

## **Report to the Local Government Board / by R. Angus Smith.**

### **Contributors**

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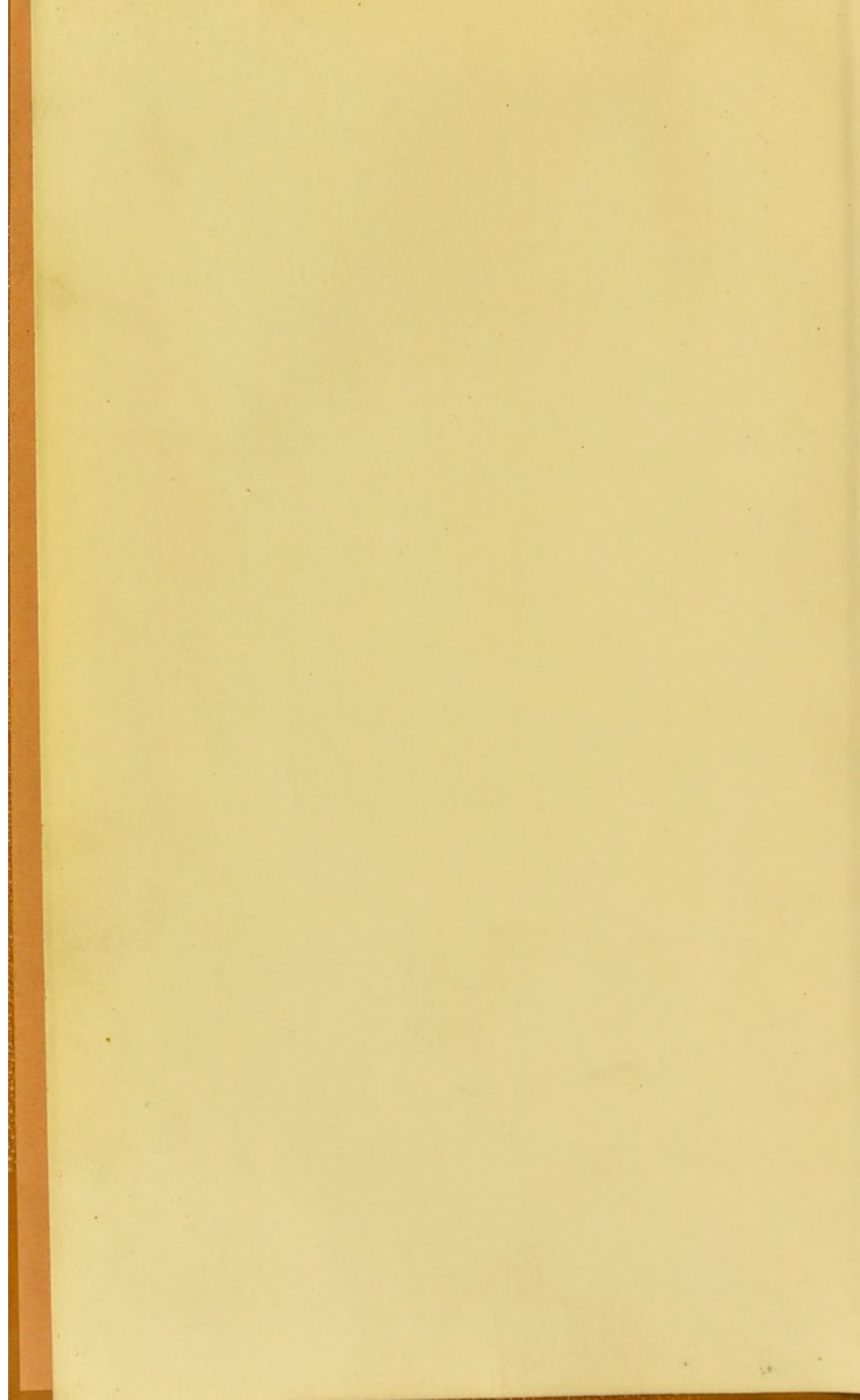
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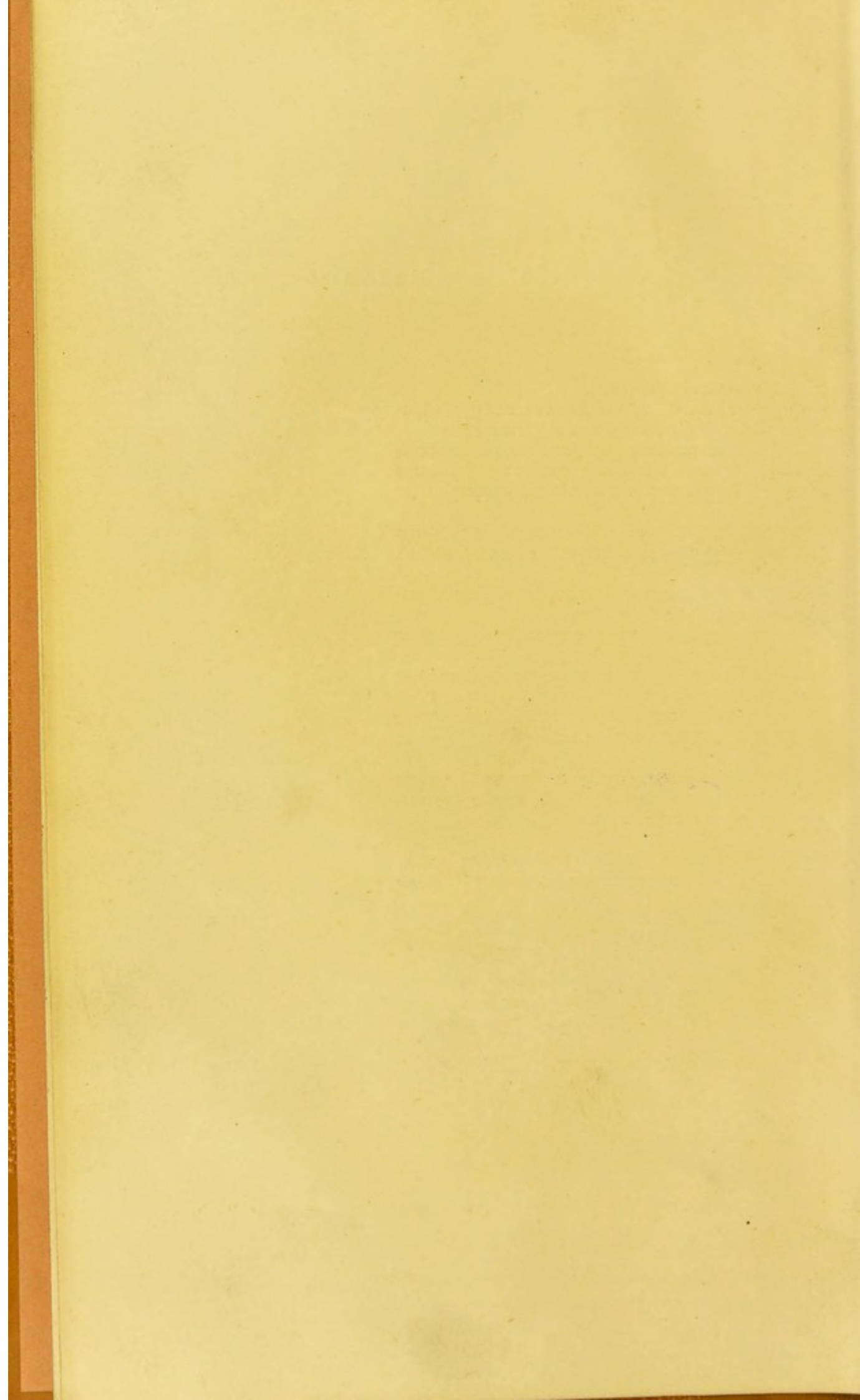




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# R E P O R T

TO

THE LOCAL GOVERNMENT BOARD

BY

1019

DR. R. ANGUS SMITH, F.R.S.,

ONE OF THE INSPECTORS UNDER THE ACT.

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Presented to both Houses of Parliament by Command of Her Majesty.

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## TO THE LOCAL GOVERNMENT BOARD.

MY LORDS AND GENTLEMEN,

THE position which I hold as Inspector under the Rivers Pollution Prevention Act has led me to consider the question of water, pure and impure, from various points of view, and I have brought forward several investigations which I hope will be found of value.

The first part relates to questions which rise to the surface when we study the analysis of water, and mainly to the decompositions which take place in the organic matter often found in water.

The second part relates to the action of air on sewage, and to the mode of treating sewage so as to hasten the aeration. This includes remarks on the relation which the results bear to the latest microscopic inquiries on the germs of disease, and water supply.

The third part relates to the purification of sulphureous liquids draining from alkali works, and to the action of air upon them; with a few experiments on effluents from several other works.

These inquiries are continuations of work done in former years, the earliest going back to 1846, if not prior.

It is really so difficult to come to a conclusion on the many questions that rise before one, that I have not attempted to do much more than to give my results, and leave them to do their work in ripening the mind. Further inquiries may modify all I have to say here, but I think the matter will in any case be of use on the road of progress. I would call attention to the decomposition of organic matter by nitrates, or vice versâ; the use of the oxygen of the nitrates in oxidizing organic matter, and giving out the nitrogen of the nitrates; to the use of aeration in preventing putrefaction, and to its use in throwing down the sulphur from the sulphides under the given conditions; that is, by the constant sulphuration and oxidation of manganese.

If in some cases I may appear to bring forward earlier papers in quotation too often, I may be forgiven, as there is always an inclination to put aside earlier work, and occasionally one feels inclined to show that in former times he has been on the right track, and not in the way of misleaders.



## PART I.—WATER AND SEWER WATER.

## No. I.

## SOME CHANGES EFFECTED BY OXYGEN ON ORGANIC BODIES IN WATER—FORMATION AND DESTRUCTION OF NITRIC ACID.

In a magnificent paper by Messrs. Gilbert and Lawes (*Phil. Trans.*, 1861, p. 508), read in 1860, it is said, when speaking of the sources of nitrogen in vegetation,—

“ Other investigations to which we have to call attention will throw some light upon the character of the molecular forces by which the decomposition of nitrogenous organic compounds is effected under such circumstances as we have been considering. These forces might be one or both of two kinds :—

“ 1. They might be of an oxidising character, analogous to that of the action of chlorine upon ammonia by which free nitrogen is evolved.

“ 2. They might be of a reducing character similar to that of a great number of substances upon the oxygen-compounds of nitrogen, by which the oxygen of the latter is appropriated, and free nitrogen given off.

“ 3. These two actions may operate in succession the one to the other.

“ It is well known that an oxidising action may be so intense as to deprive a nitrogenous organic compound of all its carbon and hydrogen, converting it into oxygen compounds, as is done by permanganic acid. The converse action of the transformation of oxygen-compounds of nitrogen into ammonia is also very well known. An intermediate stage in either of these converse actions may give free nitrogen.”

In the account of an investigation “ on the amount and composition of the rain and drainage waters collected at Rothampstead, 1881,” written by Dr. Lawes, Dr. Gilbert, and Mr. Robert Warrington, Part II., page 25, speaking of the loss of nitrates in the soil, it is said,—

“ This reduction in question has been effected by the organic matter of the soil, and has resulted in the formation of carbonic acid gas. A part of the nitric acid has probably been reduced to ammonia, while a considerable part of the nitrogen has most likely taken the form of nitrogen gas.”

The idea of such a decomposition of nitric acid by organic substances as to give out free nitrogen has been very clearly in the minds of the authors named.

I shall add some of my early work and opinions, as well as a page or two of my latest work, showing that in some conditions free nitrogen is given off by organic substances with great rapidity. It may seem at first that such a point was not of very great importance, but it has such an important bearing on the pollution of rivers question, or, we may say, rather on the purification of water, that it might have been treated even more fully than it



is, and it seems to be a suitable point with which to begin the subject afresh.

In a previous paper read in 1867, and in one in which I spoke of the importance of examining the condition of the organic matter in water, and not merely showing its amount, I divided the organic matter into seven sections:—

1. Organic matter decomposed or putrid.
2. Organic matter readily decomposed and ready to become putrid.
3. Organic matter slow to decompose.
4. Recent organic matter.
5. Old organic matter.
6. Vegetable organic matter.
7. Animal organic matter.

I might express it differently now.

I was interested in showing the development of organisms in the water as a mode of finding the quality of the organic matter. The idea was correct, and the use of the microscope for the purpose correct abstractly; but the subject must pass into the hands of men who have devoted much time to the study of the changes which take place in minute forms. I think I was right in my mode of dividing the organic matter chemically; and, seeing that the study of the germs of disease threatens to be difficult and complicated for a long time to come, it seems to be the duty of chemists to do something towards examining questions relating to organic matter in their own way. I have turned, therefore, more of late to the study of changes which take place in the ammonia, nitric acid, and oxygen, so as to find by chemical methods if the water has active organic matter in it. I do not say that I have made much progress in it, but I have done some work which seems to me interesting.

I may as well here give an extract showing some of my previous views and procedure (Mem. Lit. and Phil. Soc., Manchester, 1867):—

“If the water contains organic matter in solution, or in a condition approaching in all appearance to solution, it may be wholesome or unwholesome. The mere existence of organic matter is no proof of impurity. We must know if it brings animalcules or vegetable life, or products of putrefaction. We must know the quality as well as the quantity. If the matter is peaty, consisting of the ordinary humous class of acids and salts, the colour may be very dark, and the water very unpleasant to look at, without being in any way, so far as I have ever heard, injurious to health, although such water cannot be quite so wholesome as pure water, since the oxygen of solution is diminished. The taste and other sensible qualities will be the chief guides.

“If the matter is wholly or nearly colourless it may still be wholesome or unwholesome. It may, for example, contain the juices of plants of a wholesome character. If these juices are fresh they may do no injury; but they will not remain long fresh; they will putrefy. Water containing organic matter



ready to putrefy ought to be avoided, as we cannot tell when the moment of danger begins, whilst the quality at best is never known to us exactly.

"To ascertain the nature of the organic matter the water is allowed to stand for a day or two, in which case it may be found that *organised bodies* show themselves. Sometimes plants seem completely to fill the vessel, having come out of a moderately clear solution. When standing in this case, the water must be prevented from evaporating, and it must be in glass, so as to be exposed to light; a temperature suiting vegetation is also to be given. Animalcules may appear in great numbers. They are an indication of nitrogenous matter, and one proof of the presence of substances capable of putrefaction. It may be that some form of putrefaction will be the only result; but whether this occurs alone, or along with organised forms, an excess of organic matter is proved. Water that will not bear the test of standing will in most cases be rejected at once. If no other can be obtained, it ought to be used before the putrefactive process has begun; but this is very dangerous. The next best method is to wait till after putrefaction has terminated, and the products are separated as much as possible. This is popularly known to be the case when the water has for some time become clear and colourless and free from smell and taste."

"Water with green organic matter in suspension or semi-solution is generally full of germs of living things and nauseous to the taste."

The oxidation of nitrogen has been a favourite subject of late, but I should not think of attending to it for that reason. However, it may be known to a few chemists that I made nitric acid or nitrates from organic matter in water at a very early stage, as seen in the vol. of the Trans. of the British Association in 1848. I cannot, therefore, be said to be late in the field.

Regarding the deoxidation I may quote from my paper of 1867, speaking of nitrates: "the oxygen seems to be removed as the oxygen of the air is, leaving the nitrogen to pass off as gas." Mem. Lit. and Phil. Soc. of Manchester, vol. 4, ser. 3rd, 1867-8.

When doing the first experiments, spoken of in 1848, I used generally, if not always, yeast for the organic matter, and I did not give to the organised bodies the credit of producing the action. The interesting experiments, however, of M. Schloesing and of Mr. Robert Warington cause every one to reconsider the subject. I suppose M. Pasteur gave the first idea of the action of organisms in nitrification, but, so far as I remember, did not prove it. The idea that all nitrates are the products of oxidation of animal matter in contradistinction to vegetable is another point which compels us to think over the subject. I have always objected to the opinion that they were the products special of animal life, knowing that my own experiments were made with vegetable substances. It has, on the other hand, been said (long ago in conversation with me,—I do not remember



if the idea is published,) that probably the vegetable life passed into animalcular life, and thus nitrates were the products only of animals. This is hypothesis, and cannot go far. We must separate the idea of the action of Bacteria, or any vegetable or animal forms of organic matter, from the idea that organic matter must itself be animal before it passes into nitrates, leaving it possible that nitrates may come from decomposing vegetation.

Then, again, the drainage of peat lands frequently contains nitrates, as we know, in great abundance, but the peat itself is not remarkable for much animal life. I find Mr. Warrington thinking otherwise as to the amount of nitrates. Our experiences differ on this point, but there is a great variety of peat.

On account of these facts the conditions become complicated, and I am now led to believe the following:—

1. Animal or vegetable matter containing nitrogen produces nitrates by oxidation under certain conditions, with and without organisms.
2. Inorganic matter containing ammonia does the same.
3. Albuminous matter in a putrefactive condition, if exposed to excess of air, produces an oxidation of organic nitrogen.
4. A peculiar putrefactive condition produces a deoxidation of nitrates. In some conditions nitrogen is eliminated as gas, the oxygen going to the carbon in whole or in part. In weak solutions, containing water enough to absorb the carbonic acid, nearly pure nitrogen may be obtained with considerable rapidity.

Two of these propositions may require proof and explanation.

It will be seen in this view of the question that nitrogenous bodies have a peculiar power of taking up oxygen and of giving it out. They seem to be used for the purpose of purifying organic substances as transferrers of oxygen. Although we have not proved, so far as I know, that in cases of great impurity nitrates are formed, and their oxygen given out afterwards, yet we can prove that when the impurity is moderate nitrates are formed, and in any case they give out their oxygen in this way.

The escape of free nitrogen from solutions of organic matter has been noticed, by Reiset, for example, (see *Jahresbericht der Chemie für 1856*, p. 806,) and by myself, in the examination of the gases of putrefaction, in 1863 (*Mem. of the Lit. and Phil. Soc. of Manchester*). I certainly doubted if this was an action of organisms when I found that the nitrogen was evolved at a heat equal to 160° F. or 71·1° C. At the same time there was evolved a great deal of sulphuretted hydrogen. The putrefactive substance then used was blood very much diluted.

I had occasion lately to examine several mixtures. One was formed by the evaporation of urine, and some fæces in the process for drying employed by Mr. Alfred Fryer; and, reverting to my old idea that nitrogen might be given off, I put nitrate of potash in various amounts into solutions of the substance. Bubbles of gas began to escape next day, and in some cases came off with great rapidity and regularity, *i.e.*, about one bubble in three seconds.



Many organic fluids were tried, but the same rapidity was not obtained by any other, although nitrogen was found escaping from blood, egg albumen, and flour paste in the same conditions, that is, the putrefactive state being overpowered by nitre. It did not, however, escape so rapidly as in the liquid mentioned previously.

The nitrate of potash was decomposed and ceased to be found in the liquid. Sulphuretted hydrogen did not exist, or it was found in minute quantities only, and it was clear that the action was entirely different from putrefaction simple. The gas was frequently collected, and it was found to contain very little, sometimes only a trace of, carbonic acid. At the same time the action seemed to be caused by organisms; that is, it took place in liquids which had a great amount of organic matter ready to assert itself. And this I leave for the moment, under a belief that this may be a kind of fermentation; certainly it seems a very new kind. It is like a reversed putrefaction, and must be carefully noted down in considering the action of disinfectants.

This action not being quite the same as that found by Schloesing, where nitrogen was slowly given out, I put down here many of the experiments to illustrate it:—

1. 1100 c. c. of water, containing 10 per cent. of excreta (concentrated by Fryer's apparatus), gave off no gas during  $2\frac{1}{2}$  months.

2. 1100 c. c. of water, containing 10 per cent. of excreta and 2 grms.  $\text{KNO}_3$  (nitre), commenced to give off gas after 12 hours. The gas collected over water

$\text{N} = 98.4$  per cent.  $\text{CO}_2 = 1.6$  per cent.

3. 1100 c. c. of water, containing 10 per cent. of excreta and 2 grms. nitre, gave off 218 c. c. of pure nitrogen when collected over water. (2 grms. nitre contain 220.6 c. c. N.)

4. 340 c. c. of water, containing 10 per cent. excreta and 0.5 gm. nitre per litre, gave off 14.8 c. c. nitrogen collected over water. (The nitre contained 18.7 c. c.)

5. 350 c. c. of water, containing 10 per cent. excreta and 1.0 gm. nitre per litre, gave off 38 c. c. N collected over water. (The nitre contained 37.4 c. c.)

6. 350 c. c. of water, containing 10 per cent. excreta and 0.25 gm. nitre per litre, gave off 7.5 c. c. N collected over water. (The nitre contained 9.6 c. c.)

7. 340 c. c. of water, containing 10 per cent. excreta and 1.0 gm. nitre per litre, gave off 38.0 c. c. N collected over water. (The nitre contained 37.4 c. c.)

8. 320 c. c. of water, containing 10 per cent. excreta (fresh sample) and 0.5 gm. nitre, gave off 53.8 c. c. N collected over water. (The nitre contained 55.1 c. c.)

9. 330 c. c. of water, containing 10 per cent. excreta (as No. 8) and 1.0 gm. nitre. Gas collected over water was nitrogen only.

10. 560 c. c. of water, containing 10 per cent. excreta (as No. 8) and 5.0 grms. nitre. Gas collected over water was nitrogen only.



11. 1100 c. c. of 10 per cent. excreta from a previous experiment, with 2 grms. nitre, were mixed with a second quantity of 2 grms. nitre. Decomposition commenced at once, but continued very slowly. A gas evolution went on for many days. Liquid became strongly alkaline.

12. 1100 c. c. of 10 per cent. excreta from a previous experiment, with 2 grms. nitre, were mixed with 1,980 c. c. of water containing 2 grms. nitre in solution. Decomposition commenced at once; the gas collected over water was pure nitrogen. Liquid became strongly alkaline.

13. 440 c. c. 10 per cent. excreta (as No. 8) and 5 grms. nitre were heated to ( $120^{\circ}$ – $125^{\circ}$  F.); gave off gas after 30 hours. The speed was much slower than in those experiments at the ordinary temperature.

14. Putrid blood + 3 grms. nitre gave off much gas, which, when collected over water, consisted of pure nitrogen.

15. 1100 c. c. urine + 0.5 gm. nitrate of ammonia + 5 c. c. putrid urine, gave off 70 c. c. of N.

16. Egg and water with nitre gave off gas consisting of 77.8 per cent. N and 22.2 per cent.  $\text{CO}_2$ , collected over mercury. When collected over water the nitrogen only was obtained.

17. Blood with  $(\text{NH}_4)_2\text{CO}_3$  carbonate of ammonia and  $\text{KNO}_3$  gave off gas, which consisted of nitrogen when collected over water.

18. To a quantity of blood which had stood several weeks without apparent change about 2 grms.  $\text{KNO}_3$  were added; a brisk evolution set in after 2 days.

Gas collected over mercury = N = 92.6,  $\text{CO}_2$  = 7.4.

#### *Gases collected over Mercury.*

19. 406 c. c. blood + 1 gm.  $\text{KNO}_3$  gave off gas consisting of 96.1 per cent. N and 3.9 per cent.  $\text{CO}_2$ .

20. Flour paste + 1 gm.  $\text{KNO}_3$  gave off gas consisting of N = 97.0,  $\text{CO}_2$  = 3.0.

21. Flour paste + 2 grms.  $\text{KNO}_3$  gave off gas consisting of N = 6.4,  $\text{CO}_2$  = 93.6.

22. Egg diluted with 8 vols. of water  $\text{KNO}_3$  gave off gas slowly for some days, N = 85.4,  $\text{CO}_2$  = 14.6.

23. 205 c. c. blood + 1 gm.  $\text{KNO}_3$  gave off gas consisting of N = 84.5,  $\text{CO}_2$  = 15.5.

24. 1150 c. c. blood + 1 gm.  $\text{KNO}_3$  gave off gas consisting of N = 48.5,  $\text{CO}_2$  = 51.5.

25. 235 c. c. blood + 2 grms.  $\text{KNO}_3$  gave off gas consisting of N = 94.4,  $\text{CO}_2$  = 5.6.

In experiments Nos. 8, 9, 10, and 13 the gas evolution did not commence until the third day, the earlier specimen yielding gas much more readily. Urine when fresh did not yield gas at first, unless a small quantity of old urine was mixed with it. The solutions became more alkaline according to the amount of nitre decomposed, forming carbonate of potash.



In 11 and 12 the nitrogen came off slowly at first, but when the first charge was exhausted a second charge of nitre caused the gas to come off instantly.

The gases were exploded with oxygen and hydrogen separately, and also in conjunction with water gases. They were also treated with caustic potash and pyrogallie acid, but only carbonic acid and nitrogen were found.

## No. II.

### ABSTRACT OF WORK BY KUHLMANN, BOUSSINGAULT, SCHLOESING, AND REISET.

In 1848 (*Jahresbericht*, vol. 1, page 385) Kuhlmann found that nitrates were formed by heating sulphate of ammonia and sulphuric acid with bichromate of potash, peroxide of manganese, brown peroxide of lead, minium, or barium peroxide; also that by heating sulphate of ammonia with nitrate or chlorate of potash, the ammonia is completely converted into nitrous gas.

Kuhlmann (*Ann. Chim. Phys.*, 1847, XX., p. 223 et seq.) produces ammonia from nitrates by—

*a.* The reducing action of zinc or similar metal and dilute sulphuric acid.

*b.* The action of sulphuric acid, or, better, hydrochloric acid, upon sulphide of iron in contact with a solution of nitrate.

*c.* The action of sulphide of arsenic dissolved in solution of caustic potash.

*d.* Gradually acidulating a solution of sulphide and nitrate of potash. Ammonia is formed after some days.

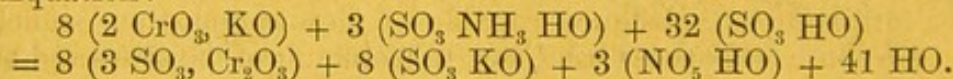
*e.* The reducing action of ferrous or stannous oxide. After several days a notable amount of ammonia is formed.

*f.* Passing a current of sulphuretted hydrogen through a solution containing  $\text{SbCl}_3$  and  $\text{KNO}_3$ .

He also obtains nitric acid from ammonia by the following reactions:—

1. By distilling a mixture of bichromate of potash, strong sulphuric acid, and sulphate of ammonia.

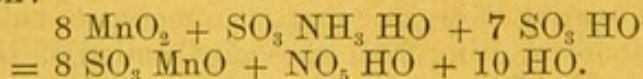
Equation:—



(There seems some error here.)

2. By distilling a mixture of weak sulphuric acid, binoxide of manganese, and sulphate of ammonia.

Equation:—



3. By heating a mixture of nitrate or chlorate of potash with sulphate of ammonia. The whole of the ammonia is converted into nitrous gas.

4. By acting with strong sulphuric acid on a mixture of peroxide of lead and sulphide of ammonium.

5. By acting with strong sulphuric acid on a mixture of peroxide of barium and sulphate of ammonia.



6. As published in 1838, by passing air mixed with ammonia through red-hot tube of porcelain, a small quantity of hyponitric acid and binoxide of nitrogen is formed.

These important facts, which I have confirmed by similar experiments, show at least that nitric acid may be formed by inorganic agents in solution, as well as by explosions in which nitrogen gas itself is oxidized.

In the *Compt. Rendu*, vol. 66, 1868, p. 177, M. Reiset speaks of the production of *nitrous gas* when the liquids become too slightly acid during the fermentation of beetroot solutions.

M. Th. Schloesing, vol. 66, 1868, p. 237, speaking of putrefaction in tobacco juice, says: "Nitrates decompose so rapidly that the solutions may be found to differ from day to day. When the nitrates are decomposed, the gases, when carbonic acid is absorbed, leave a residue containing protoxide of nitrogen. Urine was found to give out protoxide and binoxide of nitrogen." The decomposition of nitrates has not been observed when the solutions remained acid. When they became neutral or alkaline the decomposition commenced, and developed with such activity that all the nitrates disappeared in a few days.

In *Compt. Rendu*, vol. 76, p. 22, 1873, M. Boussingault speaks of the disappearance of a small amount of nitrogen in soils, but his chief object is to show that nitrates were not formed from the nitrogen of the air.

Vol. 84, *Compt. Rendu*, p. 301. MM. Th. Schloesing and A. Muntz give experiments to show that the destruction of germs by chloroform prevents the formation of nitrates. This result seems in conformity with other results, but Mr. Otto Hehner thinks a large amount necessary, as I understand him. *Chem. News*, vol. 39, pp. 26 and 53.

A fuller abstract of M. Schloesing's work may be usefully published, as below:—

*Study of Nitrification in Soils (Abstract.)*

(*Compt. Rendu*, vol. 77, pp. 203 and following.)

The necessary conditions for nitrification are known, namely, a nitrogenous substance capable of slow combustion, sufficient aeration, a carbonated base, a certain amount of moisture and heat.

These may be arranged in several categories:—

1. Conditions pertaining to the soil:—Mineral composition and the physical properties resulting therefrom, nature and proportion of the saline constituents soluble and insoluble, nature and quantity of organic matters, amount of cultivation.

2. Conditions resulting from the joint action of the soil and atmosphere:—Humidity proportion of O and CO<sub>2</sub> in the atmosphere contained within the soil, interchange of gas between the soil and atmosphere.

3. Purely physical conditions:—Heat, light, electricity.

*Influence of the Proportion of Oxygen in a Confined Atmosphere.*

Five quantities of a calcareous earth were placed in long glass vessels, at the ordinary temperature; the only difference being



the composition of the atmosphere in each, which consisted of air and nitrogen as follows:—

No. - - -	1	2	3	4	5
Per cent. by vol. of O	1.5	6.0	11.0	16.0	21.0
Humidity of the earth	15.9 per cent.				

Nitrogen in the moist earth = 0.263 per cent. A fertile earth rich in humic matter.

The air was deprived of  $\text{CO}_2$  and  $\text{NH}_3$  before reaching the earth. The experiments lasted from 5th July till November 7th, 1872.

The following are the mean results for the  $\text{CO}_2$  in the atmosphere expelled from the soils during the months of July and August. The temperature varied between 21 and 29°.

No. - - -	1	2	3	4	5
Mean T. - - -	24.3	24	23.1	24.2	25.2
Mean $\text{CO}_2$ formed in 24 hours per kilo. of earth	Mgm. 10.4	Mgm. 16.6	Mgm. 16.1	Mgm. 15.1	Mgm. 19

In the last four cases the combustion of the organic matter appears almost independent of the amount of  $\text{CO}_2$ ; and in the 1st case, where the O = only 1.5 per cent., the amount of  $\text{CO}_2$  formed is 60 per cent. of that formed in the others;—a difference between the slow oxidation in soils and ordinary combustion.

The determinations of  $\text{CO}_2$  made in September and October at temperatures between 14° and 18° call for the same remarks. They show, moreover, that temperature has a considerable influence. The production of  $\text{CO}_2$  at 16° is only half that at 24°.

The following are the results of  $\text{HNO}_3$  determinations calculated in mgms. per kilo. of earth:—

No. - - -	1	2	3	4	5
7th Nov. 1872 -	151.8	201.8	238.6	352.7	268.7
5th July 1872 -	106.1	106.1	106.1	106.1	106.1
$\text{HNO}_3$ formed -	45.7	95.7	132.5	246.6	162.6

The nitric acid present at first = 1528 mgm.

Schloesing fancies Nos. 4 and 5 have been transposed.

The production of  $\text{HNO}_3$  depends on the amount of oxygen in the atmosphere.

