h′*, (*b*) a vertical section, and (*c*) an elevation partly broken away.



(*a*) (*b*) (*c*)

FIG. 18

The lime water is fed into the top compartment of the tank at *c*, Fig. 18 (*b*), and flows into the middle compartment through the overflow pipe *d*, and from the middle to the bottom compartment through the overflow pipe *e*. A pipe from the vacuum pump is connected at *a*. This pump draws the sulphur dioxide from the sulphur ovens through the gas cooler to pipe *b*, which passes to the bottom and enters the tank at the center. The gas is drawn through pipe *b* and sleeve *f* into the dome *g*, and thence through the hollow arms *h*, *h'*, Fig. 18 (*a*), into the lime water. The gas passing up through the lime water in the bottom compartment is drawn by the vacuum through the sleeve and hollow arms into the middle compartment, and the same operation is again repeated in the top compartment. The center shaft *i* revolves, thus distributing the gas as it enters the three compartments. Wooden agitators are attached to each hollow arm *h*, and throw the liquor from the bottom up into the gas coming from the ends of the hollow arms, thus saving some of the work of the vacuum pump. The shaft *i* is supported at the top by the bridge truck resting on the beams *l*, and runs on ball bearings *t*. There is no weight on the bottom end, but merely a guide for the shaft. The tank is made of wood, while the piping, shaft, and agitator are made of bronze.

The finished product—calcium and magnesium bisulphites—in the bottom compartment is drawn off to a storage tank by means of the Y valve *n*. An indicator glass *r*, Fig. 18 (*c*), is attached to each compartment and serves to show the condition of the liquor in each. There is a manhole *o* in each compartment. The tanks are made in various sizes, each tank making acid for from 25 to 100 tons of pulp per day.

62. The Burgess absorption apparatus is very simple and compact, requiring very little labor to operate it and occupying very little space. There is only one tank to be kept air-tight, while in other systems there are three of them and sometimes four.

The lime used in all of the preceding operations is magnesia lime, well burned. This lime is first slaked in an iron tank provided with an agitator, after which it is run into a large tank, diluted to the strength required, allowed to cool, and pumped into a tank located above, for use in the absorption apparatus. The liquor from the storage tank is pumped into a reclaiming tank, from which the digesters are filled. In order to get clear liquor for the digesters, the delivery pipe should be attached to a float, so that the liquor will always be drawn from the top.

The bisulphites of calcium and magnesium are formed in this way: First the monosulphites are formed, and each molecule of these taking on another molecule of sulphurous acids is converted into the bisulphites, as shown by the following equations:

$$(1)\qquad Ca(OH)_2 + Mg(OH)_2 + 2H_2O + 2SO_2 \\ = CaSO_3 + MgSO_3 + 2H_2O$$

$$(2)\qquad CaSO_3 + MgSO_3 + 2SO_2 + 2H_2O \\ = CaH_2S_2O_6 + MgH_2S_2O_6$$

63. Preparation of the Wood.—In the sulphite process, knots, pieces of bark, and decayed wood are scarcely acted on by the bisulphite liquor, and should therefore be removed before the chips are sent to the digester. This is done in some mills by boring out the knots and cutting out the rotten parts; in other mills, where slabs are used, the slabs are sent to a knotting mill and the knots are cut out with circular saws. In some foreign countries, where labor is cheap, the chips from the chipper are thrown on an endless belt and the knots are picked out by children as the chips pass. In the United States, too little attention is paid to cleaning the wood, removing knots, etc., and as a consequence the pulp is dirtier than foreign pulp.

The chipper used in the preparation of the wood is similar to the one used in the soda process. The chips are passed through a long screen in order to remove the sawdust, dirt, etc. A convenient form of screen, and one that furnishes chips of a uniform size, consists of a double revolving cylinder. The chips from the chipper enter the inner cylinder, the larger pieces passing on to the other end while the smaller ones drop through the openings into the interior of the outer cylinder. This cylinder is covered with a coarse-mesh wire cloth, through which the sawdust and dirt pass;

the chips of the required size pass through to the other end of the cylinder, where they are caught and conveyed to the top floor of the digester room by an endless chain of buckets or some similar conveyer. The wood generally used is spruce, although hemlock, poplar, and fir are used to some extent. The best result is obtained by cooking each kind of wood separately—not mixing the chips from two or more kinds of wood and then cooking.

64. Sulphite Digesters.—The digesters for the sulphite process vary in form, the same as those used in the soda process. The sulphite digesters, however, must have a lining that will resist the action of acids. Pure lead, owing to the formation of insoluble lead sulphate, which coats the surface, furnishes a good acid-resisting material, but lead containing small quantities of antimony and copper is still better for this purpose. On account of the unequal expansion of lead and iron when heated, and the failure of the lead to assume its original condition when cooled, the lead linings have a tendency to creep, so that they have given place almost entirely to other materials for linings. A very good lining that still makes use of lead as one of the materials is the "non-antem" sulphite digester lining, which is made of lead, cement, and brick. These materials are mentioned in the order of their position from the interior to the exterior, and consist of ½-, ¾-, and 9-inch layers, respectively.

The interior of some digesters are bricked and lined with a mixture of various cements, while others are cemented on the inside and then faced with a layer of tiles. In fact, a great variety of materials is now used for linings, such as sulphite of lime, double silicates of iron and lime, glass, etc. A cement made of litharge and glycerine is extensively used between the tiles or bricks, as well as for "pointing up," stopping leaks, etc.

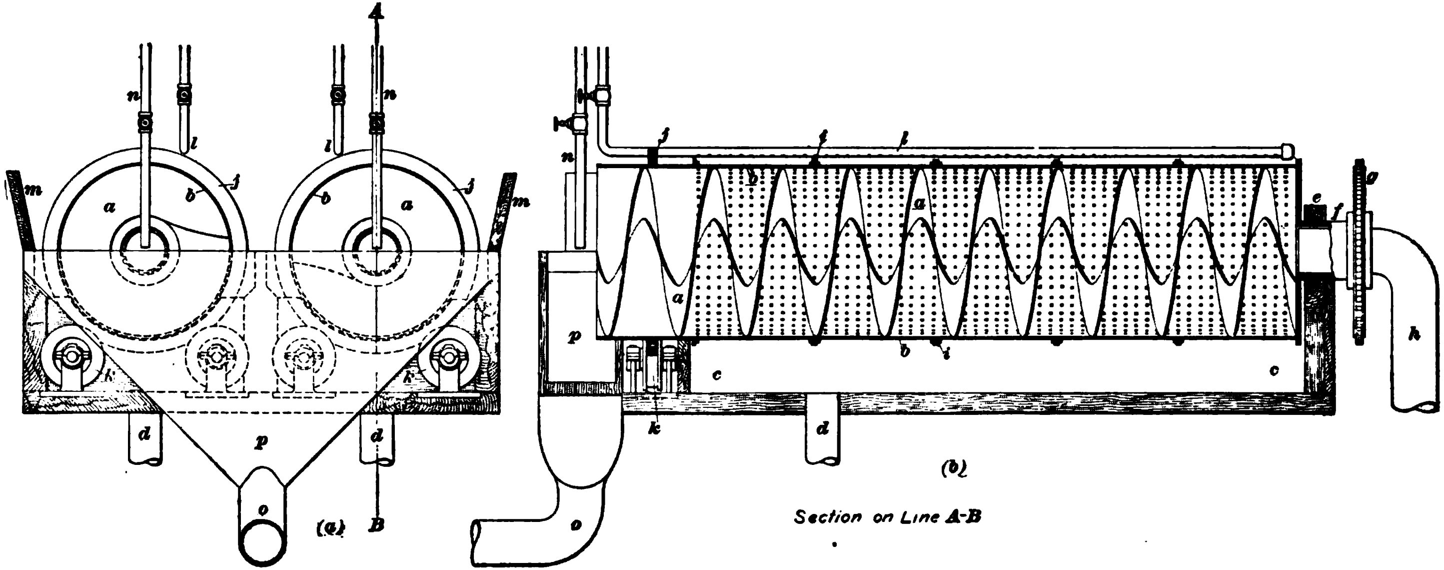
65. After every cook, the digester should be thoroughly examined, and if there are any loose places in the lining, they should be repaired before putting on another cook.

Some paper makers are of the opinion that better results can be obtained by the use of rotary digesters, quite a number of which are in use at the present time. These manufacturers claim that there is less danger of making black chips and that less liquor is used, but the most general opinion is that a better quality of pulp is produced in the upright digesters.

The digesters vary in size; some of the upright ones are 15 feet in diameter by 50 feet in length, and hold from 28 to 30 cords of wood. Those in most common use are from 12 to 14 feet in diameter and from 36 to 40 feet in length. More uniform and certain results can be obtained in large digesters than in small ones.

66. Charging and Cooking.—The chips and liquor are charged at the top, the digester being filled as nearly as possible with chips, which will settle down when the steam is turned on. The liquor is run through a large pipe in order to get it into the digester as quickly as possible. The strength of the liquor varies with the kind of wood used and with the time of cooking. A quick cook requires a strong liquor, and a slow cook a weak liquor. Hemlock requires a stronger liquor than spruce.

The pressure should not be applied too rapidly, as it will have a tendency to burn the chips if they are not sufficiently soaked with liquor. The pressure varies from 45 to 85 pounds. There is usually a thermometer arranged on the side of the digester, so that the temperature on the inside can be read at any time; also, a pressure gauge to show the pressure in the digester. The cooking is generally carried on at a temperature of about 300° F. On account of the large amount of gas generated, the temperature is a better guide to go by than the pressure. It is customary to blow the gas off at the top of the digester from time to time during the cook. The blow-off gas is recovered by sending it through a lead pipe to an absorption tank, known as the *reclaiming tank*. The lead pipe passing through a tower is cooled by water, and in this way the gas is freed from steam and the latter con-



Section on Line A-B

FIG. 19

densed. Many other equally effective methods have been proposed and are used in different works. By carefully utilizing the recovered gas, 100 pounds of pulp can be produced with about 13 pounds of sulphur. Some of the digesters are provided with a circulating device, as in the soda digesters, by which the liquor is carried from the bottom, under a perforated plate, up to the top, where it is discharged on the top of the wood, thus keeping up a continuous circulation.

67. The time required for each cook depends on the wood used, the strength of liquor, and the pressure. When boiling with a liquor containing 3.5-per-cent. sulphurous acid at a pressure of 75 pounds per square inch, the cook requires from 16 to 20 hours. From 1,000 to 1,200 gallons of this liquor is required for each cord of wood cooked. A slow cook with a weak liquor, cooked at a low pressure and a low temperature, yields the strongest fiber. When the cooking is complete, the pressure is blown down to about 30 pounds per square inch, and the pulp is discharged from the digester (this should be done as quickly as possible; otherwise, the heat in the digester, in the absence of sulphite of lime, will turn the pulp brown) into a large draining tank, called a *blow pit*, where it is washed to some extent by running water upon it. The pulp is then thinned with water and pumped up to the washers, where it undergoes a further washing.

68. **Worm-Washer.**—A very convenient form of washer, known as the **worm-washer**, is shown in Fig. 19, (*a*) being an end elevation of the end where the washed stock is delivered, and (*b*) a longitudinal section on the line *A B* shown in (*a*). This washer consists of two copper worms *a*, somewhat resembling an auger, enclosed in perforated copper cylinders *b*. The cylinders are partly enclosed by a box *c*, which catches the wash water and conveys it away through the pipes *d*. There is a support *e* at one end of the box, through which the hollow trunnions *f* of the cylinders pass. There is a large cog wheel *g* at the end of each trunnion, and an endless chain connects the cogs of the

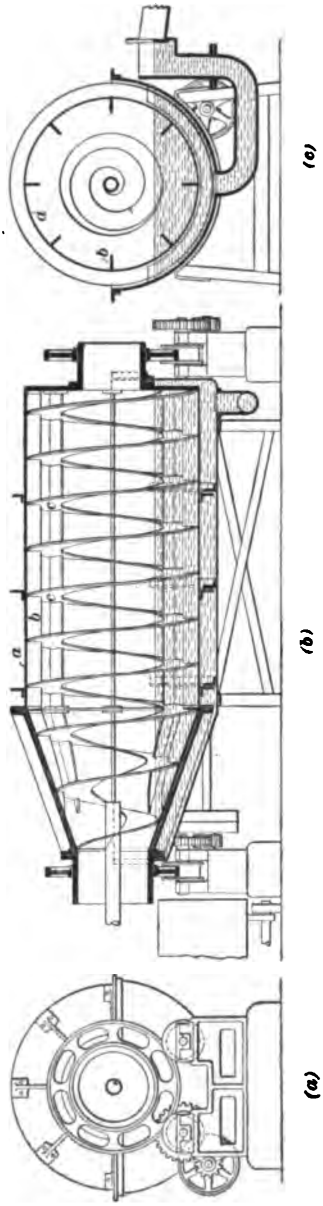


FIG. 20

two cylinders together, so that they are made to revolve at the same time. The stock enters the cylinders through the pipes *h* that pass through the hollow trunnions, which revolve around the pipe. There are heavy iron bands *i* encircling each cylinder at intervals, and at the discharge end each cylinder is encircled by a heavier band, or ring, *j*, which passes through the hollow wheels *k*, and thus holds the cylinders steady while revolving.

A perforated water pipe *l* extends along the whole length of each cylinder, and forcibly emits small jets of water against them. This water penetrates the cylinders and washes the pulp during its passage through the worms. Dashboards *m* extend from the sides of the box and are about as high as the cylinder. These dashboards prevent the water from splashing out.

The cylinders *b* are perforated, and the jets from the pipes *l* are emitted only on the surface, which is directly over the box. At the discharge end of the cylinders there is a funnel-shaped box *p*, into which the washed stock from two cylinders is deposited and washed down by water from the pipes *n* into the exit pipe *o*. The waste-water box *c* is hollowed out at this end so as to allow the drums to pass through.

In its passage through the worms the stock is turned over and over, thus exposing all surfaces to the washing action.

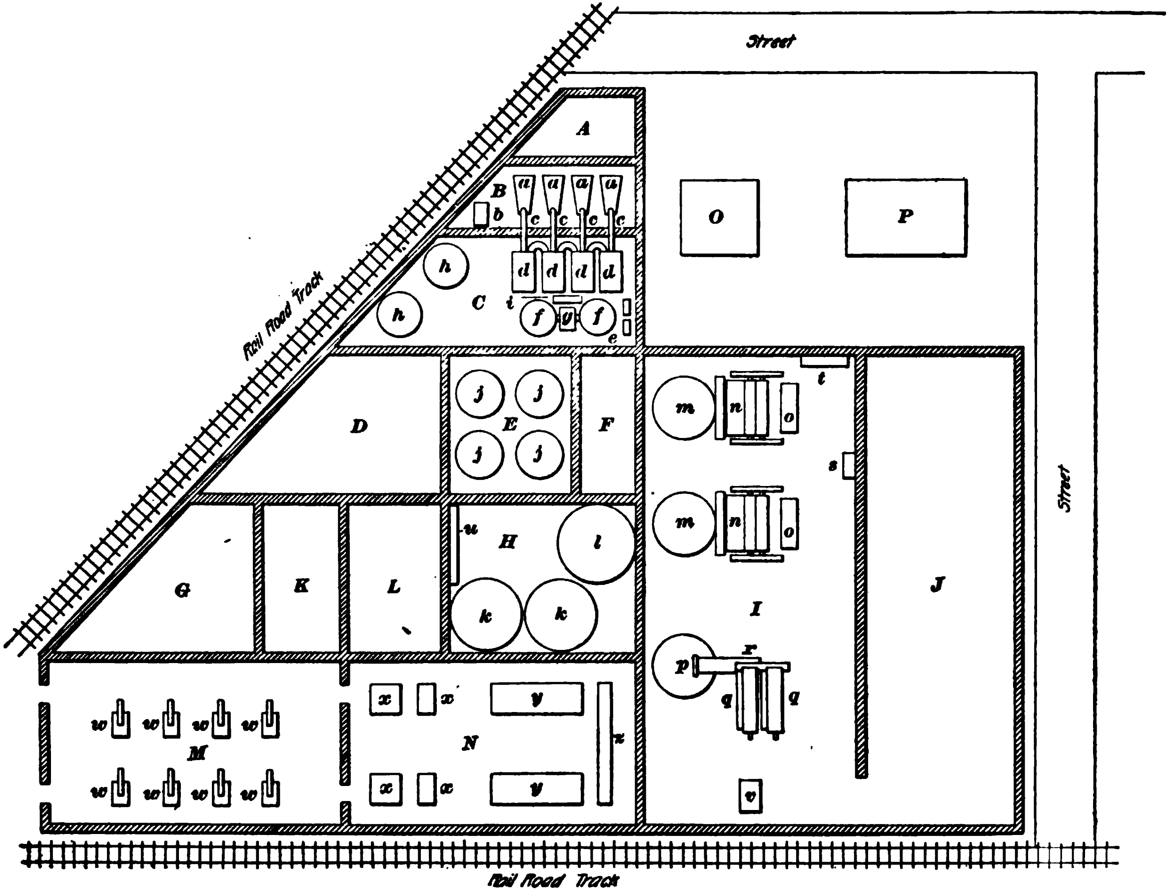
69. Fig. 20, which is taken from the Paper Trade Journal, shows an apparatus for washing pulp that is somewhat similar to the worm-washer. An end elevation is shown at (*a*), a longitudinal section at (*b*), and a cross-section at (*c*). The vat, or trough, is mounted on a suitable support and receives the drum, which is arranged horizontally and has end trunnions journaled in suitable bearings. The drum consists of a perforated shell *a*, which has a series of ribs *b* projecting inwards from its side at certain distances apart. A perforated blade *c* is wound helically around the inner periphery of the shell and extends from end to end. The water is admitted through a pipe at the conical end of the drum, while the cleansed fiber is discharged at this end through a central opening in the trunnion. The unwashed fiber is admitted through a central opening in the trunnion at the opposite end of the drum. In the bottom of the vat is a transverse, vertical web, which serves to prevent the direct passage of the clean water toward the outlet. By the rotation of the drum and helix, the fibrous material is gradually carried along the whole length of the drum and through the washing water, the level of which is kept above the helical blade to insure the immersion of the fiber carried along. During the rotation of the drum, the fibrous material is also repeatedly lifted and turned over. When the fiber reaches the conical end, it is raised up clear of the water.

From the washers, the pulp thinned with water passes to screens similar to those shown in Figs. 7, 8, and 9. The plates of these screens are made of bronze, which resists the action of the acid better than brass. The slots are usually $\frac{11}{1000}$ inch in width. Sometimes the washers are dispensed with, the pulp being washed in the blow pits and passed from these pits directly to the screens.

70. The excess of water in this pulp is usually removed by drum washers in the bleachers, the stock being pumped from the screens directly to the bleachers. In the sulphite process, unlike the soda process, the resins are not converted into soluble soaps, only the soluble parts of the resins going over with the sulphite lye. Great care should therefore be taken to wash out the dissolved resin adhering with the lye to the fiber before it hardens again. There are some forms of resin that are insoluble in the hot sulphite lye and therefore stay in the pulp, causing brown and yellowish spots to appear in the paper. The particles of resin, being lighter than water, float on the surface, and in order to remove these particles, many paper makers use laths covered with strips of long-haired felt; these float on the thin pulp when passing over the sand traps in the beaters and retain most of the resin.

Sulphite fiber is largely used in its unbleached state, as it is fairly white. When intended for use in the natural state, the excess of water is removed by wet machines and the pulp is taken off in thick sheets, which are folded and made into bundles.

71. Disposition of Waste Sulphite Liquor.—Quite a little investigation of the waste liquor from the sulphite process has been carried on, and it has been found that this liquor can be worked up and used as a sizing agent by precipitating with aluminate of sodium, but this method has never been carried out on a practical scale. In Germany, sulphite waste liquor has been used quite extensively for tanning purposes. The wood is, as a rule, not cooked so severely in Germany as it is in the United States, and consequently a clearer liquor is obtained. This liquor not only tans the hides well, but also gives a good color to them. The use of sulphite waste liquor in the United States has produced a very dark-colored leather, and, up to the present time, this liquor has been employed only for tanning uppers, the color of which is of little or no importance. As the sulphite liquor contains considerable available tannin—for


Street
A
B
a
b
c
d
C
e
f
g
h
i
O
P
D
E
j
F
m
n
o
s
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Street
G
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L
H
u
l
k
I
J
p
r
q
v
M
w
N
x
y
z
Rail Road Track
Rail Road Track

FIG. 21

instance, a sample having a density of 7½° Baumé at 60° F. showed 5.36 per cent. of available tannin—there is little doubt that in the near future means will be found to utilize this waste liquor as a source of supply for tanning extracts.

Waste sulphite liquor is used as a binding material for sand in preparing foundry cores, and a cattle food that has met with but little success has also been prepared from it. Furthermore, there is a process patented for evaporating the liquor, converting the organic matter contained therein into fuel gas, and recovering some of the sulphur contained in the liquor.

72. Ground Plan of a Typical Sulphite Pulp Mill. In Fig. 21 is shown a ground plan of a typical sulphite pulp mill.

A is the sulphur storeroom.

B is the sulphur-burner room, which contains the sulphur burners *a*, and an elevator *b* for conveying lime up to the lime storeroom above the mixers.

C is the absorption room. This room contains the up-and-down preliminary cooling pipes *c*, the coolers *d*, the vacuum pumps *e*, the lower absorption tanks *f* (the highest set of absorption tanks being directly over the coolers), the tank *g* into which the finished bisulphite liquor runs, the lime mixers *h*, and the stairs *i* leading up to the absorption tanks.

D is the boiler room.

E is the acid and liquor storage room, which contains the tanks *j* in which the bisulphite liquor and the sulphurous-acid solution used in bleaching are stored.

F is the engine room.

G is the supply room.

H is the digester room, which contains the digesters *k*, the tank *l* in which the cooked stock is given a preliminary washing, and the stairs *u* leading up to the top floor of the digester room.

I is the wet-machine room. This room contains chests *m* of bleached stock for wet machines, the screens and wet machines *n*, the tables *o* on which the pulp is folded, the chest *p* into which the washed stock passes before being pumped up-stairs to the screens and bleachers, the worm-washers *q*, the cylinder *r* through which the stock passes after coming from the washers, which gives it a thorough breaking up, the scales *s*, the stairs *t*, and the elevator *v* leading to the upper floor.

The screens and bleachers are on the second floor of the wet-machine room.

J is the pulp storeroom.

K is the pipe shop.

L is the engine room.

M is the knotting department, in which are located the saws *w*.

N is the chipper room, which contains the chippers *x*, the screens *y*, and the conveyer *z* that takes the chips up to the top of the digesters.

O is the laboratory.

P is the office.

MISCELLANEOUS PROCESSES FOR TREATING WOOD

73. Sulphate Process.—Sodium sulphate is used to some extent in cooking wood, and produces a pulp of excellent quality. This material is mixed with one-third its weight of caustic soda. The density of liquor used varies from 6° to 13° Baumé. The time required to cook the wood depends on the strength of the liquor used and the pressure at which it is cooked, and varies from 30 to 40 hours. The pressure varies from 75 to 150 pounds. Coniferous woods are exclusively used as raw materials.

The soda compounds are recovered as in the soda process, the liquor being evaporated and calcined, yielding a reddish-brown ash. There is a loss of from 10 to 20 per cent. in the recovery, which is made up by the addition of fresh sulphate, and the whole is heated with from 20 to 25 per cent. of lime. The main objection to this process is the formation of sulphur compounds of objectionable and penetrating odors, principally Na_2S. Another objection is the length of time required to cook the wood. The yield is about 10 per cent.

better than by the soda process, and the pulp is bleached with less bleaching powder.

74. Pictet and Brélaz's Process.—In the **Pictet and Brélaz process,** the wood is subjected to the action of a supersaturated solution of sulphurous acid, under reduced pressure, at a temperature not exceeding 212° F. The liquor permeates the wood, dissolving out all the cementing constituents that envelop the fibers. The digesters are lined with lead. It requires from 12 to 24 hours for complete disintegration, according to the nature of the wood used. This pulp is readily bleached with chloride of lime.

75. Barre and Bondel's Nitric-Acid Process.—In the **Barre and Bondel nitric-acid process,** the wood is digested for 24 hours in a 50-per-cent. solution of cold nitric acid. The pulp is washed first with hot water and finally with a weak solution of sodium carbonate.

76. Nitrohydrochloric Acid Process.—There have been several processes patented for disintegrating wood by the use of various mixtures of nitric and hydrochloric acids. All of these processes use more hydrochloric acid than nitric, the strength of the mixture varying according to the temperature at which the disintegration takes place. When the mixture is to be used cold, it is made of strong acids, but when it is to be used hot, the acids are diluted about twenty times with water.

Many difficulties are encountered with the use of acids. The principal one is in being able to provide vessels that will resist the powerful corrosive action. Nitric acid will form an explosive substance of the gun-cotton series; therefore, great risk is involved in drying the pulp obtained by a process in which this acid is used. The objection to using hydrochloric, sulphuric, and sulphurous acids, is that when they act on wood at moderately high temperatures, the decomposition products accumulate very rapidly and undergo a secondary decomposition, tending toward the formation of dark-colored tarry matter, which prevents the formation of pure cellulose.

MANUFACTURE OF PAPER

(PART 2)

BLEACHING AND BEATING

BLEACHING THE VARIOUS FIBERS

1. After washing the various fibers produced by any of the processes described in *Manufacture of Paper*, Part 1, they are always found to be more or less colored, owing to the fact that a portion of the non-cellulose constituents survives. The next operation is to remove this coloring matter as much as possible, and thereby produce pure-white fiber for the manufacture of the best grades of paper. This is accomplished by the *bleaching process.*

Bleaching is simply an oxidizing action, and although there are other agents to be had, the principal ones used in bleaching are chlorine or compounds of chlorine. Of these compounds of chlorine, *bleaching powder*, which is made by passing chlorine gas through slaked lime, is the one most used in the paper industry. The formula of this powder is generally accepted as

$$Ca\begin{cases}Cl\\OCl\end{cases}$$

Some authorities advocate the theory that the bleaching is accomplished as follows: The bleaching powder, when treated with water, is resolved into equal molecules of calcium chloride, $CaCl_2$, and calcium hypochlorite, $Ca(OCl)_2$, the latter, which is the active bleaching agent, splitting up into $CaCl_2 + O_2$. It is, however, most generally accepted that the bleaching action is due to the liberated chlorine combining with the hydrogen of the water, setting free oxygen, which does the work. The bleaching powder should be stored in a cool, dry place, otherwise it will lose strength; and when mixed for use, it should be used up as quickly as possible.

2. **Preparation of the Solution of Bleaching Powder.**—The tanks used in preparing the solution of bleaching powder are generally made of iron and are provided with agitators and siphon pipes, similar to those used in causticizing pans. These tanks vary in size and hold from 1,000 to 2,500 gallons. The most convenient size is one in which either one or two whole casks of bleaching powder can be used and the bleach made up to the required strength, thus avoiding the necessity of splitting casks. The temperature of the water used in mixing the bleach should not exceed 70° F., and it is better, provided the bleach settles well, to keep the water as near 60° F. as possible.

The tank is filled about two-thirds full with water, the agitators started, and the bleaching powder dumped in. The agitation is continued until all the lumps are well broken up, after which it is stopped and the bleach allowed to settle. There should not be too prolonged agitation in mixing the powder, as it will not settle so well. Agitating from 15 to 20 minutes is sufficient for a strong bleach. The washes are agitated while filling and stopped when full. In some mills, just enough bleach is used to make the liquor up to the required strength, the washes being used for making up other tanks and washes, and the final wash being made with water. The washes are made similar to those of the lime sludge in the manufacture of caustic-soda liquor. The method most generally adopted is to make the bleach up stronger than desired and to mix in a tank in the cellar with washes of other tanks until the required strength is reached. Sufficient washes should be made until practically all the chlorine has been washed out of the sludge, allowing the bleach to settle after each wash. The loss in sludge should not exceed 1 per cent. of the total amount of bleach used in making the solution. The balance of these washes, after the strong bleach is diluted to the required strength, is run into a separate tank and is used in place of water for making strong bleach. The strong-bleach solution is usually made up to about 7½° to 8° Baumé, and after dilution it tests from 3½° to 4½° Baumé, at which strength it is used in the bleachers.