Second series, differing only in the degrees of humidity which was raised to the maximum, viz., 24 per cent. In No. 1 pure nitrogen alone was used, and Nos. 2, 3, 4, and 5 had atmospheres containing 6, 11, 16, 21 per cent. oxygen.

The experiments lasted from 18th November 1872 till 3rd July 1873.

The  $\text{CO}_2$  determinations in November and December gave as means—

No. - - -	1	2	3	4	5
Per cent. oxygen in atmosphere	0	6	11	16	21
T. - - -	14.3	14.5	15.0	16.1	14.2
$\text{CO}_2$ formed mgm. per kilo. earth	9.03	15.09	16.0	16.6	16.0



The results are similar to the earlier ones. The excess of moisture favours the oxidation; the temp. being lower.

*Estimation of the Nitric Acid.*

No.	-	-	1	2	3	4	5
3rd July 1873	-	-	0.00	263	286	267	289
8th November 1872	-	-	64.0	64	64	64	64
Nitric acid	{	lost	- 64.0.				
	{	formed	-	199	222	203	225

In No. 1 the nitrates have been destroyed, doubtless by the organic matter. In the others the nitrifications have been fairly equal.

The mode of decomposition of nitrates, when the medium is a soil deprived of oxygen, has not been to my knowledge the object of an exact examination. To 12 kilos of earth from Boulogne were added 7.5 grms.  $\text{KNO}_3$  in dilute solution, the whole was placed in a 10 litre vessel with a gas evolution tube.

Moisture of the earth = 17.46 per cent.

Nitric acid { originally present = 0.844  
 added as  $\text{KNO}_3$  = 4.0095  
4.8535

The experiment commenced on the 20th November 1872.

The mercury at first rose in the evolution tube, owing to absorption of oxygen and  $\text{CO}_2$ . After five days the pressure began to increase again. On the 9th December it was equal to that of the atmosphere. On the 19th a violent evolution of gas commenced. Some gas was lost. At the end of the experiment 4200 c. c. of N and 1300 mgm.  $\text{CO}_2$  were collected, other gases were absent.

Analysis of the earth:—

Nitric acid	-	-	-	0.00
$\text{NH}_3$ in 100 grms.	{	before experiment	-	0.51 mgm.
	{	after	-	1.35 "
Gain	-	-	-	<u>0.84</u> "

2nd experiment, conducted chiefly to measure initial and final volumes of N:—

Weight of earth	-	-	-	11.4 kilos.
Moisture	-	-	-	18.2 per cent.
Temperature (surrounding)	-	-	-	5.5°.
Air introduced	-	-	-	5.0215 litres.
Do. do. (corrected)	-	-	-	4.8904 "
			N =	3.8732 "
			O =	1.0172 "

Contraction at first as in previous experiment.



## Analysis of the earth:—

Nitric acid	-	-	-	0.00
NH <sub>3</sub> in 100 grms. earth	{	before experiment	-	1.35
		after	-	3.04
Gain	-	-	-	1.69
Gain of NH <sub>3</sub> for 11.4 kilos earth	-	-	-	192.7 mgm.
NH <sub>3</sub> equivalent to 7.5 grms. KNO <sub>3</sub>	-	-	-	126.2 "
Analysis of the gas	-	-	CO <sub>2</sub>	N
Vol. at 0° and 760, recovered by the pump	{	-	3484.2	4088.5
Do., disengaged during experiment		-	89.1	809.4
			3573.3	4897.9
Nitrogen present in air at first	{	-	-	3873.2
Nitrogen present in 7.5 grms. KNO <sub>3</sub>		-	-	828.0
			4701.2	

There is thus more N given off than is present in the air and KNO<sub>3</sub>.

Boussingault has shown that in a confined oxygenated atmosphere the gaseous nitrogen does not go to form nitrates, which indeed lose a small quantity of their combined nitrogen. Schloesing confirms this last result.—Th. Schloesing, *Compt. Rendu*, vol. 77, p. 353.

## No. III.

## OXIDATION OF AMMONIA.—EXPERIMENTS MADE SOME YEARS AGO, AND LEADING UP TO THE POINTS EXPLAINED IN No. I.

The peculiar effect of the nitrates has led me into the question of the oxidation of ammonia further than previously because there seemed to be a question as to the action of organisms. I am desirous of saying that I have no desire to give my experiments in opposition to Mr. Warrington. The only experiments that were caused by reading Mr. Warrington's were those relating to the action of light and those where heat was used. I so far corroborate Mr. Warrington that light does retard the action in organic solutions. The action of organic matter is further shown by the fact that where there is most organic matter in a state readily decomposed by caustic potash that is in so-called albuminoid matter, the action of decomposing nitrates is strongest.

Pure water containing 0.1 per cent. milk, filtered through sand free from nitrites and nitrates.

The sand was about 8 inches deep and 1 inch broad.

1st. 100 c. c. filtered from December 2nd to December 20th, 1874, contained 0.185 mgm. HNO<sub>3</sub>.

2nd. 100 c. c. filtered from December 2nd to December 20th, 1874, contained 0.170 mgm. HNO<sub>3</sub>.



100 c. c. not filtered, kept in a bottle half a day, 0.148 mgm.  $\text{HNO}_3$ .

100 c. c. of the water used, filtered through sand from December 2nd to December 20th, 1874, 0.00.

The remaining portions were again filtered till 28th January 1875, making altogether 46 days, when—

1st gave	-	-	-	0.163 mgm. $\text{HNO}_3$ .
2nd „	-	-	-	0.148 „ „
Pure water	-	-	-	0.00.

There is a slight increase in the amount of  $\text{HNO}_3$  by filtration from the 2nd to 20th December, 18 days; and afterwards to January 28th, the 46th day, there is a decrease, but not so small as in the unfiltered portion. Pure water filtered through the sand for 46 days remained free from  $\text{HNO}_3$ .

Ozonized air with phosphorus vapour aspirated through water containing milk, and water made alkaline containing yeast. January 1875.

Through 50 c. c. water containing 0.01 per cent. yeast for 85 hours, extending over 5 days, strong reaction to ozone paper	-	-	-	-	} No $\text{HNO}_3$ formed.

Through 50 c. c. water containing 0.01 per cent. milk for 69 hours; 50 c. c. of caustic soda pure were then added, and the ozonized air again aspirated for 95 hours, altogether 164 hours	-	-	-	-	} No $\text{HNO}_3$ formed.

After passing the 0.01 per cent. milk solution, the ozonized air was aspirated through water containing 0.01 per cent. yeast for 164 hours	-	-	-	-	} No $\text{HNO}_3$ formed.

And finally through another 50 c. c. water containing 0.01 per cent. yeast for 164 hours	-	-	-	-	} No $\text{HNO}_3$ formed.

When the aspiration was stopped all the liquids were alkaline, and gave a reaction with ozone paper. Each portion smelled of phosphorus.

Permanganate and yeast:—

0.3 gm. yeast mixed with water and permanganate of potassium, stood 20 days	-	-	-	-	} No $\text{HNO}_3$ formed.

Hydrogen peroxide and yeast:—

0.3 gm. yeast mixed with water and 25 c. c.  $\text{H}_2\text{O}_2$  solution, stood 20 days.

The 0.3 gm. yeast contained before mixture	-	-	-	-	} 0.444 mgm. $\text{HNO}_3$ .

After mixture with $\text{H}_2\text{O}_2$ solution, and standing 20 days	-	-	-	-	} 0.193 mgm. $\text{HNO}_3$ .

There has been a decrease in the amount of  $\text{HNO}_3$ .



### Reduction of Nitrate by $\text{H}_2\text{S}$ in slightly Acid and in slightly Alkaline Solutions.

Both columns were determined in the same way by reduction with aluminium.

	Milligrammes $\text{HNO}_3$ .	
Bottle, loosely closed with paper, December 5th, 1875. 200 c. c. $\text{KNO}_3$ solution + 1 c. c. $\text{NaHS}$ solution + 0.5 c. c. Acetic Acid. Acid - - - - -	1st day.	39th day.
Bottle stoppered do. do. do. - - - - -	8.750	8.214
Open, December 5th, 1875, 200 c. c. $\text{KNO}_3$ sol. + 0.5 c. c. $\text{NaHS}$ sol. + 0.1 c. c. $\bar{\text{A}}$ - - - - -		41st day.
Stoppered do. do. do. - - - - -	8.750	8.177
Open, December 5th, 1875, 100 c. c. $\text{KNO}_3$ sol. + $\text{NaHS}$ sol. 0.25 c. c. Alk. - - - - -		42nd day.
Closed do. do. do. - - - - -	4.375	4.012
		38th day.
Open, 200 c. c. $\text{KNO}_3$ sol. + 1 c. c. $\text{NaHS}$ sol. Alk. - - - - -	8.750	8.194
Closed do. do. do. - - - - -	8.750	8.342
Open, 200 c. c. $\text{KNO}_3$ sol. + 2.5 c. c. $\text{NaHS}$ sol. Alk. - - - - -	8.750	8.405
Closed do. do. do. - - - - -	8.750	8.105
Open, 200 c. c. $\text{KNO}_3$ sol. + 5 c. c. $\text{NaHS}$ sol. Alk. - - - - -	8.750	8.356
Closed do. do. do. - - - - -	8.750	8.504
Open, 200 c. c. $\text{KNO}_3$ sol. + 5 c. c. $\text{NaHS}$ sol. + 0.5 c. c. $\bar{\text{A}}$ Alk. - - - - -	8.750	8.357
Closed do. do. do. - - - - -	8.750	8.504
Open, 200 c. c. $\text{KNO}_3$ sol. + 10 c. c. $\text{NaHS}$ sol. Alk. - - - - -	8.750	8.561
Closed do. do. do. - - - - -	8.750	8.483
Open, 200 c. c. $\text{KNO}_3$ + 0.25 c. c. $\text{NaHS}$ + 0.1 c. c. $\bar{\text{A}}$ Alk. - - - - -	8.750	8.153
Closed do. do. do. - - - - -	8.750	8.301
Closed, 200 c. c. $\text{KNO}_3$ + 10 c. c. $\text{NaHS}$ sol. + 0.7 c. c. $\bar{\text{A}}$ Alk. - - - - -	8.750	8.561
$\text{H}_2\text{S}$ was found in two bottles only. After 39 days these were alkaline.		

I have spoken of the oxidation of organic nitrogen, and we must now consider the oxidation of inorganic nitrogen or ammonia.

### Oxidation of Free and Acid Solutions of Ammonia by Hydrogen Peroxide.

	Milligrammes $\text{HNO}_3$ in the Total Liquid.	Milligrammes $\text{HNO}_3$ in the Re-agents before mixing.
10 c. c. $\text{NH}_3$ solution + 50 c. c. $\text{H}_2\text{O}_2$ solution. Tested after eight months - - - - -	14.45	0.77
10 c. c. $\text{NH}_3$ solution, acidified with 20 c. c. dilute $\text{H}_2\text{SO}_4$ + 50 c. c. $\text{H}_2\text{O}_2$ solution. Tested after eight months - - - - -	3.56	1.29
10 c. c. $\text{NH}_3$ solution, acidified with 10 c. c. dilute $\text{H}_2\text{SO}_4$ + 20 c. c. $\text{H}_2\text{O}_2$ solution. Stood ex- posed to light from February 20th, 1874, to March 24th, 1874 - - - - -	1.48	0.89
30 c. c. $\text{NH}_3$ solution + 55 c. c. $\text{H}_2\text{O}_2$ solution - - - - -	12.28	0.81



## LATER EXPERIMENTS.

## OXIDATION OF AMMONIA.

PERMANGANATE OF POTASH, AMMONIA, and SULPHATE OF AMMONIA. Oxygen and Nitric Acid in Parts per Million.  
 5 p. c. sol.                      2 p. c. sol.

	20 c. c. $\text{KMnO}_4$ sol. 3 c. c. $(\text{NH}_4)_2\text{SO}_4$ sol. 1 c. c. $\text{NH}_4\text{OH}$ sol. } 5 p. c. sol.			20 c. c. $\text{KMnO}_4$ sol. 3 c. c. $(\text{NH}_4)_2\text{SO}_4$ sol. 1 c. c. $\text{NH}_4\text{OH}$ sol. } 2 p. c. sol.			40 c. c. $\text{KMnO}_4$ sol. 6 c. c. $(\text{NH}_4)_2\text{SO}_4$ sol. 2 c. c. $\text{NH}_4\text{OH}$ sol. } 1 litre.			60 c. c. $\text{KMnO}_4$ sol. 9 c. c. $(\text{NH}_4)_2\text{SO}_4$ sol. 3 c. c. $\text{NH}_4\text{OH}$ sol. } 1 litre.		
	$\text{HNO}_3$ formed.	Avail-able O lost.	Days in Contact.	$\text{HNO}_3$ formed.	Avail-able O lost.	Days in Contact.	$\text{HNO}_3$ formed.	Avail-able O lost.	Days in Contact.	$\text{HNO}_3$ formed.	Avail-able O lost.	Days in Contact.
1880.												
1st Oct.	9.34	16	1	—	0	1	16.3	32	1	21.49	79	1
29th "	20.00	—	29	—	—	—	—	—	—	59.3	—	29
1st Nov.	—	—	32	—	—	—	—	—	—	—	—	—
4th "	23.2	47	35	2.67	0	35	23.8	126	35	104.5	379	35
12th "	17.0	47	43	6.67	16	43	23.0	632	43	206	491	43
1881.												
19th Jan.	81.5	95	111	4.45	32	111	97.8	660	111	267	679	111
29th Mar.	52.6	289	180	7.71	211	180	77.8	680	180	278	1,158	180







## OXIDATION OF AMMONIA.

SPECIMENS HEATED PREVIOUSLY. Solutions as before.

<p>1.606 gm. <math>\text{KMnO}_4</math>, 50 c. c. <math>(\text{NH}_4)_2\text{SO}_4</math> sol., 50 c. c. water.</p> <p>After heating to <math>100^\circ\text{C}</math>. for 2 hours— <math>\text{HNO}_3 = 390</math>, Permanganate still pre- sent.</p>	<p>2.339 gm. <math>\text{KMnO}_4</math>, 50 c. c. <math>\text{NH}_4\text{OH}</math> sol., 50 c. c. water.</p> <p>After heating to <math>100^\circ\text{C}</math>. for <math>\frac{1}{2}</math> hour— <math>\text{HNO}_3 = 830</math>, Permanganate still pre- sent.</p>	<p>Between 1 and 2 gm. <math>\text{KMnO}_4</math> (about 1 gm.), 100 c. c. <math>\text{NH}_4\text{OH}</math> sol.</p> <p>After heating to <math>100^\circ\text{C}</math>. for 1 hour— <math>\text{HNO}_3 = 734</math>, Permanganate all reduced. Considerable evolution of gaseous nitrogen.</p>	<p>50 c. c. <math>\text{NH}_4\text{OH}</math>, 50 c. c. <math>(\text{NH}_4)_2\text{SO}_4</math>, 1.5 gm. <math>\text{KMnO}_4</math>, 100 c. c. water.</p> <p>After heating to <math>100^\circ\text{C}</math>. for 2 hours— <math>\text{HNO}_3 = 216</math>, Permanganate all reduced.</p>	<p>5 c. c. <math>\text{NH}_4\text{OH}</math>, 5 c. c. <math>(\text{NH}_4)_2\text{SO}_4</math>, 5 c. c. <math>\text{KMnO}_4</math>.</p> <p>The permanganate was in one limb of a bent tube and the ammonias in the other; after being heated to <math>100^\circ\text{C}</math>. for 2 hours the solutions were mixed— <math>\text{HNO}_3 = 38.91</math> mgm. <math>\text{NH}_3</math> present = <math>333.65</math> mgm.</p> <hr/> <p>5 c. c. <math>\text{NH}_4\text{OH}</math>, 5 c. c. <math>\text{KMnO}_4</math>, Treated as above— <math>\text{HNO}_3 = 26.7</math> mgm. <math>\text{NH}_3</math> present = <math>297.5</math> mgm.</p>
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## OXIDATION OF AMMONIA.

Results given as NITRIC ACID in Parts per Million.

	Mixed 31st May.	Mixed 31st May.	Mixed 11th June.	Mixed 27th August.	Mixed 27th August.	Mixed 30th August.	Mixed 1st Sept.	Mixed 1st Sept.
—	10c.c. 1% KMnO <sub>4</sub> sol., 5c.c. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> sol., 100 c.c. Pure Water.	5c.c. 1% KMnO <sub>4</sub> sol., 5c.c. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> sol., 100 c.c. Pure Water.	200 c.c. KMnO <sub>4</sub> sol., 25c.c. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> sol., 50 c.c. NH <sub>4</sub> OH sol., Water to 1 Litre. KMnO <sub>4</sub> all reduced to MnO <sub>2</sub> in 1 Day.	200 c.c. KMnO <sub>4</sub> sol., 25c.c. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> sol., 10 c.c. NH <sub>4</sub> OH sol., Water to 400 c.c. Alkaline. Exposed to Daylight.	200 c.c. KMnO <sub>4</sub> sol., 25c.c. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> sol., 10 c.c. NH <sub>4</sub> OH sol., Water to 400 c.c. Neutral. Exposed to Daylight.	200 c.c. KMnO <sub>4</sub> sol., 25c.c. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> sol., 10 c.c. NH <sub>4</sub> OH sol., Water to 400 c.c. Alkaline. Kept in Darkness.	25 c.c. H <sub>2</sub> O <sub>2</sub> sol., 25c.c. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> sol., 10 c.c. NH <sub>4</sub> OH. Water to 400 c.c.	25 c.c. H <sub>2</sub> O <sub>2</sub> sol., 25c.c. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> sol., 10 c.c. NH <sub>4</sub> OH. Water to 400 c.c.
1880. May 31	0.62	0.16	2.43	6.0	6.0	6.0	0.8	0.8
June 1	..	..	446.0	1057	..	..	..	..
" 15 (about) Aug. 27	..	..	..	..	..	..	..	..
" 30	..	..	667	..	..	..	..	..
Sept. 1	..	..	..	1123	6.0	806	..	..
" 2	5.41	4.45	630	1297	7.4	..	88.9	80.0
" 17	5.53	4.84	756	1601	10.6	889	96.4	88.9
Oct. 1	..	..	741	..	..	..	..	..
Nov. 4	..	..	783	..	..	..	..	..
1881. Jan. 19	..	..	623	1630	48.9	1637	16.7	21.3
Mar. 29	..	..	..	2490	68.9	2501	7.26	9.04



## OXIDATION OF AMMONIA.

## BLOOD SOLUTIONS.—HEATED.

0.969 grm.  $\text{KMnO}_4$  and 100 c. c. 1% blood solution were heated separately to  $100^\circ \text{C}$ . for 2 hours and then mixed, 23/9/80. After 4 days' contact—

$\text{HNO}_3 = 37.36$  parts per million.

0.819 grm.  $\text{KMnO}_4$  and 100 c. c. 1% blood solution with 1 c. c. pure  $\text{NaOH}$  solution were heated separately, as above, 23/9/80. After 4 days' contact—

$\text{HNO}_3 = 29.65$  parts per million.

0.480 grm.  $\text{KMnO}_4$  and 100 c. c. 1% blood solution treated as above. After 4 days' contact—

$\text{HNO}_3 = 28.91$  parts per million.



There is here mentioned a series of trials made some years ago by passing air drawn over phosphorus, first through pure water, to find if the reagents were pure. After 60 hours the water was found to contain in 10 c. c. 0.01 mgm. of ammonia, and that in contact with phosphorus contained no nitric acid.

This phosphorised or ozonized air drawn through water for a week produced no nitric acid in it.

Then through dilute ammonia for three days no nitric acid.

Another (time not recorded) gave 0.22 mgm.  $\text{HNO}_3$ .

It will be seen from the tables that an ammoniacal condition greatly increases the nitric acid. This action of the alkaline state is probably an explanation of the effect produced in the presence of chalk, and may explain the amount of nitrates in at least some chalk waters. The water having organic matter in it and percolating through the chalk has this matter more readily oxidized.

It is clear then that oxidation is continually ready to take place when organic substances are in water, and oxygen is presented to them. This takes place rapidly if air is abundant, but it takes place much more rapidly when oxygen is presented in a concentrated form, as in nitrates, &c.

It may be asked how far this may affect the estimation of albuminoid ammonia when heat is used with permanganates.

The consequence also is that waters with little oxygen in solution are under suspicion, or rather they have or have recently had substances in solution taking up oxygen. I brought this subject forward many years ago, but it is not sufficiently attended to by chemists. Dalton saw the importance of this examination long before our time. It is a merit, which only the best water has, to have the oxygen and nitrogen in the relation of not less than 33 per cent. of the first. Sometimes I have found as much as 35. I do not know if this is an error of experiment; I think not.

We learn that by a natural process all traces of organic impurity may be removed from water, and that part of this may be done more rapidly by the assistance of organisms probably, but that it may be concluded without organisms. The only usual bodies that cannot be removed are the alkalies and their salts, of which chloride of sodium is the most striking. The attention paid to this salt has been too small. I brought this forward also in 1867, but that also was attended to before me by Dalton, and forgotten. I hope it will not again be left out. It is remarkable with what complacency many chemists look on an amount of chlorine in water far above that of the natural drainage of the district.

#### No. IV.

##### FURTHER ON THE ACTION OF THE AIR ON COMBINED NITROGEN.

The air oxidizes the nitrogen which is found in nitrogen compounds. That this is done when organic substances are absent,



is not proved, so far as I know. The oxidation of inorganic nitrogen seems to require higher oxides than the air. But we may ask, will not the ozone of the air prove to be one of these higher oxides? It is probable, and we may expect it to show its power in some cases, but it cannot be expected to reach far into sewers or heaps of refuse. We may, however, be certain that it acts as a purifying agent on substances which it meets in the atmosphere.

On the table of changes in the condition of nitrogen in water containing organic matter (p. 26) it will be observed that the nitric acid column shows a general increase in every case. There is, however, a curious observation to be made; at a certain time there is a slight diminution, and this has taken place in every instance. It cannot be supposed that amongst so many analyses no error should have occurred, but such a consistent error is not probable. Besides, a similar backward movement occurred on the occasion of a previous inquiry; and, indeed, it agrees with my early observations of the destruction of nitrates, and the later ones on the elimination of nitrogen. Those in the table given all occurred from the end of June to the beginning of August, as if the heat had been an agent, the peculiar putrefaction spoken of having occurred, I suppose.

The nitrogen of the three kinds increases (*i.e.*, of free ammonia, albuminoid ammonia, and nitric acid), being supplied by the residual albumen, which is supposed to be continually decomposing.

The effect of darkness has been to increase the growth of nitrates in the Manchester water, and the stronger blood solution. This is not apparent in the weaker.

It seems correct, from the results already given, to believe that nitric acid has a mode of growth in nature quite independent of organic matter, as well as one which is intimately associated with organic matter. We have arrived at a very firm stage, but we require to learn more. The inorganic matter from which nitric acid is made contains ammonia, and we require now to learn in what conditions nitrogen is used for forming ammonia if there be any methods of doing so.

Schönbein showed long ago that ozone caused the formation of nitric acid; and Luca (Jahresbericht, 1855, p. 318) said that, after passing air ozonized by contact with moist phosphorus for three months over potassium and potash, there was formed nitrate of potash in quantities enough to crystallize; from 7,000 to 8,000 litres of air being used. With these views before us we may look to the formation of nitrates from inorganic nitrogenous compounds in cases where ozone exists, and that may possibly be found in very pure water, where the oxygen exists to the nitrogen in a proportion above 33 per cent. Alkalinity seems an essential condition in many of the mixtures, but I have found nitrates in wells very acid. This was remarkable in the case of a polluted well, the use of which had probably caused



death to more than one of a family in Manchester before the present water supply was universal in the city.

### *Inferences.*

We may then come to the following conclusions:—Bodies containing protein compounds, when in abundance of water and in common air, may oxidise and form nitric acid.

The same organic bodies in a state of decomposition and in water may oxidise at the expense of nitrates, and give out nitrogen.

The first condition is that in which a certain amount of sewage is in the water, but is overpowered by the amount of air.

The second is when the sewage is in excess, and overpowers the nitrates.

Nitrates may be formed by the oxidation of inorganic nitrogen, but not so far as we know by contact with common air under ordinary conditions. The oxygen must be presented in a more concentrated or more active condition.

Putrefaction destroys organic matter without the influence of oxygen; it breaks up organic compounds, and destroys organisms. The evidence seems to indicate that it destroys even those bodies that produce disease, but that in certain conditions it produces others. This is a point not to be enlarged upon without more knowledge, but it is evident that by putrefaction we get rid of an enormous amount of offensive matter. Oxygen cannot enter under the surfaces of actively putrefying bodies; but whenever it is allowed to enter by the putrefaction being less active, an action begins which in time completes the destruction of the body. We are not, therefore, to suppose that the germs of disease can resist all these efforts of nature to destroy noxious things, nor are we to suppose that an invisible germ of disease can pass on from stage to stage unaffected by the putrefaction of sewage and the action of air. We must believe, for the present, that it is not so. In water we see perfect purification, nitrogen itself being lost.

In ordinary putrefaction sulphuretted hydrogen comes off in abundance, with much carbonic acid and some nitrogen. Oxygen resists this action, and if the oxygen is supplied in a concentrated condition a change takes place, nitrogen is evolved as the principal gas, and a decomposition of nitrogen compounds takes place. Nitrogenous bodies are thus destroyed, in one manner by their voluntary putrefaction, in another by oxidation. Up to a certain point not determined the greater the amount of nitrogenous bodies the more rapid is their decomposition.

The oxygen of the nitrate passes in part to the carbon; some will be retained, forming a carbonate. I have not estimated how much, or if all, is taken by the carbon.

If the solution is weak the nitrogen takes up the oxygen, and does not allow it to pass away, thus forming nitrates.



Putrefaction and oxidation are two well-known modes of destroying organic bodies at ordinary temperatures. The second is not proved to be connected with organisms.

How far then can oxidation or a great supply of air be employed to destroy putrefaction or to purify.

The bearing it has on the analysis of water will be clearly seen by chemists. The bearing on the sewage question is also interesting. Substances and living things may be carried by the rapid sewage system into the range of a new activity before undergoing that putrefaction which breaks them up in proximity to us or in the sewers themselves. It seems to point to a plan of causing the destruction of organisms by putrefaction and subsequent oxidation or by chemical action. At least it seems to me that we require to learn if it be true that any of the germs of disease, or which germs of disease, will live in an abundance of good air. We know that abundant dilution will render them all ineffective. It is probable that there will be a difference amongst them in this respect, whilst all will yield to the double action of first putrefaction and then oxidation.

On oxidation, more will follow, when speaking of its application to sewage, &c.







## OXIDATION AND DECOMPOSITION IN SEWAGE.

I feel almost ashamed to bring so many figures to prove so little, but we know that wisdom grows slowly; and the enormous amount of labour spent on sewage within 40 years shows that it has happened also to all my contemporaries as well as predecessors to give their labour to an extent which seems too great for the result. Still, I by no means think that my time is lost if I prove no more than this,—that by agitation with air sewage is kept without smell for two or more weeks in ordinary weather, and even in warm weather. This is probably the most practical portion of this part of the inquiry. The numerous analyses are not at all so telling as I expected them to be, but they do tell something of the chemistry of the sewage in relation to its loss of organic matter, and the change to inorganic. This inquiry, like all inquiries on the subject hitherto, has a preliminary character; but it is a progress in my opinion, and I am desirous of publishing it, whether found at present practicable or not, because I think that in time the practical may be forwarded by it.

The gases from putrefaction I examined some years ago, as elsewhere quoted. In 1877 I made some experiments simply to find if abundance of water increased or diminished the offensive emanations, and these I supposed to be measured by the ammonia. It is shown that the air is much more tainted with ammonia when water is not present: see "*Gases from Sewage, &c.*," p. 29. Another inquiry going further may follow this, but I look to the microscopist rather than the chemist to complete it.

*Gases from Sewage.*

The gases from sewage are continually receiving attention, but they are not frequently examined in a quantitative manner. It is very difficult to obtain them in the condition and state of dilution in which they cause illness. It has been observed that these gases produce more cases of illness than gases from excreta not producing sewage, and it seemed of some importance to know what was the proportionate amount of decomposition. The result is insufficiently shown in the table to follow. The atmosphere over the dry matter contains much more ammonia than over the wet. This may not mean that more organic matter is decomposed; it may mean only that the water keeps the ammonia in solution. Still, bubbles of gas rise rapidly from sewage in water; no such rapid evolution takes place with the dry matter. The quality of the decomposition is different. Water assists greatly the growth as well as decay of most organisms, and to these we must attribute the more rapid escape of gas. Still, the experiments point only in one direction, and we have to learn much regarding the quality of the air which comes out so rich in ammonia. This much we learn: that



water assisting the conditions of putrefaction causes a much greater destruction of organic matter, and the emanations are offensive, but we do not hear much of decided injury when they are mixed with a great profusion of air. Perhaps the paper by Dr. Henderson of Helensburgh has touched this point more directly than anything that has been done.—See “The Sewage Question in its relation to the Gareloch and neighbourhood.”—Helensburgh.

It was natural, however, to inquire what advantage could be got out of this knowledge; and at a later period, after obtaining Dr. Storer's apparatus, a fresh stimulus was given to the inquiry in a new direction.

It will be observed that in the “dry” column the ammonia rises much higher than in the “wet.” This would show that, however much gas may escape from sewage, it is never very full of the products of decomposition of animal matter. The result of breathing sewage gases, if more hurtful, must be attributed either to the supply being more abundant, although more dilute, or of a more offensive kind. This latter explanation seems the more probable one, but requires examination. This is quite in agreement with the statement elsewhere made as to the rapid destruction of organic matter in water. We know that there is a stage of great danger, and, when the sewage is diluted and exposed to the atmosphere, a rapid and remarkable stage of diminished, if not disappearing, injuriousness. The materials were kept in carboys holding about eight gallons (36·5 litres); the carboys were kept closed, a certain measure of air drawn out and washed, and an equal amount of fresh air allowed to enter.



## Gases from Sewage and Sewage Materials.

Date.	T°C.	NH <sub>3</sub> from the Solid.			NH <sub>3</sub> from the same in Water.			
		Free.	Saline.	Albmd.	Free.	Saline.	Albmd.	
1877.		Mgm. per cubic metre of air.						
October 17th - -	—	* 8.5			* 7.0			Nesslerised direct without distillation.
" 18th, 10 a.m. -	—	*10.0			* 7.5			
" " 1 p.m. -	—	*10.5			* 7.5			
" " 5 p.m. -	—	*10.0			* 5.0			
" 19th, 10 a.m. -	16°	* 8.0			* 3.5			
" " 2 p.m. -	—	* 6.5			* 5.0			
" " 5 p.m. -	—	*10.5			* 5.0			
" 20th - -	16°	* 8.0			* 7.5			
" 22nd, 10 a.m. -	18°	*20.75			*17.5			Wet, smells strong and repulsive. Dry, more intense than at first.
" " noon -	—	*20.0			*19.5			
" " 3 p.m. -	18°	*22.5			*25.0			Corks on carboys removed, and caoutchouc caps substituted.
" 23rd, 10.30 a.m.	15°	*22.5			*17.5			
" " 3 p.m. -	17°	*23.5			—			Smell from the wet becoming less intense. (The wet had another 50,000 grns. water added.)
" 24th, 10 a.m. -	17°	*31.0			*17.5			
" " 3.30 p.m.	15°·5	*33.0			*12.5			Distilled from alkaline permanganate.
" 25th, 10 a.m. -	16°	*37.5			*22.5			
" 26th, noon -	15°	*52.6			*15.5			
" 27th, 10 a.m. -	16°	*80.0			*10.0			Free. Till 24th no distillations.
" 29th, 10.30 a.m.	17°	67.5			6	—	—	
" 30th, 10.30 a.m.	17°·5	140	4.0		15	3.5		
" " 3 p.m. -	18°	105	24.0?		0	15.0	1.5	(Acidulated water used to collect the ammonia.)
" " 3.30 p.m.	—	100	1.6	—	—	—	—	
" 31st, 10.30 a.m.	—	110	2.0	8	0	0.8		
November 1st, 10 a.m. -	16°	0	180	2.0	4.8	0	2.0	
" " noon -	17°	170	0	2.5	4.0	0	1.0	
" 2nd - -	16°·5	140	0	?	—	—	—	
" 3rd, 10 a.m. -	16°	160	1.5	3.0	4.6	0.2	1.0	
" 5th, 9.30 a.m.	16°·5	160	1.0	7.5	2.6	0	1.0	
" 6th, 9.30 a.m.	16°·5	160	0	2.5	4.4	—	?	
" 7th, 9.30 a.m.	16°·5	162.5	2.0	5.0	—	1.4		Soda lime.
" " 12.30 p.m.	19°	225	—	—	—	6		
" 8th - -	—	250	—	—	—	6		Not distilled.
" 9th, 10 a.m.	17°	200	—	—	—	6		
	—	195	—	—	—	5.6		Do.
					—	8.2		
								Soda lime.