3. The percentage of available chlorine is not the only factor to consider when purchasing bleach, as the settling quality figures to a considerable extent. It is advisable that only clear liquor be used in bleaching, and for this reason a bleach that is high in available chlorine, but a poor settler, is of no more value to a concern that has a limited capacity for making bleach than a bleach that has less available chlorine, but settles well. It is due to this fact that the manufacturers of bleaching powders in the United States are unable to keep foreign bleach out of this country.

Great care should be exercised in purchasing bleaching powder, in order that the stock may be bleached economically. It should come up to the required strength, should be perfectly dry, and should settle well. Bleaching powder should be stored in a cool, dark place, and the men in charge of making up the bleach should be known to be perfectly reliable, so as to insure the most perfect extraction of bleach solution from the powder.

The sludge from bleaching powder, consisting principally of calcium hydrate and calcium carbonate, is washed out into the sewer after the last wash has been run off.

Sulphites are oxidized to sulphates by the action of hypochlorites; thus,

$$2Na_2SO_3 + Ca(OCl)_2 = 2Na_2SO_4 + CaCl_2$$

Hence, they are useful in neutralizing an excess of bleach.

4. In quite a number of mills, as has been stated, the bleaching is done in the beater; but it is customary to transfer the washed pulp, with the necessary amount of water, to what are termed *potchers*. These potchers are of various forms. Some are provided with steam pipes to heat the pulp while bleaching, and others are provided with drum washers. All potchers, however, are provided with agitators or some means of keeping the pulp in circulation during the bleaching operation.

5. Bleaching of Rags.—Pulp from rags is generally bleached in revolving barrels that are made of wood that are lined with a suitable acid-resisting material. The rags are put into the barrel through a manhole, the required amount of bleaching liquor added, and the barrel set in motion. The bleaching of rags is better accomplished by adding either hydrochloric acid or sulphuric acid during the process of bleaching. The acid should be very much diluted when added, but the addition should not be made until the bleach has been acting on the pulp for some time. When acid is added to accelerate the bleaching action, the process is termed *acid bleaching*. Acetic acid has been used extensively to assist the action of bleach liquor in the bleaching of rags, which only requires the addition of a small quantity, from the fact that during the operation the acid is regenerated according to the following equations:

$$\begin{aligned}
&(1) & Ca(OCl)_2 + 2CH_3CO_2H &= (CH_3CO_2)_2Ca + 2HOCl \\
&(2) & 2HOCl &= 2HCl + O_2 \\
&(3) & (CH_3CO_2)_2Ca + 2HCl &= 2CH_3CO_2H + CaCl_2
\end{aligned}$$

The amount of bleach necessary to produce a good color depends on the thoroughness of previous treatments, but may be given as from 2 to 5 pounds of bleaching powder for every 100 pounds of pulp.

6. Bleaching of Esparto.—Esparto fiber is very often bleached in the washing and beating engine, where it is subjected to an acid bleaching. The required quantity of bleach liquor is added, and after mixing for about ⅓ hour, the highly diluted acid is added (using about 6 ounces of acid to 100 pounds of fiber) and the bleaching continued until a good color is produced. The liquor used tests about

4° Baumé at 60° F. Esparto fiber is also bleached in large potchers made of brick and lined with cement, the agitation being accomplished by means of large revolving paddles made either of wood or iron, preferably the latter. From 10 to 15 pounds of bleaching powder is required to bring 100 pounds of esparto to a good color.

7. **Bleaching of Straw.**—Straw fiber is bleached by methods similar to those used for bleaching esparto. The amount of bleach required is from 8 to 12 pounds for each 100 pounds of pulp.

8. **Bleaching of Jute and Manila.**—Jute and manila are usually bleached in the washing engine, and chloride of lime, when used, is added in a very weak solution, which bleaches the fiber to a cream color, oxidizing it to some extent. Strong bleach should not be used, as it will chlorinate the fiber. It is better to use a weak solution of sodium hypochlorite in the bleaching of jute, as a solution of this kind will prevent the formation of the chlorinated compound. As it is difficult to bleach jute fibers to white, they are generally used for papers that do not require a high color. From 9 to 10 pounds of bleaching powder is required for each 100 pounds of pulp.

9. **Bleaching of Ground Wood.**—Owing to the fact that ground wood contains nearly all the intercellular constituents of the wood, which have to be removed by the bleach before any action takes place on the coloring matter of the fiber, it cannot be economically bleached, and is therefore used for common papers, as stated before. The color of ground wood can be considerably improved by treating it with a dilute solution of sodium bisulphite.

10. **Bleaching of Chemical Wood Fiber.**—There are many forms of bleaching potchers for bleaching chemical wood fiber made by the various chemical processes. Some potchers very much resemble a beating engine (in fact, some paper makers bleach their stock in the beaters), others are large cylindrical wooden tanks provided with an agitator,

which consists of a central rod with paddles attached at different heights, while still others are large, open, tile-lined vats made of brick, having wings attached to a revolving horizontal shaft so as to keep the stock agitated during the bleaching operation. It has been found by practice that better results can be obtained by bleaching the stock in open bleachers. All forms of bleachers have a steam line running into them, by means of which the stock can be heated during the operation. The heating must be done very cautiously, as there is great danger of chlorinating the fiber if heated too highly; there is also danger of heating it too highly in one spot (where the steam enters), with the same result. Better results can be obtained by heating the stock to the required temperature before adding the bleaching liquor. It is advisable not to exceed a temperature of 115° F. If this temperature is exceeded, there will be trouble from time to time with chlorinated fiber.

11. At times, owing to insufficient treatment in previous operations, it is difficult to bring a bleacher of stock up to color. In such a case, the action can be greatly assisted by washing out the products of the bleaching action, treating with a weak solution of alkali, and washing again. After this treatment, the most refractory pulp can be brought up to color by again treating with bleaching solution. In bleaching sulphite pulp, the fact that from 14 to 22 per cent. of bleaching powder is required indicates that the powder has to perform other actions besides bleaching. The amount of bleaching powder required increases with the amount of incrusting matter left in the pulp. Using the soda solution just mentioned before bleaching will greatly reduce the expense of bleaching.

12. In bleaching sulphite pulp, some paper makers warm the pulp in a 13-per-cent. solution of bleaching powder, and after 1 hour's time add a 2.5-per-cent. solution of sulphuric acid. The pulp is then washed for 2½ hours and rebleached with a 2-per-cent. solution of bleaching powder, finally adding a ½-per-cent. solution of sulphuric acid.

In bleaching soda or sulphite fiber, the strength of the bleach solution used is generally from 3½° to 4° Baumé at 60° F. (about ½ pound of bleaching powder to a gallon). It is advisable to keep the solution as regular as possible in order that the results obtained may be uniform. The bleaching of wood fiber requires from 12 to 25 pounds of bleaching powder for each 100 pounds of pulp, depending on the wood used, the process by which the fiber was isolated, etc. After bleaching any fiber, it must be well washed in order to remove the excess of bleach and soluble by-products. This is done in some mills by means of a drum washer in the potchers; in others, by the same operation in the beaters; and in still others, the bleached stock is pumped with a large quantity of fresh water to large drainers, or chests, having perforated bottoms and allowed to stand until it drains down solid, after which a large amount of water is added and the stock is pumped to the beaters, mixers, or pulp-machine stuff chest.

13. In order to get good results from bleaching, the stock should be well agitated. The question of agitation has caused considerable experimenting to be done by the management of the various paper mills, and as a result, some mills have adopted a system of continuous circulation. In this system, the stock, after the bleach has been added, is taken to a battery or a set of bleachers, through which it is made to pass, being pumped from the bottom of one bleacher to the top and opposite end of the other, and then from the bottom of the second bleacher, on the opposite side from where it entered, to the top of the third, and so on through a series of about six bleachers, all of which are furnished with agitators.

As nearly all bleach solutions contain some chlorate, which is inactive as a bleaching agent, it is generally advisable to add a small quantity of sulphuric acid. This acid should be added when the available chlorine has just about been exhausted, or when the stock shows a pale-blue color with iodic starch. Also, time should be allowed for its action before sulphurous acid or bisulphide liquor used as an antichlor is applied. The sulphuric acid should be very much diluted before it is added—about 1 quart of acid to a barrel of water—and should be run in very slowly. The adding of sulphuric acid will liberate the chlorine from the chlorate and will give the liberated chlorine an opportunity to assist in bleaching the stock.

In cases where the bleaching capacity of the plant is insufficient, it is advisable to add a little sulphuric acid to hasten the bleaching action. In this way it is possible to bleach more economically, and, in addition, the washing of good bleach solution from the stock is avoided. Great care, however, must be exercised in thus forcing the bleaching.

14. It is generally customary to use some form of antichlor to neutralize the last traces of bleach after the stock has come up to the required color. Sulphite and hyposulphite of soda are used to a great extent for this purpose. Sulphurous acid is also used to some extent. This acid removes the slight yellow tint left in the pulp after bleaching, bringing it to a fine white. On exposure to the atmosphere for any length of time, this yellow tint will appear again, because the coloring matter that was temporarily removed by the reducing action of the sulphurous acid will again become oxidized. When treated with an antichlor, the pulp must be rewashed.

15. **Electrolytic Bleaching.**—There has been considerable experimenting with methods of preparing bleach liquor by the electrolysis of common salt, and as a result of these experiments such a degree of proficiency has been gained that electrolytic bleach plants have been installed in a large number of mills in the United States and in Europe.

The process of bleaching with the product of the electrolysis of an alkaline chloride was first worked on a commercial basis in 1886, when M. Hermite developed the process for the production of magnesium hypochlorite by the electrolysis of a 5-per-cent. solution of magnesium chloride.

The process of electrolytic bleaching is based on certain well-known principles of electricity, a general idea of which is here given.

A metallic conductor does not suffer any apparent change when a current of electricity passes through it, but various magnetic and heating effects are produced. Some liquids, as well as solids, are good insulators, while others conduct electricity, and are termed *electrolytes*. The latter suffer decomposition in proportion to the amount of current passing through them. The *poles* are the points at which the current enters and leaves the liquid, the point at which the current enters being termed the *anode*, and the point at which it leaves, the *cathode*. The products of decomposition of the liquids are observed at the poles, and are called *ions;* that liberated at the anode is termed the *anion*, and that liberated at the cathode, the *cation*. In the process of decomposition of fused common salt, chlorine is given off at the anode and sodium at the cathode. When a solution of common salt is used, a secondary reaction takes place, due to the contact of the liberated ions, and there is a tendency toward the formation of sodium hypochlorite, which remains in solution, and hydrogen, which escapes at the cathode. There is also a decomposition of the water itself into hydrogen and oxygen, and the oxygen that is liberated at the anode will attack the material of which it is made, and, in the case of carbon, destroy it in a short time. It is the aim of the inventor to procure an anode that will resist the action of the products of electrolysis. Platinum is the best in this respect, but as it is very expensive, different forms of carbon have been used to a great extent. It is also advantageous to use as little water as possible; hence, nearly all inventors use a saturated brine solution. The quantity of electrolyte decomposed by the passage through it of a given quantity of electricity is always the same. The current efficiency of a cell is determined by dividing the quantity found by the theoretical amount.

16. That which causes electricity to flow from a point of high potential to a point of low potential is called the *electromotive force* (E. M. F.), the unit of which is the *volt*. The unit of quantity of current is the *coulomb;* the unit of rate of flow, which is 1 coulomb per second, is called the *ampere;* and the unit of resistance to the flow is the *ohm*. An electromotive force of 1 volt will send a current of 1 ampere through a resistance of 1 ohm. A current of 1 ampere, theoretically, yields 1.34 grams of chlorine and 1.51 grams of caustic soda per hour. Owing to complications due to secondary reactions, the yield in practice is only about 1 gram of chlorine per ampere per hour. The power of a current in doing work is measured in units called *watts*.

A current of 1 ampere, under an electromotive force of 1 volt, has an energy of 1 watt. One horsepower equals 746 watts.

Two pounds of coal is converted into 1 horsepower of mechanical energy, which, as stated, is equivalent to 746 watts. This is converted through the dynamo (with customary loss) into about 650 watts, which is the efficiency of the dynamo for each horsepower.

An electromotive force of from 3 to 5 volts is required between the terminals, and since the power of a circuit in watts is equal to the number of amperes flowing multiplied by the electromotive force in volts, to produce 1,000 grams of chlorine it will require (assuming the electromotive force to be 4 volts) 4,000 watts, or about 6 horsepower per hour, which means the consumption of 12 pounds of coal.

A great difficulty experienced in the process thus far set forth is in getting the caustic-soda solution free from salt, as a diaphragm is required between the anode and the cathode that will furnish as little resistance as possible and at the same time prevent the passage of brine solution through it. Several different materials are in use for diaphragms, such as unglazed earthenware, asbestos, etc.

17. A great many processes have been proposed for the production of chlorine and caustic soda by electrolysis, all of which have the same fundamental principles underlying them, namely, working with a saturated brine solution, having a diaphragm between the poles, and separating the chlorine from the soda. There has, however, been considerable difference in the designs of the apparatus.

The dynamo generally used is one so wound as to deliver a continuous current of large volume under moderate voltage, say about 1,250 amperes at 120 volts. The cells are usually arranged in multiple, and the current is conducted to them through large copper conductors.

Following are descriptions of a few of the styles of cells that have been patented and are now being worked on a paying basis at many paper mills. (For description of other cells, see *Alkalies and Hydrochloric Acid.*)

18. The Mercer Cell.—In Fig. 1 is shown the **Mercer cell,** which consists of an earthenware crock that is open at the top and sides (the side openings marked *l*, shown in (*c*), are five in number) but closed at the bottom. The brine solution is poured into the cup *b* at the side of the cell, and passes into an inner tube *c*, which extends almost to the bottom of the cell, where the brine solution is discharged. This enables the cell to be kept full and prevents the gas from escaping while filling. The crock is enlarged at *m* so as to form a groove, as shown, into which the lid, shown in (*a*), will fit and thus permit the cell to be luted air-tight. The diaphragm used is asbestos, a sheet of which is wrapped around the openings in the crock. A perforated sheet-iron jacket *k*, shown in (*e*), is securely bound around the asbestos diaphragm by means of iron bands *j*, which are in three pieces and bolted together, as shown in (*f*).

The anodes consist of round sticks of carbon *g*, shown in (*d*), four of which are attached to a lead support *h* that has a long lead projection *i* extending from its center. There are small projections *a*, shown in (*b*) and (*c*), on the inside of the crock, upon which the lead support rests. The long lead projection passes out through the lid at *d*, as shown in (*a*) and (*e*), and is luted air-tight. This lead connects with the conductor from the dynamo. The chlorine gas escapes through *e* to the gas main. Six of these shells are placed in

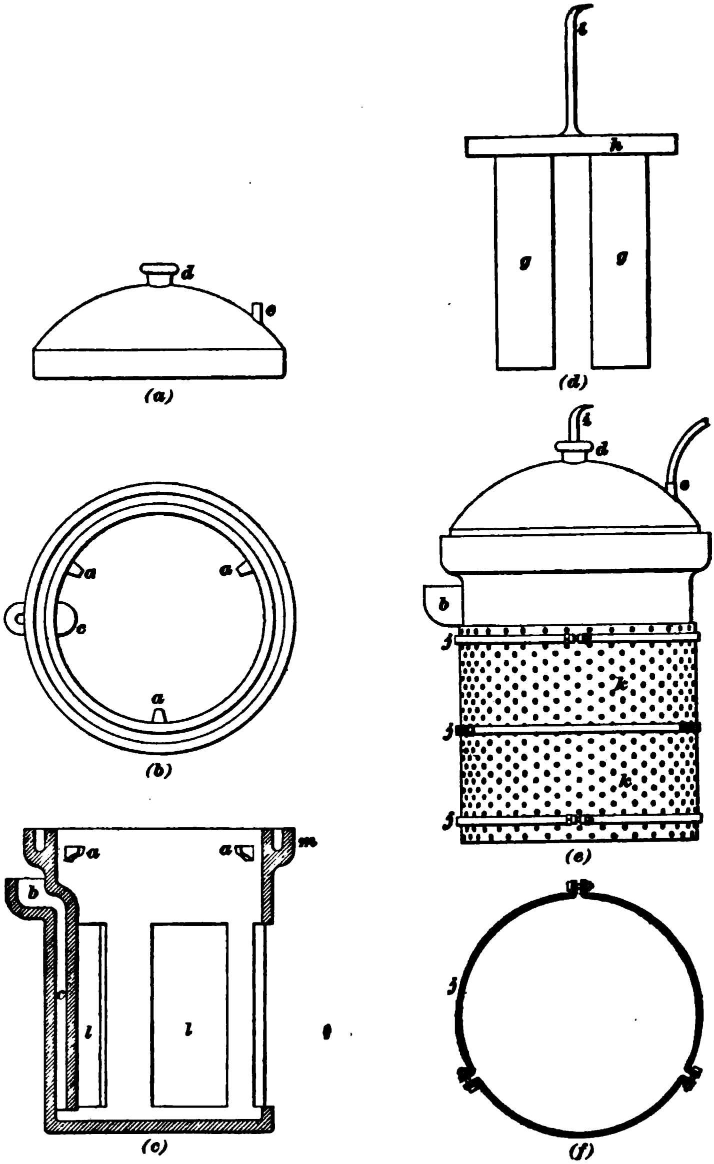

(a) (b) (c) (d) (e) (f)

Fig. 1

a long, oblong sheet-iron tank that is just wide enough to admit them. The sheet-iron jacket *k* touches the bottom of the tank and, together with the tank, forms the cathode. The tank is supported on pieces of glass.

The soda passes through the diaphragm and unites with the water, which is continually flowing in at one end of the tank and out at the other, forming caustic-soda solution. The strength of the soda solution depends on the amount of water flowing into the tank. The solution is deep enough to cover the asbestos diaphragms. The chlorine gas passes through the gas main and into the lime tower, where it comes in contact with milk of lime. The milk of lime is mixed in a tank on the second floor, and passes down the tower to a tank below, from which it is again pumped into the tank above. This continuous circulation is kept up until the bleach solution has reached the required strength, when it is allowed to settle, the liquor run off, and the lime sludge, with the addition of more fresh lime, used again. This bleach liquor is tested from time to time for available chlorine by the usual arsenious-acid tests, in order to ascertain when it is up to the desired strength. The finished liquor should contain from 1.56 to 1.75 per cent. of available chlorine. If there is not sufficient lime to take up all the chlorine to form hypochlorite, the excess of chlorine will cause the formation of chlorate, which results in the loss of the active bleaching agent. For this reason, the Baumé test is not sufficient in testing the bleach liquor made by this process, and, as just stated, the arsenious-acid test should be resorted to.

19. Outhenin-Chalandre Cell.—In Fig. 2 is shown the **Outhenin-Chalandre cell**, which consists of an inner closed anode cell *a* containing round carbon anodes *c* that are connected by means of a lead support *b* with a terminal *o*. A lead pipe *g* passing through the top carries the chlorine gas to the gas main. The sheet-iron cathode *h* forming part of the plate *m*, the top of which serves as the terminal, are contained in sloping, porous tubes. These tubes are hermetically sealed through the walls of the anode chamber, but allow free circulation of cathode liquid through them. Each tube is fastened in place by an arrangement, as shown at *i*. The anodes are suspended in rows of six between adjacent sets of cathode tubes. Water is admitted to the cathode chamber through the funnel *j*, and caustic-soda solution is drawn off at *k*. The anode solution is sodium chloride, and the cathode solution, sodium hydrate. The hydrogen produced at the cathode passes up to the tubes and is collected in the hood *l*. It is then conducted away and used for other purposes. The anode cell is filled through pipe *n*.

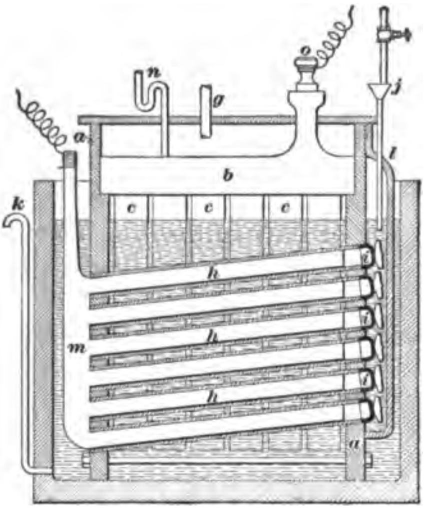


FIG. 2

It is claimed for this process that caustic soda can be made fairly concentrated, and that a sample of caustic soda made in this manner contained 97.5 per cent. caustic soda (dry basis). The chief advantages of this cell are the complete separation of soda and chlorine and the collection and utilization of the hydrogen; but, on account of the diaphragm, a high electromotive force is required between the terminals. In some mills, an evaporator somewhat similar to the Yaryan is employed to remove the salt from the caustic liquor.

20. Treatment of Bleached Stock.—The bleached and washed stock, in case the washing is not done in the beaters, follows one of the following courses: It is (1) transferred to the mixers; (2) transferred to the wet machine; (3) transferred to the pulp machine; or (4) transferred directly to the beating engine.

1. The object of the mixers, which are large, cylindrical tanks provided with agitators in the center and capable of holding several bleachers of stock, is to furnish uniform stock for the beaters, in case the pulp is worked right up into paper. The stock is passing in and out of the mixers continually.

2. The wet machine, similar to the one described in *Manufacture of Paper*, Part 1, is used in case it is desired to transfer, or ship, the pulp in folds or to weigh the amount used in the beaters. This plan is usually followed in the treatment of the sulphite fiber, after which it contains about 65 per cent. of moisture. The pulp is transferred to the beater in folds, but is opened out before it is placed in the beater.

3. Before passing over the pulp machine, the pulp first passes through a screen similar to the one described in *Manufacture of Paper*, Part 1. From the floor box of this screen the pulp passes up through a number of holes into a vat where it is mixed with more water. There is a wire-covered roll revolving in this vat, by means of which the pulp is taken up and transferred to a felt, as in the wet machine, and conveyed over one or more suction boxes through a series of press rolls and over the driers (the suction boxes, driers, and press rolls being similar to those of a paper machine, to be described later). The pulp is wound on a long reel at the end of the machine and is finally slit and rewound in rolls of a convenient size to handle (from 100 to 150 pounds each). There are usually several reels so arranged that while one is being cut another is winding, and thus the pulp is run continuously. These rolls are weighed and tied up for shipment. They contain about 7 or 8 per cent. of moisture. The rolls are either chopped up and put into the beaters in sheets or allowed to run in from a spindle.

4. The stock is pumped directly from the drainers to the beaters, where it is finally mixed for the paper machines.

BEATING

21. Beating Process.—In the **beating process,** the material is disintegrated in order to obtain a close, even sheet of paper. The amount of beating required varies according to the nature of the stock and the class and grade of paper to be manufactured. The beating process is one of the most important steps in the operation of paper making. No amount of skill of the paper maker will remedy a mistake due to carelessness or lack of skill on the part of the beaterman.

22. Beating Engine.—The **beating engine,** which has been referred to before, is shown in Fig. 3. This machine is made of wood or iron and is provided with a washer *a*, a bedplate and roll *b*, and a midfeather *c*, as in the breaking engine previously described. The washer, which is shown in Figs. 4 and 5, consist of an octagonal drum, the faces of which are made of latticework, admitting of the free

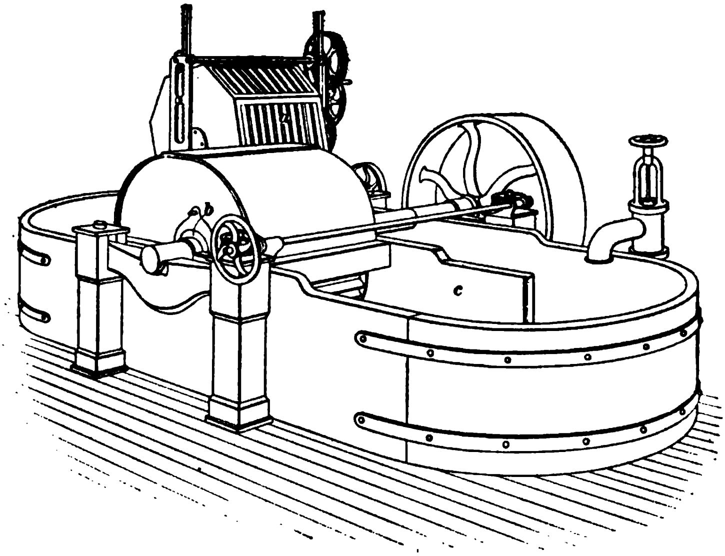


Fig. 3

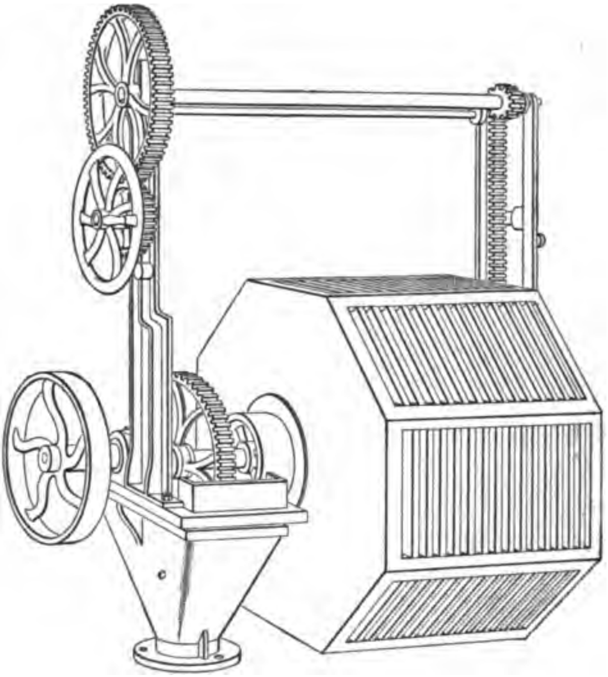


FIG. 4

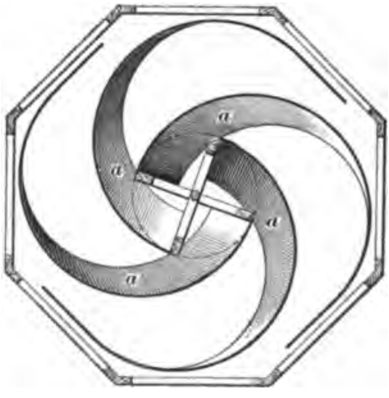


FIG. 5

passage of water to the interior, while the ends are closed in such a manner as to allow the water to pass out at the axis only. This drum is covered with a fine-mesh wire cloth, which prevents the fiber from being carried off with the wash water. The interior of the drum, shown in cross-section in Fig. 5, is so arranged that, in revolving, the arms *a* take up the water and carry it to the axis of the drum, through which it is conveyed to the trough *c*, shown in Fig. 4.

23. The engine roll, which is shown in Fig. 6, is provided with projecting steel knives that are tapered in the opposite direction to the knives in the bedplate, which are placed under the roll in the beater; thus, when the roll revolves, it produces a cutting action similar to that of a pair of shears. There is a small depression in the floor of the beater, known as the *sand trap*, in which heavy particles of dirt, sand, etc. are caught during the beating operation. It is in this engine that the stock is prepared for the paper machine. By the beating and cutting action of the roll and the bedplate, the fibers are separated and reduced in length, the fineness being regulated by varying the distance between the roll and the bedplate. The fibers obtained from straw do not require any beating; those from esparto and wood require considerable; and those from rags, on account of their length, require excessive beating and cutting. Rag stock intended for strong, thin papers must be drawn out in the washer for at least 6 hours, and in the beater for 11 or 12 hours, using blunt plates and rolls.

FIG. 6

24. The beating is carried on by gradually lowering the roll until the required effect is produced. In order to produce paper of the quality required, it is necessary to mix various fibers, which is usually done in the beating engine. In mixing these various fibers, such as rags with esparto, rags with wood, esparto with straw, sulphite stock with soda stock, ground wood with other fibers in preparing newspaper, etc., and, in fact, any of the fibers, the paper maker must use his best judgment, bearing in mind the different effects produced on the different fibers by the beating action, etc.

25. Broke Beater.—The **broke beater,** as its name suggests, is used in working up *broke*, which is partly formed paper obtained when starting the paper machine, paper damaged in passing over the drying cylinders, and imperfect or rejected paper. This engine is the same as the ordinary beating engine, except that it has a steam line by means of which the stock is highly heated. In some cases, a little caustic soda is added to the stock to assist in breaking it up again.

26. Jordan Engine.—The **Jordan engine** is an improved form of engine that will save from one-third to one-half the time required for beating, when done in the beating engine. The working of the Jordan engine will be clearly understood by referring to Figs. 7 and 8, which show the Horne-Jordan engine set up and also the interior struc-

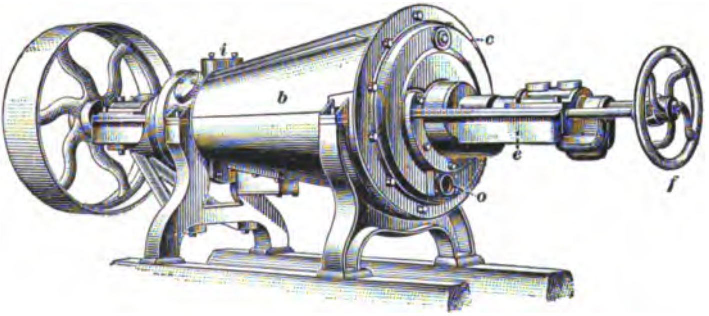


FIG. 7

ture. This machine consists of a cast-iron cone *a*, which fits into the cone *b*, forming the body of the engine. The cone *a* revolves at a speed of from 350 to 400 revolutions per minute. Both cones are fitted with angled steel knives that are held in position by hardwood wedges. The plate *c* is bolted on tightly, and the packing gland *d* is adjusted over the shaft. The arrangement shown at *e* is attached as shown in Fig. 7, and by means of the screw arrangement *f*, the cones can be adjusted to regulate the fineness of the stock.

This type of Jordan is the one in most general use, although there are other types that give very good results. Among these may be mentioned the Marshall perfecting engine. This engine differs from the Jordan in having rims on the end of each of the cones, set with knives, which cut at this point also.

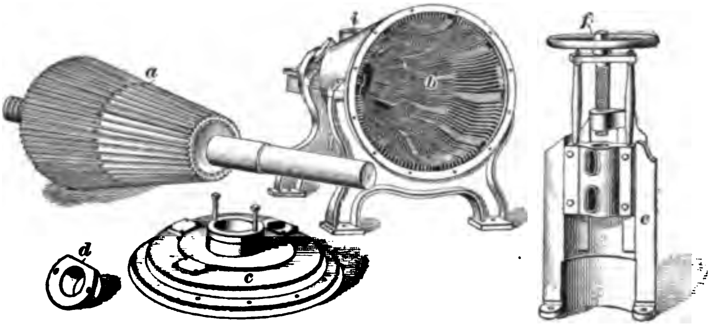


FIG. 8

The half-beaten stock from the beating engine is pumped into a supply chest located over the Jordan. From this chest the Jordan is supplied with stock by means of a pipe, the stock entering the engine at *i* and the finished stock leaving the engine at *o*. From this point the stock is conveyed through a pipe to the stuff chest, from which it is pumped to the screens of the paper machines.

SIZING, LOADING, AND COLORING

SIZING

27. It is necessary that writing paper, book paper, etc. shall not readily absorb ink or water, so that when used for writing or printing the ink will not spread, but will leave good, plain characters. This property is imparted to the paper by the use of what are known as **sizing agents,** which are assisted to some extent by the *loading agents*, which will be considered later.

28. Engine Sizing.—The process known as **engine sizing** is carried out by precipitating *rosin size* with alum, or some other precipitant, upon the fiber in the beating engine.

29. Rosin Size.—There are many ways in which **rosin size** may be prepared, but they all accomplish the same purpose—that is, getting the rosin in such shape that it can be made into a solution, from which it is again precipitated as already suggested. There has been a great deal of discussion as to what the true sizing agent is, some of the authorities contending that the free rosin is the only sizing agent, others that the resinate of aluminum is the true sizing agent, and still others that it is due to both. Practical experience inclines to favor the view that the sizing is as much due to resinate of aluminum as it is to the free rosin, as sizes in which the free rosin varied from 3 per cent. to 35 per cent. have been successfully used. When using a size containing 3 per cent. of free rosin, a larger amount of alum was required to precipitate the size, but no more rosin was required to furnish a hard-sized paper than when 35 per cent. of free rosin was used. The chief advantages of using a size containing a large amount of free rosin are the saving of considerable soda in making up the rosin soap and the saving of an enormous amount of alum or other precipitant used. It is quite probable that some classes of paper are sized best by means of free rosin, while others are sized best by resinate of aluminum.

30. Rosin size containing any amount or percentage of free rosin desired can, of course, be made by using less soda to dissolve it. When, however, a certain limit is reached, it is difficult to dissolve or to emulsify the size without causing the separation of raw rosin in sticky lumps, or masses. One of the best methods of dissolving and emulsifying high free-rosin size consists in injecting the boiling size into boiling water with a steam injector and then diluting the milk with cold water.

31. Brown Size.—In preparing **brown size,** about the same method is followed in the different mills, but different proportions are used. The rosin is first crushed and then shoveled into a hot solution of caustic soda in the mixing kettle. The boiling is continued cautiously until the rosin is saponified, the kettle being heated by either live steam or a steam coil. Any tendency of the size to boil over can be overcome by sprinkling a little cold water on it. The size should be well stirred during the boiling operation. The amount of caustic soda required varies from 18 to 22 pounds for each 100 pounds of rosin. Care should be taken not to use too much water, and the aim should be to keep the mixture at such a density that the size will float and the dirt will sink to the bottom. Salt is sometimes added to increase the density. Salt also causes the thick size to separate more thoroughly from the liquor. The separated black liquor is thrown away. The heavy size contains about 40 per cent. of water. The finished size should be drawn off and allowed to stand for about 1 week before it is used. When using, it is customary to dilute the size to a very thin solution containing over 85 per cent. of water.

32. White Size.—A very good method of preparing **white size** is the one patented by H. Hampel and Victor Zampis, of Vienna. This method has been used to some

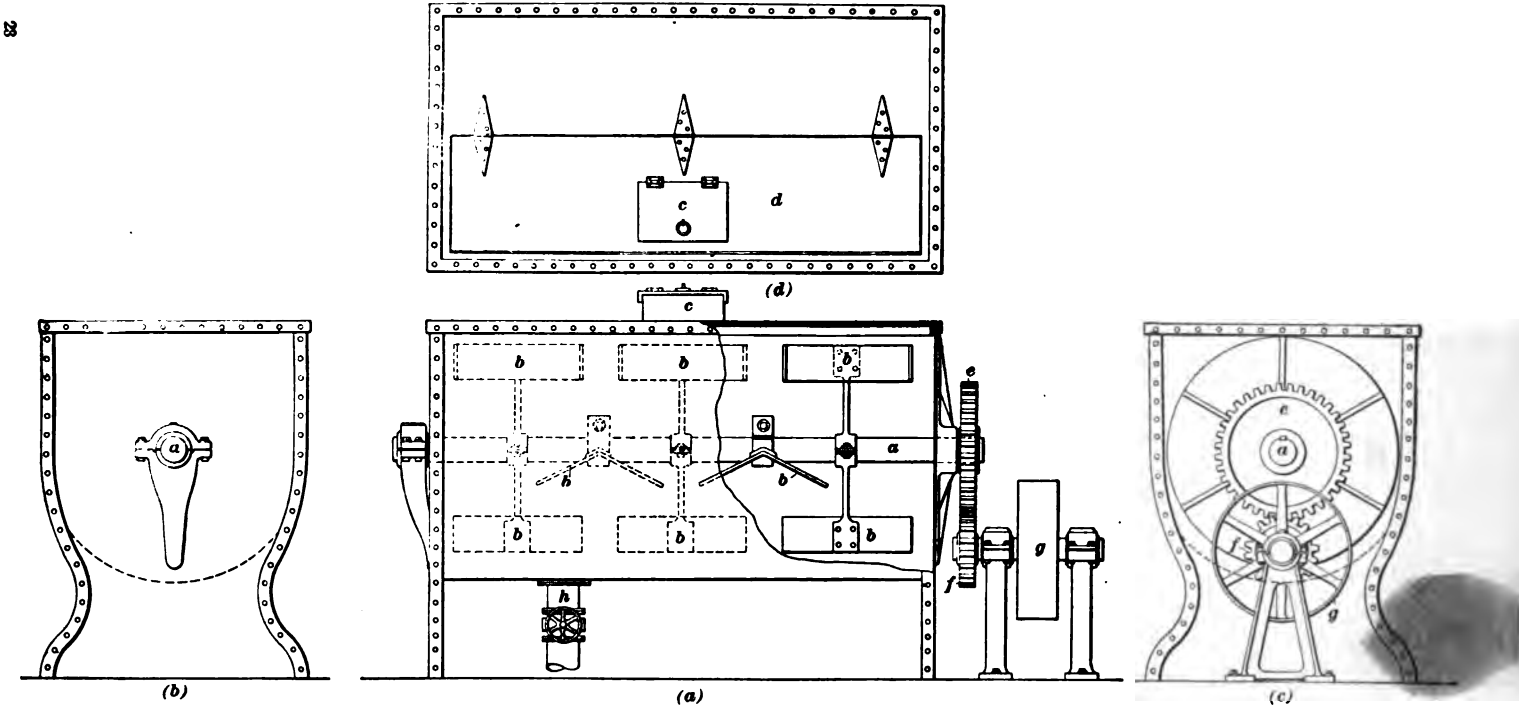


FIG. 9

extent in the United States. The apparatus for the preparation of white size consists of a large oblong tank, which has an agitator consisting of wings, or paddles, that revolve on a horizontal shaft. The cooking is not done under pressure. These tanks are of various sizes, but the proportions about to be given are for a tank that will hold 1 ton of rosin. The tank is covered by means of a large lid that has a small manhole in the top, which can also be covered, for introducing the ingredients.

Fig. 9 shows a side view (*a*), two end views (*b*) and (*c*), and a top view (*d*) of the tank used. In the figure, *a* is the shaft to which the agitator paddles *b* are attached. The shaft is run by the cog wheel *e*, which, in turn, is run by the smaller cog wheel *f* and the pulley *g*. There is a small opening, or manhole, *c* in the large door *d* on the top of the tank, through which the charge is added. When the cook is ready to be dumped into the tank, the valve *h* is opened. The dimensions of the tank shown in the figure are 4 ft. 3 in. × 2 ft. × 2 ft.

33. In making up the heavy size, 31 gallons of water is brought to a boil, the agitator started, 60 pounds of soda ash added, and the agitation continued for several minutes, to dissolve the soda. The steam is then shut off and 400 pounds of rosin, which has previously been finely crushed, is slowly added. The steam is then turned on gradually, and 1,600 pounds of rosin is added, care being taken that there is enough steam on to keep the rosin from getting too thick. The temperature is brought up to 180° F., the steam shut off, and 160 pounds of soda ash cautiously added. After all the soda ash is in, the mixture is agitated without steam for about 4 hours and then brought almost to a boil, being kept at this temperature for about ½ hour. The steam is then shut off, the agitator stopped, and the size dumped into the storage tank below. One cook will make about 300 gallons of heavy size.

The white size is made by mixing about 60 gallons of the heavy size with 2,000 gallons of water that has been heated to about 175° F., but the steam is shut off before adding the size. This mixture is agitated for about ½ hour and allowed to cool before using. A milk-white liquid containing much free rosin in emulsion is thus procured.

34. In another method of preparing white size, rosin is boiled with alkali and water under pressure in order to prevent the escape of the volatile resins. The operation of boiling is carried on in a cylindrical vessel, at the top of which is provided a manhole for charging purposes. The vessel is also provided with a perforated plate about 2 feet from the bottom, the object of which is to prevent the rosin from forming into a hard mass at the bottom of the vessel. The carbon dioxide generated is also retained; this, it is claimed, improves the size. When the cooking is complete, the rosin size is forced to the storage tanks by means of the pressure remaining in the boiler. Before adding the size to the stock, the excessive amount of water is removed from the latter by means of the drum washers and the washer is then raised. The quantity of size required is strained into the beaters in order to keep out any dirt that would otherwise enter the paper through this source. After adding the size, the stock should be allowed to circulate a short time, and the required amount of alum should then be added. This precipitates the combined rosin as resinate of aluminum, with the production of sodium sulphate,

$$3Na_2R + Al_2(SO_4)_3 = 3Na_2SO_4 + Al_2R_3$$

In the reaction expressed by this equation, R denotes resinic acids. The alum may be added in the dry state, but it is customary to dissolve it first, and knowing the strength of the solution, the amount required can be measured. The amount of alum needed depends on the amount of size used and the proportion of free rosin in the size.

35. Animal Size, or Glue.—In order to prepare **animal size, or glue,** the glue is mixed with water at a temperature of about 190° F. for from 10 to 15 hours, a little alum being generally added. The size is sometimes added to the stock in the beaters just before dumping, but it is generally added on the machines by a method called *tub sizing*, which will be described later.

36. Miscellaneous Sizes.—Starch is used to some extent as an auxiliary sizing agent, as are also sodium aluminate, sodium silicate, and casein. Casein is usually applied on the machine, and is used to give a coating or better finish to the paper; it is also used in about a 40-per-cent. solution in the beating engines.

Starch is prepared by boiling it with water, care being taken not to boil it too hard. It is only necessary to boil the starch until the globules burst. Too much boiling causes the starch to loose some of its viscosity.

Casein is the nitrogenous substance in milk, and in its original state is soluble in water. It is prepared for sizing by precipitation with magnesium sulphate or by heating milk to which sulphuric acid has been added.

37. Adaptation of Various Sizes.—The principal adaptations of the various sizing agents are as follows:

Rosin size is used to fill up the pores in the paper between the fibers and to make the paper waterproof, thus keeping ink from spreading to a greater or less degree, depending on the amount of size used.

Animal size is used mostly as a surface size. When used with rosin size, it makes the paper still better in the property of preventing ink from spreading. Animal size also gives the paper a better surface.

Casein size is of great value as a paper coating, as it gives the paper a good finish. The chief advantages claimed for casein size, however, are the production of a more elastic fiber and an increased yield of paper.

Starch at the present time is used mostly as a filler, making the paper stronger. It is claimed that paper in which starch is used has a better surface and feel. The value of the use of starch is very doubtful, as it is used in small quantities.

Sodium aluminate is sometimes used in place of sodium carbonate in preparing size. The size is added to the pulp in the usual manner and precipitated with either magnesium chloride or sulphate. Rosin, magnesia, and alumina are all precipitated at the same time, which is claimed to be an advantage.

Sodium silicate is used when a hard paper capable of producing a rattling sound is desired. It is strongly caustic and can be used in place of sodium carbonate, or it may be mixed with the size in the engine. When alum is added, there is formed a bulky, gelatinous precipitate of hydrated silicic acid, similar to precipitated alumina. The use of sodium silicate will produce a good, hard writing paper.

LOADING

38. In the manufacture of almost any kind of paper, except those of the very highest quality, it is customary to *load the stock;* that is, to add some comparatively cheap material, such as china clay, agalite, pearl hardening, etc., to the stock in the beaters, so as to give weight to the paper and also to make it less transparent and improve its surface. While, as has been stated, the appearance of a paper is greatly improved by loading, the strength of the paper is somewhat impaired, especially when a large amount of filler is used.

In some mills, it is customary to mix the filling material with water and to keep the mixture agitated continually. The strength of the mixture is known and the amount required is readily measured out, but in many mills the filler is added in the dry state.

39. The material most extensively used as a filler is a fibrous variety of magnesium silicate generally known as **agalite.** Preference is given to this material, because from 65 to 75 per cent. of it is retained in the stock. **China clay,** or **kaolin,** which is the purest form of aluminum silicate, gives a retention of almost 50 per cent.

Gypsum, or **calcium sulphate,** is used to some extent as a filler in high-class papers, but on account of its slight solubility, it does not give so good a retention as do the other two fillers just mentioned. Gypsum is sold as a filler, or loading agent, under various trade names, such as *pearl hardening*, *mineral white*, *wheelwright filler*, etc. Gypsum is not used in the raw state, but is generally burned to remove part of its water of crystallization. The retention of this filler in paper is only from 35 to 40 per cent.

Barium sulphate is sold under the name of *Blanc fix*, and an artificial compound of precipitated calcium sulphate and alumina is sold under the name of *Salem white*. Both of these compounds are used as a paper coating.

COLORING

40. Coloring is effected by adding dyestuffs or pigments to the stock in the beaters. There is a great variety of coloring matter that can be mixed with the stock to produce various shades in the finished paper. A yellow tint in the stock is neutralized by adding red or blue. The blues generally used are ultramarine, smalt, Prussian blue, and various aniline blues. The reds are usually prepared from cochineal or aniline dyes, but as the latter are affected by the use of alum, cochineal red is to be preferred. Alizarine and red ocher (oxide of iron) are also used to a great extent in producing red tints.

Yellows are produced by the use of yellow ocher, lead chromate, and some of the coal-tar dyes, the principal ones being metanyl yellow and auramine. Browns are produced by the use of pigments of the iron oxides, or the Bismarck browns (salts of triamido azobenzene). Greens are usually produced by means of malachite green or Victoria green; blacks, by the use of lampblack, Frankfort black, or blue black.

It is better to mix the coloring matters with water before adding them to the stock in the beater. The aniline colors should be dissolved in hot water and then diluted. Carmine should be dissolved in a little ammonia water and then diluted. Samples of the pulp treated are taken from time to time and matched against a sample of the paper that the paper maker is running, and the trained eye of the beaterman can readily determine when the desired effect is produced.

In order to obtain the color desired, it is first necessary for the beaterman in charge to try to match the color and then to calculate the amount of coloring matter required in the beater. This is best accomplished by mixing a definite amount of stock containing a known quantity of air-dry fiber with a convenient amount of water at about 80° F., and then adding the dyestuff from a burette, using a 1-per-cent. solution. After this the stock is squeezed out and matched, the amount of coloring matter calculated, and the required amount added to the beater.

The water from the paper machine, or *back water*, as it is called, should be used over again, and the amount of water on the machine should be so regulated that very little of it will go to waste. In this way, there will be a great saving in the loading and coloring matter, which would otherwise go to waste.

Before attempting to size or color the stock, it should be perfectly cold; otherwise, good results cannot be obtained. When the stock has been uniformly colored and well worked up in the beaters, it is passed to the Jordan engine, where it is finally prepared for the paper machines.

41. There are three classes of dyes used in the coloring of paper, namely, *acid aniline dyes*, which require acid or alum to bring out their brightest and strongest effect; *basic aniline dyes*, which show their best effect in alkaline solutions; and *substantation dyes*, which are fixed without the use of a mordant.

It is best to use only basic or only acid dyes whenever possible, and not some of each kind. The acid colors, as a rule, are faster to light than are the basic dyes. If both an acid and a basic color are to be used in coloring the same beater of stock, each color should be dissolved and added separately. If mixed, one will precipitate the other.

42. Following are the conditions to guard against in the coloring of paper:

1. *The fading of color.* This often occurs when colored paper is exposed to light or is brought into contact with

certain chemical substances. Care should be taken to select a color that will not fade when the paper is put to the use for which it is intended. The greatest difficulty along this line has been experienced in the making of colored paper for soap wrappers; it seems almost impossible to produce a paper the color of which will entirely resist for any length of time the action of the caustic alkali in the soap.

2. *Irregularity of color of the two sides of the paper.* Frequently, when pigments are used, the side of the paper next to the wire is not colored so well as the upper side. This is due to the fact that some of the coloring matter is drawn away from the lower sides by the suction boxes.

3. *Unevenness of the color.* This is generally due to mixtures of various fibers that have different affinities for the coloring matter used, and is very marked when chemical wood pulp is mixed with mechanical wood pulp.

MANUFACTURE OF PAPER FROM PULP

MAKING OF PAPER BY HAND

43. The pulp made by the various processes described is now in suitable condition for making into paper. For some fine grades of paper, this is done by hand, but by far the greatest amount of paper used is machine made. Both processes will be described.

44. In making paper by hand, the stock is passed from the beaters to vats. These are 5 feet square and 4 feet deep, and are provided with a steam pipe, to keep the pulp at the required temperature for working, and with an agitator, to keep the pulp and water well mixed. The stock is taken from the vat by hand in a mold. This mold consists of a frame that is covered first with heavy wire and then with a fine-mesh wire, upon which the sheet is formed. A movable frame is fitted upon the outside of the mold, which extends a little above the wire, forming a sort of wire-bottom tray.

The movable frame, termed the *deckle*, forms the edges of the paper, and should fit snugly to the frame. The stock is taken up in the mold, which is then shaken, the deckle removed, and the mold passed to another workman, who turns the sheet on a piece of felt, while the vatman forms another sheet. Felt is laid between all the sheets, and when about 50 deep, they are removed to a press, where the water is squeezed out. The sheets are then removed from the felts and are either hung up or laid out on a board to dry. They are then sized by spreading out the sheets in a vat of animal size, after which they are dried slowly, pressed again (preferably by running through calender rolls), and passed to the finishing room, where the specks are picked out, the imperfect sheets separated, and the balance counted and packed for shipment. Watermarked paper can be made by having the desired mark worked in wire on the bottom of the mold.

MAKING OF PAPER BY MACHINE

45. Paper Machine, or Fourdrinier.—In Fig. 10 is shown a **paper machine, or fourdrinier,** as it is called. The stock forms into a sheet upon a fine-mesh, endless wire cloth, the width of the sheet being regulated by means of a rubber strap, called a *deckle strap*, shown at *a*. The water from the pulp passes through the wire cloth, and the formed sheet is carried by means of a felt through press rolls and then over driers and calenders to reels.

The stock coming from either the Jordans or the beaters passes into a large cylindrical tank, called the *stuff chest*, which is made of either wood or iron and is provided with an agitator that extends to the bottom of the tank and is kept moving at a moderate speed. The stock is pumped from the stuff chest to the *regulating box*, which is a small box that is constantly kept filled by means of the inlet pipe at the bottom, the excess of stock being carried back to the stuff chest by an overflow pipe near the top. The discharge pipe leading to the screens is located near the bottom of the

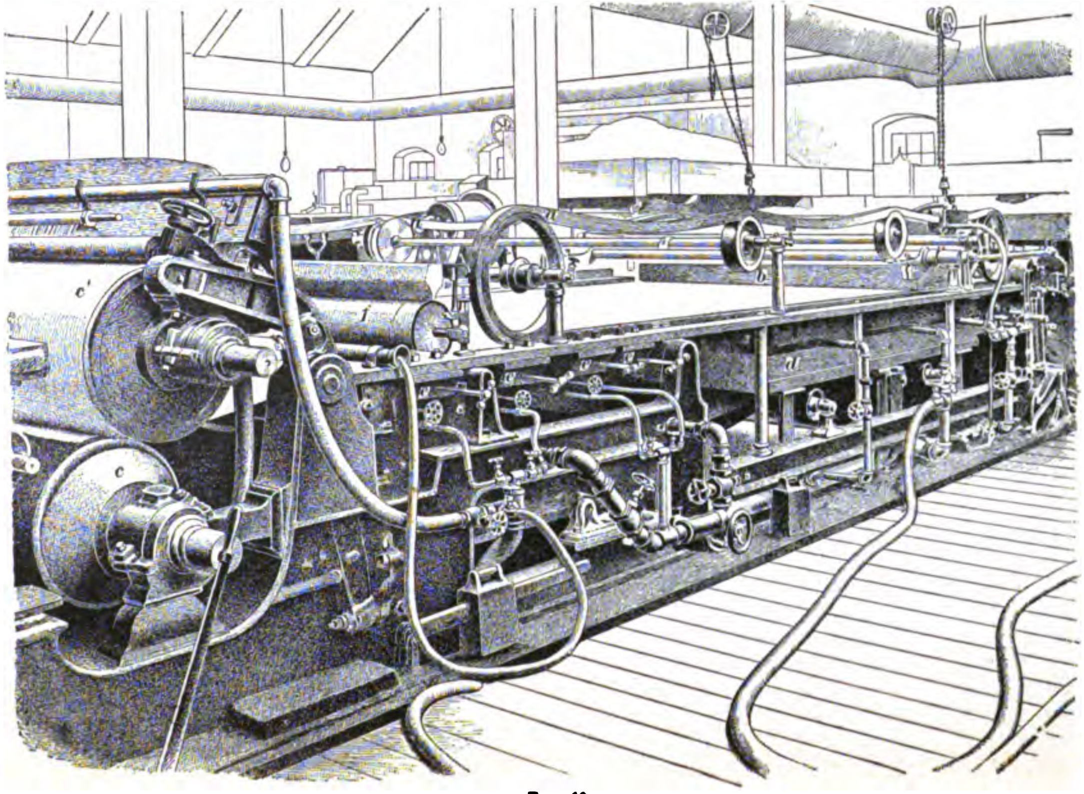


Fig. 10

regulating box, so that there is a uniform pressure at all times. The amount of stock furnished can be regulated by means of a cock on this pipe. In some mills, the stock passes from the regulating box over a *sand table*, which is a long, shallow box with a felt-covered bottom, having strips of wood placed across the direction of flow of the pulp. The object of this table is to hold back sand, etc. that has escaped removal by previous treatment. The stock then passes to the screens. However, it is not always customary to use a sand table, the stock going directly from the regulating box to the screens.

46. The *screens* are similar to those described in *Manufacture of Paper*, Part 1, and serve to remove any foreign matter, etc. that has escaped removal up to this point. After passing through the screens, the stock should be free from lumps and dirt and ready for making into paper.

Frequently, considerable trouble is caused by the frothing of the stock on the screens and also on the wires. Frothing is often caused by the liberation of carbon dioxide when hard water has been used in thinning down the stock. The addition of alum to the water before using it will usually help to prevent this occurrence; also, in some mills, a mixture consisting of 1½ gallons of linseed oil, 1 gallon of bleach, and 1½ gills of turpentine is successfully employed to prevent frothing.

After leaving the screens, the stock usually flows into what is called the *head-box*, entering at the bottom, where it is mixed with more water, which is furnished by a supply pipe. This box serves to mix the stock well before it flows on the wire; this it does by overflowing the box. The head-box also serves to catch any heavy particles of matter, as they will remain at the botton and can be washed out from time to time.

Between the head-box and the slicers is a heavy rubber apron that fits over the wires and extends across the full width of the wire and to within 1½ inches of the slicers. The purpose of this apron is to prevent any water from running through the wires and to bring the stock in its proper state of dilution and in a uniform stream right up to the slicers.

47. The beaters are sometimes so full that it is not possible to add sufficient water as they are dumped into the stuff chest. In such cases, the heavy stock goes to the bottom and is drawn into the pipe leading to the screens and thence to the head-box without being sufficiently diluted. On a heavy sheet of paper as high a difference as 5 pounds per ream will be caused by this variation in the thickness of the stock.

In order to overcome sudden changes of the consistency of the stock and to insure the production of a paper of uniform thickness and weight, the stock in a number of mills is passed from the stuff chest to a small box provided with a metal float. When the stock that enters this box becomes too heavy, the float rises and opens a valve, through which is supplied fresh water to thin the stock. When the stock is properly diluted, the float drops and automatically closes the valve.