\* Asterisks show the three ammonias given; italics the first two.



Date.	T.	Ammonia from the Solid.			Ammonia from the same in Water.			
		Free.	Saline.	Albnd.	Free.	Saline.	Albnd.	
1877.								
November 10th, 9.30 a.m.	17°	-	200	-	4.4	-	Not distilled before Nesslerising.	
					8.6	-	Soda lime.	
" 12th, 9 a.m.	16°	230		27.5	12.0	3.0	Acidulated water used to obtain the ammonia.	
" 13th - -	15°·5	150		7.5	8	2.0		
" 14th, 9.30 a.m.	14°·5	170		-	8.0	2.6		
" 15th - -	16°	215		4.5	-	8.4		
" 16th - -	16°	275		3.0	7.0	0.6	Surface.	
		290		2.0	-	-	1 ft. from surface.	
" 17th - -	-	230		5.5	5.2	1.2		
" 19th - -	15°	200		6.0	5.0	1.0		
" 20th - -	12°·5	155		2.5	4.8	1.0		
" 21st - -	12°	162.5		6.0	4.2	0.8		
	12°	140		-	-	-	By Frankland's method.	
" 22nd - -	12°	250		6.0	5.2	1.6		
		200		-	-	-	Soda lime.	
" 23rd - -	12°	212.5		7.0	4.0	1.0		
		200.0		-	-	-	Soda lime.	
" 24th - -	12°	225.0		6.0	7.0	0.0		
" 26th - -	10°	187.5		2.5	2.2	0.4		
		175.0		-	-	2.4	Dry by soda lime.	
December 1st - -	12°	-		-	-	-		
" 3rd - -	-	252.0		2.5	3.0	1.0		
" 4th - -	13°	-		-	5.0	trace		
" 5th - -	12°·5	250.0		0.5	-	-		
" 10th - -	-	-		-	2.2	1.0		
" 11th - -	14°	-		-	1.6	0.8		
" 14th - -	12°	175.0		-	0.0	*4.0	*Albuminoid and saline? Wet carboy well agitated.	
" 17th - -	12°	250.0		-	-	-		
" 19th - -	12°	275.0		-	0.0	3.6	0.0	
" 29th - -	11°	-		-	0.6	-		
" 31st - -	10°	300.0		2.5	1.0	0.0		
1878.								
January 2nd - -	10°	300.0		-	-	-		
" 21st - -	15°·5	700	10.0	9.0	10.1	1.2	5.4	
" 25th - -	10°	600		7.5	8.0	2.4	1.0	
February 1st - -	14°·5	700	8.0	7.5	11.2	0.0	1.6	
" 2nd - -	1°	190	4.5	10.5	8.8	4.2	2.6	
" 4th - -	1°·5	200	8.0	5.5	3.8	0.2	lost	
" 12th - -	Freezg.	0.00	124.0	4.5	3.6	0.2	1.2	



## Flesh, Decomposition of.

Date.	T.	Ammonia.			—
		Free.	Saline.	Albmd.	
1877.					
November 22nd	-	—	2.4	0.4	Flesh newly bought, when washed with water, showed ammonia by Nessler's test.
" 24th	-	12°	0.8	0.2	
" 26th	-	10°	6.6	?	Flesh tainted.
" 28th	-	—	2.2	—	
" 29th	-	—	2.0	—	
December 1st	-	12°	3.0	—	Flesh smell putrid.
" 3rd	-	—	4.4	0.2	
" 4th	-	13°	5.6	Trace	
" 5th	-	12°·5	11.0	1.0	
" 7th	-	—	13.0	1.4	
" 8th	-	12°	11.8	2.0	
" 10th	-	—	12.8	Trace	
" 11th	-	14°	13.0	Trace	
" 12th	-	—	19.0	Trace	
" 13th	-	11°	14.2	—	
" 14th	-	12°	18.0	—	
" 15th	-	11°	13.0	—	
" 17th	-	12°	22.0	—	
" 19th	-	12°	22.0	—	
" 20th	-	5°	21.0	0.8	
" 29th	-	11°	16.0	Trace	
" 31st	-	10°	16.0	Trace	
1878.					
January 2nd	-	10°	22.0	—	
" 21st	-	15°·5	54.0	12.4	3.0
" 25th	-	10°	70.0	2.4	2.0
February 1st	-	14°·5	70.0	1.6	3.0
" 2nd	-	1°·0	34.4	0.2	4.4
" 4th	-	1°·5	34.0	1.0	2.6
" 12th	-	Freezing	15.2	0.4	0.2



## EARLIER RESULTS—AERATION IN WATER.

This subject has long interested chemists, and aeration has formed one of the plans of engineers from a long date back. The mode of bringing down the water from the hills to Manchester has been founded on the idea that aeration is of value, the artificial falls being constructed with that view. It has also been a common saying that water is best when aerated, and mineral waters aerated to an excessive extent have been in use since first invented by Thomas Henry, F.R.S., of Manchester, last century; although it must be remembered that "aeration" by carbonic acid, as is the case in prepared waters, does not carry out the true idea of aeration which is by the oxygen of the air. "Aeration" by carbonic acid gives a secondary meaning. In order to test the purity of water to be used in distilleries, it was said jocularly in a publication, some 20 years ago, in Scotland, that one asked, "How many falls does the water fall? Talisker water comes down 80 falls." (*See Highland Drovers, Douglas, Edinburgh.*) The idea of purification by air must be considered then as a general one.

Of course water, as such alone, is not oxidized by the air, although a certain amount is held in solution; but water does not exist quite pure or unmixed in nature, and we really mean the destruction of organic matter in it when we speak of purifying water. I am obliged to approach this matter very cautiously because there are already men (one or more) who claim the aeration of water under certain conditions of impurity, such as sewage, as their invention; and it is not for me to state what is their legal position; but it is a long time since I began to study air and water, as well as sewage, as my published papers show, and I may be allowed to save myself trouble by making a few more quotations, instead of writing the old facts in new words, from a paper on "The Mud of the Clyde," Glasgow Philos. Soc. 1880, by R. Angus Smith.

P. 17.—"This raises a question to be solved, but the fact is certain that fevers have not been traced to the escape of gases of putrefaction when there has been a large amount of water and exposure to the air. But they have been found when the water is not very great in amount and the decomposition is made under cover, as in sewers. The question arises, is this owing to the concentration or to the difference of decomposition in darkness, or to the better supply of oxygen? The effect of sunlight in warm countries does not allow us to suppose that the daylight always produces in vapours an innocent state, although it has a great effect in that direction when there is little water . . . . . With us, at least, innocence in the atmosphere seems to be rather something connected with the abundance of air in proportion to the impurity. This air may act in two ways. It may act by rapid oxidation of the sub-



stances in water, or by dilution of the gases when formed; and the destruction of putrid matter in water is really very rapid when plenty of air is allowed. This air is brought to the Clyde by the water, and also by the waves, both artificial and natural, exposing a great deal of surface. The air may act also merely by rapid dispersion of the gases. Still we must not forget that these gases or vapours are not reported to us to produce any marked type of disease over the Clyde, even when they come in a state so concentrated as to produce sickness; whereas gases from sewers, in a condition which may not produce immediate illness, may produce in time typhoid fever, as we are credibly informed.

"We must conclude then that it is not mere dispersion, but that it is a more thorough putrefaction and oxidation, which takes place in the Clyde, and a more complete destruction of the organic substance by the abundance of air, than can take place in sewer water, whatever the senses may indicate to us. Of course we must ever give some credit to the flow of air up the river and the ever fresh breezes that come from the Atlantic as well as the mixture of air with water caused by steamers.

"Whilst then there is oxygen enough at present to prevent disease, there is not enough to prevent smells which disgust and cause sickness for the time."

In connection with the purification of streams the following quotation may be added, although written previously:—

"When azotized compounds decompose and form ammonia, how long is this ammonia retained in the water? On examining a very putrid stream, I estimated the amount of ammonia at the most putrid portion, where carburetted hydrogen was passing off in great volumes, and where a cubic foot could be obtained in a very few minutes by stirring.

"In the sewage stream of which I have spoken the amount of ammonia was from 0·5 to 0·7 grain per gallon. After going 14 miles the amount was only 0·07, and after 20 miles none at all was found.

"The mud of the same stream was in a state of putrefaction, and contained per cent.:—

"Ammonia	-	-	-	0·797
"a mile lower	-	-	-	0·420
"at second mile	-	-	-	0·171

"The ammonia rapidly disappeared, and the mud itself diminished very greatly in amount.

"I estimated that one grain of ammonia evaporated in some seasons from every square foot per hour.

"In taking sewage water to the land, I think it very important that the movement should be as rapid as possible.

"The water in its passage of 20 miles has lost its valuable ammonia, and that within two or three days. This is a sufficient proof that we must not trust to the ammonia as an indication of the amount of the organic matter which has been, as it is as rapidly removed as the organic matter is decomposed;



that is to say, the length of time necessary for complete putrefaction is, under favourable circumstances, no greater than the time afterwards required for the removal of its products. In this water there was no life to be observed; but the estimation of the organic matter would have shown no difference, whether vitality had been present, and the substance had been capable of entering into active and unwholesome forms, or had been ready to break up into instantaneous putrefaction, or had been preserved, like a mummy, in carbolic acid for a thousand years.

"From this observation regarding the ammonia we are clearly led to beware, in our schemes of irrigation by sewage water, that the land shall be overflowed before the ammonia is thoroughly formed, or else, if the ammonia is formed, that it shall not be subjected to loss by long exposure to evaporation.

"We see also that nature provides here for the complete obliteration of organic matter. It ceases altogether to be found in the water. It may be traced, either as such, or as ammonia and carbonic acid, long after the bubbles of carburetted hydrogen have ceased to appear, until at last it dwindles down to an amount which is rather difficult to remove from water, and which, so far as we know, may be utterly disregarded.

"In the passage of organic matter we may observe, from figures soon to be quoted, that the volatile and organic matter diminished from 9.33 grains per gallon down to 5.04, even when there was an increase of fixed matter, and that the decomposing matter in solution diminished still more rapidly, in the ratio of 283 to 17.

"The organic matter having left the water, we may next inquire whether any trace of its existence remains behind. That trace we do find in the increased amount of alkalies, sulphates, and chlorides."—Memo. Lit. and Phil. Soc., Manchester, 1867-8; also "Chemical News."

I had also, even so early as 1848, shown the oxidizing action of filtering (report to the British Association already quoted), and in a paper to the Glasgow Philosophical Society, "On the Mud of the Clyde," the following words were used:—

Page 8.—"The long stretch of water lying between Ardmore and Dumbarton is not all an accumulation of mud, which is an indication that the mud falls down,\* and is carried off mainly by the deep channels. The channel is inclined to act as a depositing reservoir, and the northern side receives the overflow water. The mud remaining in the channel is carried partly by nature, and as the water leaves the channel it becomes less disturbed and clearer. This water has, of course, some of the lighter and the soluble parts which the putrefying river brings down, but it really seems as if a very large portion of this were rapidly oxidized; and, whilst the neighbourhood is freed from the mud which might continue sending out more gases, the water is rapidly undergoing purification, and it flows then down as the tide goes out, bringing unexpectedly good water below, although, of course, not perfect. We see a rapid change of water about this district.

\* i.e. before spreading.



"I feel inclined, therefore, to repeat that this space is of great value to all the watering-places of the Clyde, and if it is ever made into arable land they will suffer severely. I only wish it were still larger."

This led to an examination of the effects on the atmosphere of the putrefaction in sewage and sewage materials. The examination, as usual, is not complete, except in one direction; and although the work was done four years ago, I have brought it forward in this Report: see p. 29. It may convey some idea of the work going on when putrefying substances in water are exposed to air in the conditions mentioned. The amount of organic matter becoming decomposed is great, and ammonia is continually given off. The experiments might be continued with advantage by finding the total amount of nitrogen and carbon from a given quantity of material in various conditions, but it is not easy to do this in conditions purely natural.

REPORT to the LOCAL GOVERNMENT BOARD by Dr. ANGUS SMITH, F.R.S., as to TREATMENT of SEWAGE.

SIR,

As requested (by Mr. Selater Booth, M.P., late President of the Board) I have the honour to submit a careful examination of five effluents, the results of processes for the purification of sewage water by different methods.

1st. From Aldershot, where irrigation alone is used.

2nd. From Coventry, where precipitation by alum and iron is used first and irrigation afterwards.

3rd. From Birmingham, where precipitation by lime is employed.

4th. From Burnley, where also lime is employed.

5th. From Aylesbury, where the A B C process is used, a precipitant of alum being employed, also of clay.

I shall extract from the larger tables some of the more important points; but I wish it to be observed that in this report I refer to quality of effluents only, and not at all to the ultimate value of processes.

FREE AMMONIA A.

	Ammonia abstracted.		Ammonia remaining.	
	Parts per 100,000.	Per Cent. of Total.	Parts per 100,000.	Per Cent. of Total.
Aldershot <i>b</i> .	11·755	97·96	0·245	2·04
Coventry - - -	2·06	79·8	0·520	20·2
Aldershot <i>a</i> .	2·913	80·10	0·747	19·9
Aylesbury - - -	2·980	74·5	1·020	25·5
Birmingham <i>a</i> .	1·425	52·9	1·275	47·1
Burnley - - -	0·120	8·3	1·330	91·7
	added	added		
Birmingham <i>b</i> .	0·520	18·8	3·220	118·8

NOTE.—Aldershot (*a*) specimen collected in wet weather; (*b*) in dry weather  
Birmingham (*a*) after lime precipitation and irrigation; (*b*) after lime alone.



Free includes saline ammonia. Its existence is of no disadvantage so far as the effect on the atmosphere is concerned, but its absorption by the soil is important as manure. Its amount indicates decomposition. So far as free ammonia is concerned, the first on the list is Aldershot during dry weather, specimen *b*; Coventry stands second. There two processes are used, both precipitation (with alum, iron, and lime) and irrigation. The next is Aylesbury. The lime processes are certainly behind.

#### ALBUMENOID AMMONIA B.

	Ammonia abstracted.		Ammonia remaining.	
	Parts per 100,000.	Per Cent. of Total.	Parts per 100,000.	Per Cent. of Total.
Aldershot <i>b</i> .	5.195	98.95	0.0550	1.05
Coventry	1.639	96.40	0.061	3.60
Aylesbury	0.59	89.40	0.070	10.60
Aldershot <i>a</i> .	1.543	88.2	0.207	11.8
Birmingham <i>a</i> .	0.840	80.0	0.210	20.0
Burnley	0.895	74.6	0.305	25.4
Birmingham <i>b</i> .	0.390	37.1	0.660	62.9

On this table Aldershot on a dry day stands best, but not on a wet day. Coventry with its double system is next best. Aylesbury with precipitation alone is almost the same as Coventry with its double purification.

Perhaps this expression "on a dry day" is not quite fair, it is meant to show that in a case of an overflow there may be little or no purification, but there is generally some unless the flood be great.

#### RESIDUAL AMMONIA C.

	Ammonia abstracted.		Ammonia remaining.	
	Parts per 100,000.	Per Cent. of Total.	Parts per 100,000.	Per Cent. of Total.
Aldershot <i>b</i> .	11.36	100.0	0.00	0.00
Coventry	5.081	99.8	0.009	0.2
Aylesbury	4.269	88.0	0.581	12.0
Aldershot <i>a</i> .	3.177	83.0	0.636	17.0
Birmingham <i>a</i> .	3.351	61.4	2.109	38.6
Burnley	1.200	29.65	2.503	70.35
Birmingham <i>b</i> .	1.530	28.0	3.930	72.0

Aldershot (dry) is again the best; Coventry next; Aylesbury third.



The two chief ammonias in a sanitary point of view are the albuminoid and residual. They are therefore added here.

TABLE D.—TOTAL ORGANIC AMMONIA, *i.e.*, Albuminoid and Residual; both Ammonias may be called "possible."

	Ammonia abstracted.		Ammonia remaining.	
	Parts per 100,000.	Per Cent. of Total.	Parts per 100,000.	Per Cent. of Total.
Aldershot <i>b.</i>	16.555	99.65	0.055	0.35
Coventry	6.720	98.97	0.070	1.03
Aylesbury	4.859	88.20	0.651	11.80
Aldershot <i>a.</i>	4.720	84.84	0.843	15.16
Birmingham <i>a.</i>	4.191	64.40	2.319	35.60
Burnley	2.095	42.73	2.808	57.27
Birmingham <i>b.</i>	1.920	29.60	4.590	70.40

TABLE E.—TOTAL AMMONIA.

Aldershot <i>b.</i>	28.31	98.9	0.300	1.1
Coventry	8.78	93.6	0.590	6.4
Aldershot <i>a.</i>	7.633	82.7	1.590	17.3
Aylesbury	7.839	82.4	1.671	17.6
Birmingham <i>a.</i>	5.616	60.9	3.594	39.1
Burnley	2.215	34.9	4.138	65.1
Birmingham <i>b.</i>	1.400	15.2	7.810	84.8

It is seen here that the lowest effluent for total ammonia is from the irrigation farm in dry weather. Coventry next. Aldershot (wet) and Aylesbury stand third nearly the same.

#### NITRIC ACID.

		Sewage.	Effluent. Parts in 100,000.
Aldershot <i>b.</i>	-	-	9.23
Aylesbury	-	None	3.19
Aldershot <i>a.</i>	-	Traces	2.79
Birmingham <i>b.</i>	-	None	2.13
Coventry	-	"	1.22
Burnley	-	-	1.20
Birmingham <i>a.</i>	-	None	1.19

Nitric acid shows the effect of oxidation on the organic matter, and here the great action of air and of a porous soil shows itself remarkably.

The best seems to be irrigation in dry weather when the land has full opportunity to act.



The use of precipitation has a decided advantage in wet weather as it raises the purity of the Coventry water above the Aldershot wet specimen. The precipitation method by alum, &c., at Aylesbury, is better in Tables B and C than in A. It is the best of the single processes in wet weather. Aldershot is the best of the single processes in dry. Coventry, the double process, is the best in wet weather. Those which are good in wet weather would probably show still better in dry if the specimens were taken frequently during the year. The precipitation processes, when alum or iron is used, have an advantage in wet weather, since the act of precipitation becomes an act of disinfection.

The effluent specimens were examined as to their tendency to putrefy. Those with lime changed most. Ammonia is in parts per 100,000.

—			Date.	Free Ammonia.	Albumenoid Ammonia.
BURNLEY, collected June 1879.	16th		June 20, 1879	1.33	0.305
			July 17, "	1.92	0.23
			" 28, "	1.92	0.30
			Sept. 4, "	2.15	0.13
BIRMINGHAM, collected June 1879.	23rd		June 25, "	3.222	0.662
			July 17, "	4.20	0.336
			" 18, "	4.15	0.336
			" 28, "	3.90	0.324
ALDERSHOT (wet) - Effluent C. -	-	-	" 7, "	0.44	0.144
			" 28, "	0.364	0.130
			Sept. 4, "	0.140	0.092
ALDERSHOT, dry -	-	-	" 16, "	0.245	0.055
			Oct. 11, "	0.240	0.058
AYLESBURY, collected July 1879.	2nd		July 23, "	0.96	0.067
			" 26, "	1.00	0.06
			" 29, "	0.96	0.06
			Sept. 4, "	0.045	0.035

Birmingham (effluent) ammonia rose in 23 days from 3.222 to 4.2; then began to fall; Burnley in 27 days from 1.33 to 1.92; Aylesbury changed none in a week; Aldershot (dry) may be said not to have changed in 25 days.

The capacity to froth when shaken is a very useful mode of finding the comparative sewage matter rapidly. It may be said to have been absent in Aldershot (dry), Coventry and Aylesbury effluents. The clearness of the liquid is very important although a popular indicator. In the Coventry sample there were a few white floating particles; when these fell the water was clear and colourless. Three specimens—Aldershot (dry), Coventry and Aylesbury were without colour, when they had stood in a large colourless glass vessel.



The total solids are in this order in the effluents; the advantage is in being low, of course:—

	Parts per 100,000.
Aldershot average of three (wet)	- 29.5
Aldershot dry	- 41.0
Burnley	- 54.0
Coventry	- 70.5
Aylesbury	- 89.5
Birmingham (b)	- 100.5
Birmingham (a)	- 112.5

During floods the volatile solids stand thus:—

Coventry	- 12.0
Aylesbury	- 13.5
Aldershot average of three (wet)	- 13.8
Burnley	- 14.0
Birmingham (a)	- 24.0
Birmingham (b)	- 26.5

The chlorine has not been found the same in the effluent as in the sewage. This, I suppose, is owing to the effluent being from sewage of a time previous to that of the specimen of sewage.

The question has been asked which of these specimens is most suited for passing into a sewer. None of these effluents can be called sewer-water in the ordinary sense. The Birmingham stream froths readily, and is not pleasant to the eye. The Burnley water was pretty clear, would do well in appearance as a stream by itself, but caused a milky deposit in the river into which it fell, arising, we may suppose, from the free lime taking up some carbonic acid from the river water and precipitating carbonate of lime. The Coventry effluent went into a stream which was very impure, and it might, so far as appearance went, pass into a shallow mountain stream without being noticed. So of Aldershot and Aylesbury.

In every respect we may say that the best result has been obtained by irrigation when the weather is not so wet as to cause overflowing. Still it was not found highly successful after lime at Birmingham.

That the precipitation with alum or alum and iron compounds is next.

That in wet weather there is an advantage in precipitation, because the action is largely, if not wholly, independent of dilution.

That the lime process is valuable but not equal to the above precipitation processes.

I must repeat that in this report I allude only to the merits of the effluent. There is a good deal to be examined before pronouncing on the ultimate value of the processes, and of course a large proportion, if not all of the remaining reasoning, must be left for Mr. Rawlinson, for whose report this may be considered as a preparation.

I am, &c.

Manchester, 16th October 1879. R. ANGUS SMITH.



# ANALYSES OF SPECIMENS OF WATERS FROM SEWAGE WORKS, expressed in Parts per 100,000.

SAMPLES from Burnley, collected 16th June 1879. (See Report by Dr. R. Angus Smith.)

	Organic Carbon.	Free Ammonia.	Albumenoid Ammonia.	Residual Ammonia.	Total Ammonia.	Nitric Acid.	Sulphuric Acid.	Chlorine.	Mineral Solids.	Volatile Solids.	Total Solids.	Alkalinity as $\text{SO}_3$ .	Hardness	
													Before boiling.	After boiling.
—														
Stream above sewage works	0.476	0.025	0.024	0.075	0.124	0.50	3.26	1.28	17.0	3.0	20.0	7.50	10.81	7.78
Do. below ditto	0.987	0.236	0.070	0.219	0.525	0.56	4.12	1.90	18.5	6.5	25.0	9.00	12.64	8.22
Crude sewage	20.33	1.45	1.20	3.703	6.353	—	6.35	5.12	49.0	148.0	197.0	13.00	—	—
Effluent from sewage works	3.737	1.33	0.305	2.503	4.138	1.20	7.38	5.06	40.0	14.0	54.0	13.00	20.92	17.16

SAMPLES from Birmingham, collected 23rd June 1879.

	Organic Carbon.	Free Ammonia.	Albumenoid Ammonia.	Residual Ammonia.	Total Ammonia.	Nitric Acid.	Sulphuric Acid.	Chlorine.	Mineral Solids.	Volatile Solids.	Total Solids.	Alkalinity.	Hardness	
													Before boiling.	After boiling.
—														
Crude sewage	20.44	2.70	1.05	5.46	9.21	None	25.23	24.16	102.0	75.0	177.0	13.83	45.0	44.0
Effluent from settling tanks	4.09	3.22	0.66	3.93	7.81	2.13	22.65	15.78	74.0	26.5	100.5	11.32	39.0	38.4
Effluent after irrigation	2.303	1.275	0.21	2.109	3.594	1.19	18.19	11.46	88.5	24.0	112.5	37.77	66.8	29.22



SAMPLES from Coventry, collected 24th June 1879.

	Organic Carbon.	Free Ammonia.	Albumenoid Ammonia.	Residual Ammonia.	Total Ammonia.	Nitric Acid.	Sulphuric Acid.	Chlorine.	Mineral Solids.	Volatile Solids.	Total Solids.	Alkalinity.	Hardness	
													Before boiling.	After boiling.
Crude sewage	11.33	2.58	1.700	5.09	9.370	None	11.33	6.85	59.0	31.0	90.0	25.35	32.80	9.85
Effluent from settling tanks (filtered).	1.418	2.40	0.245	0.511	3.156	None	7.21	6.30	55.0	16.0	71.0	22.34	37.15	15.62
Effluent after irrigation (drain out of order).	0.587	2.12	0.205	0.895	3.220	1.22	13.21	5.73	58.0	19.0	77.0	12.62	35.45	17.65

SAMPLE from Coventry, collected 10th July 1879.

	Organic Carbon.	Free Ammonia.	Albumenoid Ammonia.	Residual Ammonia.	Total Ammonia.	Nitric Acid.	Sulphuric Acid.	Chlorine.	Mineral Solids.	Volatile Solids.	Total Solids.	Alkalinity as SO <sub>3</sub> .	Hardness	
													Before boiling.	After boiling.
Effluent after irrigation	0.618	0.52	0.061	0.009	0.590	1.62	13.39	4.99	58.5	12.0	70.5	21.0	40.70	19.72



SAMPLES from Aldershot, collected 1st July 1879 (wet weather).

	Organic Carbon.	Free Ammonia.	Albumenoid Ammonia.	Residual Ammonia.	Total Ammonia.	Nitric Acid.	Sulphuric Acid.	Chlorine.	Mineral Solids.	Volatile Solids.	Total Solids.	Alkalinity as SO <sub>3</sub> .	Hardness.	
													Before boiling.	After boiling.
Crude sewage	16.90	3.660	1.750	3.813	9.223	Traces	2.04	4.38	41.0	32.0	73.0	9.40	6.71	3.38
Effluent "A" from sewage farm	—	0.920	0.276	0.803	1.999	2.69	5.14	4.54	24.0	16.0	28.0	2.50	6.57	6.29
Effluent "B" from sewage farm	2.282	0.880	0.200	0.788	1.868	1.59	1.89	3.14	15.0	11.0	26.0	1.90	5.00	4.57
Effluent "C" from sewage farm	2.240	0.440	0.144	6.318	0.902	4.08	2.40	3.20	20.0	14.5	34.5	0.70	7.86	6.86
Collected 13th September 1879 (dry weather).														
River Blackwater	0.536	0.0108	0.03	0.0542	0.095	1.56	2.40	2.46	32.50	6.00	38.50	20.40	28.55	10.88
Crude sewage (camps)	43.76	12.00	5.25	11.36	28.61	—	4.29	12.08	48.0	93.0	141.0	16.40	11.70	4.43
Effluent from sewage farm	0.970	0.245	0.055	—	0.286	9.23	4.48	15.53	24.5	16.5	41.0	Neutral	12.28	12.00

SAMPLES from Aylesbury, collected 2nd July 1879.

	Organic Carbon.	Free Ammonia.	Albumenoid Ammonia.	Residual Ammonia.	Total Ammonia.	Nitric Acid.	Sulphuric Acid.	Chlorine.	Mineral Solids.	Volatile Solids.	Total Solids.	Alkalinity as SO <sub>3</sub> .	Hardness.	
													Before boiling.	After boiling.
Crude sewage	6.76	4.00	0.66	4.85	9.510	None	14.42	7.97	76.0	29.0	105.0	35.50	48.6	20.0
Effluent from 3rd settling tank	0.633	1.02	0.07	0.581	1.671	3.19	30.21	5.44	76.0	13.5	89.5	11.20	66.40	37.1



## No. VII.

MECHANICAL AERATION OF SEWAGE, &c. TABLES OF  
EXPERIMENTS.

In the experiments noted in the previous chapter we see how long and persistently the sewage matter, both with and without water, gives out ammonia, and we must add at the same time putrid, and therefore offensive, gases and vapours. The substances were preserved in vessels partially exposed to the air; that is, the air filled the vessel excepting a very small space occupied by the sewage matter, and fresh air occasionally allowed to enter. These carboys resembled the sewers themselves and similar confined places.

I now go to entirely different conditions, and give to the sewage matter abundance of air, examining the results. I must, however, add, that in the following experiments the amount of air supplied is greater than that usually given to sewage water in nature. It does, however, show qualitatively the result of aeration, and I look on the effect as a parallel to that which we see in the Clyde and elsewhere. The oxygen does its work, and the gases of putrefaction are to a large extent modified, and in time the action itself ceases.

The aeration experiments were all made by Dr. Storer's and Mr. Cranston's apparatus, lent me for the purpose.

It consists of an earthenware vessel containing 3·3 gallons; into this was put about  $2\frac{1}{2}$  gallons of liquid, or about 14 litres, having an archimedean screw in the centre, acting on a vertical shaft, and driving the water down a cylinder which does not reach to the bottom of the earthenware vessel, called the converter. Along with the water air is driven, and the mixed water and air rise up on the outer side of the centre cylinder ready to flow in again, and so continuously. The screw was driven by a gas engine of half-horse power.

## OXIDATION, TABLE I.

We see here the condition of the sewage before treatment. It is to be observed that it is not fresh organic matter, but matter which has undergone decomposition as well as oxidation. We see the first by the ammonia in solution, and the second by the nitric acid. The amount of free oxygen shows the source.

It is a curious fact, observed frequently, that one hour's aeration removes oxygen as well as carbonic acid, and there is a general coincidence of rise and fall with free exposure. The cause of this is not clear. It may be that the motion causes the oxygen to combine; there is also a slight rise of temperature, part of which may be due to friction and part to oxidation. After an hour's aeration the effect diminishes considerably, and oxygen tends to assume its original amount. The analyses were made a day after the aeration. There were many done immediately after aeration,—that is, after allowing the bubbles to



rise,—but the differences were too great to allow of any useful table, the gases coming probably at varying speeds from the liquid. It was decided, therefore, to wait for a day.

After standing for 16–18 days, we find that the oxygen of the non-aerated has greatly diminished, and the other shows itself in proportion to the amount of aeration. Aeration, therefore, has preserved not only from all sensible signs of putrefaction, but from such chemical action as these gases would indicate.