In order to insure a good supply of stock to the stuff pump, the pipes leading from the chests should not be less than 4 inches in diameter. This pump should be capable of pumping sufficient stock to insure a good overflow when the paper machine is working at its best.

48. The thickness of the sheet is regulated by a gate, called the *slicer*. This device is made of two pieces of brass that are bolted together in the middle, and it can be lengthened or shortened to suit the width of the sheet. The slicer is placed near the point where the stock is passed on the wire, and can be regulated at different heights, according to the thickness of the sheet required, by means of screws. The height must be the same all the way across, so that the sheet will be uniform in thickness. The slicer is shown at *b*, Fig. 10.

The level of the stock behind the slicer should not be kept too high, or it will lap over the deckle strap and cause small knots to pass down on the edge. Only sufficient water should be used to close the sheet nicely, and there should be just enough shake to the wire to fill it evenly.

49. The *wire*, as it is called, is really an endless wire cloth, closely woven and having from 60 to 70 meshes per linear inch. The length of the wire is from 35 to 40 feet, and the width is usually from 100 to 130 inches, though some are made as wide as 160 inches. The wire passes around the lower couch roll *c*, Fig. 10, down under the save-all, and back to the breast roll. In its passage over the surface, the wire is supported by a large number of small brass rolls, called *table rolls*, and in returning to the breast roll, it passes over several small rolls. The frame has an attachment by which the wire is given a shaking motion from side to side, which serves to weave the fibers in their passage over the wire. Under the wire is situated the *save-all*, which is a shallow box *d*, Fig. 10, into which the waste water coming through the wire drops, and is used in place of fresh water for diluting the stock in the head-box referred to previously.

50. Near the end of the wire and under it are situated the *suction boxes e*, four of which are shown in Fig. 10. These are long, narrow boxes, which extend across the whole width of the wire and are connected with a vacuum pump. The cover of the box, which is very smooth, is perforated, and the water is further removed from the stock by having the wire pass over it. There is a screw arrangement at the end of the box by means of which plugs may be moved forwards or backwards, according to the width of the paper, so that the boxes will not lose their suction. These plugs are always kept in as far as the deckle straps.

The deckle straps *a*, Fig. 10, are heavy, square, rubber bands that rest on the wire and are carried along with it, thus regulating the width of the sheet.

51. The *dandy roll f*, Fig. 10, is situated near the end of the wire, and is used for making the "water mark" in the paper. It consists of a skeleton roll covered with a wire cloth, upon which the desired design is worked with fine wire. If the paper is required to be alike on both sides, with

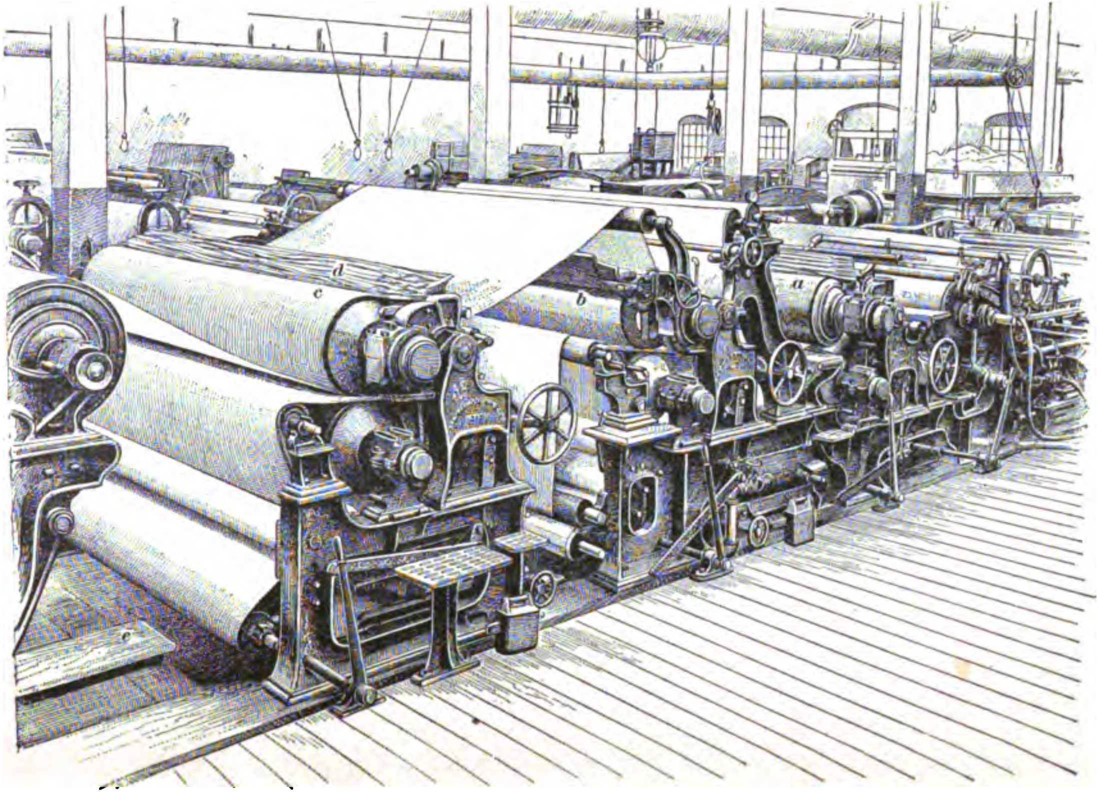


Fig. 11

no special design, the roll is covered only with wire cloth, the impression of which corresponds with the impression on the wire cloth.

Paper made in this way is known as *wove paper*. *Laid paper* is made by the dandy having a number of equidistant transverse wires upon its upper surface.

52. The paper passes under the dandy roll and is carried by the wire cloth between the *couch rolls c, c'*, Fig. 10, which are brass or wooden cylinders with a jacket of felt. In some machines, the top roll is made of wood and the bottom roll is made of iron covered with a layer of heavy rubber. There is a screw arrangement above the top roll by means of which the pressure can be regulated, thereby pressing the water out of the paper in its passage between the rolls. The paper is then carried, by means of felts and the assistance of the machine tender, through the press rolls proper. The number of press rolls varies on different machines, the machine shown in Fig. 11 having three sets, as shown at *a*, *b*, and *c*. The top roll of each set is provided with what is termed a *doctor d*, which keeps the roll clean by scraping off the pulp that sticks to it. The pressure on these rolls is also regulated by a screw arrangement. After passing through the last press roll, the sheet is transferred by the machine tender across an open space to the driers, or drying cylinders; this space *e* is wide enough for the machine tender to pass back and forth under the sheet.

53. These drying cylinders are large, hollow rolls and are heated by means of steam. The paper is carried by means of a drier felt over the series of drying cylinders, which vary in number on different machines, and can be seen in the distance in Fig. 12.

54. Tub Sizing.—After the paper has passed over a couple of the drying cylinders, it passes through a vat of liquid animal size and then between two rollers, which squeeze out the excess of size. The paper is then wound on a reel. In some mills, the paper is allowed to stand for a time and is then passed from the reels over a series of wooden drums furnished with fans, by means of which the paper is dried slowly. The most general custom is to pass the paper from the squeeze rolls over another series of driers, and thus keep the sheet in continual motion. After passing over the driers, the sheet is transferred to the calenders.

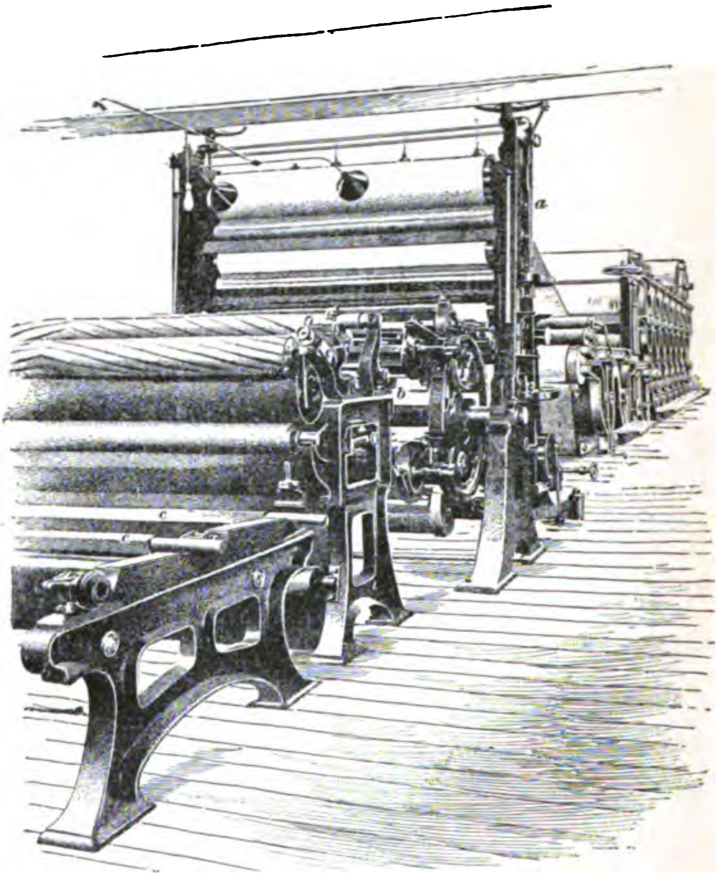


Fig. 12

55. Calendering.—In the operation known as **calendering**, the paper is given a high finish by pressing it between rolls on a machine called a *calender.* Calenders consist of a series of highly polished, revolving, iron cylinders that have a screw arrangement at the top for regulating the pressure. The number of cylinders on different machines varies, some having as high as three sets; the machine shown in Fig. 12 has only one set *a*. The paper passes over these rolls, acquiring a high finish, and thence to the reels shown at *b*. In order to give a strong glaze to the surface of the paper, one or more of the calender rolls are kept hot by passing steam through them; and, again, in order to produce what is known as a *water finish*, some of these heated rolls are also kept wet. There are usually two reels in a set, and after one has been wound to the desired thickness, the paper is cut and started on the other reel. When rewinding into rolls, only one sheet is wound at a time, being passed from the reel around a smooth brass roll and through the *slitters*, which are small, sharp-edged, revolving wheels. The slitters are arranged so as to divide the sheet into two or more sheets of equal size. The sheets formed in this manner are rewound on cores attached to shafts *c*, which are clamped down and made to revolve by means of a friction clutch.

When laying the paper in sheets at the end of the machine, as many as five reels are slit and cut at one time, as will be explained further on.

By the use of the paper machine just described, there is a continuous sheet of paper forming, passing over the machine, and winding.

56. Supercalendering.—It is sometimes necessary to have an extra-high finish on the paper; this is done on the glazing calenders, which are generally called *supercalenders.* These machines are also of various types, one being a series of rolls that are alternately of highly polished iron and compressed paper, the iron rolls being hollow and heated by steam. Another type consists of a stack of highly polished, chilled-iron rolls. The rolls are bored out and can be heated by steam; also, there is an arrangement by which one or more of the rolls can be raised, according to the finish required.

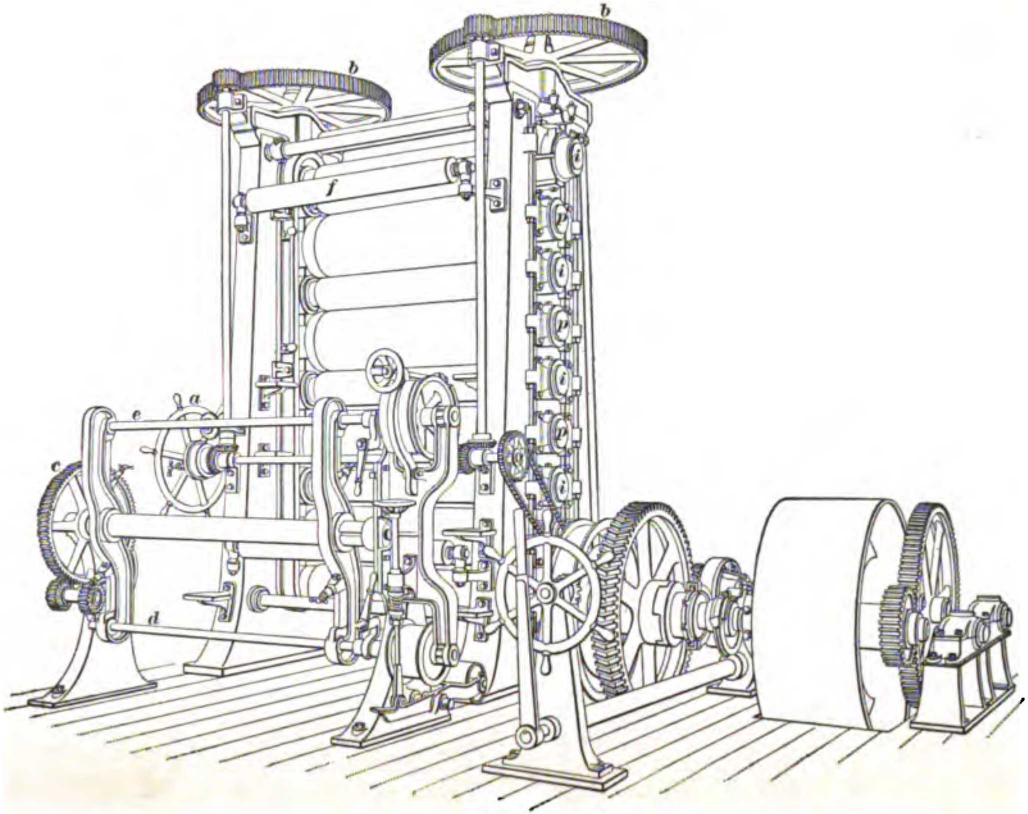


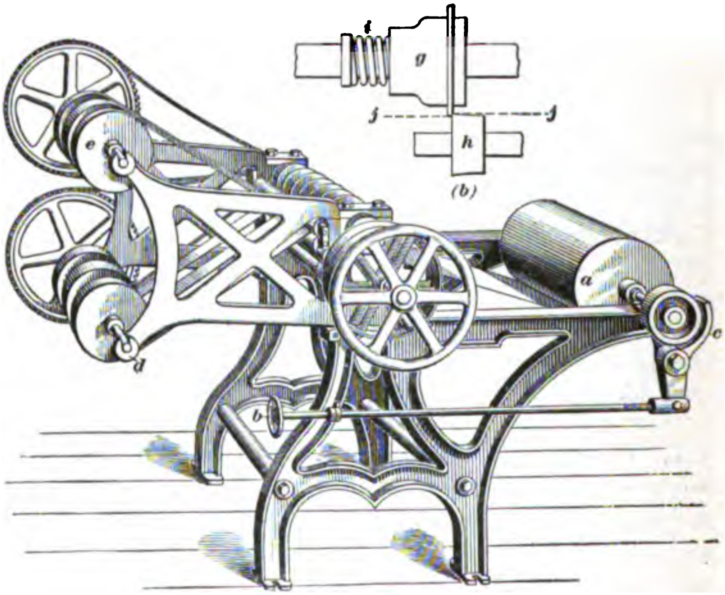
FIG. 13

The supercalender in most common use is shown in Fig. 13. It consists of a stack of rolls that are alternately of highly polished iron and compressed paper, neither of which is heated by steam. These rolls are pressed down against each other by turning a wheel *a*, which operates the large wheels *b* at the top of the calenders. The lower roll is made to revolve at a high speed, and by means of the friction exerted on the second roll, it revolves in the opposite direction, and in a like manner all the other rolls revolve at a high speed. Owing to the great friction on these rolls, they become very hot. The iron and paper rolls are designated by the letters *i* and *p*, respectively.

The roll of paper to be calendered is transferred from a small truck to the bar *d*, when, by turning a crank at *c*, the position of the roll is changed to *e*. The sheet is then passed up to a machine tender, who passes it under a brass roll *f* and then around the rolls of the calender, finally winding it on a core placed on the rod *d*. It is customary to have a perforated steam pipe extending across each side of the machine, so that a little steam can strike both sides of the sheet as it starts over the calenders. The paper coming from the calenders has a very high finish, and is transferred to the slitting and rewinding machine.

57. Cutting the Paper.—Very frequently, as previously stated, the paper is cut at the end of the paper machine, where the large reels of paper are first slit by means of small, sharp-edged wheels, under which it passes before coming to the main knife, which is a knife projecting from a revolving drum and extending across the whole width of the machine. This knife operates by passing closely against a dead knife, over which the paper passes. At every revolution of the drum, the paper that has been previously slit is cut into sheets of uniform size. These sheets drop upon traveling belts made of felt, from which they are lifted by girls or boys and placed in stacks, which operation is termed *laying the paper*. These stacks are removed to trucks and conveyed to the finishing room. It is customary to slit and cut several different reels at the same time, and in place of one sheet, there are two or more sheets laid at one time in the same stack.

When rewinding at the end of the machine, large rolls from the machine are generally slit into smaller rolls. When making paper that is to go to the supercalendering room, it must come from the paper machines in rolls, which after supercalendering, are transferred to the cutting department, where they are cut into sheets and laid as just explained.



(a)

FIG. 14

58. Slitting and Rewinding Machine.—In Fig. 14 is shown a **slitting and rewinding machine** that slits and rewinds one large roll into six small ones.

The large roll is placed on a reel, as shown at *a*. This reel can be made to run easy or hard, as desired, by turning a screw arrangement *b* that regulates the brake *c*. The end of the paper is then passed through the slitting knives, which are so arranged as to regulate the size of the smaller rolls desired, and thence to cores attached to the reels *d* and *e*, which are run by cogs and chains attached to cogs on the slitting-knife shaft. When the machine is in motion, the winding of the smaller rolls causes a continuous pull on the sheet. This unwinds the large roll, so that by tightening the brake *c* the smaller rolls are rolled tighter.

The slitting knives are similar to those at the end of a paper machine, one pair being shown in Fig. 14 (*b*). The cutting surfaces are slightly hollowed out, so as to make them sharp. The knife *g* is held against the knife *h* by the spring *i*. The sheet of paper passing through the knives is represented by the dotted line *j j*.

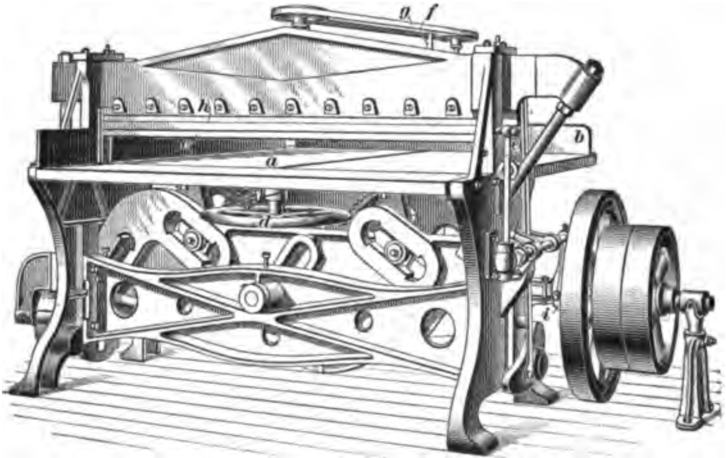


Fig. 15

59. Guillotine Paper Cutter.—The **guillotine paper cutter**, which is shown in Fig. 15, is used for trimming the edges of paper and also for cutting a large number of sheets at one time. This machine is provided with a gauge by means of which the size of the sheet cut can be regulated.

The sheets of paper to be cut are placed on the bed *a* in packs from 3 to 4 inches thick, touching the back support *b*, which can be moved backwards or forwards by turning the wheel *d*. This support is connected by means of an upright rod *f* with an endless measuring tape *g*, and the size of the sheet is read off at the pointer in front of the tape. By giving the lever *e* a slight turn and pushing it to one side, it forces a friction clutch *i* against the pulley and sets the machine in motion. The clamp *c* and knife *h* descend, and when the clamp reaches the paper its progress is arrested, thus holding the paper tight while the knife passes on down through it. The machine is so regulated that as soon as the knife has passed through the paper, the clamp and knife return to their original position. This upward-and-downward motion is kept up as long as the friction is kept on; but as soon as the lever is allowed to resume its original position the machine stops.

60. Finishing the Paper.—After cutting, the paper is passed to the finishing room, where it is counted, sorted, and packed for shipment. The sheets are gone over in this room by girls, and the defective sheets are thrown to one side, to be used up as "broke" or sold as an inferior quality of paper. The sheets that pass inspection are either packed in boxes or tied up with heavy wrapping paper, a wooden frame being placed on each side of the package so as to prevent the paper from being damaged in shipment. The sheets are packed up in reams, which consist of from 480 to 516 sheets. The rolls of paper are also well done up before shipping.

Papers are generally sold by weight; therefore, the weight per ream is also expressed when distinguishing between them. Thus, 26 × 40—80—500 means a ream of 500 sheets 26 in. × 40 in. and weighing 80 pounds.

PASTEBOARD AND PARCHMENT PAPER

61. Pasteboard, or Cardboard.—In the manufacture of **boards** all kinds of waste material occurring in the mill may be used, being sorted according to the quality of the board desired. After being well beaten, the material is mixed with a suitable amount of rag pulp, clay, etc. The boards are manufactured by superposing several sheets of paper and causing them to unite (1) by a sizing mixture; (2) by superposing several wet leaves at the time of couching; (3) by molds provided with thick deckles; or (4) by machines similar to paper machines, but having no drying cylinders, allowing the boards to dry in the open air.

62. A method employed in making cardboard with two different faces is as follows: Two pulps are mixed separately, and the first is run on the wire of a paper machine. When the water drains off to some extent, the second material, highly diluted with water, is run on—better, after the first pulp has passed over the first suction box—the water from the second draining off through the first. The paper is then passed over the machine in the ordinary way.

A good cardboard is made from shoe linings mixed with No. 1 linen rags, the larger amount being shoe linings. Cardboard made of these materials is hard-sized and has a smooth, erasable surface.

High-grade mill bristols are made of a small percentage of rag pulp, the balance being wood pulp, mostly spruce. These boards are surface-sized and allowed to dry.

Card middles, which are used for making shoe boxes, are covered on one side with coated paper. They are made of ground wood on a cylinder machine. Old printed paper is also used.

Tag boards are made mostly from spruce sulphite; some tag boards have ground wood mixed in. Jute is also largely used.

Straw is used extensively in the manufacture of the cheaper quality of boards.

63. Parchment Paper.—In making **parchment paper,** white unsized paper is dipped for ½ a minute in strong sulphuric acid of 60° Baumé and afterwards in water containing a little ammonia. The acid converts part of the cellulose into hydrocellulose, which gives the paper a gelatinous surface. Paper treated in this way becomes translucent and much stronger. In other methods, ammoniacal-cuprous-oxide solution or zinc chloride is used instead of sulphuric acid.

WATER AND ITS PURIFICATION

REMOVAL OF ORGANIC IMPURITIES

64. Water is one of the most important factors in the manufacture of paper, as it is impossible to make good papers with the use of impure or dirty water. There is such a large quantity of water used around a paper mill that the problem of water purification is of great importance.

Almost every paper mill has in connection with it a filtering plant, the size of which varies with the amount of water used and the condition of the water before filtering. If the water is very hard, it should undergo the usual treatment for boiler purposes; but for the manufacture of paper, the principal factor to be considered is the organic impurity. This causes the growth in the water of what are termed *Algæ*, which form a kind of slime, coating the pipes and eventually causing the appearance of slime spots in the paper.

65. Filtration.—The aim of the paper maker is to remove the organic impurity from the water, which is very successfully accomplished by the use of the Warren or the Jewell type of gravity filter. In each of these systems, the water undergoes a preliminary treatment, as follows:

66. In the *alum treatment*, the water is first pumped into a deep box, and before passing on to the settling basin it is treated with a solution of sulphate of aluminum, as follows: The alum is mixed up strong in one tank and then run into another tank, where it is diluted to the required strength; it then passes through the pipe *i*, Fig. 16, and valve *h* to a small oblong box *C*, from which it is conveyed by the alum pump to the incoming water. The valve is provided with a ball float *g*, which is so arranged that it will close the valve and stop the flow of the solution of alum when the box is full, thus preventing the alum from overflowing. The faster the pump works, the more alum solution flows into the box, so that it is kept at the same level all the time.

The alum pump is operated by means of a turbine wheel, which is fastened to the side of the deep box previously mentioned, right over the opening from the box to the narrow runway, so that all the water entering the runway must pass through the turbine wheel. There is a gearing on the rod *f* at the turbine that causes the rod to rotate, the speed varying with the speed of the turbine, and hence with the flow of water. The rod *f* has a similar gearing where it meets the gear-wheel *e* of the alum pump, which it causes to rotate. The pump consists of long, hollow arms *a* bent in the direction of the rotation. These arms when rotating pass through the alum solution, each one taking up its allotted portion of the same and conveying it to the drum *b*. From the drum, the solution is conveyed by six long tubes *c* to the bell *d*, where it is discharged. The bell is so arranged that it is outside of the box *C*, and deflects the alum solution so that it is deposited in the funnel *j* at the side of the box and conveyed to the incoming water.

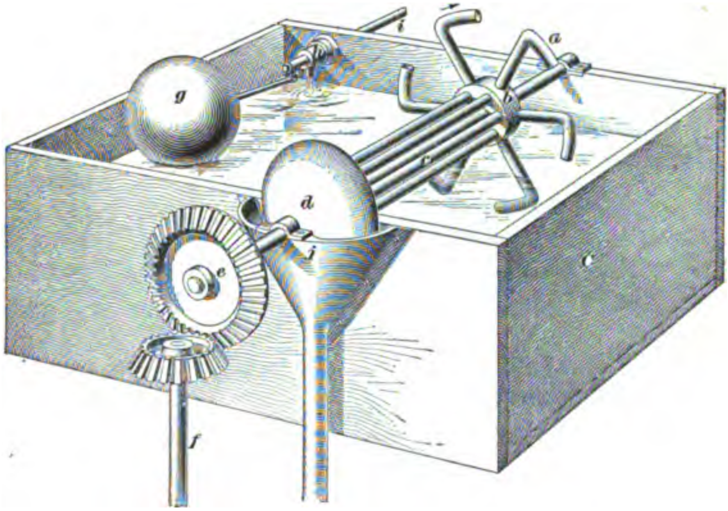


FIG. 16

67. After treatment with the solution of alum, the water, when using the Warren system, passes through a long settling basin so arranged that it moves slowly out to the end of the basin, passes around a partition that extends down to the center of the basin, and returns on the other side. The size of this settling basin varies with the condition of the water to be treated. In some cases, from 45 minutes to 1 hour is required to make the passage around the basin, but usually only from 25 to 35 minutes is required.

The object of the settling basin is to give the alum plenty of time to act and thoroughly coagulate the organic matter, some of which settles to the bottom of the basin, while the remainder passes into the filters.

This is a very convenient arrangement, as it requires no special attention and supplies a uniform proportion of alum to the water; for as the flow of the water varies, the speed of the pump varies, and, therefore, the flow of the alum solution will vary. When the quantity of alum is to be reduced, it can be accomplished by plugging up one or more of the arms; hence, the operator generally speaks of using so many "plugs" of alum, meaning the number of arms that have been left open. If the water contains considerable organic matter, it is customary to use about 1 grain of alum to every gallon of water filtered.

The following analysis shows the composition of a good alum for filter-plant use:

	Per Cent.
Sulphate of aluminum	53.98
Sulphate of iron	.42
Insoluble	.71
Free alumina	.52
Water	44.37
Total	100.00

There are several forms of pressure filters used in some mills, but the gravity filters are the ones most generally adopted.

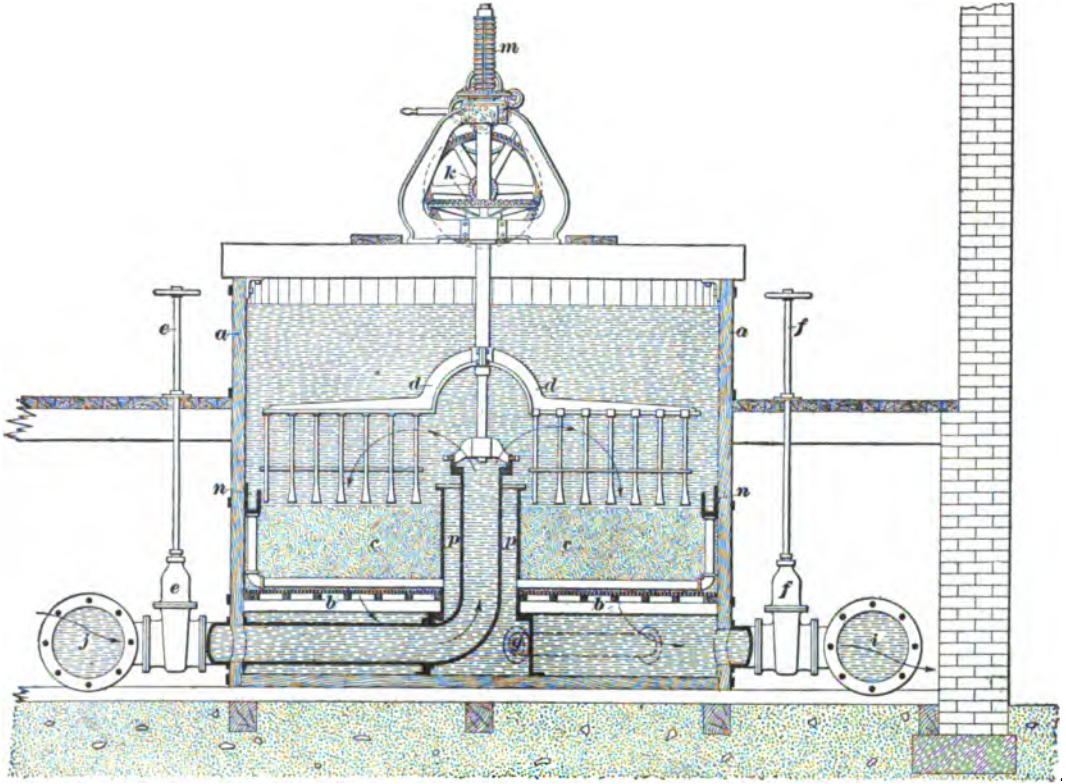


FIG. 17

FILTERS

68. Warren Filter.—The **Warren filter,** which is shown in Fig. 17, is usually constructed of wood and is 8 feet in diameter, having a bed with an area of 50 square feet. This filter contains from 20 to 24 inches of quartz sand *c*, supported on a perforated copper bottom *b*. The unfiltered water from the settling basin enters from the main *j* through the valve *e*, passes up into the filter tank *a*, and thence downwards through the bed of sand *c*, the perforated plate *b*, and through the valve *f* to the filtered-water main *i*, through which it is conducted to a storage tank. When it becomes necessary to clean the filter, which will be evident from its sluggish action, the valve *e* is closed, shutting off the unfiltered water, and the valve on pipe *g* opened, allowing the water in tank *a* to pass into the sewer. When the level in *a* falls, the water flows back from the main *i* up through the bed of sand *c*, passing down the space *p* and gutter *n*, and then through waste pipe *g*. While this operation is going on, the agitator *d*, which should be set in motion as soon as the water commences to flow back through *i*, is caused to revolve by means of the mechanical arrangement *k*. While the agitator is in motion, the teeth of the rake, which is lowered mechanically by the screw *m*, stirs up all the sand. When the water flowing up through the bed becomes clear, the agitator is raised and the waste pipe closed, and when the tank is partly filled, the valve *e* is opened and filtration is carried on as before.

Each 8-foot filter, when using alum, has a capacity of about 250,000 gallons in 24 hours.

69. Jewell Filter.—In the **Jewell filter,** which is shown in Fig. 18, the water coming direct from the alum treatment enters the subsidence basin *a* through inlet valve *i*, which is located a short distance above the bottom. This water is deflected in front of the inlet valve and flows slowly around the basin, thus depositing a great deal of the sediment before reaching the filter bed. In order to reach the filter bed, the water passes up through the central stand pipe *b* and overflows. Enough water is kept above the sand to prevent the incoming water from cutting channels through it. The Jewell filter differs from the Warren filter in being a double tank, and instead of having a perforated plate, it has a bottom made up of a series of small strainers, which empty into small horizontal pipes. These pipes empty into larger ones *c*, and thence into the main outlet pipe *h*. These strainers catch any sediment that passes through the sand.

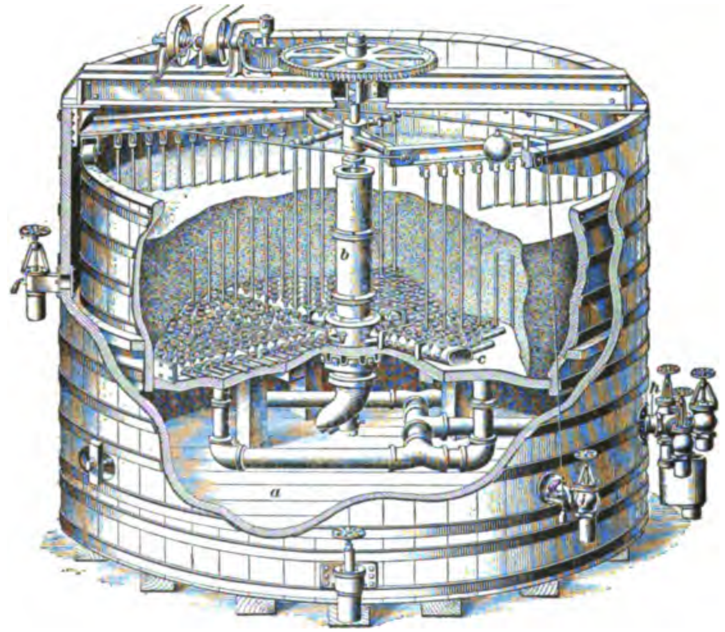


FIG. 18

In washing the Jewell filter, the rakes of the agitator, which is set in motion, stir up the sand, and the water passing through it flows over the side of the inner tank into the outer tank, and thence out at the valve *f*.

70. The coagulant used in both the Jewell and the Warren filter is generally sulphate of aluminum, which is precipitated as hydrate by the alkalinity of the water, which, if not alkaline enough, should have a small amount of caustic lime added to it. This flocculent hydrate coagulates the organic matter present in the water and carries it down, thus freeing the water of its impurity.

MANUFACTURE OF PAPER

(PART 3)

ANALYSES AND TESTS OF MATERIALS USED AND OF FINISHED PRODUCTS

APPARATUS AND CHEMICALS

1. This Section will deal with methods of analysis of the chemicals, liquors, etc. used in the manufacture of paper, and will also contain methods of making several quick tests, by means of which the manufacturer may be enabled to operate his plant on an economical basis.

It is important that the chemist in charge shall have on hand from the outset all the apparatus and chemicals that are likely to be needed at any time. Therefore, in order to give an idea of what will be required, a list of the apparatus and chemicals necessary for this purpose is here given.

2. Apparatus.—The following apparatus will be found necessary for the analytical work about to be described: A sensitive balance (enclosed in a glass case, the interior of which should be well desiccated) provided with a rider beam divided into tenths of milligrams, and a set of weights ranging from 1 milligram to 100 grams; one large and one small desiccator; several air-tight boxes with screw lids, for taking pulp samples; one large steam bath (which should be connected with a still); one hot-air bath and one water bath for slow evaporation; porcelain dishes, sizes 4 and 6 inches;

measuring flasks of the following capacities: 20, 50, 100, 250, 500, and 1,000 cubic centimeters, when filled to mark on neck; plain ungraduated flasks of the following capacities: 100, 250, 500, and 1,000 cubic centimeters; several 50-cubic-centimeter burettes, graduated into cubic centimeters and tenths of cubic centimeters, each provided with a stand; a set of pipettes, including the following sizes: 1, 2, 5, 10, 25, 50, and 100 cubic centimeters; a set of graduated cylinders of the following capacities: 100, 500, and 1,000 cubic centimeters (preferably glass-stoppered for mixing standards); several ungraduated cylinders, each having a capacity of about 200 cubic centimeters; beakers, lipped Griffin shape, from Nos. 1 to 6; watch glasses of various sizes and a pair of ground glasses and clips; one iron, one large porcelain, one small porcelain, and one agate mortar, with pestle; funnels of various sizes; a separating funnel; glass and rubber tubing, various sizes; a platinum dish having a capacity of 50 cubic centimeters; platinum crucibles, 15 and 25 grams capacity, respectively; platinum triangles for crucibles, and light and heavy platinum wire; ring-lamp stands and Bunsen burners; test tubes, various sizes; porcelain crucibles, various sizes; a condenser for distilling liquids; filter paper, various sizes; a filtering stand; a set of reagent bottles; sample bottles, various sizes; several liter bottles for standard solution; a wash bottle; a drying apparatus and train for CO_2 determinations; thermometers, 212° F. and 200° C.; short-stem Baumé hydrometers of the following ranges: 3° to 4°, 0° to 5°, 0° to 8°, 0° to 15°, and 15° to 40°; stirring rods; forceps; spatulas; and pinch cocks.

3. Hydrometers.—The **hydrometer**, whether it be on a Twaddell or a Baumé scale, is very useful about a paper mill. This instrument is used in all departments of the mill for the efficient regulation of the strengths of solutions used. The reading of the hydrometer is affected by the temperature, an increase in temperature decreasing the density of solutions. For this reason it is customary to add 1° Baumé for each 30° of temperature over 60° F. This allowance, however, will only hold good for temperatures up to about 150° F. A greater allowance should be made for temperatures above this, about 4½° Baumé being allowed for a temperature of about 185° F.

4. Drying Ovens.—There are several kinds of **drying ovens,** some of which are filled with water and heated by means of a gas burner under the bath.

The bath shown in Fig. 1 has proved on all occasions to be a very convenient form of drying oven. It consists of a

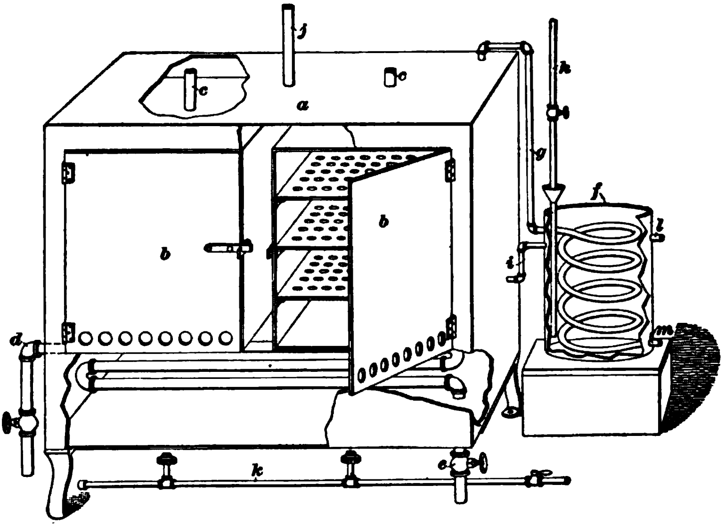


Fig. 1

large copper box *a*, which has two drying compartments *b* closed by means of doors perforated at the bottom, each having a chimney *c* extending to the outside, to permit the free passage of air through the bath. In each compartment there are perforated shelves, which can be removed if desired. The compartments are so arranged that steam circulates all around them. The bath is connected with the still *f*, which serves as a feed for it by means of the small connecting pipe *i*, the water in the bath being kept at a constant level with the overflow pipe *l* of the still. The pipe *g* comes from the top of the bath and connects with the worm of the still, the distilled water escaping at *m*. The cooling water is furnished to the still through pipe *h*. The still is at such a height that the bath is always half full of water, which is kept at a slow boil by means of the steam coil, which enters at *d* and passes out at *e*. A pipe *j* extends into the bath between the two compartments, and is provided with a valve, which when open stops the preparation of distilled water. As a precaution against the steam being turned off, a gas line *k* provided with two burners is run under the bath.

5. **Knöfler Oven.**—The **Knöfler drying oven** is so arranged that the sample to be tested can be suspended on a balance beam and lowered into the drying compartments by means of a wire cage. The weight of the pulp can be read off at any time. This oven is convenient in that it is easy to determine when the pulp has become quite dry.

6. **Chemicals.**—The following is a list of the **chemicals** necessary for all analytical tests given in the following pages. All chemicals used should be chemically pure or what is known as "analyzed chemicals."

Hydrochloric acid
Sulphuric acid
Nitric acid
Acetic acid
Oxalic acid
Arsenious acid
Sulphanilic acid
Alcohol
Aniline sulphate
Ammonium oxalate
Ammonium phosphate
Ammonium sulphide
Ammonium chloride
Ammonium sulphocyanide
Methyl orange
Manganese chloride
Barium hydrate
Barium chloride
Barium peroxide
Bromine
Calcium chloride
Ether
Carbon bisulphide
Iron perchloride
Iron protosulphate
Iron piano wire
Iron sulphide
Lead acetate
Lead peroxide
Mercury
Sodium sulphate
Sodium phosphate

Marble chips
Phenol
Platinic chloride
Phloroglucine
Phenol phthalein
Potassium iodide
Potassium ferrocyanide
Potassium permanganate
Potassium bisulphate
Potassium chromate
Potassium sulphate
Potassium sulphocyanide
Potassium chlorate
Potassium hydrate
Sodium carbonate, dry
Sodium chloride
Sodium sulphite
Sodium hydrate
Sodium acetate
Sodium nitrate
Soda lime
Silver nitrate
Starch
Zinc sulphate
Zinc chloride
Zinc oxide
Zinc shot

7. Standard Solutions.—The following **standard solutions** will be found necessary:

Normal sulphuric acid
Normal hydrochloric acid
Normal oxalic acid
Normal sodium hydrate
Normal sodium carbonate
$\frac{n}{10}$ sulphuric acid
$\frac{n}{10}$ sodium hydrate
$\frac{n}{10}$ sodium arsenite
$\frac{n}{10}$ iodine
$\frac{n}{10}$ sodium chloride
$\frac{n}{10}$ silver nitrate
Standard potassium permanganate
Standard size

Note.— $\frac{n}{10}$ **means tenth normal.**

8. The preceding standard solutions used in volumetric analysis are made up as follows:

Normal sulphuric acid should be made up very carefully, as it will furnish a good standard, by the aid of which all the other standard acids and alkalies can be made up Take 30 cubic centimeters of H_2SO_4 of about 1.84 specific gravity and mix with about 200 cubic centimeters of water. After cooling, transfer to a graduated mixing cylinder and dilute to

1 liter. Two samples are taken to standardize, or rectify, this standard. They should be measured carefully from a clean burette that has first been rinsed with some of this acid. Take the two samples, one of 10 cubic centimeters and the other of 20 cubic centimeters, and dilute to about 250 cubic centimeters in separate beakers. Bring to a boil, and, while stirring, precipitate with a $BaCl_2$ solution containing 1 gram of $BaCl_2$ in 10 cubic centimeters of water, taking care that all of the sulphuric acid is precipitated. Allow this to settle for about 2 hours, filter, wash well with hot water, dry, ignite, and weigh as $BaSO_4$. The amount of H_2SO_4 in each sample is found, the two tests averaged, and the weight of H_2SO_4, in grams, in 1 cubic centimeter of the acid solution calculated. This divided into 49 will give the number of cubic centimeters required to make 1 liter of the normal acid. In practical work, it will be found that much time cannot be spent in making up standard solutions, and it is therefore advisable to save this well-rectified standard and to use it for no other purpose than that of checking other standards.

Tenth normal $\left(\frac{n}{10}\right)$ *sulphuric acid* can be prepared by measuring 100 cubic centimeters of the normal H_2SO_4 in an accurately graduated pipette that has been well cleaned and rinsed with the acid. The contents of the pipette is carefully rinsed into a liter flask and diluted to the mark. This standard can be rectified, if desired, in the same way as in the preceding case.

Normal sodium carbonate is prepared by weighing out about 53 grams of dry sodium carbonate, dissolving in about 500 cubic centimeters of hot water, cooling, transferring to a liter flask, and diluting to the mark. This should be matched against the normal acid, using methyl orange as an indicator.

Normal sodium hydrate is prepared by dissolving 50 grams of $NaOH$ and diluting to 1 liter. Match against the normal acid, using methyl orange as an indicator. Dilute, if necessary, until 1 cubic centimeter is just equivalent to 1 cubic centimeter of normal acid.

Tenth normal $\left(\frac{n}{10}\right)$ *sodium hydrate* can be made by carefully measuring 100 cubic centimeters of the normal solution and diluting to 1 liter. This can be verified by matching against $\frac{n}{10}$ sulphuric acid.

Normal hydrochloric acid is prepared by taking 100 cubic centimeters of HCl (1.2 specific gravity), diluting to 1 liter, and matching against normal soda solution, using methyl orange as an indicator. This acid can be further rectified by precipitating with silver nitrate and calculating the number of cubic centimeters necessary to make 1 liter of strictly normal acid, as in the rectification of normal sulphuric acid.

Normal oxalic acid is made by dissolving 63 grams of pure crystals of oxalic acid in distilled water and diluting almost to 1 liter. This normal solution can be rectified by matching against a strictly normal alkali. It should be kept in a dark place.

Tenth normal $\left(\frac{n}{10}\right)$ *sodium-arsenite solution* is prepared as follows: Dissolve 50 grams of sodium bicarbonate in about 200 cubic centimeters of hot water and add 4.95 grams (accurately weighed) of chemically pure, dry, powdered arsenious acid, As_2O_3. Cover the beaker with a watch glass and allow the contents to remain almost at a boil, stirring from time to time, until all the arsenious acid is dissolved. Cool, transfer to a liter flask, and dilute to the mark.

Arsenious acid dissolves more readily in the normal carbonate, but its use is not advisable, owing to secondary reactions, which interfere with the reaction between sodium arsenite and iodine.

Tenth normal $\left(\frac{n}{10}\right)$ *iodine solution* is prepared by dissolving 12.7 grams of iodine with 18 grams of potassium iodide in 100 cubic centimeters of distilled water. If the potassium iodide is dissolved in a small amount of water, as directed, and the iodine then added, solution will take place very readily. The solution should not be heated. When dissolved, the iodine solution is transferred to a liter flask and diluted almost to the mark. In order to rectify this $\frac{n}{10}$ solution, it is matched against the $\frac{n}{10}$ sodium arsenite, using starch as an indicator.

Standard potassium-permanganate solution is prepared as follows: Dissolve about 3.25 grams of pure crystals of potassium permanganate in 200 cubic centimeters of distilled water. Filter through a layer of asbestos, cool, dilute to about 1,000 cubic centimeters and mix thoroughly. The value of this solution in terms of iron is determined by titrating a solution containing a known quantity of iron. This can be done by the use of a solution of piano wire that is known to contain 99.6 per cent. of iron. Take a small flask having a capacity of about 250 cubic centimeters, and fill it one-third full of dilute sulphuric acid (1 volume of acid to 3 volumes of water); then add a few grains of sodium-carbonate crystals. Weigh accurately .2 gram of the wire into a flask, close with a rubber stopper provided with a valve, as shown in Fig. 2, and heat gently. When the wire is all dissolved, the flask is cooled as rapidly as possible and the contents rinsed into a large beaker partly filled with recently boiled distilled water. This solution is now diluted to about 500 cubic centimeters and titrated with the permanganate solution until the faint pink tint is permanent. Since the iron wire is only 99.6 per cent. pure, there has been dissolved in reality only .2 × .996, or .1992 gram of pure iron. If it requires 25 cubic centimeters of permanganate, 1 cubic centimeter will be equivalent to .1992 ÷ 25, or .007968 gram of iron.

Standard size solution is prepared as follows: Dissolve 20 to 25 grams of good, heavy rosin size in about 250 cubic centimeters of 95-per-cent. alcohol, filter, and dilute almost to 1 liter with a 60-per-cent. alcohol solution. Add a little phenol phthalein and then add a solution of caustic soda, drop by drop, from a burette, shaking after each addition, until a faint pink color appears. This neutral-size solution is used as a standard after first determining its value. The value is determined by means of pure crystallized potassium alum, 1 part of which precipitates 2.36 parts of neutral rosin size. Weigh out 10 grams of the crystals that have previously been pressed between two filter papers, dissolve, and dilute to 1 liter. One cubic centimeter will then contain .01 gram of alum. A flask with a capacity of about 200 cubic centimeters is then filled about two-thirds full of distilled water, and 20 cubic centimeters of this size solution is run in from a burette. The alum solution is then run in from another burette, a few drops at a time. The flask is then closed with a stopper, shaken vigorously, and allowed to stand after each addition until the precipitate rises to the top, which it will do very rapidly. This is continued until the solution is left perfectly clear, after the precipitate has risen. The number of cubic centimeters of alum used multiplied by .01 will give the amount of alum, in grams, required to precipitate 20 cubic centimeters of standard size; this multiplied by 2.36 will give the number of grams of neutral size in 20 cubic centimeters of this solution. If 10 cubic centimeters of the alum solution is used, 20 cubic centimeters of the standard size will contain .236 gram of neutral rosin size.

Tenth normal $\left(\frac{n}{10}\right)$ *sodium-chloride solution* is prepared by accurately weighing 5.837 grams of chemically pure sodium chloride (which has been previously heated in a covered platinum crucible to a low red heat for several minutes and cooled in a desiccator), dissolving in distilled water, and making up to 1 liter. It is always advisable to keep this standard solution on hand to assist in making up $\frac{n}{10}$ silver-nitrate solutions.

Tenth normal $\left(\frac{n}{10}\right)$ *silver-nitrate solution* is prepared by weighing out 17 grams of pure crystallized silver nitrate, dissolving, and diluting to almost 1 liter. This solution is then matched against the $\left(\frac{n}{10}\right)$ sodium-chloride solution, using potassium chromate as an indicator, and adjusted to exact $\frac{n}{10}$ solution. One cubic centimeter of this silver-nitrate solution will then be equivalent to .00355 gram of chlorine, or .00585 gram of sodium chloride.

9. Indicators.—The following **indicators** will be found necessary:

Phenol phthalein is soluble in 50-per-cent. alcohol, and is made up for use as follows: Take a mixture of 105 cubic centimeters of alcohol (95 per cent.) and 95 cubic centimeters of water. Add to this 2 grams of phenol phthalein and stir until all is dissolved. A few drops of this indicator will be sufficient for titrating; it will produce no color in acid liquids, but the slightest trace of caustic alkali will change it to purple red. This indicator can be used in alcoholic solutions and is useful in titrating organic acids, but it is not reliable in the presence of carbonates in cold solution.

Methyl orange containing impurities that are not soluble in water should be recrystallized from alcohol. This indicator should not be used for titrating organic acids. A convenient strength is .1 gram to 100 cubic centimeters of water. One or two drops is sufficient for 100 to 150 cubic centimeters of the solution to be titrated. A good end reaction cannot be obtained if too much of the indicator is used. This indicator gives a very sharp end point in the presence of carbonates, and is therefore very useful in the titration of the alkali carbonates.

Starch is prepared as follows: About 300 cubic centimeters of water is brought to a boil in a flask having a capacity of about 1 liter. Four grams of starch is then mixed in a little cold water until all the lumps are broken and it forms a thin, pasty mass; this is added to the boiling water, and the whole allowed to boil for 5 minutes. A mixture of 5 grams of zinc chloride in a little water is then added, and the whole allowed to boil 1 minute longer. This mixture is then removed from the flame, diluted to about 900 cubic centimeters, well mixed, and allowed to stand overnight. The clear starch solution is then decanted into a bottle and is ready for use.

Iodized starch is made by taking some of the starch solution just mentioned and adding a small amount of a solution of potassium iodide.

Potassium chromate of a convenient strength is made by adding 1 gram to 10 cubic centimeters of water. A few drops of the solution will be sufficient for 100 to 150 cubic centimeters of the solution to be titrated.

ANALYTICAL METHODS

10. Analysis of Soda Ash.—The usual determination made in soda ash is for sodium oxide; if it falls below the requirement in this, free caustic soda and sulphuric acid are determined. The material should first be carefully sampled. If the soda ash is received in bags, a portion should be taken from each of seven or eight bags selected at random from each car and thoroughly mixed. This composite sample should then be quartered down until a sample of convenient size is obtained.

Determination of Sodium Oxide.—Weigh out 15.5 grams of the sample, dissolve in about 400 cubic centimeters of hot water, let cool, wash into a liter flask, and dilute to the mark. Measure out 100 cubic centimeters of this solution into a beaker by means of a pipette, add two drops of methyl orange, and titrate with a normal acid. The number of cubic centimeters of the normal acid used multiplied by 2 will give the percentage of sodium oxide in the sample. Good soda ash made by the Solvay process should contain 58 per cent. of sodium oxide; that made by the LeBlanc process, about 48 per cent. of sodium oxide.

Determination of Free Caustic Soda.—If it is desired to test for caustic soda, measure out 100 cubic centimeters of the original solution and add a slight excess of *neutral* barium chloride, to precipitate all the carbonate. Filter off the precipitated $BaCO_3$ and titrate the filtrate with normal acid, using phenol phthalein as an indicator.

Determination of Sulphuric Acid.—Take 100 cubic centimeters of the solution, equivalent to 1.55 grams of ash, acidify carefully with hydrochloric acid, bring to a boil, and precipitate the H_2SO_4 as $BaSO_4$ by means of barium chloride. Let stand in a warm place for about 2 hours, to settle the precipitate. Decant the clear liquid through an ashless filter paper, then wash the precipitate upon it, and wash thoroughly with hot water. Dry, ignite, and weigh as $BaSO_4$. The weight of the $BaSO_4$ multiplied by the factor .34335 will give the weight of the SO_3, and this multiplied by 100 and divided by 1.55, the weight of ash taken, will give the percentage of SO_3 in the ash. This is calculated to Na_2SO_4, according to the following proportion:

$SO_3 : Na_2SO_4 =$ percentage of SO_3 : percentage of Na_2SO_4;
or, $80 : 142 =$ percentage of $SO_3 : x$;
whence, $x =$ percentage of Na_2SO_4

Soda ash is usually sold on the New Castle test, which is based on the erroneous atomic weight of sodium (24). When getting the actual alkali, it is advisable also to report it in terms of the New Castle test, by multiplying actual alkali found by 1.032. Soda is sold on a guarantee of 58 per cent. Na_2O, and many chemists have rejected cars that have fallen below this test, to find later that the soda had been bought on a guarantee of 58 per cent., according to the New Castle test.

11. Analysis of Causticizing Lime.—Causticizing lime is used for converting the carbonate of soda into caustic soda. The caustic lime when added to the carbonate solution is first converted into $Ca(OH)_2$, which reacts with the sodium carbonate, forming caustic soda and calcium carbonate, the latter settling to the bottom of the tank as *lime sludge.* A good lime for this purpose should be well burned, as free as possible from impurities, and contain a high percentage of CaO. Lime that is slaked when received is not suitable for causticizing, as more of it is required to do the same work than if unslaked. In analyzing lime ordinarily, calcium oxide, carbon dioxide, and water only are determined.

Sampling the Lime.—A very large sample should be taken from different parts of the car and the whole broken up into lumps about the size of a pea. This sample should then be mixed thoroughly and quartered several times, to reduce to a small sample. This small sample should be ground very fine, well mixed, and kept in a tightly corked bottle.

Determination of Calcium Oxide.—Weigh out 10 grams of the sample, slake, and wash carefully into a 500-cubic-centimeter flask, filling it to the mark. Take 50 cubic centimeters of the clear solution, which is equivalent to 1 gram of lime, wash into a beaker, and titrate with normal oxalic acid, using phenol phthalein as an indicator. The number of cubic centimeters of normal acid used multiplied by 2.8 will give the percentage of CaO in the sample, which includes also the magnesium oxide; but as the percentage of the latter oxide in this lime is very low, its presence can for all practical purposes be disregarded.