The nitrogen being 19.97 in one case is very high, and in another 22.7 c.c. in a litre; indeed all the nitrogens are very high, but I suppose the liberation of nitrogen in the experiments already given may account for this. Perhaps time was required to remove the nitrogen, or some may have been evolved during the extraction of the gases, but it was found frequently when there was no reason for believing in a mistake.

The carbonic acid, as we may suppose, is driven out by aeration, but gradually increases on standing.

The free ammonia diminishes uniformly with aeration, but more rapidly in the first hour, as we might expect. After standing there is no difference in the free ammonia of the specimens aerated for one and for more hours.

The albuminoid ammonia is not much changed in any of the aerated specimens, and this we might expect from the absence of putrefaction; some organic substance, however, has evidently decomposed, forming free ammonia. This organic substance is that which produces the residual ammonia—the nitrogenous matter not decomposed in the treatment for albuminoid ammonia. In the non-aerated the albuminoid ammonia has increased decidedly.

The nitric acid has in every instance disappeared, when kept long, and, no doubt, has given out nitrogen in conformity with previous experiments. This is an important point in the purification of rivers, and settles the question, do rivers purify? but not the time.

In this inquiry Wanklyn's process for ammonia and albuminoid ammonia was used, but I divide the nitrogenous matter into three parts, the ammonia free and saline as one, the albuminoid, and the residual. We do not follow the stages of decomposition when we estimate the total nitrogen only.



## OXIDATION.—TABLE I.

DISSOLVED GASES, MANCHESTER SEWAGE:—1st GROUP of FOUR examined the DAY after AERATION.

		2nd		16-18 DAYS							Ammonia and Nitrate.			
		Oxygen, c. c. per Litre.	Nitrogen, c. c. per Litre.	CO <sub>2</sub> , c. c. per Litre.	Total Gas, c. c. per Litre.	Oxygen, % of Total.	Nitrogen, % of Total.	CO <sub>2</sub> , % of Total.	O + N = 100, % O.	O + N = 100, % N.	Free NH <sub>3</sub> , per Million.	Albd. NH <sub>3</sub> , per Million.	HNO <sub>3</sub> , per Million.	
Manchester Sewage, from Miller's Lane, received 12/1/81:—														
Before treatment	.....	4.00	18.24	21.51	43.75	9.22	41.59	49.19	18.28	81.72	48.0	10.8	4.07	
Aerated 1 hour, 12/1/81	.....	2.71	19.03	12.86	34.60	7.69	54.09	38.22	14.76	85.24	34.0	—	4.63	
“ 2 hours, 13/1/81	.....	4.42	18.15	18.12	40.69	10.88	44.57	44.55	19.6	80.4	31.68	10.6	3.71	
“ 4 hours	.....	3.94	18.18	21.37	43.49	9.00	42.20	48.80	17.59	82.41	25.6	10.4	5.19	
Manchester Sewage, from Miller's Lane, received 12/1/81:—														
Before treatment	.....	1.88	20.80	31.73	54.41	3.45	41.67	55.88	8.27	91.73	32.0	13.4	0.00	
Aerated 1 hour, 12/1/81	.....	1.94	19.97	—	21.94	8.84	91.02	—	8.86	91.14	32.0	8.40	0.00	
“ 2 hours, 13/1/81	.....	2.76	22.70	19.4	44.86	6.15	50.61	43.24	10.84	89.16	33.0	7.70	0.00	
“ 4 hours	.....	3.48	19.15	30.40	53.03	6.57	36.12	57.31	15.4	84.6	33.0	8.52	0.00	



TABLE II.

*Glasgow Sewage.*

After half an hour's oxidation the carbonic acid fell as before. The oxygen was very low at first, and rose but only a little. The addition of lime has lessened both the carbonic acid and oxygen. This in part explains the increase of nitrates when lime is used. There seems no increase of nitrates by aeration with the apparatus alone, but there is some formed after 22 days.

The free ammonia diminishes by the use of agitation, but increases by standing.



TABLE II.

DISSOLVED GASES, GLASGOW SEWAGE partly with LIME:—1st GROUP of FOUR examined the DAY after AERATION.

			2nd	Two	22 DAYS	Ammonia and Nitrate.		
						Free NH <sub>3</sub> per Million.	Albd. NH <sub>3</sub> .	HNO <sub>3</sub> .
Oxygen, c. c. per Litre.	Nitrogen, c. c. per Litre.	CO <sub>2</sub> , c. c. per Litre.	Total Gas, c. c. per Litre.	Oxygen, % of Total.	Nitrogen, % of Total.	CO <sub>2</sub> , % of Total.	% Oxygen, O + N = 100.	% Nitrogen, O + N = 100.
Glasgow Sewage, received 8/2/81:—								
Before treatment	Examined 9/2/81 -	30.10	42.70	1.03	28.47	70.50	3.5	96.5
Aerated $\frac{1}{2}$ hour alone, 9/2/81	" 10/2/81 -	20.10	34.41	2.04	39.64	58.32	4.9	95.1
" and $\frac{1}{2}$ hour with lime.	" "	0.02	17.26	0.70	99.19	0.11	0.71	99.19
" and 1 hour with lime.	" "	4.40	22.69	0.25	80.36	19.39	0.30	99.7
Glasgow Sewage, received 8/2/81:—								
Before treatment	Examined 4/3/81 -	97.88	118.48	1.17	16.21	82.62	6.77	93.23
Aerated $\frac{1}{2}$ hour alone, and 1 hour with lime, 9/2/81.	" "	39.47	54.32	3.52	23.82	72.66	12.87	87.13
Glasgow Sewage, received 8/2/81:—								
Aerated without, and then with, lime...	Examined 4/3/81 -	0.15	19.97	6.92	92.34	0.74	6.97	93.03
							66.0	7.0
								7.41







*Summary of Experiments, Aeration of Sewage.*

In all cases putrefaction is delayed by aeration. The oxygen recovers itself in the aerated specimens better than in the non-aerated. Nitrates are formed more readily in the aerated than in the non-aerated specimens.

Ammonia is lost by agitation, but specially by the previous addition of lime. The amount of lime added was .171 gr. per litre, or 12 grains to the gallon.

---

TABLE IV.

The experiments were made with water containing 10 cub. cent. of putrid blood to 15 litres.

They show a diminution of oxygen and of carbonic acid by agitation; also an increase of nitrates.

The peculiarities came out more strongly here than with the sewage.

The diminution of oxygen is not observed so much in the aerated as in the non-aerated.

The oxygens rise and fall very irregularly; this may come from changes of temperature.

The nitrates always rise up to a certain point, and then begin to fall.

It appears as if the putrid matter were able to contain nitrates to a certain extent before the action which destroys them both commences. This also depends on temperature.







TABLE V.  
DISSOLVED GASES. WHITE OF EGG. EFFECT OF TIME AND AERATION.

	Oxygen, c. c. per Litre.	Nitrogen, c. c. per Litre.	CO <sub>2</sub> , c. c. per Litre.	Total Gas, c. c. per Litre.	Oxygen, % of Total.	Nitrogen, % of Total.	CO <sub>2</sub> , % of Total.	% Oxygen, O + N = 100.	% Nitrogen, O + N = 100.	Ammonia and Nitrate.		
										Free NH <sub>3</sub> , per Million.	Albd. NH <sub>3</sub> , per Million.	HNO <sub>3</sub> , per Million.
White of one egg in 15 litres water, mixed 31/12/80:—												
Not treated	4.44	13.56	0.49	18.49	24.04	73.36	2.60	24.68	75.32	0.80	15.12	5.18
"	2.67	20.33	2.45	25.45	10.48	79.88	9.64	11.69	88.31	—	—	—
"	2.77	14.00	4.96	21.73	12.78	64.38	22.84	16.69	83.31	8.08	10.40	2.70
White of egg in 15 litres water, mixed 31/12/80:—												
Aerated 1 hour, 31/12/80	3.86	10.83	0.61	15.30	25.25	70.73	4.02	26.31	73.69	0.84	17.60	5.92
"	4.40	20.74	4.30	29.44	14.90	70.46	14.64	17.49	82.51	0.90	16.50	20.01
"	4.94	19.00	7.06	31.00	15.92	61.29	22.79	20.62	79.38	5.70	6.30	2.00
White of egg in 15 litres water, mixed 31/12/80:—												
Aerated 4 hours, 31/12/80	3.34	20.50	0.24	24.08	13.89	85.11	1.00	14.01	85.99	0.90	12.00	0.00
"	4.97	16.76	1.70	23.43	21.20	71.52	7.28	22.87	77.13	2.12	9.40	2.89



TABLE VI.  
DISSOLVED GASES. YOLK OF EGG. EFFECT OF TIME AND AERATION.

	Oxygen, c. c. per Litre.	Nitrogen, c. c. per Litre.	CO <sub>2</sub> , c. c. per Litre.	Total Gas, c. c. per Litre.	Oxygen, % of Total.	Nitrogen, % of Total.	CO <sub>2</sub> , % of Total.	% Oxygen, O + N = 100.	% Nitrogen, O + N = 100.	Ammonia and Nitrate.		
										Free NH <sub>3</sub> per Million.	Albd. NH <sub>3</sub> per Million.	HNO <sub>3</sub> per Million.
Yolk of one egg in 15 litres water, mixed 3/1/81:—												
Not Treated	2.51	20.60	1.90	25.01	10.04	82.36	7.60	10.86	89.14	1.25	12.00	—
"	0.65	16.18	2.89	19.72	3.28	82.09	14.63	3.85	96.15	0.48	18.00	—
"	0.84	9.26	4.20	14.30	5.87	64.75	29.38	8.32	91.68	1.12	11.25	2.30
Yolk of one egg in 15 litres water, mixed 3/1/81:—												
Aerated 1 hour, 3/1/81	3.76	18.75	2.64	25.15	14.94	74.58	10.48	16.69	83.31	0.60	12.50	—
"	1.58	15.06	1.79	18.43	8.55	81.74	9.71	9.47	90.53	8.08	13.30	7.86
"	2.12	15.35	4.82	22.29	9.49	68.86	21.65	12.12	87.88	0.96	11.10	3.59



## No. VIII.

## CONNECTION OF THIS WORK WITH RECENT MICROSCOPIC INQUIRIES.

It may be interesting to connect this subject with the progress of microscopic inquiry. After writing the opinion on the action of the air, I made many examinations of aerated sewage, and found that the act of aeration prevented putrefaction. It was my intention to examine the matter microscopically; and, indeed, I did so, but not with that fullness which a professed microscopist attains. I am therefore glad to allow this part of the subject to pass into other hands, so far as sewage is concerned, remarking that the chemical change is most decided. An hour's aeration will enable sewage water to keep without putrefaction from two to three weeks in weather ranging from the beginning of July 1880 in Glasgow, where experiments were first made with Storer and Cranston's apparatus, till the end of spring 1881 in Manchester.

My idea was to kill, by the use of air, the germs of disease and of putrefaction, whatever they might be, judging this possible simply from the fact that they seemed to be killed when they passed from sewers into rivers. Still it seemed to me that it would be better if putrefaction were allowed its full action first, so that many organic substances should be decomposed, and some living organisms themselves broken up into gases or into intermediate products, when afterwards the oxygen would purify the solution. This is a plan that may be adopted systematically in some places, as I believe it is adopted practically, but without intention, in many places. The action in the sewer rivers is partly this; and when there is little water, that is, when there is a strong solution of sewage, this is probably the chief action. The oxidation takes place very rapidly after putrefaction. (On this point I have only general observation, not measured results.) As we seldom can allow the water to stand long enough to undergo complete putrefaction, it comes from the sewers into the rivers in a condition which, so far as I know, has not been characterised microscopically with a knowledge up to the latest date. I am therefore speaking somewhat vaguely when I say that we may take it for granted that the minute organisms causing disease have not been acted on sufficiently to be destroyed. It would be interesting to know at what stage they are destroyed. The mixture of the sewage water with river water will produce an act of oxidation to a certain extent, and will, in cases where there is water enough, produce an act of purification so far, but a further flow will increase the oxidation. In the Clyde and the Irwell (as in the Thames before the new sewage system was adopted) the action of putrefaction is decided, but it is limited by the struggle with oxidation. A part of the river becomes a reservoir for putrefaction, although probably not to its utmost, and the lower part a place for oxidation. For this reason it is suitable to have the first part confined, so as to allow the putrefaction full force, and after this



to have the water spread as much as possible to allow of fullest oxidation. A fair example of this is given in the action in the Clyde above Dumbarton as putrefactive, then down to Greenock as oxidizing; and if by no means satisfactory, it is so far good and nature's method.

This is entirely regardless of the comfort of the inhabitants, who may object to the part of the river being devoted to purification by putrefaction. That, however, brings in another subject. For irrigation purposes *solely*, rapid transference is best.

To return again to the effect of oxidation, I wish to introduce an extract from two papers; and, first, that already quoted, Chem. News, 1865, p. 304.

*"On the examination of Water for Organic Matter."*

"The gases of pure water contain 34 per cent. of oxygen.

"Dalton found cistern water almost deprived of its oxygen, and I have found every per-centage of oxygen, from 34 downwards. I go further into this point in my chapter on water, which I hope to bring out soon. Meantime, I may say that the examination for oxygen is a very important one.

"The loss of the oxygen with peaty matter and no vegetation indicates, as already said, the formation of carbonic or a bitter acid. The loss of oxygen with evolution of sulphuretted hydrogen indicates putrefaction. But there are two conditions which externally resemble each other very much,—the growth of vegetable matter with diminished oxygen, and the growth of vegetable matter with excess of oxygen. Water in the first of these conditions may contain, as I imagine, the most dangerous ingredients. Germs of all kinds may exist in such waters,—we do not know to what extent; and as we are very ignorant on the subject, it is well to be alarmed at the conditions until we have examined them and made distinctions."

I add, perhaps too cautiously, but still believing in the power of oxidation, even when vegetable matter was growing in it:—"We do not know much about the second of these two (*i.e.* with excess of oxygen), and if I think it is less dangerous it is perhaps more from a prejudice in favour of the abundance of vital air, and of those hill waters which do not contain bitter peat."

So far as this purification by air is concerned, it is interesting to see that it is the right track, and to be able to look at the researches of Pasteur and of Dr. Ogston as confirming the views, if indeed there was any need of confirmation of the fact that air purified. Yes, there was need, as there have been questions as to organisms on the hills acting with all their poisoning vigour after being brought down by rivers. It was my belief at one time that the effect of dilution was the purifier, but now that may be supplemented by the effect of oxygen preventing putrefaction as proved here, and by weakening the action of the germs, at least of some diseases, as shown by Pasteur in his researches on the chicken cholera, and by Dr. Ogston on the micro-organisms in pus.



The words of Pasteur may be given here, as introduced into the "Chemical News," 22nd April 1881:—

*"On the Attenuation of the Virus of Chicken Cholera,  
by L. Pasteur."*

"Now that we have arrived at this point, a question presents itself which relates to the cause of the attenuation of virulence.

"The cultivations of our virus must take place in contact with air, because our virus is aerobian, and, without air, its development becomes impossible. We are then naturally led to ask whether the attenuation of the virus is not due to contact with the oxygen of air? Would it not be possible that the small organism which constitutes the virus, when left in contact with the oxygen of pure air, in the medium of cultivation in which it has developed, may have been modified, and the change remains permanent, even after the organism has been withdrawn from the modifying influence? We may also inquire whether some chemical principle in the atmosphere, other than oxygen, does not intervene in this phenomenon, the singularity of which almost justifies my hypothesis.

"It is easy to understand that the solution of this problem, in case it depends on our first hypothesis, that the phenomenon is due to the oxygen in the atmosphere, may be tried by experiment. If oxygen is in reality the cause of the attenuation of virulence, we may have, to a certain degree, a proof of it by noting the effect of suppressing it.

"To test this, let us conduct our cultivations in the following manner:—We may take a certain quantity of our chicken broth and place in it the most virulent virus, and fill with it a series of glass tubes up to two-thirds, three-quarters, &c. of their volumes. These tubes may then be closed over the lamp. By the presence of the small quantity of air left above the liquid the development of the virus may be started, which is ascertained by the increasing turbidity of the liquid. The development of the cultivation gradually absorbs all the oxygen contained in the tube. The turbidity then diminishes, the growth is deposited on the sides of the tube, and the liquid becomes limpid. This takes place generally in two or three days. The microscopic organism is then deprived of oxygen, and will remain in this condition as long as the tube is not opened. What will become of its virulence? To be sure of our results we will have prepared a great number of such tubes and an equal number of flasks, which last will continue to be left in contact with pure air. We have already spoken of what becomes of cultivations carried on in presence of air. We know that they experience a progressive attenuation of their virulence, and we will not return to this subject. Let us now only pay attention to the cultivations in closed tubes. Let us open them—one after an interval of a month, another after three months, and so on until we open one that has stood ten months. I have



not gone any further at the present time. It is a remarkable circumstance that the virulence in all these cases is of the same degree as that of the liquid which served to fill up the tubes. As to the cultivation exposed to the air, they are found either dead or in a condition of feebler virulence.

"The question we have proposed is then solved: it is the oxygen of the air which attenuates and extinguishes the virulence.

"To all appearances we have here what is more than an isolated fact. We must have reached to a general principle. We may suppose that an action which is inherent to atmospheric oxygen, an agent present everywhere, has the same influence on other viruses. At any rate it is worthy of interest that possibly a general cause of attenuation exists dependent on an agent which is in a manner cosmical. Can we not suppose even now that it is to this cause that we can attribute in the present, as in the past, the limits set to great epidemics.

"The facts which I have had the honour to communicate to the Academy suggest many proximate and remote inductions. From all these I must hold back with reserve. I will not feel authorised to present them to the public unless I make them pass into the domain of demonstrated truths."

Also from Dr. Alex. Ogston:—

*From a "Report upon Micro-organisms in Surgical Diseases," by Alexr. Ogston, M.D.—Brit. Med. Jour., 12th March 1881.*

"The results, so far as has been gone, may be summed up as follows:—

"Cold abscesses contain no micro-organisms, and their pus is harmless.

"Acute and pyæmic abscesses always contain micrococci.

"Pus whose micrococci have been killed by carbolic acid or high temperature is harmless.

"Pus containing micrococci is resisted by animals if the dose be minute, or if it be injected into the peritoneal cavity.

"Doses of one or two minims injected into the sub-cutaneous tissue may cause death by blood-poisoning, or may cause sphacelus of the site of the injection, or may be resisted by an unusually insusceptible animal.

"As a general rule such doses produce acute inflammation, accompanied by blood-poisoning and ending in abscess.

"The third part, upon micrococci in wounds and suppurations, is summed up as follows:—

"Suppurating wounds contain micrococci, whose numbers and activity are proportionate to the intensity of the suppuration.

"Listerian dressings prevent micro-organisms from gaining access to wounds.

"Micrococci in wounds withstand most antiseptic applications.

"Where no micrococci are present in wounds, no pus is produced; the discharge is serous.



"Micrococci exist wherever pus occurs, save in chronic suppurations, such as cold abscess, chronic acne vulgaris (?), &c. Micrococci in man produce the same varying effects as in animals; they may produce blood-poisoning without suppuration, they may cause suppuration, or they may be resisted by strong individuals under favouring circumstances. Lastly, there are possibly micrococci that do not produce suppuration."

An account of numerous cultivation experiments is given, and the certain opinion is expressed that the cultivation must go on in absence of air, *i.e.* air is hurtful to the cultivation of the micrococci. The most successful method employed was to inject the seed fluid to the end of an egg opposite to a very small puncture made to admit a hollow needle. Antiseptic precautions were taken to exclude the action of germs in the air.

"To sum up, micrococci do not produce putrefaction. They develop best when removed from the atmosphere. The preceding facts prove that they are able, under suitable circumstances, to give rise to blood-poisoning, to acute inflammation, and to suppuration."

The experiments described in this report show that aeration delays putrefaction. If it does not kill the germs or organisms which produce putrefaction, it weakens them, as in the case of chicken cholera. It is possible that they may die in the oxygen, and the liquid may be again supplied with them.

A curious question arises then: What is the value of a process of oxidation which does not kill the germs of putrefaction; because, if they are not killed, what proof have we that the germs of diseases are not killed? We have no proof; but we are told by Pasteur that in certain cases at least the germs of disease are made innocent by the action of air; and I find as a distinct fact that the germs of putrefaction are also so weakened that they produce no effect until after considerable time. If the germs of all diseases are affected as the germs of chicken cholera and putrefaction are, then we must look to the aeration as a cure for a certain time. This time being long and measured by weeks, the water or sewage treated can in almost all cases be far removed, and sent to places where its impurities will be without effect.

The proposal quoted from my previous papers to examine the growth of the organisms in water was not carried out by me, but I am glad to have been in the right track so long ago, and to have been so also with the inquiries as to oxidation. The results obtained by Koch and also by Klebs must receive the attention of chemists. It does not appear that even if we kill all the germs in any process that much advantage is gained if they are so readily producible from neighbouring sources. The discussion whether those which are most common in smaller numbers, and are in constant supply, can by some peculiar change of condition not visible to us become so abundant as by



their very bulk to be deadly, or by their character to be active, virulent, and equally destructive to higher animal life, is one which must greatly interest chemists as well as biologists. As chemists we can only exhibit the inorganic phenomena so far; we have no test for vitality. The advice I gave so long ago has not been sufficiently taken by myself, but Koch has made it easier to take, and we must not forget the results. At the same time, as chemists we must not forget that chemical tests are not exhausted, and the two inquiries must go on until they blend into one, as they must ultimately do.

These researches do not prove to us that the germs spoken of are destroyed by oxygen; they become weak, and this weakness increases to absolute ineffectiveness, and so far we are guarded; and they may be supposed also from their weakness to increase less rapidly, or to cease to play a prominent part, but ready to begin again. Analogy, however, would lead us to believe in complete annihilation of the first series in the case of those that produce putrefaction, so that they may make room for their successors. The relation of the succeeding to the first is not known to me at least, and I judge simply from analogy that the first organisms will be destroyed with the mass of the organic matter which is destroyed. The destruction is so great in the case of putrefaction that we see the bubbles rising before us rapidly. The gases given out were found to be carbonic acid, hydrogen, carbonic oxide, carburetted hydrogen, nitrogen, sulphuretted hydrogen.

Still there is a limit to the proportion of organic matter destroyed by putrefaction, and I suppose oxygen to be the body which comes and concludes the process. There is, however, an oxidation going on slowly in sewage before putrefaction, but it is not a very rapid one, and what time is required to destroy the several classes of organisms has not been made out. I see no reason as yet for Pasteur's hypothetical influence other than oxygen.

When Dr. Storer came to me with a proposal to use his apparatus for aerating sewage, we had not the investigations of Pasteur to go upon, but I was very glad to have the opportunity of using the means put into my hand, Dr. Storer's apparatus, as the time for considering the subject was come.

To the opinions and facts already given we must add the remarkable observations recorded in the Royal Agricultural Society's Journal, No. XXXIII, Part 1, 1881, by Dr. W. S. Greenwood.

It seems clearly proved there that sewage that has undergone no putrefaction or sufficient oxidation is a very destructive agent when it contains the *débris* of diseased action in the human body, in some if not all cases. It seems to follow as a natural conclusion that as disease has not been observed to any very decided extent as following the use of sewage irrigation, that the putrefaction and oxidation are in ordinary cases sufficient. But there are some differences of opinion, and it is pro-



bable that these processes of destruction and purification, in cases where the sewage has been injurious, have been interrupted too rapidly by the rapid transfer of the sewage to the soil. On this point we must refer to the remarkable inquiry by Dr. Greenwood. At a mill near Bingley, woolsorters' disease and malignant pustules had broken out amongst those who worked with mohair coming from Van. To disinfect the wool it was exposed to the air on a field. In a few days a cow died in a field which received the village sewage, and next month cattle and sheep were attacked by anthrax. In a series of experiments carefully made it was abundantly proved that the disease had come from the wool,—which, however, seemed to have been roughly torn, let us hope, from dead animals, as some of the skin and flesh was at times found attached.

In relation to this report on impure wool, I may mention a circumstance elsewhere mentioned, as it occurred many years ago. I was rather disgusted on entering into a room in a large paper-works where rags were sorted. These rags came from all the miserable wretches that lived or died in unwholesome dens, prisons, workhouses, and hospitals on the continent, and seemed to call up every variety of human bodily misery lingering in our civilisation. What diseases might not be there, and must have been there. In this room dust was flying about, and a number of young people, about 20 years of age, were working diligently there. I certainly never had seen more healthy looking specimens of young women. They were much beyond the average in bulk, their cheeks were ruddy, and their complexions remarkably good, different decidedly from other women in the neighbourhood. I asked if none of them were ever poisoned: no such thing was said to be known. I asked the owner to weigh them, but he never did so. I have often considered this case, and every time I came to the conclusion that the original substances had undergone a transformation, and the germs of disease had been destroyed by an act, if not of putrefaction, of at least some analogous chemico-organic change. This first showed me the value of putrefaction as a purifying agent.

I may add here that I had attempted by the use of fermentation to estimate the amount of vitalized matter in the air, and I give one attempt here from the 10th Annual Report, pp. 42 and 43.

#### “ SOME HIDDEN QUALITIES OF TOWN AIR.

“ Some years ago I made inquiries into the effect of various substances in preventing putrefaction; the effect was measured in one set of trials by the amount of sulphuretted hydrogen produced, and in another set by the amount of gases of decomposition evolved. Lately I made another series, with the view of finding if there were any bodies in the atmosphere of large towns which prevented decomposition, the opinion being that the sulphurous gases must have this effect. I did not find that putrefaction was a satisfactory method of trial, and I trusted to



fermentation of sugar as one more under our command. The air of the town was used first, that is, a certain quantity of air was washed with pure water, and a fixed quantity of sugar and yeast added. At the same time there was a control experiment made, lest the yeast should be peculiar. This was done simply by using the same amount of yeast and sugar in pure water, without adding any air washing. There was no mode, however, employed of preventing ordinary contact of the air.

"The results of these experiments are very irregular, as one might suppose when dealing with such substances as yeast. Sometimes the amount of carbonic acid obtained was almost nothing, and at other times, apparently with the same quality of substance, there would be disengaged a large amount. It was needful, therefore, to make numerous experiments, satisfied that absolute exactitude could not otherwise be gained, if it even then could. The results, however, are not without interest if we take the averages, because in them we see a uniformity which it is impossible to see in the list of apparently struggling individual experiments.

"These trials were made at various times, occupying a portion of every month for two years. It seemed to me that nothing would come of them, and that much time was lost. However, I did venture to look the whole in the face lately, and summed them up, bringing out the averages. It is apparently true that the air of a town influences fermentation in sugar to a certain extent."

The researches of Dr. Koch, however, have obtained results far superior, and by using a part of his process I am obtaining very promising results, to be spoken of later.

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Having now given some of the principal points connected with the idea of aerating sewage, I may make some further investigation into the result. What advantage would it be to any city to send down its sewage into a river in a condition in which it did not putrefy, if it were to have an appearance of impurity as great as ever? I think this would be an advantage, but not a sufficient one. We demand more. Indeed, the appearance is quite as much a matter to be considered as any other point. Perhaps we may say that it is the chief point. We have not proved any disease to occur from the sewage below Glasgow or Manchester, although I see that some one has observed a peculiarly poisonous centipede in the mud opposite Liverpool, and fears, probably too well founded, are rising on the Clyde where shores are left bare. The appearance of a river is, to say the least, a prominent point; next, the fish question is an important one; and although sewage is an excellent feeder of fish, these do not enter the places where sewage is very strong, and, I believe, never at all where there is putrefaction going on. We do not effect enough by removing the tendency to putrefy. We may then ask, what more is to be done?

A very common plan is to allow the sewage to pass into tanks and deposit. This generally brings on purification by putrefaction, and of course would receive favour if it were thorough enough,—which it seldom, if ever, is. In most cases there is not ground enough for it; and although some towns take



room enough by converting the rivers into putrefying tanks, and so purifying the water, the result has the objection already mentioned. This certainly has the advantage of being well tried. I might have mentioned, as an argument in favour of putrefaction and the destruction of diseases in rivers, that the Thames water not long ago was considered the best of all water on ships, after it had stood and putrefied in the barrels on board. I am therefore on safe ground. Still it is desired that the water be cleared, and it is cleared at present very slowly by putrefaction and subsequent subsidence or filtration in its own bed.

For sewage filtration unaided has been given up, but filtration with lime is a possible process.

The use of lime has now been long tried, and it has been shown to possess many good qualities. It clears the sewage with great rapidity to a certain extent. But I need not describe its action, as this has been done so well before, and especially by Dr. Wallace, of Glasgow, who has made a special study of the subject. It may be even asked, what advantage can we obtain by any aeration if lime is used?

It is agreed that the effluent from lime is still liable to putrefaction, although this action is postponed for a time and diminished also. Dr. Wallace finds that if the sewage water of Glasgow is allowed to mix with twelve times its bulk of river water, the result will be entire freedom from further smell or putrefaction. It has, among other results, been oxidized. By aeration, then, we seem to do that something for a time which twelve times its bulk of water does to the sewage permanently. The absence of putrefaction after aeration, even with the solid remaining in the water, is a very great result; still I am unable to decide on its ultimate value from present results.

Lime, then, does not disinfect in such a way as to prevent putrefaction as long as aeration does, but it clears the liquid much more thoroughly, and if the effluent is removed the putrefaction resulting cannot be equal to that which would take place in the aerated sewage after a certain time.

This seems to lead to another point, namely, is it not best, then, to use both processes—the lime and the aeration? The lime to clear, and the aeration to delay putrefaction, until the water flowed out of the reach of danger. It is probable that in this case none would take place whatever in any of the circumstances usually found at towns.

The results here are given of a great many experiments, but they are all laboratory experiments, we must remember. I have, however, seen enough of lime precipitation to make me believe that something more would not be a disadvantage.

This account does not contradict anything already said of the great value of the use of alum and iron salts, and it is thought well to append the account previously given, 1879. The matter of expense must be settled by others.



## No. IX.

## EXTRACTION OF AMMONIA.

I have not at all considered independently the expense of aerating in this manner a million gallons, but I am assured that the apparatus is not at all likely to be too expensive. It has been considered that one hour's agitation will be enough. This has been variously calculated for expense. I shall not give my calculation. The amount arrived at is much higher than that obtained by Messrs. Storer, but I must yield to their greater experience.

When sewage is aerated, and left with the solid matter in it, there is, of course, abundant room for a new succession of putrefactive material, and it is necessary to remove that rapidly by precipitation or by filtration. These methods may both be useful; namely, precipitation, so as to allow the deposit to leave a considerable amount of clean water above. After this filtration may be used for collecting the deposit, if it is true that the improvements in filters is as great as I hear of. I have read and been told of several inventions in this direction which seem to me of great value, but I have not entered practically on a study of them. It was found, however, that ammonia came off more readily when the sewage was not filtered.

This subject has baffled all engineers. Sewage has caused expense, and it has failed to produce profit in cases which cannot be called exceptional. It is not proposed to describe the causes, but one certainly is pre-eminent,—the great bulk of water now used for supplying towns. And this cause allies itself to another, namely, the great mass of water as rain, which in some parts of the country weakens the sewage in its flow or in the fields already drenched. The amount of ammonia, as we have long known, is great in sewage, but we have not known how to remove it. It has truly almost as little weight in proportion to the sewage itself as a man has to a castle.

In working with the apparatus described, a constant loss of ammonia was observed, and sometimes this was found by the smell itself. The sewage was tossed about; the volatile part was carried up by the currents of air, and it had no opportunity of returning. Here it was thought was at last a method of obtaining a revenue from sewage ammonia. If we take a grain of ammonia only out of a gallon of sewage, we have from a million gallons a million grains, equal to 142·81 lbs.—let us say 140 lbs.; let us for a large city like Glasgow multiply this by 50, and we have 7,000 lbs. of ammonia daily = 1,140 tons per annum, which at 60*l.* a ton, its present market price, is 68,400*l.* per annum.

Can we obtain a grain out of every gallon? In the laboratory with a small apparatus this has not always been done unless



lime has been used in sewage containing six grains of ammonia. In an experiment made in Glasgow with one hour's aeration without lime, two grains per gallon were obtained from sewage containing about nine grains of free ammonia, I am told. This appeared as a very remarkable and cheering fact, opening up a new field of action for sewage operations.

The question now came to be, How is this to be proved? We know that the world will not spend its money unless it can receive the hope of a good reward.

There is, however, a second question :—When the ammonia is removed from the liquid, how is it to be retained; that is, removed from the air which carries it up, and held in a concentrated form? The present ideas on that point have not been subjected to proof, but it is contemplated using either an acid or a solution of a salt, such as chloride of calcium; from which the ammonia, which has always carbonic acid along with it, would throw down carbonate of lime in fine division, and leave chloride of ammonium in solution.

It was found, however, that the idea had come into the mind of another, ten years before, and had been thrown away. A provisional specification of a patent had been made out in 1870: was it right to throw it aside, and must I do the same? The first projector seems to have acted from theory, and his plan was so imperfect that success, we can easily see, was impossible. A liquid must be very rich in ammonia before such a process would allow any important quantity to be taken from it, as there is simply a bubbling of air through the liquid. Another patent was taken out by Messrs. Hills and Biggs in 1872, one by Messrs. Welch and Scott in 1876, and one by W. L. Wise in 1878. I have tried only Dr. Storer's, and it is not for me here to give opinions of the comparative merits.

#### *Ammonia removed by Exhaustion.*

In aerating water by the method just spoken of, there is a removal of the gases contained in the water, and a substitution of air. This displacement is not effected without using a large amount of air, as one part of fresh air removes a small part only of the gases contained in the water. We cannot expect to do the same work with a small amount of air, unless we first remove the gases contained in the water. This may be done to a large extent by pumping them out; and it is remarkable how much is done, at least on a small scale, in a minute or two by this method. I cannot say that a result has been obtained equal to that by a current of air; and we must remember that the current acts oxidizingly as well as by displacement; but a great deal is effected by the exhaustion methods. The gases come off in a condition strongly impregnated with organic matter, and very disagreeable to the senses. They may in this case be sent through a disinfecting process; say, by passing a fire, if necessary, and if the ammonia cannot be got out. It was expected



that by taking them out in a concentrated state they could be passed through acid, and the ammonia removed in a small absorbing space, thereby getting over the difficulties which may be expected when we try to absorb the ammonia from a large amount of air. This, however, was not found in practice to take place to a sufficient extent; very little ammonia was removed by pumping. At the same time it is very probable that the failure was not inherent to the process, but caused by the limited and imperfect scale of laboratory operations. In some cases it is probable that ammonia would come off in this way; that is, when the sewage was stronger than usual.

If this method of pumping out the gases were adopted it would only be as a preliminary to aeration, which might be effected either by allowing the air to enter, or by assisting it.

How far this plan will be found useful in extracting ammonia from various decomposing bodies, other than sewage and solutions, is still to be found out, but it certainly seems to recommend itself in many cases where putrefaction causes offence, because the putrid gases are drawn out at once and may be treated by fire or otherwise rapidly. It is a new mode of disinfection.

Some enquiry is necessary to enable us to find if the plan of previous pumping out of the gases, and then aerating, is to be recommended in any case in preference to the mode of passing air through the sewage at first. My belief is that such cases may exist when ammonia is to be extracted, but they are more likely to be found where purification and oxidation are required, without looking to the ammonia. This pumping simply draws out the gases which are not very soluble in water, and makes room for others to enter. Those which enter are expected to be oxidizing agents; and first we must look to the action of common air. The sewage could be rapidly deprived of its gases, and then simply allowed to flow away. When it had flowed even a very short time the air would enter, and during this period more would come out. Still it cannot be denied that if the sewage smells badly, the removal of all the air that can be pumped out does not quite remove the smell. It does, however, diminish the quantity of gases and of vapour capable of causing a smell. If, however, the oxygen were caused to enter in a condition more concentrated than it is in the atmosphere, the oxidation would go on more rapidly. It has been a matter of thought to supply the concentrated oxygen to the sewage. We know what wonderful effects are caused by permangates and by peroxide of hydrogen; and I have shown also what high oxides, such as nitrates, effect. A careful study is not required to show that pure oxygen gas, at the present price of materials, is too expensive if we are to saturate the solution, or to give it two per cent. only. At the same time I have not ascertained how much would be necessary. Unless the action were very rapid, the amount would be rapidly diminished by diffusion, and the most active agents for supplying solid oxygen are too expensive.



Viewing the matter in this way, I have called to mind my experiments made long ago in the absorption of gases by charcoal. It was at one time apparently certain to me that oxygen could be filtered out of the air by charcoal; and, indeed, I have found large proportions of oxygen taken out by charcoal. Indeed, we may say that the amount removed from the air is, as a rule, 30 to 40 per cent. I have not, however, been always successful in obtaining it back by pumping it out of the charcoal; occasionally it has come out very well, but it has sadly disappointed me. The plans, however, are not all exhausted. The amount of gas regained from the charcoal usually has less oxygen than the air.

Finding that charcoal was not manageable I have had recourse to water. Pure water absorbs air, not exactly as such, but in the proportion of one-third and a little over of oxygen, the rest being nitrogen—leaving out traces. In other words, we can pump out of water a mixture containing about 13 per cent. more oxygen than common air contains. Such a great increase of per-centage of oxygen has a remarkable influence in most cases, and I suppose will have in oxidizing the substances in sewage. There is a disadvantage, namely, in the small total volume of air that can be obtained from water. In some cases this is of little consequence, because the water is abundant, and one would suppose a stream to be an endless source. In other places, it may be said, where should we obtain water? Water may be used as a filter; when it has been exhausted of air it begins again to drink it in; and the same may be repeated for ever. The question, however, remains, How rapidly can this be done? For example, what surface and depth of water are necessary to supply continuously a cubic foot of air having 13 per cent. of oxygen added to its present amount.

If this mode of obtaining oxygen were manageable, the water would not require to be pumped high; but it could be put into a closed vessel, first pumped for a short time and then allowed to pass off for more air. This water would require to be kept pure.

These are ideas regarding the supply of oxygen:—Methods of hastening the action of the air. Another method consists of using pressure to save time. The water, after being exposed to a vacuum, might be exposed to pressure with common air, or with the richer air from water, and pressure might be applied so as to finish the process very rapidly.

These methods of increasing the purifying action going on in water, are based on the first facts; namely, that a large and important effect is produced in one hour by passing air alone; next, that a more rapid effect is produced by pumping out the gases before passing air. The next effects, namely, of stronger mixtures of oxygen, may be considered certain, although not tried. The mode of obtaining oxygen is certain also, as shown by Mallet. The analysis of the air at successive stages is very



interesting (*see* 2nd Supplement, Watts's Dict., "Oxygen"), but the practicability of the process on a large scale has not been put to the test to my knowledge.

I send out these writings, being chiefly the description of work done, but partly of course looking forward to work that may be better done after the information here has been considered.

## No. X.

### AERATION OF WATER SUPPLIES.—DRINKING WATER.

This is not quite a new subject to speak of, but it has not been well worked out. These latest ideas as to the value of air compel us to turn to it again. We have now many towns supplied with surface water without filtration. The result of this must be that there is some deposit in the reservoirs if the solid matter is not carried away. Perhaps I ought first to have said that there is solid matter in all cases nearly, although there may not be much. Indeed it is not easy for us to suppose that the washings of fields can be free from floating bodies. When the water sinks deep into the ground we have magnificent filtration and clear brooks. The experience described by Dr. Greenwood must not be forgotten, and we do not know the limits of the impurities from manured land. As a rule, however, it seems to be true that the organisms washed from fields, and coming into our streams, rivers, and reservoirs, are not hurtful. And why not? When we have the great dilution and the great aeration together we may draw the conclusion that the researches of Pasteur empower us, even when no opportunity is given for that destruction by putrefaction which has received favour in this Report. Still we have this fact before us, that in great floods there is little time for change, and the increase of material washed off the soil is equal to a diminished opportunity of oxidation. In such cases it does seem right that water should have some time to undergo its changes, or that it should be filtered, or both. The reason for filtration is twofold: we remove solids by it; and in removing visible although minute floating matter, we remove also much which is insensibly small. But this is not all: the act of filtration in a good filter is really an act of oxidation,—in sand, for example, and other porous bodies. Of this I have spoken elsewhere. When this is not sufficiently done, would it not be well to use mechanical aeration for drinking water? It is certain that many of our water supplies do not contain as much oxygen as the best water. Manchester, for example, has a fair supply of water, but it varies considerably, and the oxygen passes down to 27 in the 100 of air dissolved in it. How far this could be remedied by the use of more oxygen, it is not possible to say without trial, and it is a trial which ought to be made. This is rather an addition to the duties of waterworks proprietors, but it is one which comes with the changes of our habits. Our reservoirs are filled by streams in flood, and we do not wait until these rough



waters pass away leaving the calmer streams to be taken, such as are filled by the water filtering through the soil, and thereby purified, as they often are, to brilliancy.

In speaking of this it is natural to consider the use of lime now proposed in so many cases of purification. In Clark's process, for example, lime is used, and carbonic acid is removed. It has been asked if it would not be an improvement to add carbonic acid. I believe it would, and probably air also. In the first proposals for purifying water by Thomas Henry, F.R.S., Manchester, about a century ago, lime was used, and after precipitation carbonic acid was employed to neutralize any excess. Any excess of carbonic acid over the lime would be an improvement. Free lime in water is a great disadvantage. Indeed we must look carefully to our streams whenever lime is used for precipitation. It is a favourite poison for fish, and I have seen a clear solution from a precipitating tank become suddenly whitish on entering a river of clear water. The process was intended for purifying the river, but it was in reality adding a new poison. It was in small amount, certainly; but who knows the amount used at times? There must be a careful measure of lime used in all cases where a river may be affected.

This use of carbonic acid might take place along with air, and if the water were to be used rapidly, it would add sapidity, which is not obtained at once by natural aeration, and is best obtained by deep filtration or by carbonic acid.

We may now consider generally the effect to which the newest information regarding germs of minute life seems to point. Water, when standing long with germs of life, has, or may have, according to the weather, increase of growth. Abundance of air will be preventive of or destructive to many of the lower forms, certainly those that cause putrefaction. Stagnation allows the oxygen to be consumed. Filtration and aeration ought to take place just before the water is to be used, according to these views.

#### *Note on Depositing or Filtering.*

The use of filtration is great, and nature provides us by its means the best of water, which comes through soils holding many unlovely things, and still without carrying them forward. It is an important matter to imitate this, and we try with some success, but we cannot imitate the self-purification in nature as fully as we wish; we cannot remove the carbon so rapidly and make it from a constituent of a filthy compound to one of a pure gas. The consequence is that our filters become covered with much impurity, and through this all our water supplies go, that is, there is an accumulation which is not an imitation of nature as we find it on the soil, but a simple product of art. I do not ignore the fact that various modes have been devised of removing this, and I have much good feeling towards the oxidizing filters used, especially those with compounds of iron or iron itself, and I will not say that in some cases they are not by far the best to



be chosen; but it has seemed to me that it would be a fine thing if we could avoid completely the passage of water through an impure deposit, and if we could remove that as rapidly as it is formed.

#### *Note on Mechanical Filters.*

There are several such filters, and a remarkable one is devised by Mr. Bowing, in which the liquid to be filtered is pressed against canvas or cloth, which lies on a perfectly plain surface of metal. The water works its way between the metal and the cloth. The fact is curious, and the result is remarkable. How far this would do for finer water I do not know; it would probably be insufficient; but when applied to less pure liquids the result has been shown to be excellent. The advantage of the mechanical filter is that the deposit is removed rapidly, and is not allowed to remain and putrefy; and if it could be so applied for drinking water as to produce an unobjectionable result, we should rejoice.

I doubt if Mr. Bowing's filter, as made by Manlove and Alliott of Nottingham, has been tried otherwise than for sewage; but even then it seems as if it were too much to expect a good result on account of the enormous bulk of sewage to be passed. If, however, a deposit were allowed first, and mechanical filtration applied to it afterwards, we might obtain something of more value. I have nothing to say of new modes of filtration, but am looking to experiments on a large scale. I have not given sufficient attention to the spongy iron filter of Mr. Bischof's, but having got remarkable results from iron filings in 1848, I am much in favour of iron, and must give it more attention.

#### *Precipitation in Drinking Water.*

The very great attention given to precipitation of sewage has led us from its application to drinking water, and it is remarkable that we have so much neglected the possibility of improvement in this direction. We know the old methods of adding alum to muddy water and finding it rapidly cleared,—a method used in India and China, and probably elsewhere. We send many tons of alum to Asia for this purpose, as it is supposed. But then these Easterns are so careless that the water which they call not good for drinking is to us horrible, and that which they consider just drinkable is bad to our sight and smell. The wonderful clearness obtained by throwing down flocculent precipitates has been often remarked. It has occurred, however, to Mr. Peter Spence, of Manchester, to use an aluminous salt not merely for sewage and very impure waters, but also for town supplies, and the results obtained in Manchester water are remarkable. The substance he uses is called by him alumino-ferric cake, but the name can be readily altered. The salt is a sulphate of alumina, with only 0.7 per



cent. of oxide of iron in it. It is made from bauxite, a mineral containing chiefly soluble alumina.

The Manchester water is considered a very fair one; it is a little yellow, being coloured by peaty matter. But when this sulphate of alumina is added, and it is allowed to settle for two days, it obtains a brilliancy equal to all we can desire. I made some experiments, and obtained the following results. The estimation of the purity of tint made by my new method is as follows. (See for explanation, No. XI., p. .)

The highest numbers show the greatest transparency; but it must be remembered that it is only proportionate, that is, the same water does not give the same numbers on every trial, because the amount of light differs.

People may be afraid that alum will remain in solution, but there is rarely a water to be found so free of lime as not to decompose the small amount of sulphate of alumina used in these experiments. This point must of course be remembered, and the water kept alkaline.



TRANSPARENCY of the specimens, WEAK LIGHT, but STRONG SOLUTION to COMPENSATE, 50 c. c. contained 0.3 gm.  $\text{SO}_3$  + 0.5 gm. KI.

		Pure distilled Water.	Manchester Water purified by Alumino-Ferric Cake.	Manchester Water purified by Ferric Chloride.	Manchester Water after filtration through Blotting Paper.	Manchester Water.
		c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.
1881.						
November 9th	-	25.0	25.0	21.0	17.4	13.6
" 10th	-	16.0	16.7	12.1	7.9	7.0
" 14th	-	4.2	3.9	2.9	—	1.1
" 15th	-	26.9 26.9	25.0	23.0	—	19.1 19.0
" 16th	-	30.5	29.0	26.0	—	22.0
" 17th	-	50.0	48.5	46.0	—	41.0
" 18th	-	23.5	21.0	19.5	—	13.0



Could this result be obtained in great reservoirs? I can only say that it is so remarkable that it ought to be tried. It is certainly far beyond any method of filtering used at any water-works seen by me; it can only be compared to deep soil filtration. I must mention that I have not seen either the recent iron filters or the carbide of iron ones at use on a large scale, and cannot allude to them.

The alumina which falls takes down organic colouring matter, but the alumina may be dissolved out of the precipitate. How far it can be dissolved again is a point into which I have not entered. Mr. Spence says that for sewage this may be done repeatedly; in treating drinking water it may not act so well a second time, but the expense is certainly small. The amount I used for Manchester water was .7 grains per gallon, or about a ton for 20,000,000 gallons, which ton would cost 50s.

The results of analysis are as follows, but it is enough to judge by the effect in brilliancy already mentioned:—

EFFECT OF PRECIPITANTS ON MANCHESTER WATER.  
Analyses in Parts per 100,000.

—		Total Solid Matter.	Free Ammonia.	Albumenoid Ammonia.	Alkalinity as $\text{SO}_3$ .
Manchester water	- - - - -	6.75	0.0022	0.0076	1.37
Do.	with 1 part aluminio-ferric cake per 100,000.	7.00	0.0028	0.0056	1.03
Do.	with 1 part ferric chloride	7.16	0.003	0.0060	1.00

If this turns out as well as it promises it will be necessary to give up the method of using surface or flood water. Hitherto it has been allowed to settle only, but we can neither remove the colour nor the germs of life by any such process, and by precipitation we remove at least the visible part of the organic matter, and some of the very material on which organisms live. That none should be left, considering the very vital conditions of the world, it is not for us to expect even if it is to be hoped for.

Examination of this process continues. I look on it as chiefly valuable for throwing down fine floating matter, taking, however, some organic matter out of solution.



## MODE OF ESTIMATING THE TRANSPARENCY OF WATER.

In the 16th Report under the Alkali Act, also in the proceedings of the Royal Society, Vol. XXX., I gave an account of a mode of measuring the amount of light over any given period of time. Finding that the idea had previously occurred to Dr. Leeds of the United States, I gave him of course the credit. However my intention was to pursue it for the purposes of my office, and to endeavour to measure the influence which fogs natural and artificial or smoke have on the amount of light transmitted through the atmosphere immediately above us. I also said that I intended to apply the knowledge to an estimation of the transparency of water. I have in my 16th Report under the Alkali Acts given a table of the total comparative light during six hours of the day for above a year, and in this report under the Rivers Pollution Prevention Act I now describe the same method as applied to water.

A few of the results are given, and I may say that they are most satisfactory. The order of the figures is certainly the same as I made out for myself by using the tube when the waters were brought to me without description; but I had a difficulty in judging. Time was required, a certain amount of anxious consideration was needful, and in one case I gave a decision, which, on reconsideration, I reversed. I may add that I am not behind in this mode of judging; two pairs of young eyes belonging to chemists were less correct and constant in their judgment, at least on this occasion. I say this to show the accuracy of the experiment, and to prove that we save time by it and uncertainty. However, this is not all. We obtain exact numbers, such as the eye cannot pretend to determine.

I always use of course as a standard distilled water, and it is necessary to have it in the experiment, as the numbers are not definite in a continuous sense on account of the constant change of light. They are comparable with pure water; but the same numbers do not occur on every experiment, as the light differs. The exact law of change requires study, but the order is certain.

Every new idea has its own mode of development, and I cannot tell how this may grow, considering all the various changes of colour in impure streams in this country; but for natural streams there is less difference of shade. I have here used it to define the brightening effect of precipitation as an example unless otherwise mentioned.



TRANSPARENCY.—TABLE I.

TRANSPARENCY of WATER with different PROPORTIONS of CHLORIDE of IRON in SOLUTION.

50 c. c. Solution containing 0.060 gm.  $\text{SO}_3$  + .5 gramme Potassium Iodide.

	Pure Water.	Pure Water + $2\frac{1}{2}$ c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.	Pure Water + 5 c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.	Pure Water + 10 c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.	Pure Water + 20 c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.	Pure Water + 50 c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.	Pure Water + 60 c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.	Pure Water + 70 c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.	Pure Water + 80 c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.	Pure Water + 100 c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.
	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$	c. c. $\text{Na}_2\text{S}_2\text{O}_3$	c. c. $\text{Na}_2\text{S}_2\text{O}_3$	c. c. $\text{Na}_2\text{S}_2\text{O}_3$	c. c. $\text{Na}_2\text{S}_2\text{O}_3$	c. c. $\text{Na}_2\text{S}_2\text{O}_3$	c. c. $\text{Na}_2\text{S}_2\text{O}_3$	c. c. $\text{Na}_2\text{S}_2\text{O}_3$
July 5th, 1881. 8.45 a.m. to 6.15 p.m.	5.7	4.9	4.4	3.4	3.0	2.5	1.5	1.4	1.0	0.8
July 8th, 1881. 8.45 a.m. to 6.15 p.m.	3.0	2.0	2.0	1.0	0.7	0.3	0.0	0.0	0.0	0.0
July 9th, 1881. 8.40 a.m. to 2 p.m.	4.0	3.5	3.0	2.0	1.0	0.5	0.0	0.0	0.0	0.0
July 11th, 1881. 8.35 a.m. to 6.30 p.m.	3.4	3.0	2.6	1.8	1.0	1.0	1.0	0.8	0.5	0.4

1 c. c. Standard Ferric Chloride = 10.15 mgms.  $\text{Fe}_2\text{Cl}_6$  + 6.75 mgms.  $\text{HCl}$  (free).



TRANSPARENCY.—TABLE II.

TRANSPARENCY OF WATERS WITH CHLORIDE OF IRON IN SOLUTION. DUPLICATE EXPERIMENTS SHOWING CONSTANCY.

50 c. c. Solution containing 0.060 gm.  $\text{SO}_3$  + .5 gramme KI in 50 c. c. Flasks.

	Manchester Water.	Manchester Water + 5 c. c. Standard $\text{Fe}_2\text{Cl}_6$ per Litre.		Manchester Water + 10 c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.		Manchester Water + 20 c. c. $\text{Fe}_2\text{Cl}_6$ per Litre.
	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.		c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.		c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.
York Place—						
June 28th, 1881	-	59.5 57.0	57.75 55.75	52.50 53.50	47.25 49.00	
June 29th, 1881	-	8.85 8.85	8.5 8.5	7.7 7.7	7.0 7.1	
June 30th, 1881	-	6.8 6.8	6.5 6.5	5.9 5.9	5.3 5.3	
July 1st, 1881	-	12.1 12.0	11.4 11.5	10.9 10.9	10.55 10.6	
July 2nd, 1881	-	8.55 8.5	8.3 8.2	7.9 7.75	6.5 6.5	



## TRANSPARENCY.—TABLE III.

## TRANSPARENCY OF MANCHESTER WATER and PEATY WATER.

50 c. c. Solution containing 0.060 gm.  $\text{SO}_3$  + .5 gramme Potassium Iodide.

				Distilled Water.		Manchester Water.		Peaty Water.	
				c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.		c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.		c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	
1880, May 26th.	After 21 hours	-	-	-	12.0	-	7.0	-	4.5
May 27th.	-	-	-	-	3.2	-	3.0	-	1.6
May 28th.	After 3 hours	-	-	-	4.2	-	1.2	-	0.6
May 29th.	After 16 hours	-	-	-	2.0	-	1.0	-	0.0
May 29th.	After 44 hours	-	-	-	50.0	-	38.5	-	27.2
May 30th.	After 3 hours*	-	-	-	47.0	-	28.0	-	18.0
May 31st.	After 24 hours	-	-	-	14.5	-	9.6	-	4.6
June 1st.	After 1½ hours	-	-	-	10.7	-	6.5	-	4.2
June 1st.	After 5 hours	-	-	-	7.5	-	5.6	-	2.6
June 2nd.	After 16½ hours	-	-	-	7.1	-	5.5	-	2.4
June 2nd.	After 7 hours	-	-	-	6.9	-	3.7	-	1.6
Average		-	-	-	15.0	-	9.96	-	6.1

\* This contained 0.300 gm.  $\text{SO}_3$ .



TRANSPARENCY.—TABLE IV.

MANCHESTER WATER and PEATY WATER. LITTLE LIGHT and MODERATE LIGHT.

Solution 50 c. c. containing 0.300 gm.  $\text{SO}_3$  + .5 gm. Potassium Iodide.

		Manchester Water.	Manchester Water containing 1 % Peaty Water.	Manchester Water containing $2\frac{1}{2}$ % Peaty Water.	Manchester Water containing 5 % Peaty Water.
		c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.
1880, June 9th.	After 2 hours, 11 a.m. to 1 p.m.	7.1	6.4	4.2	1.3
June 9th.	After $2\frac{1}{2}$ hours, 1 p.m. to 3.30 p.m.	5.9	6.0	3.1	1.1
June 10th.	After 3 hours, 9.45 a.m. to 12.45 p.m.	6.46	6.0	4.4	1.8
June 11th.	After 3 hours, 12 noon to 3 p.m.	6.7	4.5	4.2	2.0
June 12th.	After $\frac{1}{2}$ hour, 10 a.m. to 10.30 a.m.	8.6	8.6	5.6	1.6
June 12th.	After 17 hours -	25.8	25.8	20.0	17.3
June 10th.	After $21\frac{1}{4}$ hours, 1.45 p.m. to 11 a.m.	17.3	16.5	15.0	12.0
Average -		11.2	10.5	8.07	5.3

One per cent. is very decided on the average numbers, but has variations. After one the result is decisive.



TRANSPARENCY.—TABLE V.  
MANCHESTER WATER with SEWAGE and PEATY WATER. A FAIR AMOUNT of LIGHT.

Same Solutions in each.		Manchester Water.	Manchester Aq. containing 3.52 % Sewage.	Manchester Aq. containing 7.04 % Sewage.
		c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.	c. c. $\text{Na}_2\text{S}_2\text{O}_3$ sol.
1880, June 5th.	After 18 hours	10.4	7.0	3.2
June 6th.	After 45 hours	25.5	18.3	10.7
		Manchester Water.	Manchester Water containing 2.8 % Peaty Water.	Manchester Water containing 5.6 % Peaty Water.
1880, June 2nd.	After 23 hours	5.5	3.2	2.0
June 4th.	After 24 hours	13.0	3.0	2.0
June 5th.	After 24 hours	9.4	4.0	2.7
June 6th.	After 45 hours	26.4	13.0	10.0

TRANSPARENCY.—TABLE VI.  
DISTILLED WATER. MANCHESTER WATER and SEWAGE in WEAK LIGHT.  
Solutions containing in 50 c. c. 0.06 gramme  $\text{SO}_3$  + .5 gramme KI.

		Pure Distilled Water.	Manchester Water.	Pure Water + $2\frac{1}{2}$ % Sewage Water.	Pure Water + 5 % Sewage Water.	Pure Water + 50 % Sewage Water.
1880, June 22nd.	10 a.m. to 4.30 p.m.	2.5	2.0	1.7	0.7	0.3
June 23rd.	10 a.m. to 4 p.m.	1.45	1.39	1.1	0.9	0.4
June 24th.	10 a.m. to 4 p.m.	5.0	4.1	3.8	3.6	0.3



## PART II.

## EFFLUENTS FROM PRINTWORKS, DYEWORKS, &amp;c.

*Precipitation.—General Rules.*

If the effluents from dyeworks or printworks are alkaline, containing organic substances coloured or otherwise, an acid generally throws down a decided amount of solid matter. If the effluent contains soap, the fatty matters are separated, and fall or rise to the surface. These fatty matters may contain a large amount of colouring matter which may or may not be of value.

If acid is expensive at the place of precipitation a similar result can be obtained by chloride of calcium or any cheap metallic or earthy salt. Chloride of calcium is the simplest, and has a great influence. Its effect is not limited to the soap, but is observed in the effluents from paper works, and other cases where the liquids are alkaline.

Salts of calcium are, therefore, very valuable; and as they are found at bleachworks, printworks, and paperworks, and wherever bleaching is done, they have a great influence on the discharges. This influence is not always seen at once; it requires some time, and it would appear as if settling tanks were absolutely necessary. It would be very good if we could hasten this precipitation. To some extent this is done by adding metallic or aluminous salts, but it is done also by stirring or shaking, as we often find in a laboratory, and previous to allowing the solution to rest. Thinking of this, one would have supposed that very violent action would have assisted still more the fall; but this was not the case; we found that by agitating the effluents after mixture with the precipitant, these could be reduced to a state of division so fine as to delay their fall.

The advantages of chloride of calcium are that it is frequently a waste product, and a great deal could be obtained if it were wanted.

Lime will certainly throw down the fatty matter of soap, and it will also take a great deal of solid matter out of the effluents of paper and other works, but it will not neutralize in such cases; on the contrary, it causticises these liquids. Chloride of calcium also can be thrown in considerable quantities into a river without injury, whereas this is not the case with lime.

The first thing to be done with the effluents from works generally is to allow them all to mix together, when large precipitates occur, and frequently complete neutralization, arising from this, namely, that the processes have required equivalent amounts of acid and alkali, although they escape separately. Cases exist, however, in which such a mixture would be of no advantage; and in other cases, as in alkali works, the mixture of the acid and sulphide liquors produces intolerable results.



The works, however, specially under consideration give out liquids which by this treatment cause considerable and sometimes large precipitates. The addition of chloride of calcium causes a second precipitate frequently, and it may be that this will be in some cases a sufficient treatment.

When better results are required, it is apparently essential to use salts of iron or aluminum; and few waters from these works under consideration will not become clear after this treatment; most, if not all, can be made also nearly colourless.

It would be quite wearisome to detail all the experiments made to come to these conclusions, but various results will be here given, and they may be compared also with those from sewage treatment.

### Effluents from Paper Works.—May 1878.

#### Discharge Water from Settling Ponds, Carron Grove Works.— 19th April 1878.

- (1.) After filtration,—  
 10 lbs. Alum } per 1,000 galls.      The filtrate was slightly acid;  
 2.5 lbs. Lime }      colour = 0.1 c. c.  $\text{NH}_4\text{Cl}$  with  
                      Volatile = 4.9 gr. per gall.      Nessler. No permanent froth  
                      Mineral = 65.94      „      on shaking.  
                      Total = 70.84      „
- (2.) After filtration,—  
 8 lbs. Alum } per 1,000 galls.      The filtrate was faintly alkaline;  
 2.5 lbs. Lime }      colour = 0.4 c. c.  $\text{NH}_4\text{Cl}$  with  
                      Volatile = 5.67 gr. per gall.      Nessler. No permanent froth  
                      Mineral = 57.33      „      on shaking.  
                      Total = 63.00      „
- (3.) After filtration,—  
 4 lbs. Alum } per 1,000 galls.      The filtrate decidedly coloured.  
 2.5 lbs. Lime }      Permanent froth on shaking.

#### Sample received 29th April 1878.

- (4.) After filtration,—  
 10 lbs. Alum } per 1,000 galls.      Similar to No. 1.  
 2.5 lbs. Lime }      Volatile = 0.28 gr. per gall.  
                      Mineral = 76.16      „  
                      Total = 76.44      „
- (5.) After filtration,—  
 8 lbs. Alum } per 1,000 galls.      Similar to No. 2 as to froth.  
 2.5 lbs. Lime }      Filtrate slightly coloured.  
                      Volatile = 11.48 gr. per gall.  
                      Mineral = 77.55      „  
                      Total = 89.04      „
- (6.) After filtration,—  
 6 lbs. Alum } per 1,000 galls.      Filtrate decidedly coloured.  
 2.5 lbs. Lime }      Froth lingered slightly.



Sample received 19th April 1878.

- (7.) After filtration,—  
 $2\cdot5$  lbs.  $\text{Fe}_2(\text{SO}_4)_3$  }  
 persulphate of iron. }  
 Lime quant. suff. } The lime was added immediately after the iron  
 sol. Filtrate slightly coloured.
- (8.) After filtration,—  
 $1\cdot25$  lbs.  $\text{Fe}_2(\text{SO}_4)_3$  }  
 Lime quant. suff. } The lime was added five minutes after the iron  
 sol. Filtrate was colourless.
- (9.) After filtration,—  
 $0\cdot7$  lb.  $\text{Fe}_2(\text{SO}_4)_3$  }  
 excess powdered }  
 chalk. } The ppt. settled readily. Filtrate clear; did not  
 froth.

Clarification of Logwood Waste Liquors.—March 1879.  
 Exit Liquor from Works.