Determination of Carbon Dioxide.—Carbon dioxide can be very accurately determined by treating a carefully weighed sample in a flask with hydrochloric acid and absorbing the liberated CO_2 in a Geissler bulb containing a solution of potassium hydroxide (1 to 1). This method, however, necessitates the use of a drying apparatus for the air that passes through the flask and also a train of **U** tubes with an aspirating bottle at the end of the train. For all practical purposes, the CO_2 may be determined as follows:

After shaking, take 50 cubic centimeters of the solution used for the calcium-oxide determination, add from a burette an excess of normal hydrochloric acid, and titrate the excess of acid with normal sodium hydrate. The number of cubic centimeters of hydrochloric acid used less the number of cubic centimeters in excess, as found by the sodium-hydrate titration, is the total number of cubic centimeters neutralized by the CaO and $CaCO_3$. The number of cubic centimeters thus found less the number of cubic centimeters of normal oxalic acid used in the estimation of calcium oxide, is the number of cubic centimeters of hydrochloric acid used in titrating the

$CaCO_3$. This number multiplied by 5 will give the percentage of $CaCO_3$ in the sample. To find the percentage of CO_2, multiply the percentage of $CaCO_3$ by .44.

Determination of Water.—The amount of water can be determined by weighing 1 gram of the lime sample in a platinum crucible, gently heating at first, and gradually raising the temperature to a strong red heat. Cool in a desiccator and weigh quickly. Repeat until a constant weight is obtained. The loss in weight will be due to water and CO_2. Determine the CO_2 as in the previous case. Subtract the weight of the CO_2 in 1 gram from the total loss of weight on heating. The difference will be the loss due to water. This weight multiplied by 100 will give the percentage of water in the sample.

12. Complete Analysis of Lime.—When a complete analysis of lime is desired, the following determinations are usually made: Silica, sesquioxides of iron and aluminum, calcium oxide, magnesium oxide, sulphuric acid, and carbon dioxide.

Determination of Silica.—Weigh out 2 grams of the carefully prepared sample and fuse in a platinum crucible with about 8 grams of sodium carbonate. Dissolve the fused mass with hot water in a porcelain dish with the use of a slight excess of dilute hydrochloric acid, keeping it well covered with a watch glass. Boil and evaporate to dryness. Moisten thoroughly with strong hydrochloric acid, and again evaporate to complete dryness. Take up in dilute hydrochloric acid, boil, and filter through an ashless filter, using a "policeman," or rubber-tipped glass rod, to remove the fine particles of silica from the dish. Wash thoroughly with hot water. Collect the filtrate and washing in a 200-cubic-centimeter flask, cool, and fill to the mark. Transfer the filter paper and residue to a crucible, ignite, and weigh. The weight of the residue multiplied by 50 will give the percentage of SiO_2 in the sample.

Determination of Sesquioxides of Iron and Aluminum.—Take 100 cubic centimeters of the filtrate from the silica determination, heat nearly to boiling, add a few drops of nitric acid, and precipitate the iron and aluminum with a slight excess of ammonium hydrate. Then take up again in a slight excess of hydrochloric acid, and reprecipitate with a slight excess of ammonium hydrate, bring to a boil, and allow to boil gently until the odor of ammonia is no longer perceptible. Allow the precipitate to settle, decant the clear liquid through an ashless filter, wash several times by decantation, boiling with water each time, and finally collect the precipitate on the filter. Dry in an oven, transfer to a weighed crucible, ignite, and weigh as $Al_2O_3 + Fe_2O_3$. This weight multiplied by 100 will give the percentage of these mixed oxides in the sample.

Determination of Calcium Oxide.—Heat the filtrate from the previous analysis to boiling and add a slight excess of ammonium-oxalate solution, stirring for several minutes. Allow this to settle for about 3 hours, wash well with hot water, and dry. Transfer the precipitate to a platinum crucible, burn the filter paper, and add its ash. Treat with a few drops of dilute sulphuric acid, heat gently, to drive off the excess of H_2SO_4, then heat to redness, cool in a desiccator, and weigh as calcium sulphate. This weight, multiplied by .412 × 100 will give the percentage of CaO in the sample.

Instead of treating the precipitate with H_2SO_4, it may be converted directly into CaO by igniting to constant weight, which requires a long ignition over the blast lamp. This weight multiplied by 100 will give the percentage of CaO.

Determination of Magnesium Oxide.—The filtrate from the calcium-oxide determination is acidified with HCl, an excess of sodium phosphate added, and concentrated by evaporation to about 200 cubic centimeters. It is then cooled, preferably in ice water, and NH_4OH added drop by drop, while stirring, until a precipitate begins to form. After standing about 15 minutes, 50 cubic centimeters of strong NH_4OH is added. Allow to settle for about 2 hours, filter, and wash with ammonia water made of 1 part of ammonia hydroxide (.96 specific gravity) and 4 parts of water. Dry, transfer the precipitate to a porcelain crucible, burn the filter, and add its ash. Then ignite to constant weight, over the blast, and weigh as magnesium pyrophosphate, $Mg_2P_2O_7$. This weight multiplied by .36036 × 100 will give the percentage of MgO in the sample.

Determination of Sulphuric Acid.—Take the remaining 100 cubic centimeters of the filtrate from the silica determination, heat to boiling, and precipitate the sulphuric acid as $BaSO_4$ with barium chloride. Let stand in a warm place for about 2 hours, or until the precipitate is settled. Decant the clear liquid through an ashless filter, wash twice by decantation with hot water, and finally on the filter with hot water, until a few drops of the filtrate give no test for chlorides with silver nitrate. Dry, transfer to a crucible, burn the filter as before, and ignite to constant weight. The weight of the $BaSO_4$ multiplied by .34335 × 100 will give the percentage of SO_3 in the sample.

Determination of Carbon Dioxide.—The carbon-dioxide determination should be made as described in Art. **11.**

The following analysis shows the composition of a good causticizing lime:

	PER CENT.
Silica, SiO_2	.62
$Fe_2O_3 + Al_2O_3$	.84
Calcium oxide, CaO	95.91
Magnesium oxide, MgO	.51
Carbon dioxide, CO_2	.92
Water	1.15
Undetermined	.05
Total	100.00

13. Analysis of Magnesia Lime.—Magnesia lime is used for making up bisulphite liquors for the sulphite process. The lime should be well burned, contain high percentages of both calcium and magnesium oxides, and be fairly free from impurities. The same determinations are made as in causticizing lime and the same methods used.

In the determination of calcium and magnesium oxides, owing to the fact that some magnesium oxalate will be precipitated with the calcium oxalate, the following precautions should be taken: Precipitate the calcium oxalate in the usual manner, and, after a slight washing, redissolve the precipitate in hydrochloric acid, make ammoniacal, reprecipitate the calcium, filter, wash, and treat the calcium oxalate, as previously described. The filtrates are combined, the whole acidified with HCl, sodium phosphate added, evaporated to 200 cubic centimeters, cooled, and the magnesium precipitated with ammonia, as in the preceding article. In accurate work, it is essential that a double precipitation of the calcium be made, both in the case of a causticizing lime and a magnesia lime. It is also advisable to make a double precipitation of the magnesia.

The following is an analysis of a good magnesia lime for the sulphite process:

	Per Cent.
Silica and insoluble	.22
$Fe_2O_3 + Al_2O_3$	.19
Calcium oxide, CaO	50.92
Magnesium oxide, MgO	44.32
SO_3	1.51
Water	1.23
Carbon dioxide, CO_2	1.48
Undetermined	.13
Total	100.00

14. Analysis of Sludge From Causticizing Pans. The sludge from the causticizing pans is tested in order to determine the loss in per cent. of soda, etc. at this point. After the liquor from the third wash has been run off as low as possible, the sludge is well agitated and a sample taken. The determinations usually made are insoluble matter, sodium oxide, calcium oxide, calcium carbonate, and moisture.

Determination of Insoluble Matter.—Weigh out 20 grams, or more if necessary, of the sample in a small beaker. Transfer to a porcelain dish, take up with an excess of hydrochloric acid, and evaporate to dryness to expel all HCl.

Take up again in hydrochloric acid and water, boil, filter, and wash the residue thoroughly with hot water. Ignite in a crucible to constant weight. This weight multiplied by 100 and divided by the weight of the sample taken will give the percentage of insoluble matter.

Determination of Sodium Oxide.—Weigh out approximately 45 or 50 grams of the sample, transfer to a porcelain dish and evaporate to dryness with a little ammonium carbonate. Take up with water and repeat this evaporation with ammonium carbonate. Take up again in hot water and allow to remain almost at a boil for some time. Filter into a 500-cubic-centimeter flask, wash thoroughly with hot water, cool filtrate and washings, and fill up to the mark. Take 100 cubic centimeters of this filtrate and titrate with a normal acid, using methyl orange as an indicator. The number of cubic centimeters of acid required multiplied by .031 will give the weight, in grams, of the sodium oxide in 100 cubic centimeters of the solution. This weight multiplied by 5 × 100 and divided by the weight of sludge used in making the sample solution will give the percentage of Na_2O in the sludge.

Determination of Caustic Lime.—Take 100 cubic centimeters of the sludge, weigh in a 100-cubic-centimeter flask, wash into a beaker, and titrate with normal oxalic acid, using phenol phthalein as an indicator. The number of cubic centimeters required less the number of cubic centimeters neutralized by the Na_2O, as calculated for the weight of sludge used from the data obtained in the sodium-oxide determination, is the number of cubic centimeters of normal oxalic acid neutralized by the CaO. This number multiplied by .028 (the value of 1 cubic centimeter of normal oxalic acid in lime) × 100 and divided by the weight of the sludge taken will give the percentage of calcium oxide, or caustic lime.

Determination of Calcium Carbonate.—Take about 10 grams of the sludge, after agitating well, and titrate with normal hydrochloric acid, using methyl orange as an indicator. The number of cubic centimeters of acid used less the number required for sodium oxide and for caustic lime, as previously determined for the same weight of sample, is the number of cubic centimeters of normal acid neutralized by the calcium carbonate. This number multiplied by .05 will give the weight of calcium carbonate in the sample taken. This weight multiplied by 100 and divided by the weight of sludge taken will give the percentage of calcium carbonate.

Determination of Moisture.—The determination of the amount of moisture is made by weighing out about 50 grams of the sample as quickly as possible and drying at 100° C. to constant weight. The loss in weight multiplied by 100 and divided by the weight of sample taken will give the percentage of moisture. Other constituents of sludge may be determined by methods given in Art. **12.**

The following is an analysis of a lime sludge:

	Per Cent.
Moisture	76.780
Silica, SiO_2	.090
$Fe_2O_3 + Al_2O_3$	.250
Magnesium oxide, MgO	.085
Sodium oxide, Na_2O	.350
Calcium hydrate, $Ca(OH)_2$	1.070
Calcium carbonate, $CaCO_3$	21.290
Undetermined	.085
Total	100.000

15. Analysis of Bleaching Powder.—The value of bleaching powder depends on the percentage of available chlorine in it. On standing, bleaching powder loses its strength, especially if kept in a damp place. A good bleaching powder should contain from 36 to 37 per cent. of available chlorine, but it is generally accepted if it tests over 35 per cent.

Sampling.—In order to get a fair sample from a car, small samples should be taken from at least five casks. This is best done by means of a long, ½-inch copper tube, which is thrust into the cask after boring a hole in it, withdrawn, and the contents transferred to the sample bottle by gently tapping the tube. The sample bottle should be perfectly dry and kept closed as much as possible. Analysis should be made as soon as sample is taken, and as quickly as possible.

Determination of Available Chlorine.—Weigh out 7.1 grams of the well-mixed sample, transfer to a porcelain mortar, add a little water, and grind with the pestle, taking care to avoid loss. Allow to settle for a moment and decant into a liter flask. Repeat this three times, and finally wash the contents of the mortar into the flask, using a clean finger to rub off the mortar and pestle. Fill to the mark with water, shake well, and transfer 50 cubic centimeters to a beaker by means of a pipette. Titrate with $\frac{n}{10}$ sodium-arsenite solution, stirring while adding the standard. The end point is reached when a drop of the solution no longer gives the blue coloration to iodized-starch paper (this paper is prepared by soaking strips of filter paper in iodized-starch solution). When the quantity of sample just mentioned is used, each cubic centimeter of the standard used is equivalent to 1 per cent. of available chlorine. With practice, this test can be made rapidly and with good results.

The bleaching powder should be tested as soon as possible after sampling, and after starting to test there should be no delay, as otherwise the results will come too low.

Determination of Chlorate.—Sometimes it is necessary to determine the amount of chlorate present in bleaching powder. For all practical purposes, this can be done by adding a little dilute sulphuric acid to the sample that has been titrated for available chlorine and rapidly titrating again, thus determining the chlorine present as chlorate.

The following is a complete analysis of bleaching powder:

	Per Cent.
Available chlorine	36.80
Chlorine as chlorate	.22
Chlorine as chloride	.42
Lime, CaO	43.98
Magnesia, MgO	.39
$Fe_2O_3 + Al_2O_3$	.41
Water (by difference)	17.78
Total	100.00

16. Analysis of Bleach Sludge.—It is important that the bleach sludge should be tested from time to time, to ascertain the loss of available chlorine in the dump. The sludge, after drawing off the wash as closely as possible, should be agitated and the sample taken.

Determination of Available Chlorine.—Measure 50 cubic centimeters of the well-mixed sample into a beaker by means of a pipette, which is rinsed out into the beaker. Titrate with $\frac{n}{10}$ sodium arsenite as before. The number of cubic centimeters used multiplied by .071 gives the number of grams of available chlorine per liter of sludge, and this multiplied by 3.785 (the number of liters in 1 gallon) gives the weight of available chlorine in 1 gallon. This weight multiplied by 3 gives the approximate loss of bleaching powder in 1 gallon, and, knowing the cubical contents of the tank and the number of inches dumped, the loss in the dump can be easily calculated.

In a bleach that settles well, this loss ranges from .6 per cent. to 1 per cent. of the bleach mixed. If the bleach does not settle well, the loss will reach 3 per cent. and may go even higher.

17. Analysis of Black Ash.—Black ash is the ash that is recovered after the liquor used in the soda process, in which the wood has been cooked, has been evaporated and burned.

Preparation of Sample.—Quite a large sample should be taken, ground up, mixed, and quartered several times. The last portion should be ground very fine and well mixed in the sample bottle. Weigh out 50 grams of this carefully prepared sample and boil up with water. Stir well from time to time for at least 1 hour, filter into a liter flask, wash well, cool, and dilute to the mark. It is customary to make determinations of caustic soda, sodium sulphide, sodium carbonate, sodium sulphate, and sodium chloride.

Determination of Caustic Soda.—Take 50 cubic centimeters of the clear liquid and precipitate the carbonate with a slight excess of neutral barium-chloride solution in a 200-cubic-centimeter flask, add hot water, shake well, cool, fill to the mark, and after again shaking, allow to settle. Take 100 cubic centimeters of the clear portion and titrate with normal acid, using methyl orange as an indicator. Multiplying the number of cubic centimeters of acid used by 4 and dividing by 1.25 will give the percentage of $NaOH$ in the ash. This also includes any Na_2S present, and if it is considerable, the number of cubic centimeters of standard acid neutralized by it must be deducted from the whole before the calculation of the caustic soda is made.

Determination of Sodium Sulphide.—Take 25 cubic centimeters of the clear liquor, equivalent to 1.25 grams of the ash, dilute to 200 cubic centimeters with recently boiled water, acidify with acetic acid, and titrate quickly with $\frac{n}{10}$ iodine solution, using starch as an indicator. The number of cubic centimeters of standard used multiplied by .39 and divided by 1.25 will give the percentage of Na_2S in the ash.

Determination of Sodium Carbonate.—Take 25 cubic centimeters of the original clear liquor and titrate with normal hydrochloric acid, using methyl orange as an indicator. The number of cubic centimeters of acid used less the number of cubic centimeters neutralized by the caustic soda, as determined for the same volume of liquor, multiplied by 5.3 and divided by 1.25 will give the percentage of Na_2CO_3 in the ash.

Determination of Sodium Chloride.—Take 25 cubic centimeters of the clear liquor, neutralize with nitric acid, and boil to expel hydrogen sulphide. Filter, wash, cool, add a little potassium-chromate indicator, and titrate with $\frac{n}{10}$ silver-nitrate solution. The number of cubic centimeters of silver nitrate required multiplied by .585 and divided by 1.25 will give the percentage of sodium chloride in the ash.

Determination of Sodium Sulphate.—The amount of sodium sulphate can be determined by dissolving 25 grams of ash in hot water, filtering and washing well, acidifying the filtrate slightly with hydrochloric acid, boiling to expel all CO_2, and precipitating with a slight excess of barium-chloride solution. Let stand in a warm place until settled, filter, and wash thoroughly with hot water. Dry, ignite in a crucible, and weigh as $BaSO_4$. Calculate to Na_2SO_4 by multiplying by .6094. The weight of Na_2SO_4 multiplied by 4 will give its percentage in the ash.

The following is an analysis of a sample of black ash:

	Per Cent.
Sodium carbonate	78.15
Sodium hydrate	1.83
Sodium sulphate	2.55
Sodium sulphide	.50
Sodium chloride	6.60
Carbon	4.30
Silica	5.10
Calcium carbonate	.72
Undetermined (difference)	.25
Total	100.00

18. Analysis of Alum.—In the paper industry, the term *alum* is applied to sulphate of aluminum, $Al_2(SO_4)_3 \cdot 18H_2O$, which, strictly speaking, is not an alum. The analysis of an alum is quite long and complicated, but if carried on with care, very good results can be obtained. The following determinations and tests are usually made:

Determination of Water.—Weigh out 2 grams of the well-mixed sample into a platinum crucible. Heat gradually until a low red heat is reached, and allow to remain at this temperature until fumes of SO_3 are perceptible. Cool in a desiccator and weigh. The loss of weight gives the amount of water, together with some SO_3. The loss of SO_3 may be determined as follows:

Add about 10 cubic centimeters of hot, concentrated, hydrochloric acid to the contents of the crucible and allow to stand in a warm place for about half an hour, when the lumps will be all broken down, provided the heating was not too high or too long when driving off the water. The contents of the crucible should then be washed into a small beaker with hot water, diluted to about 50 cubic centimeters, and heated until all is dissolved, except what little insoluble matter there may be in the alum. Filter and wash well with hot water. Precipitate the sulphuric acid in the filtrate with barium chloride, as in the determination of sulphuric acid described in Art. **10.** Filter, wash well with hot water, dry, and ignite to constant weight. The weight of $BaSO_4$ multiplied by .34335 will give the weight of SO_3. This weight subtracted from the weight of the total SO_3 in the same weight of sample, as found by a separate determination, will give the loss of weight due to SO_3. Subtracting this loss from the total loss on heating will give the loss due to water, and this multiplied by 50 will give the percentage of water in the alum.

Determination of Insoluble Matter.—Weigh out 20 grams of the alum and dissolve in about 300 cubic centimeters of hot water. Filter through an ashless filter into a liter flask, and wash well with hot water. Dry, ignite, and weigh the residue, the weight of which multiplied by 5 will give the percentage of insoluble matter in the alum. Cool the filtrate and dilute to the mark.

Determination of Alumina.—The alumina and ferric oxide are determined together. The ferric oxide is determined in a separate portion and subtracted from the mixed oxides, giving the alumina.

Take 50 cubic centimeters of the filtrate from the insoluble determination (equivalent to 1 gram of alum), dilute to 200 cubic centimeters, add a few drops of nitric acid, and precipitate with a slight excess of ammonium hydrate. Neutralize the excess of ammonia with hydrochloric acid, add NH_4OH gradually, drop by drop, until its odor can be detected in the solution. Bring to a boil and allow to remain so, after covering with a watch glass, until the odor of ammonia can no longer be detected. The volume of liquid should be kept as nearly constant as possible by additions of a little hot water. Allow to settle, and decant the clear portion through an ashless filter. Boil up again with hot water, settle, and decant. Repeat this several times. Finally wash the precipitate upon the filter, wash well with hot water, dry, ignite, and weigh as $Al_2O_3+Fe_2O_3$.

The preceding analysis will hold good provided there is no zinc in the alum; but when zinc is present (which can be detected by precipitating with ammonium hydrate, filtering, and adding a few drops of yellow ammonium-sulphide solution, which will give a flocculent, white precipitate), the iron and aluminum oxides should be precipitated as basic acetates. Take about 50 cubic centimeters of the original solution and dilute to about 450 cubic centimeters. Bring to a boil, and add about 2 grams of sodium acetate and a few drops of acetic acid. Boil the solution for about 15 minutes, allow to settle, and decant through an 11-centimeter ashless filter. Wash several times by decantation, bring to a boil each time, and finally wash on to the filter with hot water containing a little ammonium acetate. Evaporate the filtrate to about 150 or 200 cubic centimeters, and filter again through a separate filter paper. Wash well and add to the first residue. Dry, ignite, and weigh as $Al_2O_3 + Fe_2O_3$.

Determination of Zinc.—The filtrate from the aluminum and ferric hydrates should be neutralized as nearly as possible, and the zinc precipitated as the sulphide with ammonium sulphide. The reagent should be added drop by drop, to avoid a large excess. Boil for about 20 minutes, and allow to settle. Test with a drop of ammonium sulphide to make sure that all the zinc is precipitated, filter, wash, dry, and ignite to constant weight at a strong heat. This weight multiplied by 100 will give the percentage of zinc oxide in the alum.

Determination of Iron.—1. Take 10 grams of the alum, dissolve in water, filter into a flask that holds about 300 cubic centimeters, and dilute to about 150 cubic centimeters. Add 8 or 10 grams of granulated zinc and about 40 cubic centimeters of concentrated sulphuric acid. Close the flask with a valve made as shown in Fig. 2. This valve consists of a glass tube *d* passing through a cork *e*. On the end of this glass tube is slipped a rubber tube *b*, having a slit *c* for the escape of gas. The upper end of the tube *b* is closed by a glass plug *a*. This allows the generated hydrogen to escape, but does not allow the air to enter. Set the flask on the hot plate until the zinc is dissolved. This will be sufficient to reduce all the ferric iron to the ferrous state. Boil for about a minute to drive out any remaining hydrogen, cool as quickly as possible, and transfer to a larger beaker. Dilute to about 500 cubic centimeters with distilled water that has been recently boiled, and titrate with standard permanganate solution. The number of cubic centimeters used multiplied by the factor for the solution will give the number of grams of iron in 10 grams of alum. Calculate this to Fe_2O_3 by multiplying by 1.4285. The number of grams of Fe_2O_3 multiplied by 10 will give the percentage of Fe_2O_3 in the alum. The solution may also be run through a Jones reductor and then titrated with permanganate.

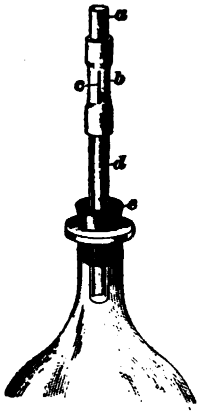


FIG. 2

2. The percentage of iron oxide can also be determined by dissolving 20 grams of alum in water, bringing to a boil, and adding a large excess of potassium-hydrate solution. The aluminum hydrate formed is dissolved by the KOH, while the ferric hydrate is not affected. Filter, wash, and dissolve the precipitate in warm, dilute hydrochloric acid. Heat to boiling, and reprecipitate the iron with ammonium hydrate. This precipitate will now be free from alumina. Filter, washing first by decantation and finally on the filter paper, dry, ignite, and weigh as Fe_2O_3.

Determination of Sulphuric Acid. –Take 50 cubic centimeters of the prepared sample solution (equivalent to 1 gram of alum), dilute to about 200 cubic centimeters, acidify with hydrochloric acid, bring to a boil, precipitate with barium chloride, and treat as in Art. **10**. The weight of the $BaSO_4$ multiplied by .34335 × 100 will give the percentage of SO_3 in the alum.

Determination of Free Acid.—It is very important in determining the value of an alum to know the amount of free acid present, as this attacks the coloring matter and at the same time injures the machinery of the mill. Many methods have been suggested for the quick determination of the free acid, but they are all very unsatisfactory. Three methods are here given.

1. Digest a weighed quantity of alum for about 15 hours in strong alcohol. Filter, wash with alcohol of the same strength, and titrate with $\frac{n}{10}$ alkali, using phenol phthalein as an indicator. Calculate the percentage of free acid.

2. Dissolve 2 grams of alum in 5 cubic centimeters of water and add 5 cubic centimeters of cold saturated solution of ammonium sulphate, stirring thoroughly. Now add 50 cubic centimeters of 95-per-cent. alcohol, filter, evaporate the filtrate on a water bath, take up in water, and titrate with $\frac{n}{10}$ alkali, using phenol phthalein as an indicator.

3. The following is the most accurate method for the determination of the free acid in alum: First, make a complete analysis of the alum. Determine the amount of sulphuric acid necessary to combine with all the bases. If there is more acid than is necessary to combine with all the bases, the excess may be considered as free sulphuric acid. If there is not acid enough to combine with all the bases, combine the acid with all the bases except alumina, and then use up all the latter possible, reporting the balance as basic alumina, Al_2O_3.

Sizing Test.—The standard size is prepared as described in Art. 8. Dissolve 10 grams of alum in water and dilute to 1 liter. Fill a 200-cubic-centimeter flask about two-thirds full of distilled water, and run in from a burette 20 cubic centimeters of size solution. Now, add the alum solution from a burette, a few drops at a time. Shake violently, and allow the precipitate to rise after each addition. Toward the end, the alum should be added a drop at a time. When the precipitate, on rising, leaves the solution perfectly clear, take the reading of the alum burette. The number of cubic centimeters of alum solution multiplied by .01 will give the number of grams of alum necessary to precipitate 20 cubic centimeters of standard size, and this divided into the factor for neutral dry size in 20 cubic centimeters of standard size will give the number of parts of neutral dry size precipitated by 1 part of alum.

The foregoing is a good quick test for the precipitating power of alum, but it does not give much of an idea as to the quality of alum, as it may be a very acid alum and still have a good precipitating power.

Ultramarine Test.—The ultramarine test in connection with the sizing test will give a fair idea as to the fitness of an alum for paper maker's use, provided, however, the alum contains a low percentege of iron.

Weigh out .2 gram of ultramarine, transfer to a 100-cubic-centimeter flask, and fill to the mark with distilled water. Shake well, in order to mix the ultramarine thoroughly, taking care that none remains on the bottom of the flask. Weigh out 2 grams of the alum to be tested, and also 2 grams of an alum that has already been well tested and with which the sample is to be compared. Dissolve each sample in 100 cubic centimeters of distilled water. Take 50 cubic centimeters of each of these and transfer to two properly labeled 100-cubic-centimeter flasks. Now, to each of the alum solutions add 10 cubic centimeters of the ultramarine mixture, which should first be well shaken. Allow them to stand for some time, with frequent shaking, and note the effect of the alum on the color of each mixture. This is only a comparative test as to the action of the alum on ultramarine.

Samples of alum analyses in which the different elements were determined and bases combined with acid are given in Table I.