- (1.) 100 lbs. Alum Cake } per 1,000 galls. Colour almost gone.  
 $7\cdot5$  lbs. Lime }
- (2.) 20 lbs. Alum Cake } per 1,000 galls. 97 % colour removed.  
 $1\cdot5$  lb. Lime }
- (3.) 10 lbs. Alum Cake } per 1,000 galls. 95 % colour removed.  
 $0\cdot76$  lb. Lime }
- (4.) 6 lbs. Alum Cake } per 1,000 galls. 90 % colour removed.  
 $0\cdot76$  lb. Lime }
- (5.)  $4\cdot74$  lbs. Ferric Chloride } per 1,000 galls. 99·8 % colour removed.  
 $6\cdot00$  lbs. Lime }
- (6.)  $2\cdot16$  lbs. Ferric Chloride } per 1,000 galls. 98 % colour removed.  
 $4\cdot56$  lbs. Lime }
- (7.)  $0\cdot66$  lb. Ferric Chloride } per 1,000 galls. 70 % colour removed.  
 $2\cdot28$  lbs. Lime }

NOTE.—There was a little free HCl along with the  $\text{Fe}_2\text{Cl}_6$ , ferric chloride or perchloride of iron.

- (8.)  $18\cdot5$  lbs. hydrated alumina per 1,000 galls. 60 % colour removed.
- (9.)  $4\cdot12$  lbs.  $\text{Fe}_2\text{Cl}_6$  }  
 $12\cdot5$  lbs. HCl } per 1,000 galls. Colour destroyed. The ppt.  
 $5\cdot0$  lbs. Lime } settles rapidly and perfectly.
- (10.)  $2\cdot1$  lbs.  $\text{Fe}_2\text{Cl}_6$  }  
 $6\cdot25$  lbs. HCl } per 1,000 galls. Colour destroyed. The ppt.  
 $2\cdot5$  lbs. Lime } settles rapidly and perfectly.
- (11.)  $1\cdot25$  lbs.  $\text{Fe}_2\text{Cl}_6$  }  
 $2$  lbs. Lime } per 1,000 galls. Filtrate faintly coloured. Ppt.  
 $3\cdot75$  HCl } settled fairly, but left a tur-  
 bidity in the liquid, which,  
 however, was readily re-  
 moved by filtration.
- (12.)  $0\cdot85$  lbs.  $\text{Fe}_2\text{Cl}_6$  }  
 $2\cdot5$  lbs. HCl } The ppt. behaved as in No. 11, but the filtrate was  
 $1\cdot5$  lbs. Lime } distinctly coloured.
- (13.) 200 lbs.  $\text{CaCl}_2$ , chloride of calcium, per 1,000 galls. removed 60 % of the  
 colour.



## Clarification of Liquors from Woollen Mill.

Contents of last Tank before entering "Lade," Copperas, or protosulphate of iron, or ferrous sulphate.

- (a.) 8 lbs. Ferrous Sulphate } per 1,000 galls. 66 % colour removed.  
0.5 lbs. Lime
- (b.) 8 lbs. Ferrous Sulphate per 1,000 galls. 39.3 % colour removed.
- (c.) 12 lbs. Ferrous Sulphate } per 1,000 galls. 84.5 % colour removed.  
0.5 lb. Lime
- (d.) 12 lbs. Ferrous Sulphate per 1,000 galls. 78.7 % colour removed.
- (e.) 2.6 lbs.  $\text{Fe}_2\text{Cl}_6$  } per 1,000 galls. 89.4 % colour removed.  
(?) Lime
- (f.) 8 lbs. Alum } per 1,000 galls. 71 % colour removed.  
0.5 lb. Lime
- (g.) 8 lbs. Alum per 1,000 galls. 72.5 % colour removed.
- (h.) 6.5 lbs.  $\text{Fe}_2\text{Cl}_6$  } per 1,000 galls. 95.6 % colour removed.  
5.6 lbs. Lime
- (i.) No. (h) with 8 lbs. Copperas per 1,000 galls. 98.9 % colour removed.  
The ferrous salt was added to destroy the chromate which was left by the ferric salt.
- (j.) 3.7 lbs.  $\text{Fe}_2\text{Cl}_6$  } per 1,000 galls. 96.5 % colour removed.  
8.0 lbs. Copperas  
2.75 lbs. Lime
- (k.) 3.7 lbs.  $\text{Fe}_2\text{Cl}_6$  } per 1,000 galls. 97 % colour removed.  
20 lbs. Copperas  
2.75 lbs. Lime
- (l.) 7.4 lbs.  $\text{Fe}_2\text{Cl}_6$  } per 1,000 galls. 96.5 % colour removed.  
4.0 lbs. Copperas  
5.5 lbs. Lime
- (m.) 3.7 lbs.  $\text{Fe}_2\text{Cl}_6$  } per 1,000 galls. 92 % colour removed.  
2.75 lbs. Lime
- (n.) No. (m) with 8 lbs.  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  per 1,000 galls. No further change.  
Comp. (h) and (i).
- (o.) No. (n) with 1.4 lbs. Lime per 1,000 galls. 98.2 % original colour removed.

The liquid flowing from the ppt. obtained in expt. (j) gave—

Volatile matter	-	-	-	8.4 grs. per gall.
Mineral "	-	-	-	24.5 "
Total	-	-	-	32.9 "

Before clarification the liquid contained—

Volatile matter	-	-	-	81.9 grs. per gall.
Mineral "	-	-	-	119.0 "
Total	-	-	-	200.9 "

- (p.) 5 lbs.  $\text{CaCl}_2$  } per 1,000 galls. Filters slowly. Filtrate coloured  
1.5 lbs.  $\text{Fe}_2\text{Cl}_6$  } (neutral iron sol.) blue.  
11.0 lbs.  $\text{SO}_3$
- (q.) 5 lbs.  $\text{CaCl}_2$  } per 1,000 galls. Similar to (p.)  
1.5 lbs.  $\text{Fe}_2\text{Cl}_6$  } (neutral iron sol.)



- (r.)  $\left. \begin{array}{l} 5 \text{ lbs. CaCl}_2 \\ 1.5 \text{ lbs. Fe}_2\text{Cl}_6 \text{ with} \\ 3.0 \text{ lbs. HCl} \end{array} \right\} \text{ per 1,000 galls.}$  Filters clear. Filtrate slightly yellow.  
(Acid solution of iron.)
- (s.)  $\left. \begin{array}{l} 5 \text{ lbs. CaCl}_2 \\ 1.5 \text{ lbs. Fe}_2\text{Cl}_6 \\ 2.0 \text{ lbs. HCl} \end{array} \right\} \text{ per 1,000 galls.}$  Filtrate blue and turbid.  
(neutral iron sol.)
- (t.)  $\left. \begin{array}{l} 5 \text{ lbs. CaCl}_2 \\ 1.5 \text{ lbs. Fe}_2\text{Cl}_6 \\ 3.0 \text{ lbs. HCl} \end{array} \right\} \text{ per 1,000 galls.}$  Filtrate coloured; not very clear.  
(neutral iron sol.)
- (u.)  $\left. \begin{array}{l} 5 \text{ lbs. CaCl}_2 \\ 3 \text{ lbs. HCl} \end{array} \right\} \text{ per 1,000 galls.}$
- To the filtrate from the foregoing—  
 $\left. \begin{array}{l} 2 \text{ lbs. Fe}_2\text{Cl}_6 \text{ (neutral) per 1,000 galls.} \\ ? \text{ Lime (till faintly alkaline).} \end{array} \right\} \text{ The filtrate from the iron was good.}$
- (v.)  $\left. \begin{array}{l} 5 \text{ lbs. CaCl}_2 \\ 4 \text{ lbs. SO}_3, \text{ sulphuric acid calculated} \\ \text{as anhydride.} \end{array} \right\} \text{ per 1,000 galls.}$  Filtrate slightly alkaline.
- (w.)  $\left. \begin{array}{l} 5 \text{ lbs. CaCl}_2 \\ 20 \text{ lbs. SO}_3 \end{array} \right\} \text{ per 1,000 galls.}$  Filtrate slightly turbid.

### Mixture of polluted liquids from Woollen Mills.

- $\left. \begin{array}{l} 20 \text{ lbs. sulph. acid} \\ 4.12 \text{ lbs. Fe}_2\text{Cl}_6 \\ 12 \text{ lbs. CaO} \end{array} \right\} \text{ per 1,000 galls.}$  Filtrate colourless.
- $\left. \begin{array}{l} 20 \text{ lbs. sulph. acid} \\ 0.82 \text{ lb. Fe}_2\text{Cl}_6 \\ 5.0 \text{ lbs. CaO} \end{array} \right\} \text{ per 1,000 galls.}$  Filtrate colourless.
- $\left. \begin{array}{l} 1 \text{ lb. O. V.} \\ 0.41 \text{ lb. Fe}_2\text{Cl}_6 \\ 4.0 \text{ lbs. CaO} \end{array} \right\} \text{ per 1,000 galls.}$  Filtrate slightly coloured.
- $\left. \begin{array}{l} 5 \text{ lbs. CaCl}_2 \\ 8\frac{1}{2} \text{ lbs. Fe}_2\text{Cl}_6 \\ \text{CaO} \end{array} \right\} \text{ per 1,000 galls.}$  Colourless.
- $\left. \begin{array}{l} 2.5 \text{ lbs. CaCl}_2 \\ 2.1 \text{ lbs. Fe}_2\text{Cl}_6 \\ 6.6 \text{ lbs. HCl} \\ ? \text{ CaO} \end{array} \right\} \text{ per 1,000 galls.}$  Colourless.



# CLARIFICATION OF SPENT LOG-WOOD DYE LIQUORS.

Very strong. Direct from Vat, and Undiluted.

ALUMINO FERRIC CAKE.				FERRIC CHLORIDE.			
Lbs. Chemicals per 1,000 galls.	Al <sub>2</sub> O <sub>3</sub> per 1,000 galls.	Equivalent of Fe <sub>2</sub> O <sub>3</sub> .	% of Colour removed.	Lbs. Chemicals per 1,000 galls.	Fe <sub>2</sub> O <sub>3</sub> per 1,000 galls.	Equivalent of Al <sub>2</sub> O <sub>3</sub> .	% of Colour removed.
17.5 lbs. cake	-	Lbs. 2.4	-	10 lbs. ferric chloride	-	Lbs. 3.8	-
4.6 lbs. lime	-	-	99	4 lbs. lime	-	-	98.4
10 lbs. cake	-	1.4	-	5 lbs. ferric chloride	-	1.9	-
2.3 lbs. lime	-	-	95.8	2.6 lbs. lime	-	-	84.0
5 lbs. cake	-	0.7	-	3 lbs. ferric chloride	-	1.14	-
2 lbs. lime	-	-	88	1.6 lbs. lime	-	-	75.6
4 lbs. cake	-	0.56	-				
3.5 lbs. lime	-	-	82				
3 lbs. cake	-	0.42	-				
1.6 lbs. lime	-	-	71.6				



*Miscellaneous Trials on Coloured Waters.*

*Spent Tan Liquids.*—The acid liquid from a spent bark vat treated in Storer and Cranston's apparatus. Four hours' aeration did not alter its appearance, or render it more amenable to filtration.

By precipitation with a per-salt of iron and lime, a much better result was obtained in the liquid before aeration. The aerated specimen gave a much more coloured filtrate.

When the liquid was made alkaline with lime and then aerated, it darkened rapidly and considerably in colour. The colouring matter was somewhat soluble, and gave a strongly coloured filtrate.

A fair clarification may be obtained by adding lime to the unaerated liquid (which may require dilution), separating the insoluble, and aerating the clear liquid. A second ppt. is obtained, after the separation of which the liquid appears fairly pure.

*Peaty Water.*—A sample of strong peaty water was aerated in Storer's converter. After two hours' action 20 per cent. of the colour was destroyed; further aeration was of no benefit. Two grains lime per gallon were then added, when half an hour's action destroyed another 30 per cent. of the colour; *i.e.*, 50 per cent. of the original was destroyed. Further aeration was not of use.

Two grains of lime per gallon added to the same water without aeration intensified the colour considerably.

*Dye-house Liquids.*—A sample of liquid from Bradford chiefly contaminated with logwood was aerated. No apparent change took place after two hours' treatment; but the addition of 25 gr. CaO per gallon, and half an hour's further aeration, gave a better result than the simple addition of lime without aeration.

A sample of logwood liquor from Brinscall was aerated. After  $1\frac{1}{2}$  hour there was a decided diminution in the colour of the filtered liquid compared with the original liquid likewise filtered. 13.2 gr. CaO per gallon were now added, which further lessened the colour of the filtrate; continued aeration (two hours) was of little use.

A sample of the above liquor from Messrs. Wood's was pptd. with 26.5 gr. CaO per gall., and the filtrate aerated. Two hours' aeration destroyed 20 per cent. of the colour, five hours' 24 per cent. of the colour.

Logwood was examined qualitatively with BaO<sub>2</sub>, BaS, CaS, and H<sub>2</sub>O<sub>2</sub>.

BaO<sub>2</sub> gave the best result; then came BaS, soda waste, H<sub>2</sub>O<sub>2</sub> and CaS. This arrangement is according to the immediate effect. The H<sub>2</sub>O<sub>2</sub> continued to act slowly, and gave a better result after standing some time.



Logwood liquor treated in the converter with soda waste for two hours had a stronger colour than by simple lime precipitation (20 grm. waste to 15 litres liquor).

Logwood liquor which had been treated with lime and afterwards aerated was submitted to the action of ozonized air in the converter, but no further decrease of colour ensued.

A quantity of logwood liquor was enclosed in a glass tube along with oxygen under pressure of two atmospheres, but no apparent change took place after 10 days.

### *Iron and Tin Plate Works.*

The solution coming from these works consists entirely of sulphate of iron with a little extra acid. The acid is in nearly all cases sulphuric. I have proposed some rules which for the present are very mildly stated.

"Some Rules applicable especially to Works in South Wales."

1. After the 31st day of December 1880, it is expected that at every tin and iron work the solutions of sulphate of iron or copperas, being the liquids remaining after the processes in which the acid solutions called "black pickle" and "white pickle" are used, shall be treated or removed in such a manner as shall prevent any of it flowing to any river or stream.

2. It is not proposed to insist at present that the water used for washing the plates which have been taken out of the acid or pickle shall be treated in such a way as to remove all the acid. It is, however, known that there are two methods by which it may be done; one by passing the plates singly through rollers, and thus removing the acid almost entirely. If the water should contain a little carbonate of lime in solution, it may be enough, and it is in a known case in the district more than enough to neutralise all the remaining acid. The second plan is to dip the plates in a cistern of water before exposing them to the great rush of wash water. This cistern removes nearly all the acid, and will last a long time. The solution will require to be boiled down along with the so-called pickles, or otherwise treated so as to be innocuous.

I wish to call attention to this point, namely, that at present I should not think it right to give a certificate under the Act unless one of these methods is adopted, or a better.

3. Dregs of the crystallising vessels containing sulphate of iron are not to be thrown on the ground in such places as render them liable to be washed into streams. The dregs ought to be thrown away only after the copperas is fully washed out.

4. All the work must be done in such a manner as to be easily inspected. It must be open and free to the surface in every possible case.



*Encroachments on the Rivers.*

I propose that in every case causing suspicion, fear, or complaint a retaining wall of about 3 ft. high from the surface be made adjoining the river, and marking the limit of deposit of refuse or "tipping." This wall to be not less than twelve inches in breadth, and to be kept in good order. The heaps or refuse not to extend to the edge of the top of the wall next the river, but to be limited to the inner edge of the wall. When this point is reached grass to be sown on the refuse. Grass will grow, although slowly, on almost every kind of heap, and if there is any difficulty a little dusting of earth is sufficient to raise it. A small amount is sufficient to show that no trifling with the rule takes place, but that "tipping" at the spot has ceased.

## ALKALI WASTE HEAPS AND DRAINAGE.

## ON AERATION AND OXIDATION IN WATERY SOLUTIONS OF SOLUBLE SULPHIDES.

The waste heaps made near alkali works, or by the tank waste from alkali works, wherever laid down, have been a frequent source of complaints. They give out, according to their condition, sulphurous acid or sulphuretted hydrogen; and the drainage water from the ground covered by the waste containing much sulphide gives out the latter gas in great abundance, according to the condition of the air or the rain whilst the influence is felt as far as the stream flows. Sulphur in the meantime is deposited, as it is not a simple sulphide, but a double or a penta-sulphide, or a mixture of sulphides, which is contained in the yellow fluid. I may as well extract from the reports relating to the Alkali Acts 1877 and 1878, p. 12, the following general observations which will introduce the subject:—

"Many attempts have been made to recover the sulphur from the great heaps of lime salts so frequently seen about soda works. These heaps contain at first a large amount of sulphide of calcium. This sulphide of calcium is not very soluble, and it seems at first to be a mono-sulphide; gradually, however, it absorbs oxygen, and, being moist in the condition in which it is laid down, gives out sulphuretted hydrogen. First the carbonic acid of the air along with water decomposes the sulphide so that sulphuretted hydrogen passes off; next the oxygen of the air oxidizes the calcium, which sets free sulphur, which again in its nascent state becomes oxidized; these two processes forming hypo-sulphite of calcium (*i.e.* thio-sulphate). Another process, which may either be called a third or fourth, is the formation of sulphurous acid. This is formed, I suppose, by the heat igniting the sulphuretted hydrogen, but not entirely so. The heat decomposes the gas, and in the absence of air produces fine sulphur, which is seen deposited on the heaps and in



all the gas passages. This sulphur is ignited as the heat advances, and it burns according as the oxygen is supplied; the process may be so slow that the heap cools before the sulphur receives its supply of oxygen. The action of the air, if followed further, leads to an oxidation of the hypo-sulphite into sulphite, and afterwards slowly to sulphate, when the final stage is reached.

"The result to the atmosphere may be, first, the spread of sulphuretted hydrogen, second, the spread of free and sublimed sulphur, and third, the spread of sulphurous acid. If it is asked why these two gases, sulphuretted hydrogen and sulphurous acid, are put together as being in the atmosphere, seeing that they decompose each other, I then add that they do not decompose instantly when in a very dilute state in the air, and I might also add that it is not proved that they come from the exact same point of the decomposing or oxidizing substances.

"In any case these gases are offensive, but if in a concentrated form, or rather if a considerable quantity of each is put together, or if they meet in water, the result is that the sulphur of both is thrown down in a free state, and no smell of either gas of course can be perceived; both have ceased to exist. It has therefore been the object of several inventors to cause the sulphur to be partly oxidized into sulphurous or more conveniently into hyposulphurous acid, so as to form hyposulphite of lime, a salt whose acid is converted into sulphurous acid and sulphur when acted on by any strong acid. This result has been attained, especially by Mr. Mond, who oxidizes a certain portion of the sulphur in the waste by blowing air through it; and when the exact amount of hyposulphurous acid is formed capable of destroying the sulphide of hydrogen or calcium remaining, he dissolves in water all that will dissolve, and adds hydrochloric acid, which releases both the acids so as to let them act upon each other. The result is that the sulphur is thrown down free and useful instead of combined and noxious.

"Not many people have used this process; it was said to be troublesome, it required considerable capital to establish; still there was, and I suppose still is, a profit on the sulphur regained. This is fully established by Mr. Worsley, of Netham, near Bristol, who, however, showed that the profit was not great, and that most of the manufacturers preferred to use their capital in another direction. It was a question whether they ought not to be compelled to adopt some plan of purification. Where capital is abundant, it might not be a hardship; where money is scarce it was said to be decidedly so.

"Then it was said that the remaining waste or undissolved lime salts which still contained some sulphur combined in sulphide of calcium, decomposed more readily than when Mr. Mond's process was not used, and that they sent out (for a shorter time certainly) but still for a time, more of the offending gases. I do not think that this was a valid objection by any means; when the waste is well oxidized by this method, it certainly is more porous, but if well washed the oxidation does not produce offensive gases to an



extent that could be perceived twenty yards off. This was the result of examining the heap at Netham.

"Another objection was that the remaining lime compounds being loose did not form such a solid base for building on as the old waste. I do not see that this is correct; the old waste swelled out very much for many years, and was often a very dangerous heap, as, if high, it was apt to fall in great masses. The waste formed by Mond's process does not swell out so much as the ordinary, because the sulphur is removed, and less oxygen and water are required to form the sulphate of lime. Time has not allowed us to see any structures built on the new waste or that from Mond's process. The waste by the old plan must lose a very large amount of soluble matter by rain, as the hyposulphite is very soluble in water. The lightness of the waste is probably caused in the blowing apparatus in which it is puffed up; if so, it will return by pressure to the normal weight of a sulphate.

"It is in the drainage that the difference of the two is most seen. The old method gives waste which sends out sulphureous solutions for many years. The new method may be so employed as to send out drainage in which the senses cannot detect sulphur: this I saw effected at Netham. A similar result was observed where Emil Kopp's method is used at Dieuze.

"The ultimate results of the two will be that in the old waste there will be more sulphate, and by the new processes more carbonate. Besides this there will be more lime dissolved out by Mond's and by the new processes in the condition both of sulphide and hyposulphite. The sulphates are not so suited for a foundation as the carbonates, being more soluble in water; the first about one in 400.

"There is another plan of treating the waste to be seen at Dieuze in Alsace. It was developed chiefly by Dr. Emil Kopp. Sulphate or chloride or any soluble salt of iron is thrown on the waste in small quantities, less than five per cent. The quantity is not important, but if very small the action will take a longer time. The iron is converted at once into a sulphide, and if turned over and exposed to the air it becomes an oxide, and the sulphur is set free, and in this way it is converted and reconverted until a sufficient amount of sulphur is removed from the calcium. The oxidation of the iron is always accompanied by the oxidation of sulphur into a hyposulphite. The excess of lime in the mass dissolves the sulphur, the heating of the whole being sufficient for this purpose. The solutions of sulphide and hyposulphite are mixed so as to contain the necessary proportions.

"These processes demand acid in order to set free the sulphurous and hydrosulphuric acids, and hydrochloric acid is the most suitable, but it has been presumed too often in estimating the value of these processes that it has little or no marketable value. When bleaching powder is in demand, the acid is valuable, and in all places, so far as I know, where it is made on the continent it is of a decided value. To avoid using too much, Mr. McTear has invented a process in which sulphurous acid takes its place to a considerable extent."



*Process of Dieuze.*

"This process, I believe, was first proposed by Dr. Emil Hofmann, developed by E. Kopp, and advanced under the care of M. Marchal. A report on the process was written by Professor Rosenstiehl, of Mulhouse, and communicated to the British Association by Mr. I. Lothian Bell, M.P., but I do not find that anything above a short notice has appeared in English. I shall extract from the memoir by Professor Rosenstiehl whatever may seem to be of interest to English alkali makers at the present time.

PROCESS, as used at DIEUZE, for recovering SULPHUR from the WASTE HEAPS, REPORT by PROFESSOR ROSENSTIEHL, of Mulhouse, 1867 (and still in use in 1878).

"The solid residue left on lixiviating crude soda is called "marcs de soude" or "charrée." The elements which compose this substance are sulphur, carbonate of lime, caustic lime, silicates, and water, in proportions which greatly depend on the purity and division of the materials employed in the manufacture of soda. Generally the fresh "waste" contains 12 to 16 per cent. of sulphur according to the quantity of water remaining with it.

"The residual liquors from the manufacture of chlorine contain the chlorides of manganese, iron, and barium, free chlorine, free hydrochloric acid and water, in proportions which vary with the nature of the manganese employed.

"The following is the composition of the liquors at Dieuze according to an analysis made by M. Hofmann:—

Manganous chloride	-	-	-	22
Ferric "	-	-	-	5.5
Baric "	-	-	-	1.06
Free chlorine	-	-	-	0.09
Hydrochloric acid	-	-	-	6.80
Water	-	-	-	64.55
				<hr/>
				100.00

"These are the residues in question which it is proposed to transform into inoffensive residues or useful products, but in either case without the consumption of fuel.

"The different steps in the process may be summed up as follows:—

1. Transformation of the waste into soluble sulphur compounds (yellow liquors).
2. Precipitation of the sulphur by the acid in the chlorine residues; neutralization of these.
3. Elimination of iron by fractional precipitations.
4. Precipitation of manganous sulphide.
5. Combustion of this sulphide.
6. Utilization of the ash of the sulphide.



1.—*Transformation of the Waste into Soluble Sulphur Compounds. (Production of Yellow Liquors.)*

When acid is poured into a mixture of two molecules of a polysulphide and one molecule of a hyposulphite, all the sulphur contained in these bodies is precipitated, and neither sulphuretted hydrogen nor sulphurous acid is evolved. One molecule of hydrochloric acid thus producing at least one atom of sulphur ( $S=32$ ) and at most two atoms, according as the solution contains a bisulphide or a pentasulphide.

We may thus with a small expense of acid produce a relatively large quantity of sulphur and avoid all evolution of gas. On this reaction the regeneration of sulphur is based. It is necessary to convert the sulphide of calcium in the waste into a polysulphide and hyposulphite.

When the waste is exposed to the air the simultaneous action of carbonic acid, oxygen and water, induces the formation of soluble compounds of which I have spoken.

But the reaction is slow; it requires not less than 8 to 10 months for completion, that is to say, to furnish a residue no longer containing sulphides. The necessary consequence of this tardy action is, large surfaces of ground for the decomposition of the daily yield of waste.

This process, condemned by practical men, has been so successfully modified at Dieuze that it allows the extraction of 44 per cent. of the total quantity of sulphur contained in the waste, in the form of soluble compounds, and that in the space of 8 days.

This modification, which forms the novelty of the process, consists in the incorporation of a certain quantity of sulphides of iron and manganese with the waste. These sulphides are obtained by treating the neutralized chlorine residues with a little waste until almost all the iron is precipitated as sulphide; at this time the greater part of the manganese is still in solution; this liquid is run off, and the residue is mixed with the waste, which is allowed to remain exposed to the air for 6 or 8 days.

The air acts energetically on this mixture, and the sulphuretted compounds are formed rapidly. The formation of these polysulphides and hyposulphite requires the presence in the mass of free sulphur. Now, according to the observation of M. Hofmann, sulphide of manganese exposed to the air is transformed into oxide and free sulphur; the oxide of manganese may again be made into sulphide, and pass through the same changes; a part of the waste is thus found decomposed into caustic lime and free sulphur.

Analyses made by the chemist already cited prove in fact that the final residue contains a larger proportion of free lime than the waste itself.

In the theory described, I have intentionally ignored the presence of sulphide of iron. Its action is not yet *defined* by direct experiment, and from its proneness to oxidation might readily favour the formation of calcium sulphate, and thus have a less



useful effect than the sulphide of manganese. The liberated sulphur forms polysulphides with a portion of the sulphide of calcium, and hyposulphite with another portion, under the influence of the air.

For practical purposes it was very important to know how to produce separately one or other of these compounds. The advantage was thus obtained of mixing them in such proportions that an evolution of sulphuretted hydrogen or sulphurous acid should be completely avoided when acted upon by acid.

This important result was obtained by observing carefully the progress of the oxidation.

The waste containing the sulphides of iron and manganese is exposed to the air in heaps for eight days. The interior of the mass heats and would arrive at incandescence if care were not taken to turn over the heap during the interval. In this manner the temperature rarely exceeds  $90^{\circ}$  (C.) The lixiviation of this modified waste furnishes a saturated solution of a polysulphide of calcium; there is only a small quantity of hyposulphite produced; doubtless the high temperature destroys this latter compound, it being decomposed at  $50^{\circ}$  (C) into polysulphide and sulphate.

After this first lixiviation the residue is again exposed to the air for two or three days, then it is washed a second time. In this case the temperature is less elevated, and considerable quantities of hyposulphite are formed. The residue from the second washing, exposed to the air, again heats, the sulphides of iron and manganese being oxidised, in this case no product is obtained by washing.

According to an analysis of M. Hofmann, this residue is composed of—

Sulphate of lime	-	-	-	66.248
Carbonate „	-	-	-	1.320
Caustic lime	-	-	-	20.982
Oxide of iron and alumina	-	-	-	7.
Oxide of manganese	-	-	-	1.500
Insoluble matter	-	-	-	2.800
				<hr/>
				99.85
				<hr/>

This residue does not occupy more than two-thirds of the original volume of the waste; it does not now contain any substance which, by dissolving in the drainage water, could injure vegetation or manufactures.

I have often examined the drainage water from heaps of the residue, and have been able to prove the absence of soluble sulphides; this fact is important from a sanitary point of view.

It has been said that the result of the first washing is a solution of polysulphide of calcium in which acids produce an abundant precipitate of sulphur and an evolution of sulphuretted hydrogen.



The second washing gives a mixture of polysulphides and hyposulphite in such proportions that an acid produces a feeble disengagement of sulphurous acid, and at the same time an abundant precipitate of sulphur. These two solutions are employed separately; the first is used by preference for the neutralization of the chlorine liquors and the production of sulphur, and the second serves for the production of sulphide of manganese.

From their beautiful golden colour these liquors are called the yellow liquors, and to distinguish them from each other the first is called sulphuretted yellow liquor (*eaux jaunes sulfurées*), and the second oxidised yellow liquor (*eaux jaunes oxydées*).

## 2.—*Neutralisation of the Residues from the manufacture of Chlorine; precipitation of Sulphur.*

These residues contain three substances which unite in precipitating sulphur; they are hydrochloric acid, free chlorine, and ferric chloride.

Into one pit is brought a mixture, in convenient proportions, of the two yellow liquors so as always to maintain a slight excess of sulphurous acid and the acid residues from the preparation of chlorine. The moment of neutralization is known by the precipitated sulphur, which at first is pure yellow, becoming grey from the presence of a trace of sulphide of iron. The precipitated sulphur is very abundant, and of such a consistence that it settles rapidly and permits the easy passage of liquids; it is washed on a filter, pressed, and dried.

## 3.—*Separation of the Iron.*

The preceding operation has neutralized the residues from the manufacture of chlorine; at the same time the free chlorine has disappeared, and the ferric chloride has been reduced to ferrous salt.

According to the process described in the memoir of M. Buquet, the neutralized liquid was pumped into certain reservoirs, where the iron was eliminated by fractional precipitation by adding gradually a solution of the sulphuretted yellow liquors to the mixed chlorides of iron and manganese, a precipitate was thus obtained of sulphide of iron containing 45 per cent. of sulphur, and equalling *pyrites smalls* for the manufacture of sulphuric acid. This manufacture of sulphide of iron has been stopped, as the ashes resulting from the roasting are of no value, and form a cumbersome residue; moreover, the sulphide of iron in the form of paste has a singular consistency which may be compared to that of tar or of a fatty body; it is washed and drained with difficulty, and attaches itself to all bodies with which it comes in contact, and it is only removeable by excessive and violent washing. The workmen show a certain unwillingness to work with it. It is therefore preferable to employ the sulphuretted yellow liquors for the preparation of the sulphide of manganese,



which is more advantageous and an easier operation, and the iron is eliminated by sending into the liquid a little waste mixed with caustic lime; the precipitate, which is a very impure mixture of sulphide and oxide of iron, is added to the total mass of waste and serves to induce oxidation.

#### 4.—*Precipitation of Sulphide of Manganese.*

The liquids coming from the preceding operation contain only the chlorides of manganese and calcium. After clarification in a special tank, the sulphuretted yellow liquors are added, and a beautiful rose red precipitate of manganous sulphide free from iron but mixed with sulphur is obtained. The use of yellow liquors containing hyposulphite is carefully avoided in this operation because the latter compound does not precipitate salts of manganese, and the corresponding sulphur would be lost.

When the precipitate is formed, it is allowed to settle, and the clear liquid is decanted and allowed to flow into the river; the sulphide of manganese is collected, washed, drained, and dried on warm plates.

The preparation of sulphide of manganese on the large scale permits of the close study of the chemical properties of this body.

As it is obtained at Dieuze, it contains 58.6 per cent. of sulphur; sulphide of carbon dissolves two-thirds of the sulphur if it has been dried rapidly, there is therefore only one third of the sulphur combined with the manganese.

According to these data it would contain—

Sulphur	-	-	-	-	40
Manganous sulphide			-	-	55
Oxide of manganese	-	-	-	-	5
					<hr/>
					100
					<hr/>

approximately 3 atoms of sulphur for 1 of manganese; whence we may conclude that the sulphuretted yellow liquors contain tersulphide of calcium. Exposed to the air it becomes brown rapidly. This colouration is due to a remarkable phenomenon of oxidation effecting the separation of the sulphur from the manganese which forms an oxide. This combustion is continuous, and, from the observations of M. Hofmann, the final result would be the total decomposition of the sulphide; no sulphate is formed. The quantity of heat disengaged during this exposure to the air is considerable; it accumulates sufficiently from fragments of sulphide in heaps 2 to 3 decimetres high, so that after five minutes the heat disengaged is sensible to the hand, and at the end of twenty minutes it is sufficient to inflame the sulphide. At Dieuze there has been constructed a small furnace which permits of this experiment being conducted on a larger scale, and to give most striking evidence of this singular fact. This furnace is a cylindrical space about 1 metre high; the grate is a simple arch of dry



stones; it communicates with a sulphur burner which receives the products of combustion. This small furnace is charged from above with large pieces of sulphide, the aperture is closed with bricks luted with clay. The feeble draught of the sulphur burner produces a current of air sufficient to traverse the interstices of the grate; the oxidation commences; the temperature being elevated, in five minutes the sulphide catches fire, and in a few moments the mass is at a bright red heat, which is maintained so long as there is any sulphide remaining.

This proneness to combustion necessitates precautions to avoid accidents. It has been observed that the sulphide when in the form of powder does not inflame spontaneously, no doubt because the air then penetrates too slowly. If it is wished to place the sulphide in heaps, the workmen must crush the lumps with his shovel; under these conditions no ignition has been observed. However, it is rare to have any considerable quantity stored, the sulphuric acid manufacture consuming it as it is produced.

#### 5 and 6.—*Combustion of the Sulphide of Manganese; Utilization of the Ashes.*

As we have just seen, there is no difficulty in burning the sulphide of manganese; this combustion is performed simply in the furnaces in which Sicilian sulphur is burned, the sulphurous acid being conducted to the lead chambers.

The residue from combustion contains, according to M. Hofmann,—

Manganous sulphate	-	-	-	44.5
Binoxide of manganese	-	-	-	18.9
Protoxide	-	-	-	36.6

The weight of the ash is half the weight of the sulphide used.

The manganous sulphate produced in this reaction would appear to be a serious obstacle to the employment of sulphide of manganese; its formation causes a loss of sulphur, and from its solubility it is as inconvenient a residue as the chloride. This difficulty has been overcome by so ingenious a process that not only is the loss of the sulphuric acid corresponding to the manganese sulphate avoided, but the oxide of manganese is in a great measure recovered. The process described in the memoir presented to the Industrial Society has been modified; the sulphate of manganese is no longer separated by washing. It has been remarked that the presence of oxide does not at all change the conditions of success; at one step the cost of evaporating the solution of the sulphate has been avoided, and a superior yield of binoxide has been obtained.

The ash of the manganous sulphide is mixed with an equivalent quantity of nitrate of sodium; this mixture, heated in a sulphur or manganous sulphide furnace, disengages the nitrous fumes necessary for the formation of sulphuric acid. The residue from the calcining is a mixture of neutral sodium sulphate and oxide



of manganese, containing 55 per cent. of the binocide, and equalling the native manganeses. In certain cases it may be advantageous to the manufacturer to produce a richer oxide; pure manganous sulphate is then employed, and an oxide containing 70 per cent. of binocide is obtained.

To recapitulate: the process adopted at Dieuze converts two troublesome and offensive residues,—

1st. Into a solid residue, composed of sulphate of lime, carbonate of lime, oxide of iron, and oxide of manganese, substances which are insoluble and inoffensive.

2nd. Into a liquid residue, containing part of the calcium, and all the chlorine from the manganese residues, in the form of calcium chloride. This neutral salt, dissolved in a certain quantity of water, is inoffensive, and may with impunity flow into a river.

It furnishes as useful products:—

1st. Sulphur either free or combined with manganese.

2nd. An oxide of manganese, which can be used for the preparation of chlorine.

It will be seen that this process still produces residues; it does not, therefore, attain to the ideal of chemical manufacture, but these residues, not being hurtful to any manufacture, will not readily induce litigation.

Some attempts have been made at Dieuze to utilize the calcium chloride.

The production of pure calcium sulphate by the action of sodium sulphate was tried; the fibrous structure of this body seemed to indicate it as a substitute for kaoline in the paper manufacture; but this product has not been accepted hitherto, and this part of the Dieuze process still remains a proposal.

Two useful products have been obtained, viz., sulphur equal to 36 per cent. of the total quantity in the waste, and sulphate of manganese, which contains a further amount of from 8 to 10 per cent. of that substance.

Before entering upon the financial part of this report, it is necessary to examine the value of the products obtained.

Grey sulphur contains about 90 per cent. of pure sulphur; it is, therefore, almost equal to Sicilian sulphur, which contains from 2 to 5 per cent. of impurities.

On the REGENERATION of the SULPHUR employed in the ALKALI MANUFACTURE, as conducted at the works of Messrs. CHARLES TENNANT & Co., St. Rollox, by the "MACTEAR" PROCESS.

*Read before Section B, British Association, Plymouth,  
7th Aug. 1877.*

The "Mactear" process owes its origin to the great nuisance produced by the natural oxidation of the enormous heaps of



alkali waste, and its subsequent lixiviation either by rainfall or by springs under the heaps, and differs in the first instance from Mond's process, in that it proposes simply to deal with the drainage liquors from the deposits, and not by any special separate treatment of the waste.

The principle on which all these processes for the recovery of the sulphur have been based is identical, and lies in the decomposition of sulphuretted hydrogen by sulphurous acid, or such decompositions as are to all intents and purposes equal to this.

It is of course necessary that the lime sulphur compounds must be in such proportions that, on the addition of hydrochloric acid with proper precaution, there shall be practically no evolution of sulphuretted hydrogen; and in Mond's process it has been found extremely difficult to obtain in practice liquors of the required composition, and if the workmen are at all careless there is apt to be a considerable evolution of sulphuretted hydrogen.

In the "Mactear" process the apportionment of the various sulphur compounds is very simple, and the evolution of sulphuretted hydrogen, except in cases of the most gross carelessness, is very slight indeed. Although this process has until very recently only been in use at the works of Messrs. Charles Tennant & Co., at St. Rollox, yet by it more sulphur has been recovered than by any other process hitherto introduced.

The heaps of alkali waste at the St. Rollox Works have been accumulating for over 40 years, and are chiefly deposited on the surface of an old "bog" or "peat moss," which has been formed in a natural basin in sandstone rock. This bog is of large extent, and contains many springs of water, which, rising up under the waste, dissolve out the soluble sulphur compounds, and give rise to a large flow of what is commonly called "yellow liquor," which is a complex sulphide of calcium, holding also in solution free sulphur. This liquor was for many years allowed to flow with the natural drainage of the land into a stream called the "Pinkston Burn," which, after traversing a considerable portion of the city of Glasgow as a covered sewer, falls into the river Kelvin at some little distance from its junction with the Clyde. This burn in its course receives liquid refuse of all sorts other than mere sewage, notably refuse from distilleries, and these being acid gave off from the sulphide of calcium liquors sulphuretted hydrogen in such quantities as to give rise to a most intolerable nuisance, of which the public had good reason to complain.

The writer's two predecessors in the management of the works of Messrs. Charles Tennant & Co., the late Messrs. C. T. Dunlop and John Tennent, used their best endeavours to abate or remove the cause of complaint, but in the then state of knowledge it was not found possible to overcome it, although a large sum of money was expended in the attempts.

An effort to abate the evil by intercepting the springs of



water which were supposed to exist under the deposits was made, a shaft being sunk to the sandstone rock some 40 or 50 feet in depth, and a series of mines or galleries were then driven in various directions, extending in one direction to nearly 300 yards, and following up all water sources that were met with. A large amount of water was thus drained off, and it was pumped out of the mine and run away. This was continued night and day for years, and must no doubt have decreased the amount of sulphide of calcium liquor, which, however, existed still to the extent of about 30,000 gallons per day, of from  $11^{\circ}$  to  $14^{\circ}$  Twaddell.

The rainfall of Glasgow being about 42 inches per annum, and one inch of water being equal very nearly to 100 tons per acre, the amount of drainage due to the rainfall alone, supposing half the total amount of rain to pass through the mass of waste (which is of rather a porous nature), would be very nearly 1,300 gallons per acre. The deposits covered at this period about 10 acres, so that there would be equal to at least 13,000 gallons per day due to rainfall alone.

The damp climate of Glasgow thus adds to the difficulties in the way of utilizing the waste and prevention of nuisance.

In the year 1864 an iron pipe of some 9" diameter was laid direct from the St. Rollox Works to the River Clyde, and the sulphide of calcium liquors were thereafter run away by this channel, a large reservoir being constructed to enable the liquid to be stored up, so that it might only be allowed to flow away into the river while flooded with rain, which in our climate is not seldom.

Still the nuisance, although it had been removed altogether from the district in which it had formerly given such cause of complaint, was only transferred in a lessened degree to another, and serious complaints were made as to smell, and also as to an alleged action of the water of the Clyde on the copper sheathing of the ships which lay in the river. The late Professor Anderson made an investigation, and prepared a long and interesting report on the subject for the Clyde Trustees in 1865, and thereafter, year by year, pressure was brought to bear on the Messrs. Tennant by the authorities, in order to force them to take such steps as were possible to prevent nuisance arising from this drainage.

And here it is worth considering one of the greatest difficulties in dealing with a question of this kind. It is this:—

The drainage comes chiefly from heaps of waste which have been some time deposited, not from the fresh waste, and if the usual cry of the aggrieved public were to be acted upon, and the works abolished or forced to remove, the drainage would still remain, and continue for years to be as great a nuisance as before; indeed, were an alkali work compelled to close on account of its waste heap drainage nuisance, there would be no hope whatever of the nuisance being reduced for years to come. On the other hand, by such a process as that now in use at St. Rollox, the alkali work, while it produces hydrochloric acid, can utilize this



waste drainage liquor without nuisance; and thus the best means of removing cause of complaint of alkali waste drainage, is by encouraging the alkali works to remain and to undertake the production of sulphur.

In the year 1867 the writer's firm erected plant for the sulphur recovery process of Mr. Mond, which we proposed working on a modified system, in which the drainage liquors were to be used instead of water for lixiviating the oxidised waste.

So far as the production of sulphur was concerned, this process succeeded admirably, but the evolution of sulphuretted hydrogen when the liquors were not of exactly the correct proportions for decomposition, and also that given off during the oxidation of the waste, which, in the large scale on which the process was employed at the St. Rollox Works, was considerable, caused serious complaints in the immediate neighbourhood of the works.

The very large amount of plant required also, and the fact that it was not found possible to work up by it all the drainage liquors, induced the writer to again carefully study the subject in all its bearings; and after a long series of experiments, many of them, like those of former workers in the same direction, failures, he succeeded in developing the process which has been so successfully worked at St. Rollox, and bears his name.

As has been said, the principle of all the processes for the recovery of sulphur from alkali waste lies in the mutual decomposition of sulphuretted hydrogen and sulphurous acid.

The "Mactear" process depends on the decomposition of the sulphides of calcium by hydrochloric acid, in the presence of a source of sulphurous acid.

The process has various modifications, each of which is applicable under special circumstances:—

- 1st. The drainage liquor usually called "yellow liquor" is mixed with a small proportion of lime, and then treated with sulphurous acid, which it absorbs, giving a small quantity of sulphur. The liquid containing this sulphur in suspension is then decomposed at a temperature of about 140° Fahr.

This method gives good results, but is difficult to regulate, and is subject to the same objection as Mond's process, in that it is difficult to regulate the composition of the liquors, even when only a portion of the yellow liquor is treated with sulphurous acid, and then mixed with the remaining portion and hydrochloric acid.

It is also, in consequence of this difficulty, apt to give rise to an evolution of sulphuretted hydrogen, and cause a nuisance.

- 2nd. The modification actually worked for the past five years is that of using a solution of sulphurous acid in water. This is obtained either from pyrites, or from the refuse sulphur from the process.

The condensing towers are built of wood, common flooring boards, well jointed, and bound with iron corner-pieces and



tie rods. These towers, after five years' use, seem at this date almost as good, and the wood as fresh, as when new.

These towers are filled with coke in three stages, strong cross joints dividing the tower into three divisions. A tray, with a large number of little tubes of lead, covered over with lutes to avoid entrance of air, divides the water into fine streams, and the sulphurous acid gas is then lead up one tower, down to the bottom, and up another tower.

The solution of sulphurous acid in water, in practice, is only of about 2° Twaddell, and in this lies the worst feature of this modification of the process, viz., the heating to the proper temperature for decomposition of such a large bulk of liquid.

The solution of sulphurous acid is led, by means of a wooden shute, to the decomposing vessels, and is mixed on its way with a stream of the yellow liquor or sulphide of calcium; it then runs into the decomposing vessel, where it is met by a stream of hydrochloric acid, the whole kept carefully at as near 145° Fahr. as possible. With moderate care, little sulphuretted hydrogen is evolved, and the decomposition is regulated in the easiest manner by a very simple means of testing:—A burette is fixed to a wooden upright, and filled with the yellow liquor, a sample is drawn from the decomposing vessel, a drop of solution of sulphate of iron added, and then the yellow liquor run in from the burette; the number of divisions required to blacken the solution indicate the acid still present.

The sulphur is allowed to settle, and the clear liquor run off through a catch pit, so as to retain any sulphur that might otherwise be lost; and after some 5 or 6 operations, the sulphur sludge is run off into a drainer.

After draining into a stiffish mud, it is transferred to a melting vessel, where it is melted by steam; and, if necessary, the arsenic removed by an application of the well-known fact that alkaline sulphides dissolve sulphide of arsenic. This process was first applied at St. Rollox in 1869, while working Mond's process, and has been adopted by almost all those manufacturers who recover sulphur. It has the drawback, however, that it also removes a quantity of sulphur, which is of course just so much loss.

The plant required is simple, and, looking at the results obtained, very inexpensive.

It consists of:—

- 1st. Pumping arrangement and cistern for the yellow liquor.
- 2nd. Kilns for burning pyrites or sulphur, and producing  $\text{SO}_2$ .
- 3rd. Condensing towers, and water supply.
- 4th. Steam boiler.
- 5th. Wooden decomposers, with stirring gear.
- 6th. Wooden drainers for the sulphur.
- 7th. Steam melting arrangements.



And the following is an estimate of the cost of the plant now at work at St. Rollox:—

### MACTEAR'S SULPHUR RECOVERY PROCESS.

#### COST OF PLANT.

To produce 30 to 35 tons weekly.

	£	s.	d.
Sulphur burners - - - -	38	0	0
Cast-iron tunnel - - - -	130	0	0
Lead tunnel - - - -	22	0	0
Scaffolding for pipes - - -	16	0	0
Condensing towers - - - -	162	0	0
Pipes and fittings, &c. - - -	35	0	0
Wooden decomposing vessels -	163	0	0
Engine and gearing - - - -	160	0	0
Valves, runs, taps, &c. - - -	64	0	0
Water tank - - - -	24	0	0
Steam and water pipes - - -	50	0	0
Pumping engine - - - -	40	0	0
Steam boilers - - - -	600	0	0
Brickwork and fittings - - -	110	0	0
Melters and fittings - - - -	151	0	0
Square draining tanks - - -	120	0	0
Roofs - - - -	134	0	0
	<hr/>		
	£2,019	0	0

All this plant is substantially erected, and likely to last for many years, with ordinary repair.

It is capable of making 35 tons of sulphur weekly, from yellow liquors of about 11° Twaddell; when less than this strength, the increased bulk of liquid prevents the necessary amount being worked in the decomposers.

The following statement shows the cost of manufacturing one ton, with the consumpt of coals, acid and pyrites:—

#### DETAILED COST OF ONE TON OF SULPHUR BY "MACTEAR" PROCESS.

	Cwt.	Qr.	Lb.	Rate.	Cost.
Pyrites Sulphur - - - -	8	0	25	39/	16·03/
Salt - - - -	35	1	18	16/	28·33
Vitriol - - - -	29	3	27	30/	45·00
Coal - - - -	114	2	7	4·4/	25·20
Repairs - - - -	—	—	—	—	4·00
Wages - - - -	—	—	—	—	38·50
					<hr/>
Off Sulphate of Soda - - -	39	0	21	49/	157 06
					96·01
					<hr/>
Nett cost of one ton of Sulphur -	—	—	—	—	61·05/



It will be seen that the cost, which is based on an experience of five years, and extracted from the annual accounts of my firm, shows that a ton of sulphur has been made for an expenditure of about 61/ per ton. In this nothing is charged for hydrochloric acid; it is usual to treat hydrochloric acid in this way when used in the manufacture of bleaching powder, and therefore it is the proper way to compare the results on the same basis.

We may assume that the Weldon process is the one by which bleaching powder is now almost universally made, and that it requires in the usual practice the acid of

55 cwt. of salt to 20 cwt. of bleaching powder.

If we take the lowest cost of bleaching powder as being

5*l.* 10*s.* per ton,

and compare it with sulphur, when

36 cwt. of salt yields 20 cwt. of sulphur,

at a cost of, say 3*l.* 5*s.*

we have—

	Cost.	Price.	Margin.
Bleaching Powder -	5 <i>l.</i> 10 <i>s.</i>	7 <i>l.</i> 0 <i>s.</i>	1 <i>l.</i> 10 <i>s.</i>
Sulphur - - -	3 <i>l.</i> 5 <i>s.</i>	6 <i>l.</i> 10 <i>s.</i>	3 <i>l.</i> 5 <i>s.</i>

Or for each one ton of salt decomposed, the profit obtained will be—

In the case of bleaching powder,

say 11*s.*,

While in the case of sulphur it will amount to,

say 36*s.*,

A larger profit in favour of the manufacture of sulphur to the extent of

25*s.* per ton of salt

used in producing the acid required for its manufacture.

These figures will of course be modified from time to time by the market price of the articles.

It will at once be seen that the manufacture of sulphur by this process is a much more profitable means of using hydrochloric acid than is the manufacture of bleaching powder, and I am of opinion that it will long continue so, because, in the first place, Sicilian sulphur cannot be reduced much below its present price without shutting up some of the mines, and reducing considerably the production there; and secondly, the effect of the Alkali Acts and recent Royal Commission has been to increase the manufacture of bleaching powder, and by an excess of production over demand, to keep the price at a point at which it is no longer remunerative to the manufacturer.

So far as the question of removal of nuisance is concerned, this process has been amply successful in dealing with the sulphide of calcium liquors which used to flow into the Clyde from our works; and on the last occasion on which a complaint of smell was made, it was traced to the escape of coal gas, which, owing to some accident at the city gas works, had been allowed to pass into the pipes unpurified



for some little time; the gas escaped into the sewer, and a series of complaints of the frightful nuisance of those chemical works was the result. As the complaints came not only from the neighbourhood of the works and the sewers in connection therewith, but also from the other side of the river, the town authorities traced the complaint to its real source, and exonerated us from all blame in the matter.

3rd. The third modification of this process is intended for use when the liquors are very weak in strength, say  $5^{\circ}$  to  $8^{\circ}$  Twaddell, in which case the cost of fuel becomes much enhanced.

It consists in obtaining a stronger solution of sulphurous acid by the production of a bisulphite of lime, or at least of a solution of sulphite of lime in sulphurous acid, which is used just as the sulphurous acid solution in the 2nd modification is employed.

As the old waste contains large quantities of sulphite of lime, it is utilized in this modification of the process by grinding it in water to a milk and treating this with sulphurous acid; thus obtaining a solution of sulphite of lime in sulphurous acid, and thus reducing considerably the amount of sulphur required to form sulphurous acid.

More hydrochloric acid is of course required by this method, but it has great advantages to recommend it.

There can be no doubt that the application of one or other of the modifications of the "Mactear" process to the waste drainage, from the heaps at the great centres of the alkali trade, such as Widnes and St. Helens, would reduce very greatly the nuisance complained of there.

The St. Helens manufacturers have recently decided not to put any acid drainage into the celebrated Sankey Brook, and this will lead to its utilization in one way or another. The most probable direction for it to take is that of the manufacture of bleaching powder, an article of which I am sorry to say there is at present a very great over-production.

Were, for instance, a combination of manufacturers along the course of the Sankey Brook to collect the drainage liquors, pump them to a convenient spot (in which my experience of nearly ten years shows there is little difficulty), and treat them with the acid of either one or various works, obtained by arrangement, I am confident the nuisance complained of in that district would be much reduced, and a handsome profit realised by the manufacturers.

The result of this method is a drainage without colour and scarcely scented.

#### *The Solution from the Waste.*

The rain falling on the waste brings down oxygen, and the result already mentioned takes place, so that we may have a clear



yellow stream, or with some iron a dark bluish one, which becomes decomposed by the carbonic acid of the air, and gives off sulphuretted hydrogen. If this stream is not kept within bounds, but allowed to overflow the fields, the acid rain falling on such a great surface still further decomposes the sulphide, and more sulphuretted hydrogen is formed,—a very common occurrence. If a stream of water containing acid meets this stream of sulphide, the formation of sulphuretted hydrogen is abundant, and the liquid becomes opaque and yellow from free sulphur. This acid stream is frequently found coming from chemical works where muriatic acid is made.

The sulphur solution is that which nature has formed from the heaps, and which Mr. Mond forms by mechanical oxidation; at least it is so to a great extent. It does not contain the exact amount of hyposulphite to form the decomposition wanted, but by a little further oxidation the proper state may be produced. The two acids, hyposulphurous and hydrosulphuric, do not decompose each other when united to the calcium, but if that base is removed the former acid is decomposed, leaving sulphur to fall, and sulphurous acid to decompose the sulphuretted hydrogen. It is on the solution made by nature from the heaps that Mr. McTear begins his process.

*Angus Smith's Process for treating Sulphide Solutions.*

The process which I proposed in 1877, or earlier, was not given to the public till 1879. However, the date has been preserved so far that after I had made trials for about a year Mr. McTear was good enough to make an experiment for me, and the account of them is dated 8th August 1878. (See Report for 1877 and 1878, p. 38.) I say this more particularly because of some mistakes having been made in this respect, and it abundantly shows that I could have taken the idea from no one in any sense. But as ideas grow from their ancestry, and this ancestry I described clearly, I shall repeat the account here.

I have already mentioned that the manager of Mr. Tennant's works told me that he had tried the burnt pyrites for purifying the solutions at the base of the waste heap, and that for a time they came through the iron quite clear; that he had given up the plan, however, as the clearness did not continue. We know, of course, that nothing will continue. The removal of the sulphur from soluble sulphides by hydrated oxide of iron has not been able to make a successful process. The action is slow; and with great quantities only, and by allowing a great space, can it be expected to succeed even with the hydrate. The same slow process must be allowed for the re-oxidation, when the iron will be able to begin its work again.

When I saw from the evidence of Mr. Shaw given before the Noxious Vapours Commission that the drainage from the heaps at the South Shields Works was deodorized by means of



the waste oxide of iron from the manganese solutions, I went to examine the process. I could scarcely call it a finished process, since the matter was merely thrown down and rarely stirred, the chief work being left to the air. I had no faith in the iron from my former experience. I had also tried manganese at the same time, and did not expect sufficient results from that. Something new must be added that I had not known before, and this was found in other processes, namely, blowing air through the solution to supply the oxygen. It was not intended to try the chloride of iron; that, we knew, would act as least by equivalents; it was known also what chloride of manganese would do, since it was proposed as a disinfectant by James Young, F.R.S., and it was only necessary to try the oxide.

With this in view, a solution from the waste heaps was treated with peroxide of manganese, and sulphuration took place immediately, part of the oxygen of the manganese going to form a thiosulphate. The mixture was shaken in a bottle with air, and an oxide of manganese was formed, whilst sulphur fell.

The process was then complete in theory, and it was desired to make it continuous. This was done in a very simple manner. The solution to be freed from sulphur was put into a tall glass vessel, a little of the peroxide of manganese was added, only  $1\frac{1}{2}$  gramme to a litre, and air was blown in. This completed the conversion; but it was not yet a continuous process. A syphon was then added to the vessel, one end reaching to the bottom, the other being outside to draw off the purified solution whilst the fresh sulphide entered above. This acted well, but some of the solid matter rose with the liquid and was lost. The mouth of the syphon was then enlarged by adding a small inverted funnel to it, and covering this with calico, so that the liquid came off clean and quite free from any sulphide.

As a sanitary process it is perfect, but is it so as a manufacturing process?

The first quantitative trial was made on a mixed sulphide of calcium obtained by heating lime milk with sulphur. To this solution 1.025 gramme of peroxide of manganese was added, and air passed through. After  $3\frac{1}{4}$  litres had been oxidized, the precipitate gave 2.89 grammes of sulphur.

Next 1 gramme manganese peroxide oxidized 9 litres of sulphide of calcium solution, the precipitate having 17.5 grammes of sulphur, or 72.3 per cent.

3.9 grammes peroxide of manganese added to waste liquor, or liquor from the soda waste heaps, containing 17.6 grammes of sulphur per litre, diluted 20 times or to .88 grammes sulphur per litre in sulphide, and 1.54 as hyposulphite, was oxidized continuously for three weeks and a half. The supply of liquid was at first  $\frac{1}{2}$  a litre per hour, but at last it rose up to 2.7 litres. 140 grammes of precipitate were obtained containing 77 per cent. of sulphur. The remainder was principally carbonate of lime. 160 litres altogether of the dilute solution were used, giving



67.6 grammes per 100 litres, or 108 grammes of S out of 140 in the original solution.

Another sample of drainage liquor from Widnes gave .14 grammes from 1.8 litres, or only 7.7 per 100 litres.

The precipitate of sulphur is mixed with carbonate of lime, and, unless carefully washed, some hyposulphite, also with a high oxide of manganese when thoroughly oxidised by passing an excess of air.

It is not often, however, that the exact numbers quoted are obtained, because some manganese remains with the sulphur. This is no great objection if the sulphur is to be burnt, as the sulphide of manganese burns readily, at least when tried on a small scale, and leaves a porous friable mass which is capable of being used again, and this could be repeatedly done were it not for the lime remaining, which gradually increases. If the lime were removed by acid this would introduce a feature which it was desired to avoid, but the amount of acid although small might be saved by throwing away the whole, the manganese being so small in amount in comparison to the sulphur gained.

It is also to be remarked that the process has never succeeded in strong solutions. That which usually flows from the heaps requires to be diluted until the amount of sulphur, as in a sulphide, is equal to one-tenth per cent.

This is an objection, as water must be added; but it is not a great evil, since the supply of fresh liquor may be proportionately small. It demands that the vessels be larger, and necessitates more pumping than would otherwise be required.

The reason that the process is not successful in strong solutions is, at least partly, that the sulphur is re-dissolved as soon as precipitated. It has already been said that the sulphide dissolves sulphur readily.

A solution of sulphide of calcium, sodium, or barium gives off sulphuretted hydrogen when common air is passed through it. It is slowly oxidized. Three hours were required to destroy the sulphide of the first, using a solution of the same strength as that taken to compare the oxides of iron and manganese. The sulphur is partly precipitated. An experiment comparing the use of air alone, and air with oxide of manganese, gave—

With air alone -	-	-	73
With oxide of manganese	-	-	582

In the first case sulphuretted hydrogen is given off, not in the second.

#### *Calculation for Work on a large scale.*

Some idea of the amount of work to be done may be estimated in this manner: let us suppose an acre to receive 537,600 gallons of rain annually after deducting one-third for evaporation; and let us suppose this drainage to be of the strongest kind that flows



from waste. Then, judging from the size of the vessels used on a small scale, a vessel holding 1,000 gallons would be sufficient to pass 1,200 gallons through it purified every 12 hours. This would require to be in action for 224 days, night and day, to overtake the drainage. This is not a supposition that strains us much; the amount of sulphur obtained from such a solution as is here spoken of would be, according to the longest experiment made, 1.76 per cent., or 63.36 tons, equal, at 6*l.* a ton, to 380*l.*, to pay for the working, an amount quite sufficient but not highly remunerative. In the case of weaker solutions the amount of sulphur would be less, but the time required would be less also. Some of them are weak enough to require no dilution. The exact expense and the settlement of the many possible questions I cannot of course foresee.

Mr. Weldon has used air for oxidising sulphide of iron, but not manganese with sulphides in solution, and I may state that I have no desire to take from him the credit of using air, although my idea came in the way represented.

The chief objection to the process is that the sulphur of the hyposulphite is not precipitated. To do this would require the aid of Mond's process.

#### *Sulphide of Barium with Oxides of Manganese.*

The action of the manganic oxides on the calcium sulphides induced me to try them on barytic sulphides, and here is a result with three sets of experiments.

The simple CaS, as obtained by decomposing sulphate of lime with C in the fire, was found to be dissolved to the extent of 1.3 per cent. If allowed to stand free from air no change is perceived. If shaken with air or peroxide of hydrogen the colouring is immediate.

The result, at any rate in the heaps, is, that by oxidation a mixture of sulphide and hyposulphite is formed, but the inquiries on the sulphates now show that oxygen may be obtained from them without the external air.

Glasgow, 8th August 1878.

DR. ANGUS SMITH, F.R.S., &c.

I HAVE now the pleasure to send you the remaining details of the experiments on the oxidation of the bog liquor by air and manganese, regarding which I sent you the details of the first experiments on the 6th of May last.

3rd Experiment.—On the oxidation of yellow liquor draining from alkali waste by means of a small proportion of manganese oxide.

#### *Details of Experiment.*

Filled oxidizing vessel  $\frac{2}{3}$  full of water, added a small quantity of black oxide of manganese (prepared by Dunlop process), and



turned on the current of air from a blowing engine ; kept a small stream of yellow liquor constantly running into the oxidizing vessel at the rate of about 2 gallons per hour.

At this rate the air could not quite oxidize it as it ran in ; but as, for sundry reasons, it was only run in during the day while the air was kept on night and day, the oxidation was complete enough in the morning ; in fact in two cases the manganese had been raised to the black colour, indicating its oxidation to the state of peroxide.

*Measurement of liquors.*—The fresh liquor was carefully measured in a cast-iron cistern made specially for measuring purposes, and the oxidized liquor was also carefully measured in a similar cistern.

Each morning, after the complete oxidation of the liquor in the oxidizer, the air was turned off, the precipitate allowed to settle, and about  $\frac{1}{3}$  of the liquor run off and measured. A fresh amount of liquor was then allowed to flow slowly into the oxidizer, while the air was again turned on. This alteration was carried on until there had been used 216 gallons of yellow liquor. Samples were taken from each operation, and the amount of the sulphur compounds estimated. The precipitate was at the completion of the experiment washed and dried, and its sulphur contents also estimated.

The following give the results :—

Yellow liquor used 216 gallons at  $8\frac{1}{2}^{\circ}$  Twaddell.