19. Analysis of Agalite.—Agalite is a silicate of magnesia of a fibrous nature and is retained very well in the paper, the retention being from 60 to 90 per cent. of the

TABLE I

ALUM ANALYSES

Alum Sample	Water Per Cent.	Insoluble Per Cent.	$Al_2(SO_4)_3$ Per Cent.	$FeSO_4$ Per Cent.	$ZnSO_4$ Per Cent.	Na_2SO_4 Per Cent.	Free H_2SO_4 Per Cent.	Basic Al_2O_3 Per Cent.	Parts of Neutral Dry Size Precipitated by 1 Part of Alum	Remarks
A	41.83	.170	49.18	.62	6.36			1.54	3.47	This alum is very good with ultramarine
B	41.65	.046	56.76	.68				.61	3.59	Fair with ultramarine
C	45.59	.035	53.49	.51			.25		3.51	Strong action on ultramarine
D	45.28	.060	53.26	.41			.81		3.53	Strong action on ultramarine
E	43.57	.047	54.98	.33				.85	3.58	Fair with ultramarine
F	44.18	.100	54.88	.32				.41	3.55	Slight action on ultramarine
G	43.16	.070	52.02	.38	3.68			.76	3.55	Fair with ultramarine
H	43.63	.076	51.83	.62	1.35	.7		1.24	3.41	Good with ultramarine
I	41.90	.600	54.29			3.0		.30	3.41	Slight action on ultramarine
J	42.32	.040	56.85	.25				.45	3.63	Slight action on ultramarine
K	43.29	.056	55.59	.57	.05			.19	3.49	Acts considerably on ultramarine

amount used. Agalite usually contains more grit than clay, but should not contain much soluble matter, as this cuts down its retention. In analyzing, the following determinations are usually made:

Determination of Water.—Weigh out 2 grams of the agalite in a platinum crucible and heat for some time at a red heat. Cool in a desiccator and weigh. Repeat until a constant weight is obtained. The loss of weight multiplied by 100 and divided by 2 will give the percentage of water in the sample.

Determination of Silica.—Fuse 1 gram of the agalite in a platinum crucible with 10 grams of a mixture made up of 1 part sodium carbonate and 1 part of potassium carbonate. Cool the bottom of the crucible in cold water, which will cause the solidified mass to break away from the sides. Transfer with the aid of hot water to a 4-inch porcelain dish. Cover with a watch glass, add about 100 cubic centimeters of hot water, and then cautiously add hydrochloric acid until the mass is broken up and effervescence ceases; then proceed with the determination of silica as directed in Art. **12.** The weight of the silica multiplied by 100 will give its percentage in the agalite.

Determination of Sesquioxides of Iron and Aluminum. Treat the filtrate from the silica determination in exactly the same way as in the determination of the sesquioxides of iron and aluminum in Art. **12.** The weights of the mixed oxides $Fe_2O_3 + Al_2O_3$ multiplied by 100 will give their percentages. Unless the presence of iron is very marked, it is unnecessary to separate the Al_2O_3 from the Fe_2O_3; but if desired, proceed as in Art. **18** in the determinations of alumina and iron.

Determination of Calcium Oxide.—Evaporate the filtrate from the previous determination to about 200 cubic centimeters, and precipitate the calcium as oxalate with ammonium oxalate in the usual way, as described in Art. **12,** taking all the precautions mentioned in the analysis of magnesia lime in Art. **13.** Calculate the results as described in Art. **12.**

Determination of Magnesium Oxide.—The amount of magnesium oxide present is determined in the filtrate from the calcium-oxide determination by precipitation with sodium phosphate in the usual manner (see Art. 12, Determination of Magnesium Oxide). The weight of the magnesium pyrophosphate, $Mg_2P_2O_7$, multiplied by the factor .36036 and by 100 will give the percentage of MgO in the agalite.

The following is an analysis of agalite:

	Per Cent.
Water (loss on ignition)	2.67
Silica, SiO_2	61.82
$Fe_2O_3 + Al_2O_3$	1.59
Lime, CaO	3.65
Magnesia, MgO	29.98
Manganese	trace
Undetermined	.29
Total	100.00

20. **Analysis of Clay.**—Clay is chemically a silicate of aluminum. The value of clay depends on the percentage of silicate of aluminum present and on the absence of iron oxide and grit. In analyzing clay, the following determinations are usually made:

Determination of Moisture.—Weigh out 2 grams of the clay in ground watch glasses. Dry in an air bath at 100° C. to constant weight. The loss of weight multiplied by 100 and divided by the weight of the sample taken will give the percentage of moisture in the sample.

Determination of Combined Water.—Weigh out 2 grams of clay in a platinum crucible and ignite at a red heat to constant weight. The loss of weight multiplied by 100 and divided by 2 will give the total percentage of water in the clay. Subtracting the percentage of moisture from this will give the percentage of combined water in the clay.

Determination of Silica.—Take 1 gram of the sample, heat in a platinum crucible at a low temperature for a few minutes, and then mix with 10 grams of a mixture made up of 1 part of sodium carbonate and 1 part of potassium carbonate. Fuse and proceed as directed for the determination of silica in Art. **19.** The weight of the silica multiplied by 100 will give its percentage in the clay. Collect the filtrate from the silica in a 200-cubic-centimeter flask and fill to the mark.

Determination of Sesquioxides of Iron and Aluminum. Take 100 cubic centimeters of the filtrate from the silica determination (equivalent to .5 gram of clay), dilute to 200 cubic centimeters, and precipitate with NH_4OH in the usual manner. Proceed as in the same determination in Art. **12.** If a separation of the oxides is desired, use the methods given in the analysis of alum in Art. **18.** Calculate the results in the usual manner.

Determination of Calcium and Magnesium Oxides.—The filtrate from the iron- and aluminum-oxide determinations should be tested for CaO and MgO, and if present, they should be determined as directed in Art. **12.** The weights of the oxides found multiplied by 100 and divided by .5 will give the percentages of these oxides in the clay.

The following is an analysis of a good clay:

	PER CENT.
Moisture	.55
Combined water	12.32
Silica, SiO_2	46.32
Al_2O_3	40.25
Fe_2O_3	.31
CaO and MgO	trace
Undetermined	.25
Total	100.00

21. Analysis of Ocher.—Ochers are colored clays, their color being due to the presence of sesquioxide of iron, Fe_2O_3. The greater the amount of iron, the deeper the color. The value of an ocher depends not only on its coloring power, but also on the absence of gritty substances, which tend to make the paper harsh and also injure the calenders. The following determinations and tests are usually made:

Grit Test.—The presence of grit is determined by means of a flotation test, which will give the approximate amount of grit present if carried out carefully. This test serves well for the comparison of two ochers.

Weigh out 5 grams of the ocher, transfer to a large beaker, fill with water and stir for about a minute. Allow to settle 5 minutes and decant the cloudy portion. Repeat this operation until the water becomes perfectly clear, after settling 5 minutes. Filter, wash on the filter paper, dry, ignite, and weigh. When comparing two samples, weigh out equal amounts and treat each in exactly the same manner, when the better one in this respect can readily be determined. An idea as to the grit present can be determined by grinding a little of the ocher between the teeth.

Determination of Strength of Color.—A good quick method for testing two ochers as to strength of color is to mix them with zinc oxide and linseed oil, spreading on a piece of glass and comparing the depth of color.

Take .1 gram of a good, strong ocher and mix well on a glass plate with 1 gram of zinc white, ZnO, using as little linseed oil as possible. After these are thoroughly mixed and of uniform color, spread some of the mixture on a strip of glass. When this glass is turned over, the color produced by the ocher on the zinc white can be plainly seen. Now weigh out .1 gram of the ocher to be compared with the standard, and mix with 1 gram of zinc white, as before, on a clean glass plate. Place this mixture alongside of the standard mixture on the glass, where the stronger one can be readily selected. By this method, it is possible to keep mixing with larger and larger amounts of zinc white and to determine approximately the per cent. of difference between the ochers compared.

For example, if it requires 1.1 grams of zinc white to produce the same shade with one ocher as 1 gram will produce with the same amount of the other, the former is 10 per cent. stronger than the latter. Two ochers may also be approximately compared as to the presence of sesquioxide of iron by weighing out equal amounts in test tubes, adding equal volumes of strong hydrochloric acid, placing the tubes in a beaker of boiling water for some time (until all the oxide of iron is dissolved), and removing both at the same time. The ocher containing the greater amount of sesquioxide of iron will color the acid the deeper.

Determination of Silica and Insoluble Matter.—Weigh out 1 gram of ocher, and heat for some time in strong hydrochloric acid in a 4-inch porcelain dish. Evaporate slowly to dryness and drive off the excess of acid. Proceed as directed in the determination of silica in lime in Art **12.** Weigh the residue as SiO_2 and insoluble matter. This weight multiplied by 100 will give the percentage in the ocher.

If it is desired to determine SiO_2 alone, fuse the preceding residue in 8 grams of a mixture containing equal proportions of sodium and potassium carbonates. Proceed exactly as directed for the fusion of lime for silica in Art. **12.** Weigh as SiO_2; this weight multiplied by 100 will give its percentage in the ocher.

Determination of Sesquioxides of Iron and Aluminum.—The sesquioxides of iron and aluminum are determined in the filtrate from the silica and insoluble matter in the usual manner, as directed for the same determination in lime in Art. **12.**

Determination of Calcium and Magnesium Oxides.—If a qualitative test shows the presence of much of the calcium and magnesium oxides, they should be determined in the filtrate from the iron and aluminum-oxide determination, as directed in the analysis of lime in Art. **12,** and the percentages calculated in the usual manner.

Determination of Moisture.—Weigh out between watch glasses 10 grams of ocher, and dry to constant weight at 100° C. The loss of weight is due to moisture. This loss multiplied by 10 will give the percentage of moisture in the ocher.

Determination of Combined Water.—Weigh out 2 grams of ocher in a platinum crucible, and ignite to constant weight at a low red heat. The loss of weight multiplied by 50 will give the total percentage of water. Subtract the percentage of moisture found, and the difference will be the percentage of combined water.

The following is an analysis of a good ocher:

	PER CENT.
Moisture	.78
Combined water	8.47
Fe_2O_3	20.05
Al_2O_3	7.11
Silica, SiO_2	62.62
Lime, CaO	trace
Undetermined	.97
Total	100.00

22. Analysis of Ultramarine—Ultramarine is an artificial compound consisting of silica, alumina, sulphur, and soda. This compound is readily attacked by mineral acids, which destroy its color and liberate hydrogen sulphide. Its color varies from reddish to greenish blue. Ultramarine poor in silica is acted on by alum solutions, which destroy the color, while one rich in silica withstands this action. It is therefore advisable to use ultramarine rich in silica in paper manufacture. The following are the usual tests and determinations made in ultramarine.

Color Test.—Weigh out 2 grams of alum and dissolve in water in a 100-cubic-centimeter flask. Dilute to the mark, and take two 50-cubic-centimeter samples of this alum solution in 100-cubic-centimeter flasks. Mix .2 gram of a good ultramarine in water in a 100-cubic-centimeter flask and fill to the mark. In another 100-cubic-centimeter flask, mix up .2 gram of the sample to be tested and fill to the mark. After shaking well, take 10 cubic centimeters of each of the ultramarine mixtures and add to the preceding alum solutions in the flasks. Allow them to stand for some time, with frequent shaking, and note the difference in color. The injurious effect of the alum can at once be told.

Determination of Moisture.—Weigh out between watch glasses 2 grams of the sample and dry to constant weight at 100° C., cooling in a desiccator. The loss in weight multiplied by 50 will give the percentage of moisture.

Determination of Silica.—Weigh out 1.5 grams of ultramarine, transfer to a porcelain dish, and treat with dilute hydrochloric acid; heat for some time; finally remove the cover glass to one side and evaporate to dryness. Proceed as directed for the determination of silica in lime in Art. **12.** Weigh as SiO_2 and earthy residue. This weight multiplied by 100 and divided by 1.5 will give the percentage of silica and earthy residue in the sample.

Determination of Sesquioxides of Aluminum and Iron.—Take 100 cubic centimeters of the filtrate from the silica determination that has been made up to 300 cubic centimeters in a graduated flask, and precipitate with ammonium hydrate in the usual way, proceeding as directed in the same determination in lime in Art. **12.** The weight of the ignited residue multiplied by 200 will give the percentage of Al_2O_3 and Fe_2O_3 in the sample.

Determination of Calcium Oxide.—If a qualitative test of the filtrate from the $Al_2O_3 + Fe_2O_3$ determination shows the presence of CaO, precipitate as oxalate, as directed for the same determination in lime in Art. **12.** Calculate in the usual manner.

Determination of Sulphuric Acid.—Take 100 cubic centimeters of the filtrate from the silica determination, dilute to 200 cubic centimeters, bring to a boil, and precipitate with barium chloride, as in the determination of H_2SO_4 in lime in Art. **12.** The weight of the $BaSO_4$ multiplied by .34335 × 200 will give the percentage of SO_3 in the sample.

Determination of Sodium Oxide.—Take the remaining 100 cubic centimeters of filtrate from the silica determination, precipitate, and wash the $Al_2O_3 + Fe_2O_3$ as before (this precipitate may be used as a check on the $Al_2O_3 + Fe_2O_3$ determination). Acidify this filtrate with H_2SO_4, evaporate to a small bulk, and transfer to a weighed platinum dish. Evaporate very cautiously on a water bath, and finally over a low flame. At this point, care should be taken to avoid loss by sputtering. Heat cautiously until fumes of H_2SO_4 are no longer given off, and then raise the temperature to red heat. Cool in a desiccator and weigh as Na_2SO_4. This weight will include $CaSO_4$ and $MgSO_4$, if calcium and magnesium are present. In the latter event, the amount of these elements present must be calculated to sulphates, and the weight of these sulphates must be subtracted from the weight of the mixed sulphates to get the weight of pure Na_2SO_4. The weight of Na_2SO_4 multiplied by .43694 × 200 will give the percentage of Na_2O in the sample.

The extra precipitation of the $Al_2O_3 + Fe_2O_3$ may be avoided by running the filtrate from the original $Al_2O_3 + Fe_2O_3$ determination into a 200-cubic-centimeter flask, and using 100 cubic centimeters for the Na_2O and the other 100 cubic centimeters for the CaO determination. This, however, gives only a .25-gram sample to work on, and better results can be obtained by using a new sample.

Determination of Sulphur.—Weigh out 1 gram of the sample and mix in a platinum crucible with 2 grams of magnesium oxide and 1 gram of sodium carbonate, saving a little of the magnesium-oxide and sodium-carbonate mixtures to cover over the top of the charge. Heat at a low red heat for about 20 minutes, and then stir with a platinum rod. Keep at this temperature, stirring from time to time, until the blue color disappears, which will take about 2 hours. Cool and wash into a small beaker with hot water, using a rubber-tipped glass rod to remove the last traces from the crucible. Add 10 cubic centimeters of bromine water, boil for about 1 minute, and filter. Wash well with hot water, add 10 cubic centimeters of hydrochloric acid, and boil until all the bromine is driven off. Precipitate with barium chloride, as usual. The weight of $BaSO_4$ multiplied by .13734 × 100 will give the percentage of sulphur in the sample.

The following is an analysis of ultramarine:

	PER CENT.
Silica and earthy residues	42.90
Sulphur	11.78
$Al_2O_3 + Fe_2O_3$	23.63
Lime, CaO	.16
Soda, $NaOH$	19.44
Sulphuric acid	2.00
Undetermined	.09
Total	100.00

23. Analysis of Rosin.—Rosin is the residue from turpentine distillation, and consists principally of the anhydride of abietic acid, the latter being $C_{19}H_{29}CO_2H$. Rosin is readily soluble in alcohol and also in alkali solutions. The principal test of a rosin is for saponifiable rosin.

Test for Saponifiable Rosin.—Weigh out 2 grams of rosin, dissolve in 30 cubic centimeters of absolute alcohol, and pass a current of dry HCl gas through the solution until the gas is seen to escape. This will take about ¾ hour. Allow the flask to stand about 1 hour, to insure complete etherification. The resinic acids will separate on the top as an oily layer. Dilute the contents of the flask with five times its volume of distilled water, and boil until the aqueous solution becomes clear. Transfer the contents of the flask to a separating funnel, and rinse the flask with ether. Shake vigorously, allow to separate, run the acid layer off, and wash until the last trace of HCl is removed. Rinse the funnel with 50 cubic centimeters of alcohol into a beaker, and titrate with normal sodium hydrate, using phenol phthalein as an indicator. The resinic acids combine at once with the alkali. Adopting 346 as the combining equivalent for rosin, the number of cubic centimeters of normal sodium hydrate used multiplied by .346 will give the amount of saponifiable rosin in the sample taken.

24. Analysis of Rosin Size.—When rosin and soda are boiled together, they combine to form resinate of soda, or rosin soap. The abietic acid and the sodium carbonate are supposed to react according to the following equation:

$$2C_{19}H_{29}CO_2H + Na_2CO_3 = 2C_{19}H_{29}CO_2Na + CO_2 + H_2O$$

Rosin size prepared by different processes is analyzed by the same methods.

Determination of Water.—Weigh out a quantity of size that will contain about 1 gram of rosin, and dry at 100° C. in a flat-bottomed metal dish for 1 hour. The loss of weight multiplied by 100 and divided by the weight of the sample taken will give the percentage of water in the size.

Determination of Free Soda.—Weigh out in a small beaker a quantity of size that will contain about 10 grams of rosin, dry until nearly all the water is drawn off, and dissolve in hot, strong alcohol. Filter, wash with strong alcohol, and heat the residue in the steam bath for a few minutes to drive off the alcohol. Take up the soda in hot water and titrate with standard acid, using methyl orange as an indicator. The number of cubic centimeters of acid used multiplied by the soda factor for each cubic centimeter, and this product multiplied by 100 and divided by the weight of sample taken, will give the percentage of free soda in the size.

Determination of Free Rosin.—Dissolve a quantity of size containing about 2 grams of rosin in about 100 cubic centimeters of distilled water, and transfer to a separating funnel. Add about 50 cubic centimeters of ether, agitate gently, and allow to separate. Draw the lower solution off as closely as possible, wash the ether solution several times with water, drawing the washings off into the original aqueous solution, and finally run the ether solution into a platinum dish that has been previously dried and weighed. Evaporate the ether, heat for 1 hour at 100° C., and weigh. This weight less the weight of the dish is the weight of the rosin, and this multiplied by 100 and divided by the weight of the sample taken will give the percentage of free rosin in the size.

In the case of a size containing a very high percentage of free rosin, it is a very difficult matter to extract the free rosin without the formation of a permanent emulsion. For this reason, the shaking with ether should be done very gently, and if an emulsion that separates with difficulty is formed, the addition of a small amount of powdered common salt will often hasten the separation. It is always advisable to make a second extraction of the aqueous solution with about 25 cubic centimeters of ether, as the first extraction is generally incomplete on account of insufficient agitation with ether. It is better to allow the solution to stand overnight, when there is a more complete separation.

Determination of Combined Rosin.—Return the aqueous solution from the previous determination to the separating funnel, add an excess of dilute sulphuric acid, which separates the combined rosin, shake with ether, and allow to separate. Draw off the lower layer, wash as before, and transfer to a weighed platinum dish. Proceed and calculate the results exactly as in the previous determination.

Determination of Combined Soda.—The percentage of combined soda is usually estimated by difference. The sample in which the moisture was determined is taken up with about 75 or 100 cubic centimeters of hot water, cooled, and titrated with standard acid, using methyl orange as an indicator.

Another very satisfactory method is as follows: Weigh out about 10 grams of thick size in a platinum dish, and heat over a low flame until the water is driven off. Then increase the flame until the rosin takes fire and allow to burn as long as it will. Now heat over a full flame for a few minutes, and allow to cool. Extract the residue with water, filter, and titrate with standard acid, using methyl orange as an indicator.

Either method will give the total soda in the sample. The combined soda is then found by subtracting the amount of free soda determined previously and calculating the percentage in the usual manner. The following are analyses of various sizes:

	Per Cent. Brown Size	PerCent. Dry Basis
Water	86.350	
Free soda	.012	.088
Free rosin	2.560	18.754
Combined rosin	9.180	67.253
Combined soda	1.830	13.407
Undetermined	.068	.498
Total	100.000	100.000

	Brown Size (With Small Amount of Free Rosin) Per Cent.	Dry Basis Per Cent.
Water	86.370	
Free soda	.800	5.87
Free rosin	.296	2.17
Combined rosin	10.920	80.12
Combined soda	1.610	11.81
Undetermined	.004	.03
Total	100.000	100.00

	White Size Per Cent.	Dry Basis Per Cent.
Water	97.8000	
Free soda	trace	trace
Free rosin	.7145	32.48
Combined rosin	1.2681	57.64
Combined soda	.2149	9.77
Undetermined	.0025	.11
Total	100.0000	100.00

25. Testing of Glue, or Animal Size.—Glue, or animal size, is made by heating the clippings of bones, horns, etc. with water. The best grades of glue for paper-mill use have been thoroughly washed, and are ready for mixing up for sizing purposes without any previous purification. Glue is insoluble in cold water, but will absorb six to eight times its weight of water and swell up. The best glue should absorb eight times its weight of water at a temperature of 15° C. in 24 hours. Glue is readily soluble in hot water, the solution gelatinizing on cooling. The following tests may be made to determine the quality of glue for paper makers' use:

Determination of Power of Absorption.—Weigh out 10 grams of the sample into a beaker and fill with cold water, taking care that all of the glue is covered by the water. Do not allow the temperature to rise above 15° C. for 24 hours. At the end of that time, pour off the excess of water and weigh again. The increase of weight will indicate the amount of water absorbed. The absorptive power is expressed as the number of times its weight of water absorbed.

Determination of Moisture and Ash.—The moisture is determined by drying a sample of the glue to constant weight at 100° C., the loss of weight being considered as moisture. For the determination of the ash, ignite the same sample and weigh the ash. The bone glue gives a fusible ash, while hide glue does not produce a fusible ash.

Comparison of the Value of Glues.—A good practical test that serves as a comparison of two glues as to money value is made as follows: Weigh out 10 grams of the higher-priced glue in a small beaker, and then weigh out an amount of the lower-priced glue that will be equivalent in price to the 10 grams of the former. Add 100 cubic centimeters of water to each at the same time and heat gently, keeping both at the same temperature and stirring in the same manner until all the glue is dissolved. Remove and allow to cool and gelatinize. Compare the strength of the two mixes. If neither gelatinizes, it will be necessary to take larger samples. A good glue for paper makers' use should gelatinize at 75° F. when mixed in the proportion of 10 grams of glue to 100 cubic centimeters of water.

ILLUSTRATION.—Two glues marked A and H, and costing 12½ cents and 12 cents, respectively, were compared. Treated in the manner just described, it required 11.5 grams of H to gelatinize from the same amount of water as 10 grams of A. Therefore, if H is worth 12 cents per pound, A is worth 13.8 cents, and as A sells at 12½ cents per pound, other things being equal, it is by far the cheaper glue.

26. Analysis of Salt.—Common salt, or sodium chloride, is used in the paper mill for the preparation of a bleach solution by electrolysis. The crude salt is used, but it should be as free as possible from calcium chloride. The following determinations are usually made:

Determination of Moisture.—Weigh out 5 grams of salt in a covered platinum crucible. Heat gently at first over a low flame, gradually raising the temperature to a low red heat. Keep at this temperature for a few minutes, cool in a desiccator, and weigh. The loss in weight multiplied by 20 will give the percentage of moisture in the salt. During the heating, great care should be taken to avoid loss by decrepitation.

Determination of Insoluble Matter.—Weigh out 5.85 grams of salt. Dissolve in hot water and filter into a 500-cubic-centimeter flask. Wash well with hot water, dry, ignite, and weigh. This weight multiplied by 100 and divided by 5.85 will give the percentage of insoluble matter in the salt.

Determination of Chlorine.—Cool the filtrate from the previous determination and fill to the mark. Take 25 cubic centimeters of this in a beaker by means of a pipette, dilute to about 50 cubic centimeters, add a little potassium-chromate indicator, and titrate with $\frac{n}{10}$ silver-nitrate solution. When the solution changes from yellow to faint pink, take the reading. The number of cubic centimeters required multiplied by 2 will give the percentage of sodium chloride in the sample. This percentage multiplied by .6239 will give the percentage of chlorine.

Determination of Calcium Oxide.—Dissolve 5 grams of salt in water and a little hydrochloric acid, if necessary. Filter off the insoluble matter and make alkaline with ammonia. Precipitate the calcium as oxalate in the usual manner, as described in Art. **12**, in the determination of calcium oxide.

If there is no sulphuric acid in the sample, the calcium oxide found is calculated to the chloride, and its equivalent of $NaCl$ subtracted from the $NaCl$ found.

Determination of Sulphuric Acid.—If a qualitative test shows the presence of sulphuric acid, it should be determined in the usual manner by precipitating with barium chloride, as has been described. The weight of $BaSO_4$ multiplied by 100 × .34335 and divided by the weight of the sample taken will give the percentage of SO_3 in the salt.

The following is an analysis of salt used:

	PER CENT.
Moisture	.480
Insoluble matter	.038
Calcium chloride, $CaCl_2$	1.100
Sodium chloride, $NaCl$	97.690
Calcium sulphate, $CaSO_4$	trace
Undetermined	.692
Total	100.000

27. Analysis of Sulphur, or Brimstone.—Sulphur is used in the manufacture of bisulphite liquor. For every 100 kilograms of sulphur there should be a yield of 190 kilograms of sulphur dioxide. A good sulphur should contain less than 1 per cent. of foreign matter.

Determination of Moisture.—An average sample of from 50 to 75 grams of sulphur should be taken and dried, without grinding, at 100° C. for 12 hours. If the sample is first ground, some of the moisture will be lost by evaporation. The results are calculated in the usual manner.

Determination of Ash.—Burn 50 grams of sulphur in a weighed platinum dish, weigh, and calculate the percentage of ash.

Determination of Sulphur.—1. Weigh out 50 grams of the finely ground sulphur, and digest in 200 cubic centimeters of carbon bisulphide in a stoppered bottle at the ordinary temperature. Take the specific gravity of the liquid. Reduce this to specific gravity at 15° C. by means of the following formula:

$$D = g + .0014\ (t - 15),$$

in which D = specific gravity at 15° C.;
g = specific gravity at actual temperature;
t = temperature (degrees C.) of solution.

This formula will hold good up to 25° C. In Table II, which has been carefully computed, is given the percentage of sulphur in the sample of brimstone for each specific gravity of the foregoing solution.

2. Weigh out .5 gram of the sample into a porcelain dish having a capacity of 250 cubic centimeters. Heat to 30° C. and add 6 cubic centimeters of bromine. After keeping at this temperature for about 10 minutes, add 15 cubic centimeters of concentrated nitric acid heated to 30° C. A violent action takes place, with the formation of sulphuric and hydrobromic acids, the remaining bromine distilling off. Heat with caution at first, and then bring to a boil in order to drive off the nitric acid. Add a small amount of a solution of $NaCl$, to avoid loss of sulphuric acid when evaporating, and evaporate to small bulk. Add hydrochloric acid and evaporate to small bulk again, and repeat this three or four times, finally evaporating to dryness. Heat gently to drive off hydrochloric acid, and take up with 5 cubic centimeters of half-strength hydrochloric acid and about 100 cubic centimeters of water. Filter into a 500-cubic-centimeter flask and wash

TABLE II

PERCENTAGE OF SULPHUR IN THE SAMPLE FOR EACH SPECIFIC GRAVITY

Specific Gravity	Percentage of Sulphur	Specific Gravity	Percentage of Sulphur	Specific Gravity	Percentage of Sulphur	Specific Gravity	Percentage of Sulphur	Specific Gravity	Percentage of Sulphur	Specific Gravity	Percentage of Sulphur
1.282	10.4	1.297	25.2	1.312	39.6	1.327	54.0	1.342	68.4	1.357	84.0
1.283	11.6	1.298	26.0	1.313	40.8	1.328	55.2	1.343	69.6	1.358	84.8
1.284	12.4	1.299	26.8	1.314	41.6	1.329	56.0	1.344	70.4	1.359	86.0
1.285	13.6	1.300	28.0	1.315	42.4	1.330	56.8	1.345	71.6	1.360	87.2
1.286	14.4	1.301	28.8	1.316	43.6	1.331	58.0	1.346	72.4	1.361	88.4
1.287	15.6	1.302	30.0	1.317	44.4	1.332	58.8	1.347	73.6	1.362	89.2
1.288	16.4	1.303	31.2	1.318	45.2	1.333	60.0	1.348	74.4	1.363	90.8
1.289	17.6	1.304	32.0	1.319	46.4	1.334	60.8	1.349	75.6	1.364	92.0
1.290	18.4	1.305	32.8	1.320	47.2	1.335	61.6	1.350	76.0	1.365	92.8
1.291	19.2	1.306	34.0	1.321	48.4	1.336	62.4	1.351	77.2	1.366	94.4
1.292	20.0	1.307	34.8	1.322	49.2	1.337	63.6	1.352	78.4	1.367	96.0
1.293	21.2	1.308	35.6	1.323	50.4	1.338	64.4	1.353	79.6	1.368	97.2
1.294	22.4	1.309	36.8	1.324	51.2	1.339	65.6	1.354	80.4	1.369	99.2
1.295	23.2	1.310	37.6	1.325	52.4	1.340	66.4	1.355	81.6		
1.296	24.0	1.311	38.8	1.326	53.2	1.341	67.6	1.356	82.4		

well with hot water. The residue can be ignited and weighed for the determination of insoluble matter.