Containing :—

	Lbs.
Sulphur as hyposulphite of lime	- 1.015
„ sulphate of lime -	- .712
„ sulphides of calcium	- 53.569
Total sulphur	- <u>55.296</u>

Manganese used 10 lbs., containing 68 per cent.  $\text{MnO}_2$  (Dunlop's recovered black oxide).

Oxidized liquors :—

421.8 gallons of  $4\frac{1}{2}^{\circ}$  Twaddell.

(The specific gravity varied from  $1^{\circ}$  in the beginning to  $6\frac{1}{2}^{\circ}$  at the end of the whole experiment.)

Containing :—

	Lbs.
Sulphur as hyposulphite, $\text{CaS}_2\text{O}_3$	- 34.377
„ sulphite, $\text{CaSO}_3$ -	- 1.350
„ sulphate, $\text{CaSO}_4$ -	- .506
Total sulphur	- <u>36.233</u>



## No SULPHIDE.

Precipitate :—

It weighed wet 52 lbs., and contained :—

		Lbs.
Sulphur as sulphate $\text{CaSO}_4$	-	1.235
„ sulphide $\text{MnS}$	-	1.940
„ free sulphur	-	15.140
		<hr/> 18.315 <hr/>

Total sulphur started with	-	Lbs.	55.296
„ at finish of experiment in solution		Lbs.	36.233
„ at finish of experiment in precipitate			18.315
			<hr/> 54.518 <hr/>

0.648 lbs. lost.

This loss occurs by evolution of  $\text{H}_2\text{S}$ , spills of liquor, and inaccuracies in the measurement.

Calculated on to percentage results are—

For 100 parts of sulphur started with there has been obtained—

In solution	-	-	-	65.65%
In precipitate	-	-	-	33.18
Lost	-	-	-	1.17%
				<hr/> 100.00 <hr/>

In the precipitate there exists—

As available sulphur, say for melting			
out for sale	-	-	27.3%
As sulphide	-	-	3.64%

Lime :—

The lime  $\text{CaO}$  in the yellow liquor was equal to 43.9 lbs.  $\text{CaO}$ , and the  $\text{CaO}$  in oxidized liquor amounted to 37.2 lbs. The difference = 6.7 lbs.  $\text{CaO}$  had been thrown down as carbonate or sulphate. All the lime as carbonate is equal to at least two equivalents of free sulphur.

6.7 lbs.  $\text{CaO}$  = 15.26 per cent. of the  $\text{CaO}$  in original liquor. Say that the lime equals two equivalents of sulphur  $\frac{6.7 \times 32}{28}$  = 7.66 lbs. sulphur. Then, as total sulphur precipitated

was equal to 18.315 lbs., and the sulphur equal to loss of  $\text{CaO}$  in liquor was equal to 7.66 lbs., we have  $\frac{7.66 \text{ lbs.} \times 100}{18.315 \text{ lbs.}}$  = 41.8 per cent. of the sulphur precipitated, due either to the formation of



sulphate or carbonate of lime. As the amount of sulphate is not high, it would seem as if the  $\text{CO}_2$  had done nearly as much work in precipitating the sulphur as did the oxidation and reduction of the manganese.

The amount of air used was enormous compared with the work actually done.

From all the results obtained I would be much inclined to think that if gases such as those from a chimney were forced through DILUTE yellow liquors (perhaps washing first to get rid of acid vapour) the results would be from every point of view much more satisfactory. I intend trying this, and will report to you the results.

Yours, in haste,  
JAMES MACTEAR.

The amount of free sulphur obtained by Mr. McTear is less than that obtained by me. He used a large excess of air, and this seems to explain much. If we use as little oxygen as possible we limit the amount of thiosulphate formed. If we use no air, but only the lower oxide of manganese or carbonate of manganese, for example, we obtain with difficulty any result. Some of the solutions have stood for weeks with oxide of manganese without losing the yellow colour, but those with carbonate of manganese are decomposed more rapidly.

*Abstract.* (p. 45 of Report.)

$\text{MnO}$ , protoxide of manganese, added to the solution without air, the  $\text{CaS}_2$  is not decomposed.

If  $\text{MnO}_2$  or any oxide above  $\text{MnO}$  be added the sulphur is taken down rapidly and the calcium is oxidized, but no sulphur, so that no thiosulphate is formed.

No sulphurous acid or sulphite is formed.

No sulphuric acid or sulphate is formed.

If this sulphide of manganese is exposed to air it becomes oxidized, and sulphur is thrown out in a free state.

If air is passed through the liquid in which the sulphide of manganese lies oxidation takes place, and oxide of manganese is formed, at first white and afterwards dark, according to the continuation of the current of air. During this oxidation there is hyposulphite formed by the oxidation of part of the sulphur.

Carbonate of manganese may be used instead of oxide.

If air is passed through the sulphide solution by itself hyposulphite is formed, and some sulphur is deposited, and the action is slow, but there is still some, and  $\text{H}_2\text{S}$  is given off.

When solutions of sulphide of sodium were deoxidized with manganese (p. 36 of Report) a constant formation of hyposulphite of sodium took place.



*Gas Lime.*

It was then held possible that the same process might apply to the sulphuretted lime of the gasworks so much complained of, and it was found that by treating with water, and removing the sulphur from the water solution by means of manganese, there is obtained a liquid quite free from smell, and a considerable supply of that sulphur which in part had existed in the gas is precipitated in a free state, and will probably be found extremely pure.

*Apparatus used.*

A drawing is given of the apparatus by which the experiments were made in the laboratory. I have not made any attempt to use larger apparatus, but I should not suppose that it would be well to imitate this particular form. It is probable that a revolving water-wheel raising the fluid mixed with the manganese and allowing a stream of gas to pass through would present a very much larger surface than any gas forced into the liquid in proportion to the power applied. If, however, pressure is important the advantage would be against the wheel; and pressure is of advantage, as the experiments show, if not too expensive.

Since writing the above I have used a small dash wheel to make spray, and have very much quickened the process.

When this was published I received a visit from Dr. Storer, of Glasgow, a gentleman whom I had not seen before. His object was to show me an apparatus which he considered well adapted for mixing the air with the solutions to be aerated. He had also new views regarding the substances which might be aerated. He had already been interested in aeration, and had been applying his knowledge successfully to the treatment of oils, so as to make drying oils. He had also been oxidising sulphates and chlorides of iron after adding lime.

He also spoke of applying the process to the oxidizing of manganese in the Weldon process, and in oxidizing sulphur liquors in soda works, a purpose also laid down in my report.

This, of course, was interesting to me, but I was at the time engaged in examining questions relating to water, and it was in this department that I was inclined chiefly to renew my interest.

MESSRS. HELBIG AND SCHAFFNER'S PROCESS: FROM PROFESSOR LUNGE'S WORK ON "SULPHURIC ACID AND ALKALI."

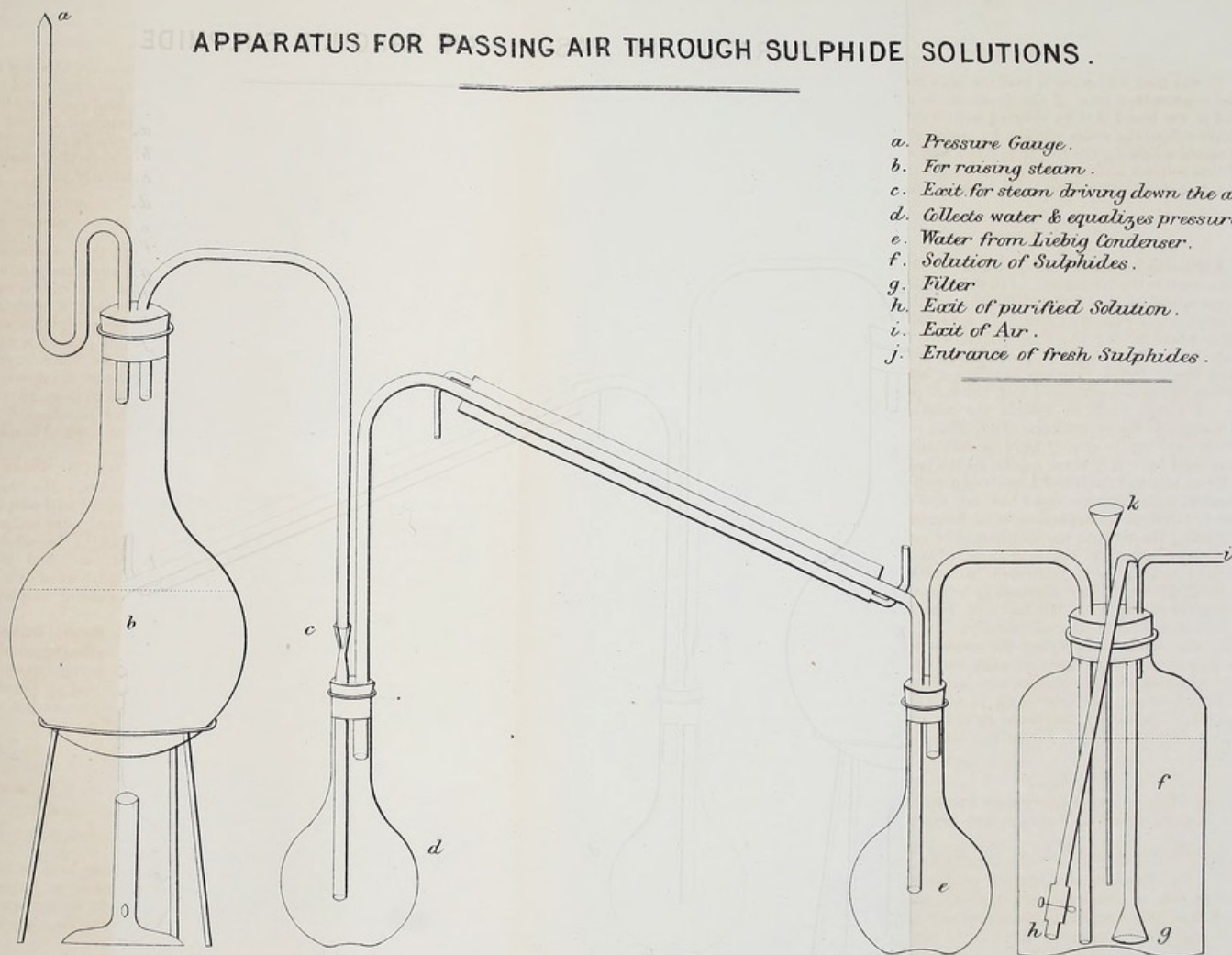
*Complete recovery of Sulphur and Lime from Tank-waste.*

"We shall conclude this chapter by describing in *extenso* the new process of Schaffner and Helbig (patented in England, March 9th, 1878), which, if it succeeds as well in the long run as it has done hitherto, seems destined to put the final touch to



# APPARATUS FOR PASSING AIR THROUGH SULPHIDE SOLUTIONS.

- a. Pressure Gauge.*
- b. For raising steam.*
- c. Exit for steam driving down the air.*
- d. Collects water & equalizes pressure.*
- e. Water from Liebig Condenser.*
- f. Solution of Sulphides.*
- g. Filter*
- h. Exit of purified Solution.*
- i. Exit of Air.*
- j. Entrance of fresh Sulphides.*







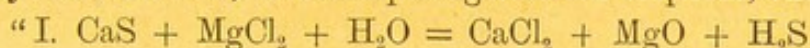


Leblanc's process, since it entirely does away with the only serious drawback attached to that process, viz., the tank waste.

"The sulphur recovery processes hitherto in use are based essentially on oxidizing the tank waste to a certain extent, dissolving out the sulphur liquor, and precipitating the sulphur by muriatic acid. In the best case, however, only 50 to 60 per cent. of the sulphur are thus recovered; the other 40 to 50 per cent., together with lime, form a new waste, containing undecomposed calcium sulphide along with sulphite and sulphate. This new waste is not a nuisance similar to fresh tank waste; but, owing to its great bulk and its very slight utility, it is a great burden upon alkali works. This will be done away with by the invention of Schaffner and Helbig, which recovers by far the greatest portion of the sulphur and also the lime.

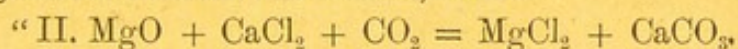
"It is chiefly based on:—

"(a.) The applicability of magnesium chloride, hitherto not employed in the arts, to decomposing calcium sulphide, thus:—



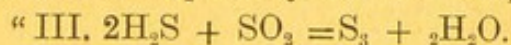
(calcium carbonate not being acted upon by  $\text{MgCl}_2$ ).

"(b.) The recovery of the magnesium chloride by exposing the residue from the first operation (consisting of magnesia, calcium chloride, and the impurities of soda-waste), after driving off the  $\text{H}_2\text{S}$  to the action of carbonic acid, by which calcium carbonate and magnesium chloride are formed, thus:—



A portion of the magnesium chloride can be replaced by the simultaneous action of muriatic acid, by which the separated magnesia is always dissolved again, and again becomes active. This reaction might be applied where an excess of muriatic acid is obtained, and at the same time yields calcium chloride in case the latter is not got otherwise as a by-product. In this case the mud, after being treated with boiling water, is allowed to settle, and a corresponding portion of the clear  $\text{CaCl}_2$  liquor is drawn off. Of course the action of  $\text{CO}_2$  can only recover as much  $\text{CaCO}_3$  as corresponds to the  $\text{MgCl}_2$  employed.

"(c.) The sulphuretted hydrogen escaping in the first operation is transformed into sulphur by means of sulphurous acid:—



Ordinarily this reaction does not take place as smoothly as the formula would indicate, but, as we have seen before, large quantities of pentathionic (or tetrathionic) acid are formed; and it would fail to be available in this case, as it has done in all previous cases, unless Schaffner and Helbig had discovered a plan for preventing to a great extent the formation of pentathionic acid, or, if the latter has been formed, precipitating the sulphur from it. This consists in the application of solutions of calcium or magnesium chloride, also of other mineral salts and acids.



If aqueous solutions of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  are mixed in the proportions expressed by the above equation, a milky liquid is formed, from which, by addition of a solution of calcium or magnesium chloride, a flaky readily settling precipitate is obtained, which corresponds to the theoretical quantity. An excess of one gas or the other is found unchanged in the liquid, and does not interfere with the reaction. It is not known what part the chlorides play in this case, but so much is certain, that an amount of  $\text{CaCl}_2$  or  $\text{MgCl}_2$  equivalent to the total sulphur is required.

"The greatest impediment to the application of the mutual decomposition of  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , which, even more than the formation of polythionic acids, had baffled all previous endeavours in this direction, was the milky state in which the sulphur is precipitated, which prevents its separation of subsidence or filtration. This is completely obviated by the employment of solutions of salts (as stated above), which is the most important feature of the new process.

"The  $\text{MgCl}_2$  obtained in the second operation is employed for decomposing new quantities of tank-waste, and the calcium carbonate in the black ash mixture.

"The operations are practically carried out as follows: the decomposition of tank-waste by magnesium chloride takes place in a large air-tight iron vessel provided with an agitator, with contrivances for charging and discharging the materials, gas delivery pipes, &c. Here the mixture is exposed to heat. Either the tank-waste is gradually introduced into a charge of  $\text{MgCl}_2$ , or, inversely, the  $\text{MgCl}_2$  solution is run upon the waste, or both are simultaneously introduced in equivalent proportions. The apparatus must be so arranged that the operation can be arrested at a moment's notice; nor should any  $\text{H}_2\text{S}$  be able to escape into the air. This is prevented by producing a draught from without by means of a chimney, fan-blast, or pump, and by always keeping an excess of  $\text{SO}_2$  in the decomposers over and above that corresponding to the arriving  $\text{H}_2\text{S}$ , so that the latter can never be in excess. According to Stingl and Morawski this process is to be explained thus: first magnesium chloride and calcium sulphide decompose into calcium chloride and magnesium sulphide; the latter at once reacts upon the water present, magnesium hydrate and sulphuretted hydrogen being formed.

"The cinders and other impurities of the tank-waste must be removed from the residue remaining after the just described treatment. They cannot be left in the recovered lime, because accumulating they would make it unfit for black-ash mixing. These impurities are completely removed in a very simple manner, either by levigation or by passing the residue through a fine sieve. The cinders, coal excess, limestone, &c., contained in the tank-waste are heavier and coarser than the magnesia separated in the first operation; they amount to 25 or 30 per cent. of the whole dry weight of the tank-waste. The residue thus purified is now treated with more or less impure carbonic acid in order to recover



the magnesium chloride and calcium carbonate as previously mentioned. The way in which this is done will be apparent from the subsequent description of the apparatus.

"The sulphuretted hydrogen from the first operation is now brought into contact with sulphurous acid and a solution of calcium or magnesium chloride, which can be done either in tubs or towers. In the latter case the  $H_2S$  should be introduced at the bottom of the tower, the  $SO_2$  a little higher up. The precipitated sulphur settles down with striking rapidity, owing to the action of the chlorides; it is separated from the liquid by decantation or filtration, and the same solution used over and over and over again for running down in the tower. The gas pipes must be easily accessible from without, for rapid cleaning. The requisite  $SO_2$  is made by burning pyrites, sulphur, or sulphuretted hydrogen, or taken from any metallurgical process; it is either conveyed directly into the decomposer, or first condensed in an ordinary acid condenser to a solution of  $SO_2$  in water, or in a solution of  $CaCl_2$  or  $MgCl_2$ .

"This process is applicable not merely to tank-waste, but also to calcium or barium sulphate after their previous reduction to  $CaS$  or  $BaS$ ; it also permits the utilisation of the  $SO_2$  evolved in many metallurgical operations. Its advantages are: it is easy and safe in its execution; the working-up of the tank-waste costs much less time and wages than hitherto; at least 90 to 95 per cent. of the sulphur contained in the waste are recovered, as against 50 to 60 per cent.; 80 per cent. of the total lime are recovered as calcium carbonate adapted for black-ash mixing. The  $CaCl_2$  and  $MgCl_2$  are all recovered except the unavoidable mechanical losses, which can be made very small; in any case they are as nothing compared with the saving in wages and in the muriatic acid required in the processes hitherto employed. If the requisite  $SO_2$  is made from pyrites the production of sulphur can be increased by 50 per cent. over and above that recoverable from the waste. The ultimate residue only amounts to about 20 per cent. of the fresh waste, thus saving a great deal in carriage and depositing ground."

#### SOME RESULTS OF THE STUDY OF WASTE.

The question now arises, what result or advantage to the public will result from using any of these processes?

1st. It is clear that streams of yellow liquid giving out sulphuretted hydrogen may be converted into streams quite innocent, in a sanitary point of view, so far as the effect on the atmosphere is concerned.

A sub-question, however, arises, is it possible to apply the plan to streams containing very little sulphur unless at an unreasonable expense? On this point it may be considered enough to say that it is not well to begin our reforms with the most innocent, let us begin with the larger evils. It is certain that in many places small streams may be made to run together



and form a large one, and this may be treated as one. I am not, however, inclined to say that it is necessary to have any streams at all from the waste heaps. I may say, as already said, that if a well were dug in the middle of a heap the drainage would go into that well so long as it was properly pumped. The rainfall would go inwards, instead of outwards as at present, and the heap as well as its drainage would be innocent. There is no doubt of this, it is a certainty. Let us suppose cases where the heaps are large and the drainage great, as at St. Helens; we have only to use the method proposed, and we cease at once to allow any yellow liquid to flow into the river, but we obtain the sulphur in a profitable form. The manufacturers have imagined that they invented something valuable when they removed the acid from the brook at St. Helens, but the evil is only slightly diminished. The brook does not smell so badly, but it does smell, and as to appearance it is worse, whilst its effect on land cannot be much altered. This collective mode of treating the drainage from the waste will make the heaps give up some of their treasures.

In cases where this collective action is not required the same of course may be done by individuals: but in such cases, and, indeed, in all cases, the question arises, whether it would not be better to treat the tank waste beforehand and take out the sulphur before it reaches the heap. The various modes of doing this may be studied. I am not sure, of course, how far the newer plans are to be recommended, which have not been tried on a large scale, and none of the alkali makers have been pioneers of late, Mr. Chance excepted; but Mr. Mond's plans are well known, and they are now so well tried that proof is unnecessary.

But we know enough to say that, with all these facts together, there is no reason for allowing waste and drainage to be left to their natural and offensive decompositions.

This is perhaps scarcely the place to enter very fully on the plans for carrying out the new "Alkali, &c. Works Regulation Act," but so far as our streams are concerned it is necessary to speak of the subject here, and it may from this find its way to the alkali makers also.

It seems to be certain that no mode of laying down fresh tank waste has succeeded in avoiding offence. I must say, after abundant experience, that every method tried has been a decided failure. The offences have been twofold; one is by sending gases direct into the air, the other by sending solutions from the heaps, hurtful as solutions and ready themselves also to send sulphuretted hydrogen into the air.

Are there no exceptions to this rule? There may be practically; that is, there are a few places where the waste is laid in places not observed. These cases injure no one at present; it is not possible to say when they may cause injury. One cannot tell into what unlikely places men may take their habitations,



or what horrors may be caused by some day finding that houses had been built on waste from which there was no drainage, and which had remained long unoxidised. We have no right to spoil ground for our posterity; at least, if we have a legal right, it is not a humane act to exercise it.

But some of these places may be so situated that drainage comes from them; in which case oxidation goes on, and perfect innocence of ground will follow, such cases being common. The answer is, certainly this is true, but this drainage is an offensive sulphureous solution, and if it flows away must be objectionable; if it is retained it may remain long unchanged, as stated above. If it is allowed to flow, can it do so without being a nuisance? Such cases may exist, but they must be few.

Is the mode of covering heaps with soil not sufficient? I have never seen it done well, and on inquiry, I meet so many objections that I do not expect it to be done so well as to be a complete remedy for untreated waste.

It has been lately a favourite belief of alkali makers that the waste should be patted down; it was once a favourite belief that it should be put in small heaps; one is to prevent oxidation, the other to hasten it. But neither have been fully successful, judging by the senses or by any way. Covering would do very well, if it were done very completely. If no oxygen is allowed to enter, then combustion does not begin; and this result might be obtained by digging deep pits, and putting the waste into them, as has been done in some places. But in nearly all cases this would be too expensive. There are, however, cases in which considerable depth can be obtained without inordinate expense, and I have seen this used without offence. It is probable that a very small depth would be enough if the soil were immediately put over the waste, but it must be done at once; any delay in putting on the soil allows the heating to begin. Still, any mode of laying the soil without previous desulphurising renders a careful mode of drainage quite essential, unless in cases where the waste is thrown so deep that the drainage never reaches the surface. If well beaten down it is probable that it would lie in a deep pit for ages unaltered.

Unless in cases where the waste (or let us call it the sulphides of calcium, since it ought not to be *waste*) is put out of the reach of oxidation and drainage, we must make up our minds to let nature partially oxidize it, or we must do it ourselves. After oxidation the liquid must be treated to remove the sulphur. There is a choice; there is no monopoly of method; and more than one method pays at least its own expenses, and at times is said to do a great deal more.

I have objected to the mode of laying down the waste. It is not sufficient to pat it as usually done, simply because it is never done well enough to destroy its porosity. It is possible, perhaps. It is also, as said, possible to cover it over with earth sufficient to



keep out air, but it is not desired to keep out air so entirely that the stream from it is not partially oxidized and of a bright yellow. The monosulphide is very slightly soluble or coloured, and without oxidation we should have it permanent.

In one of my reports I have shown (the 14th + 15th Report, p. 41) that sulphide of calcium decomposes sulphate of lime, and intermediate products are formed. This is abundantly proved by the inquiries made. Now, it seems to me, but it is only a proposal, that it would be a possible way of applying this knowledge to mix up the old waste with the new at the time of laying it down. How much of each I do not know. The result would be, as I suppose, that the new waste would not heat so rapidly, because it would be exposed to cool surfaces. But it is probable that a part would oxidize nearly as rapidly, whilst the heat produced would be thrown out or dispersed at a lower temperature, because being dispersed throughout a greater mass. Next, the action of the sulphides would be to begin oxidizing themselves at the expense of the sulphates and sulphites, and thus there would be less air required or used for oxidation, whilst the oxidation which was caused by the oxygen salts would not produce heat, as there would be a simple interchange with no diminution of the volume of oxygen. I must add, that a trial made of this for me by Mr. Henry Brunner has not been successful.

It would be well to make a complete trial of this plan. It certainly would cause some expense, because the manipulation of the old waste would require to be paid for; it would be rough work, although probably less expensive than the present methods of oxidizing. However, the only real cure is to lay down no waste till the sulphur is removed, and to this we must rapidly come.

This report may be said to be chiefly on the VALUE OF OXYGEN in destroying putrefaction, in oxidizing impurities of nearly all kinds, and of course in preserving water and air from the unwholesome agencies to which they are exposed.

R. ANGUS SMITH.

August, 1881.

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## APPENDIX.

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December 1881.

Having visited the works of Messrs. Schaffner and Helbig at Aussig, I may mention that I brought away a specimen of the waste after treatment there by Mond's process. The analysis gave—

### WASTE FROM AUSSIG.

Sulphur as Sulphide	-	0.09 %
Thiosulphate	-	3.64
Sulphite	-	0.72
Sulphate	-	0.84
		5.29

Total sulphur (direct oxidation) = 5.40 %.

### ANOTHER TREATMENT OF "YELLOW LIQUORS."

When examining the action of steam and air I found that so much sulphur was oxidised that hyposulphite was formed. The plan was abandoned.

It was also found that with strong or hot solutions above 130°–140° F., the sulphur was dissolved when it was thrown down in the manganese process.

On p. 34 of my 14th and 15th combined report it is said:—

"This solubility of the sulphur applies also to strong solutions of caustic soda and potash, so that an attempt to precipitate from them will fail unless care is taken to pour them into a weak solution in which the manganese oxide is acting, and at such speed as to keep up a constant moderate strength.

"But the solubility may be taken advantage of in making hyposulphite of soda, because if a hot solution of caustic soda is used and an excess of sulphur, the sulphur will dissolve as soon as precipitated, and at every precipitation and solution some will be oxidised until the whole is converted into hyposulphite of soda.

"A similar experiment was tried with the waste itself so as to convert all its sulphide of calcium into hyposulphite, but the action was slow and unsatisfactory, the reason being in the insoluble character of the monosulphide. Still I think this might be made to succeed if it were desirable."

I had tried therefore hot solutions as well as aeration without manganese, but Mr. Dryden, at the works of Messrs. Chance, has



brought forward a plan which carries out Mond's process by using warmed solutions, and thus takes advantage of the formation of hyposulphites.

By partially oxidising the yellow solutions, and then adding hydrochloric acid, sulphur is thrown down. This is unquestionably a valuable process when acid can be had cheaply. I leave him to describe it in his own words. It is the latest phase of the sulphur process.

MESSRS. CHANCE'S ALKALI WORKS, near Birmingham.

*Treatment of Yellow Liquors to render them innocuous, and to recover the Sulphur contained in them.*

The question of the best method of treating yellow liquors having become an urgent one, and hydrochloric acid being available for the purposes of such treatment, I naturally proposed neutralisation by this means, the collection of the precipitated sulphur by filtration, and the running off of the clear and innocuous filtrate. The large quantity of sulphuretted hydrogen evolved I proposed to burn, the resulting sulphurous acid to be carried into the chambers, arrangements for this process being already in existence in the works.

But it seemed to me that it would be much more satisfactory if the yellow liquor process could be made complete in itself, and to this end it became necessary to prevent the evolution of sulphuretted hydrogen gas, and to procure the whole of the sulphur in the solid form of a precipitate. This result was, of course, quite attainable if the liquor could be made to contain a quantity of hyposulphite of calcium in proportion to its sulphides, sufficient, on the addition of acid in slight excess, to bring about the reaction upon which Mond's process depends, that is, the complete precipitation of the sulphur.

Oxidation by means of a stream of air having in Mond's case when applied to moist vat waste brought about the result he desired, I proceeded to try the effect of passing a stream of air through the yellow liquor, but after continuing this experiment for a great many hours the desired end was not achieved. Moreover a considerable quantity of sulphuretted hydrogen was given off. This experiment was made with *cold* liquor and *cold* air.

I next proceeded to repeat the experiment, accompanying the stream of air with a jet of steam blown into the liquor, and I found that the liquor, being thus kept hot, had after several hours blowing and steaming assumed a condition which permitted the precipitation of its sulphur on addition of acid, without any evolution of sulphuretted hydrogen gas, and found too that the quantity of sulphuretted gas given off during the oxidation was so inappreciable as to be in no way offensive; and, as to the constitution of the liquor before and after blowing, I found that two corresponding portions, tested for precipitable sulphur at the beginning and the end of the operation, gave one-fifth more in the latter case than in the former.



Experiments made with known quantities of acid gave a yield of sulphur at the rate of one ton sulphur for less than 50 cwt. of acid at 28° Tw.

The operations having been removed to their present site, a powerful Körting's blower was introduced, and the mixing of the liquor and the acid is now effected, after about three hours' blowing of the liquor, without the slightest trace of sulphuretted hydrogen being liberated; in fact the only escape from the mixing vessel is of quite another character, consisting of a little sulphurous acid arising from decomposition of hyposulphite, in excess of what is necessary for the reaction. This formation of excess of hyposulphite (by overblowing) is, indeed, the chief thing to be guarded against in the process, being followed, as I find, by the formation in the sulphur precipitate of an undue proportion of insoluble lime salts, one sample tested having contained as much as 13 per cent. of fixed residue. Ordinarily the proportion does not exceed 3, and has been as low as 0.75 per cent.

The batch, as soon as mixed, is run straight into wooden boxes lined with canvas, in which the sulphur is deposited, the chloride of calcium liquor draining off, and then passing through a tank containing crushed limestone, by which any free acid is neutralised, and thence into the canal.

I ought to mention that Messrs. Chance are making the only complete trials of Messrs. Helbig and Schaffner's process that I know of. The production of the sulphuretted hydrogen and its combustion are a complete success. As to the rest, I have not full results to record.

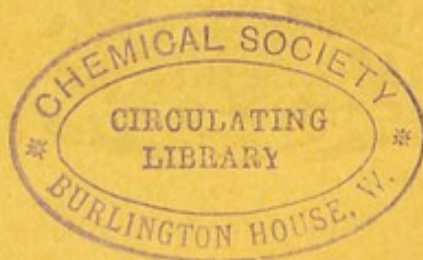
### *Supply of Sulphur.*

I have in this report and on a former occasion spoken of digging deep wells in the mounds at St. Helens, and causing all the yellow drainage to run into them instead of into the rivers. I find that Messrs. Chance are treating a mound close to their works at Oldbury in this manner, and removing the sulphur from the yellow liquid obtained. This is the true method of relieving the streams, and preventing the evil arising from old waste heaps. New waste heaps may be treated much more effectually.

After considering all the methods now known, I see no reason why a very large amount of sulphur, which is wealth and power, ought not to be saved to the country. Enormous quantities of waste are thrown away daily. It is difficult to find room for the great masses, which are unsightly and for a long time unpleasant. They destroy land and every pleasant property of air, water, and landscape, besides causing illness in many cases. So useless is this matter held that it is taken out in steamboats built for the purpose, or dragged out in barges down the Tyne, to the ocean, where it is thrown out. The great sea does not allow us to observe the movements of the waste, but we do not know



if such a finely divided mass may not be easily driven on some part of the shore, affecting the harbour. At any rate it is an outcast product, and its 15 per cent. of sulphur is thrown away. We may say that all the sulphur used on the Tyne is thrown into the sea after it has done its first work, heedless of the fact that it cannot be destroyed, and is quite willing to do the same work again if it is only brought back to its original condition, or rescued from its bondage. This rescue certainly promises, and more than that it makes, profit.



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