Dilute the filtrate to the mark, take 100 cubic centimeters and precipitate the sulphur as $BaSO_4$ with barium chloride in the usual manner, filter, dry, ignite, and weigh as $BaSO_4$, and calculate to sulphur by multiplying by .13734. The weight of the sulphur thus found multiplied by 1,000 will give its percentage in the sample.

The following is an analysis of sulphur:

	Per Cent.
Moisture	.24
Foreign matter	.63
Sulphur	99.13
Total	100.00
Ash	.27

28. Analysis of Bisulphite Liquor.—Bisulphite liquor, which is used in the manufacture of "sulphite pulp," consists principally of calcium bisulphite, $CaH_2S_2O_6$, magnesium bisulphite, $MgH_2S_2O_6$, and calcium sulphate, $CaSO_4$, together with free sulphur dioxide, SO_2.

The ordinary tests made to control the working of the liquor are volumetric tests for total sulphur dioxide, SO_2, by titrating with $\frac{n}{10}$ iodine solution, using starch as an indicator, and for free SO_2 by titrating with $\frac{n}{10}$ sodium-hydrate solution, using phenol phthalein as an indicator. For each of these tests, 2 cubic centimeters of liquor should be used. The difference between the total SO_2 and the free SO_2 is the combined SO_2. The term *available* SO_2 would be better to use than free SO_2 to express the total acidity. There would then be no confusion about what is meant. Some designate as free SO_2 only that SO_2 which is in excess of that necessary to form *bisulphites* with the bases present, while others call free SO_2 all that is present in excess of that necessary to form *monosulphites* with the bases present.

A complete gravimetric analysis of the liquor is often required, and can be made according to the following methods:

Determination of Silica.—Take 10 cubic centimeters of the liquor in a porcelain dish and weigh; add 5 cubic centimeters of hydrochloric acid and evaporate to dryness. Drive off the excess of acid by gently heating, and take up in 5 cubic centimeters of dilute hydrochloric acid. Dilute to about 100 cubic centimeters, boil, filter, wash well with hot water, dry, ignite, and weigh as SiO_2.

The specific gravity of the liquor should be taken, and this multiplied by 10 will give the weight in grams of the liquor taken for the test. The weight of silica found multiplied by 100 and divided by the weight of liquor taken will give the percentage of silica.

Determination of Sesquioxides of Iron and Aluminum.—Treat the filtrate from the silica determination with NH_4OH, to precipitate the hydrates of iron and aluminum. Proceed as in Art. **12.** The weight of the oxides multiplied by 100 and divided by the weight of liquor taken, as found in the silica determination, will give the percentage of these oxides in the liquor.

Determination of Calcium Oxide.—Concentrate the filtrate from the preceding determination to about 200 cubic centimeters. Heat to boiling, and precipitate the calcium as oxalate with ammonium oxalate, as in Art. **12.** Calculate the percentage of CaO in the usual manner.

Determination of Magnesium Oxide.—Evaporate the filtrate from the calcium-oxide determination, and proceed as directed in Art. **12.** The weight of the magnesium pyrophosphate multiplied by 100 × .36036 and divided by the weight of liquor taken will give the percentage of MgO in the sample.

Determination of Sodium Oxide.—Take 25 cubic centimeters of the liquor, precipitate the heavy bases with ammonia carbonate, filter and wash, and after treating with a little dilute sulphuric acid, evaporate the filtrate in a platinum dish. Ignite until all sulphuric acid is driven off, cool, and weigh as Na_2SO_4. The weight of the Na_2SO_4 multiplied by .43694 × 100 and divided by the weight of the sample taken will give the percentage of sodium oxide.

Determination of Sulphuric Acid.—Treat 10 cubic centimeters of the liquor in a porcelain dish with 5 cubic centimeters of hydrochloric acid, and evaporate nearly to dryness to drive off the sulphur dioxide; dilute and precipitate with $BaCl_2$. If the mixture of sulphuric and hydrochloric acids should come to dryness, take up with a little hydrochloric acid, dilute, and precipitate with barium chloride, as directed in Art. **12.** The weight of $BaSO_4$ multiplied by 100 × .34335 and divided by the weight of the sample taken will give the percentage of SO_3 in the liquor.

Determination of Sulphur Dioxide.—Oxidize 10 cubic centimeters of the liquor with 10 cubic centimeters of bromine water, pouring the liquor into the bromine water. Heat, dilute, and boil to drive off the excess of bromine. Precipitate with barium chloride, as in Art. **12.** Calculate the SO_3 as in the previous analysis, and subtract the amount found there from the amount just found. The difference will be the SO_3 from the oxidation of the SO_2. This weight multiplied by 100 × .18001 and divided by the weight of the sample taken will give the percentage of SO_2 in the liquor.

In calculating the results of the liquor analysis, the sulphuric acid is combined with lime to form calcium sulphate, $CaSO_4$. If there is less lime than is necessary to saturate the SO_3, the balance of the SO_3 is calculated to magnesium sulphate, $MgSO_4$.

Any excess of lime is calculated to calcium bisulphite, $CaH_2S_2O_6$. If there is more SO_2 than is necessary to combine with all the lime, the magnesium oxide is calculated first to the monosulphite, $MgSO_3$, and if there is an excess of SO_2, to the bisulphite, $MgH_2S_2O_6$. Any further excess is reported as free SO_2.

The following is an analysis of a good bisulphite liquor:

	PER CENT.
Silica, SiO_2	.07
$Fe_2O_3 + Al_2O_3$	.02
Bisulphite of lime, $CaH_2S_2O_6$	2.76
Bisulphite of magnesia, $MgH_2S_2O_6$	3.19
Calcium sulphate, $CaSO_4$	.16
Free sulphur dioxide, SO_2	.14
Water and undetermined	93.66
Total	100.00

Ordinarily, the total acidity as determined by titration with standard soda solution, with phenol phthalein as an indicator, is calculated as free SO_2. This is, of course, the SO_2 over and above that required to form the monosulphite instead of the bisulphite, as expressed in the preceding analysis.

29. Analysis of Caustic Liquor.—Caustic liquor is used for digesting the wood in the soda process. The strength of this liquor varies in different mills from 11° to 12° Baumé at 60° F. In order to get good results, the liquor should be from 93.5 to 94 per cent. caustic; that is, this percentage of the soda present should be caustic. This test is practically the only one made.

Determination of Causticity.—Make up a weak solution of sulphuric acid (about 6 cubic centimeters of strong acid to 1 liter of water is a convenient strength). Take about 5 cubic centimeters of the caustic liquor (the amount should be varied according to the strength, but should never be so great as to require more than 50 cubic centimeters of the acid), dilute in a small beaker to about 50 cubic centimeters, and add a few drops of phenol phthalein. Titrate with the dilute sulphuric acid until the pink color just leaves, and take a reading. Now add a drop of methyl-orange solution, titrate cautiously until a slight pink tint is reached, and take a second reading. Subtract the first reading from the second, multiply the difference by 2, and subtract from the second reading. This remainder divided by the second reading and the result multiplied by 100 will give the percentage of causticity.

ILLUSTRATION.—The first reading when the pink color disappeared was 42.6 cubic centimeters. After adding methyl orange and titrating again until pink, the reading was 43.9 cubic centimeters. Following out the calculations as explained, $43.9 - 42.6 = 1.3$; $1.3 \times 2 = 2.6$; $43.9 - 2.6 = 41.3$; $41.3 \div 43.9 = .9407$; $.9407 \times 100 = 94.07$, which is the percentage of causticity.

Another method that gives very accurate results is as follows: Measure out 25 cubic centimeters of the caustic liquor and titrate with a normal acid, using methyl orange as an indicator. This will give the total alkali. Take 100 cubic centimeters of the same liquor and precipitate the carbonate and sulphate with neutral barium chloride in slight excess. Dilute to the mark in a 200-cubic-centimeter flask, shake well, and allow to settle. Take 50 cubic centimeters of this clear solution and titrate with the normal acid, using phenol phthalein as an indicator. This will give the amount of $NaOH$ in 25 cubic centimeters of the caustic liquor. The number of cubic centimeters of acid used in the second titration divided by the number of cubic centimeters used in the first titration and multiplied by 100 will give the percentage of causticity.

The liquor should also be tested for salt, especially where caustic liquor from an electric bleach plant is used in the liquor. This is done by titrating 5 cubic centimeters of the liquor with silver nitrate, using potassium chromate as an indicator.

30. Color Value of Pigments.—The price of a pigment does not always indicate its value. This is determined by the coloring power of the pigment. A chemical analysis will determine the value of a pigment, but there are simple methods of comparing colors and dyes that can be applied by persons not having a knowledge of chemistry. Under the analysis of ochers, in Art. **21**, a method was given for comparing colors, by mixing the ocher with zinc white and linseed oil. A method similar to this may be used for comparing all colors and dyes.

Comparison of Pigments.—To compare two pigments, weigh out 1 gram of the higher-priced one and mix with 10 grams of a good, dry china clay. Now weigh out as many grams of the lower-priced pigment as can be bought for the price of 1 gram of the higher-priced one, and mix with 10 grams of the same clay. Mix separately in a mortar with water to a thin, pasty mass. Spread each upon a strip of glass side by side and dry in a steam bath. The colors can now be compared, and the pigment having the higher color value selected. This test may be carried still further by weighing out a larger amount of clay and adding to the one giving the strongest tint in the preceding test until it matches the other.

By noting the difference in the amount of clay used, the difference in value of the two pigments can be determined.

Comparison of Soluble Colors.—All soluble colors, such as aniline colors, are dissolved in the proportion of 1 gram to the liter. Some colors have greater affinity for paper fibers than have others; also, some colors have greater affinity for one kind of fiber than they have for other kinds of fibers. In order to compare such colors in regard to their relative coloring power, the comparison must be made on the same paper stock, or combination of fibers, on which the colors are intended to be used.

If, for instance, it is desired to compare the relative strength of two aniline blues for use in coloring or whitening newspaper made up of 75 per cent. of ground spruce wood and 25 per cent. of spruce sulphite fiber, then some newspaper stock made up of those two pulps in the proportions given should be used in making the comparison. This is done as follows:

A quantity of the pulp is taken, thinned with water, and thoroughly mixed to a uniform mixture. The dilution should be such that 200 cubic centimeters will contain about 1 gram of dry fiber. Of this thinned pulp, exactly the same volume (200 cubic centimeters) is measured out for each color to be compared. These portions are poured into white-china bowls. With a pipette, the same measured amount of each color solution is run into each of the bowls. In the case of acid colors, alum is added, the same quantity of alum solution being added to each vessel, so that everything connected with each test is the same. In case of basic colors, no alum is added, as none is required; in fact, alum may prove injurious to colors of this kind. The mixtures of pulp and color are stirred from time to time and allowed to stand for about ½ hour. By this time the colors have gone on to the fibers to their maximum extent. The contents of each bowl is now poured on a wire cloth of fine mesh, and the water draining off, leaves a sheet of colored paper formed on the wire. A sheet of muslin is spread over this sheet of wet paper, and a sheet of blotting paper is then placed on this muslin and pressed so as to absorb some of the water from the wet paper. When the muslin is stripped off, it carries the sheet of colored paper with it. This is next pressed between two fresh pieces of muslin and blotting paper, and the sheet of colored paper is then stripped off from the pieces of muslin and hung up to dry. When dry, the sheets are compared as to the strength or depth of color. All conditions being identical, the color that produces the strongest coloring effect is, of course, the strongest color.

In order to tell just how much stronger one color is than another, the same measured quantity of the same thinned pulp used in the first comparative test is taken, and 5 per cent. less of the stronger color than was used in the first test is added. To another measured portion 10 per cent. less color is added; to another 15 per cent. less; and so on, until a sheet is obtained that is colored to exactly the same extent as with the weaker color. This, of course, shows how much stronger the one color is than the other.

In order to determine whether a dry, powdered soluble color is a straight color or a mixture of two or more colors, a very simple test is to wet a piece of filter paper and then blow some of the powdered color on it. Where each speck of color strikes the wet filter paper, it colors the paper with its own individual color. For example, suppose it is desired to learn whether a red-shade blue color, such as is ordinarily used for newspaper, is a straight blue of uniform red shade or a mixture of a blue-shade blue with some red color. By blowing some of the powder on a wet sheet of filter paper it will be found that if the color is straight, each particle will produce the same kind of blue spot on the wet paper, but if the color is mixed, there will appear both blue and red spots. It is sometimes preferable to wet the filter paper with alcohol instead of water, as the former dissolves some colors better than the latter and consequently the colored spots show up better.

31. Analysis of Wood Pulp.—The analysis of soda and sulphite pulps are taken up separately.

Determination of Cellulose in Wood.—Weigh out 5 grams of the finely divided substance and boil four or five times in water, using 100 cubic centimeters each time. Pour off the water and dry at 100° C. Now exhaust with a mixture of equal parts, by measure, of benzine and strong alcohol, to remove the rosin, fat, wax, etc. Dry the residue and boil several times in water, to every 100 cubic centimeters of which 1 cubic centimeter of strong ammonia has been added. This treatment removes the pectous substances and coloring matter. Treat the residue in a closed bottle with 250 cubic centimeters of water and 20 cubic centimeters of bromine water containing 4 cubic centimeters of bromine to the liter.

TABLE III

PERCENTAGE OF CELLULOSE IN VARIOUS WOODS

Wood	Percentage of Cellulose	Wood	Percentage of Cellulose
Alder	54.61	Oak	39.50
Beech	45.49	Pine	57.00
Birch	55.52	Poplar	62.80
Chestnut	52.64	Scotch pine	53.27
Ebony	30.00	Spruce	53.00
Fir	53.30	Willow	55.72
Linden	55.09		

When the yellow color of the liquid disappears, add more bromine water and repeat until the yellow color remains and bromine can be detected after standing 12 hours. Filter off the liquid, wash the residue with water, and heat to boiling with 1 liter of water containing 5 cubic centimeters of strong ammonia. If the liquid and tissue are colored brown, filter off the undissolved matter, wash, and treat again with bromine water, as before. When the action seems complete, heat the residue as before with ammonia water, and if the brownish tint is again imparted to the liquid, repeat the preceding operation. The cellulose is thus obtained in a pure white state. Wash with boiling water and then with hot alcohol.

Dry at 100° C. and weigh. The percentage of cellulose is calculated in the usual manner.

Table III gives the percentage of cellulose in representative woods as determined by the foregoing method.

32. Analysis of Soda Pulp.—Soda pulp is made by the soda process. Samples from the rolls and from the wet and the pulp machine should be taken from time to time and tested. In taking samples from the roll for shipment, cut through at least ten layers of the pulp and take two strips about 12 inches long and ½ inch wide. Tear these into small pieces and put them in a weighed sample box, keeping the lid on as much as possible. A sample should be taken from every tenth roll.

Determination of Total Moisture.—Weigh the box containing the sample and empty it on a clean piece of paper in the drying oven. Dry at 100° C. for about 6 hours. Return the sample to the box, cool in a desiccator, and weigh again. Repeat until the weight is constant. The loss in weight multiplied by 100 and divided by the weight of the sample taken will give the percentage of moisture in the pulp.

The folds from the wet machine are tested in the same way.

Determination of Air-Dry Moisture.—Pulp that contains moisture due only to the atmosphere is known as *air-dry pulp*. The amount of moisture present is rather indefinite, owing to the difference in humidity. It is determined by drying a sample until bone dry, weighing, and exposing to the atmosphere at ordinary temperature for at least 24 hours. The increase in weight will indicate the amount of air-dry moisture. All pulp is generally sold on the air-dry basis, and not on the bone-dry basis. It is an almost universal custom to figure air-dry pulp as containing 10 per cent. of moisture. This is calculated by determining the bone-dry weight, which is then multiplied by 100 and divided by 90. Some pulp testers add to the bone-dry weight 10 per cent. of itself and call the result the air-dry weight; this, however, is obviously incorrect.

Determination of Ash.—Weigh out about 5 grams of the pulp sample in a platinum crucible. Ignite until all carbonaceous matter is burned off. Cool in a desiccator and weigh. The weight of the ash multiplied by 100 and divided by the weight of the sample taken will give its percentage in the pulp. Soda pulp that has been run over the driers usually contains from 7 to 8 per cent. of moisture and about 1 per cent. of ash. Pulp after leaving the last press roll and before passing over the driers contains about 65 per cent. of moisture.

33. Analysis of Sulphite Pulp.—Sulphite pulp is made by the sulphite process. It is shipped in folds from the wet machine, and contains from 60 to 70 per cent. of moisture.

Determination of Moisture.—Cut strips 10 inches long and ½ inch wide from folds taken at random from different parts of the lot sampled, taking care that a good average sample is selected. Tear these strips into small pieces and put them in a sample box. Weigh the box and contents and transfer the sample to the drying oven. Dry at 100° C. for from 18 to 24 hours. Return to the box and weigh again. Subtract the weight of the box to get the weight of bone-dry fiber. Dividing by the weight of wet pulp taken will give the percentage of bone-dry fiber. The weight of the bone-dry fiber divided by 90 and multiplied by 100 will give the percentage of air-dry fiber in the sample.

The following is a convenient method for the determination of moisture and gives results sufficiently accurate for all practical purposes. The results are expressed in percentage of air-dry fiber. This method is used when samples are taken from time to time from the wet machine to ascertain how the pulp is running and to figure out the percentage of fiber made daily.

Take 100 grams of the sample, weighing as quickly as possible, and transfer to the drying oven, after separating the different layers as much as possible. Dry from 18 to 24 hours and rapidly weigh again. The weight of the dried sample divided by 90 and multiplied by 100 will give the percentage of the air-dry fiber.

Determination of Ash.—The ash of sulphite pulp is determined the same as the ash of soda pulp in Art. 32. For sulphite pulp, it is usually from .6 to 1 per cent.

34. **Paper Testing.**—Samples of paper are tested in the same way as pulp for moisture and ash, taking about 50 grams for the determination of moisture and 3 or 4 grams for the ash.

Determination of Retention of Filler.—The retention of filler is determined as follows: The percentage of ash of the paper and the percentage of ash in the paper stock itself to which no filler has been added are determined. This latter percentage is deducted from the former, and the difference is the ash due to the filler used. As the fillers ordinarily used suffer more or less loss in weight on ignition, a sample of the filler used must be ignited by itself and the loss on ignition determined. Agalite ordinarily loses about 4 per cent., while clay loses from 15 to 20 per cent. The percentage of "ash due to filler," as just determined, must therefore be corrected for the "loss on ignition" of the filler used, in order to get the true percentage of original filler contained in the paper. The percentage of filler furnished to the paper maker being known, it is of course a simple matter to calculate what percentage of this amount was found in the paper, or, in other words, the percentage retained.

Microscopic Fiber Test.—The various fibers in paper are detected by means of a microscopic examination, while at the same time there are several chemical tests that are useful in identification.

Prepare the sample to be examined under the microscope as follows: Cut small pieces of paper from different parts of the sample and boil in a 1-per-cent. solution of caustic soda. The fibers may now be separated by shaking in a bottle containing a few pieces of broken glass. The fibers are placed on a glass and covered with a drop of glycerine and a cover glass.

Mechanical Wood Fiber.—Under the microscope, *mechanical wood fiber* is distinguished from *chemical wood fiber* by the fact that the fibers are rarely separated, they being generally bound together in bundles. The ends also are torn and jagged.

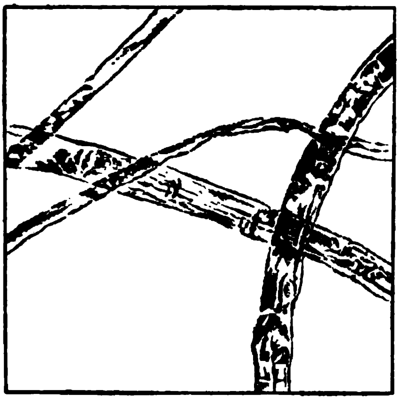


FIG. 3

Linen Fiber.—In Fig. 3 is shown an illustration of *linen fiber*. The ends of this fiber are usually drawn out into numerous fibrils and fibers of a cylindrical form.

Esparto and Straw Fibers. The esparto and straw fibers are very much alike, and consist of serrated cells and fibrovascular bundles. Straw may be distinguished from esparto by the presence of small, oval-shaped cells and the absence of the fine hairs that always line the inner surface of the leaf of the esparto plant.

FIG. 4

Chemical Wood Fiber. The fibers of chemical wood are flat and ribbon-like and have unbroken ends, very much like cotton, but are distinguished from it in that they are not twisted. Pine-wood fiber is detected by the presence of small pitted vessels.

Cotton fiber is shown in Fig. 4, poplar fiber in Fig. 5, and spruce fiber in Fig. 6.

To assist in the determination of different fibers under the microscope, a reagent made up as follows will be found of great help: Dissolve 2.1 grams of potassium iodide and

.1 gram of iodine in 5 cubic centimeters of water and mix with 20 grams of zinc chloride dissolved in 10 cubic centimeters of water. The mixture should be allowed to stand and the clear liquid decanted. This reagent will color cotton, linen, and hemp, wine red; esparto, straw, and wood cellulose, bluish violet; mechanical wood pulp and unbleached jute, yellow; and manila hemp, blue and bluish gray to yellow.

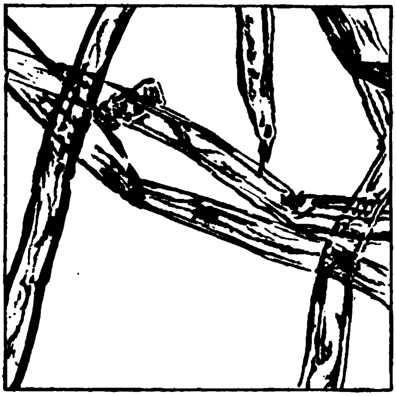


Fig 5

Chemical Tests for Constituents of Paper.—When a small quantity of paper that has been beaten up, separated, and moistened with iodine is examined under the glass, the fibers can be separated, owing to the fact that the ground wood and jute will be colored yellow; cotton, hemp, and linen, brown; while bleached straw, esparto, and chemical wood fiber will remain uncolored.

Fig. 6

Detection of Mechanical Wood Pulp.—Nitric acid gives a brown stain on paper containing mechanical wood pulp. Phloroglucinol gives a deep magenta in the presence of mechanical wood pulp. The latter test is the one mostly used for this purpose. Phloroglucinol is prepared by dissolving 2 grams of the reagent in 25 cubic centimeters of 95-per-cent. alcohol and adding 5 cubic centimeters of concentrated hydrochloric acid. Apply a drop to the paper to be tested and allow to evaporate. In the presence of ground-wood pulp, the deep magenta coloration will be developed.

In some papers, the coloring matter used acts as an indicator for acids and will turn red when treated with acid. In papers where these colors are present, it is difficult to test for ground wood with phloroglucinol, as the acid in the mix develops the red color. In papers where "yellow mix" is used, this color is developed by the acid in the phloroglucinol. Aniline sulphate develops a deep yellow in presence of ground wood, and is prepared by dissolving in water. This reagent should be substituted for phloroglucinol in tests where colors such as those just mentioned have been used in the paper.

The *percentage* of ground wood may be roughly estimated by comparing the depth of color produced by the phloroglucinol on the sample with the depth of color produced on several standard samples in which the percentage of ground wood is known. This test can be applied only when the chemical fiber present has been perfectly reduced.

Detection of Sulphite Pulp.—Sulphite pulp can be detected by means of a dilute solution of sodium-auric chloride, which imparts to the paper moistened with it a reddish-brown color when unbleached sulphite pulp is present, and a bluish color when bleached sulphite pulp is present.

Detection of Straw and Esparto.—Straw and esparto can be detected by boiling the paper for some time in a 1-per-cent. solution of aniline sulphate, which produces a red color in the presence of these substances.

Detection of Animal Size.—Heat a small fragment of paper in a test tube with distilled water, transfer the clear solution to another tube, cool, and add a solution of tannic acid. If any animal size is present, a milky, flocculent precipitate will be formed, the consistency of which will depend on the amount of animal size present.

A very delicate test for animal size is to soak a small strip of paper in a reagent prepared by dissolving a small amount of quicksilver in an equal weight of fuming nitric acid, cooling, and adding an equal volume of water. In the presence of animal size, the paper will develop a red color, the depth of which will depend on the amount of size present. This reagent will keep only about a month, and hence must be made up frequently.

Detection of Starch.—Starch may be detected in paper by adding a drop of very dilute solution of iodine, which, if starch is present, will develop a deep-blue color. This test is better carried out by boiling some of the paper in water for about 20 minutes, pouring off the water into another vessel, and adding the dilute iodine solution.

Detection of Rosin Size.—The presence of rosin size may be detected by heating some of the paper in absolute alcohol and pouring the alcoholic solution, after cooling, into five times its volume of distilled water. If a precipitate is formed or there is a cloudiness, the presence of rosin size is indicated.

By wetting the sheet with the mouth and holding it to the light, a well-sized paper will not be transparent, while if poorly sized, it will be transparent, the degree of transparency varying inversely with the amount of size used.

Detection of Chlorides.—Boil the paper in distilled water, filter, add a few drops of nitric acid, and then a few drops of silver-nitrate solution. A cloudiness or a precipitate indicates the presence of chlorides.

Detection of Alum.—An excess of alum can be detected by boiling a quantity of the paper in a small amount of water, filtering, and testing the filtrate for aluminum by precipitating with ammonium hydrate and ammonium chloride.

The *nature* of the filler can be determined by an analysis of the ash.

Determination of Coloring Matters.—Sometimes, coloring matters can be determined by an examination of the ash. When ultramarine has been used, the ash is blue.

35. Mechanical Tests of Paper.—There are several mechanical tests to which paper should be subjected in order to determine its quality.

Determination of the Direction in Which the Paper Came From the Machine.—In order to determine the strength of paper, the direction in which the paper came from the machine must be ascertained. This is done as follows: Cut a disk from the center of the sheet of paper, float it on water, and allow it to rest on the palm of the hand, when it will curl up. The direction of the axis of the cylinder formed is the direction in which the paper came from the machine.

Determination of the Strength of Paper.—The strength of paper can be determined roughly by tearing the sheet. Two papers can be compared in this respect by means of a testing machine, for which test strips are cut (taking care that they are cut in the same way, as to coming from machine, and are of the same size). The strips are then subjected to tension in the testing machine, and the weight necessary to break them read off and compared. Two sheets can be roughly compared in this respect by cutting strips an inch in width from each sample, and suspending them from an iron bar. Weights are then cautiously attached to each until the sheets break; the difference in weights required will give the comparative strength of sheets.

Detection of Dirt.—Dirt in paper can be detected by holding a sheet to the light.

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NOTE.—All items in this index refer first to the section (see the Preface), and then to the page of the section. Thus, "Brimstone burners, §1, p25," means that brimstone burners will be found on page 25 of section 1.