PART II.

EFFLUENTS FROM PRINTWORKS, DYEWORKS, &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.
2·5 lbs. Lime }
Volatile = 4·9 gr. per gall.
Mineral = 65·94 „
Total = 70·84 „

The filtrate was slightly acid; colour = 0·1 c. c. NH_4Cl with Nessler. No permanent froth on shaking.

(2.) After filtration,—
8 lbs. Alum } per 1,000 galls.
2·5 lbs. Lime }
Volatile = 5·67 gr. per gall.
Mineral = 57·33 „
Total = 63·00 „

The filtrate was faintly alkaline; colour = 0·4 c. c. NH_4Cl with Nessler. No permanent froth on shaking.

(3.) After filtration,—
4 lbs. Alum } per 1,000 galls.
2·5 lbs. Lime }

The filtrate decidedly coloured. Permanent froth on shaking.

Sample received 29th April 1878.

(4.) After filtration,—
10 lbs. Alum } per 1,000 galls.
2·5 lbs. Lime }
Volatile = 0·28 gr. per gall.
Mineral = 76·16 „
Total = 76·44 „

Similar to No. 1.

(5.) After filtration,—
8 lbs. Alum } per 1,000 galls.
2·5 lbs. Lime }
Volatile = 11·48 gr. per gall.
Mineral = 77·55 „
Total = 89·04 „

Similar to No. 2 as to froth. Filtrate slightly coloured.

(6.) After filtration,—
6 lbs. Alum } per 1,000 galls.
2·5 lbs. Lime }

Filtrate decidedly coloured. Froth lingered slightly.

Sample received 19th April 1878.

(7.)	After filtration,— 2·5 lbs. $Fe_2(SO_4)_3$, persulphate of iron. Lime quant. suff.	The lime was added immediately after the iron sol. Filtrate slightly coloured.
(8.)	After filtration,— 1·25 lbs. $Fe_2(SO_4)_3$ Lime quant. suff.	The lime was added five minutes after the iron sol. Filtrate was colourless.
(9.)	After filtration,— 0·7 lb. $Fe_2(SO_4)_3$ 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, 7·5 lbs. Lime per 1,000 galls.	Colour almost gone.
(2.)	20 lbs. Alum Cake, 1·5 lb. Lime per 1,000 galls.	97 °/o colour removed.
(3.)	10 lbs. Alum Cake, 0·76 lb. Lime per 1,000 galls.	95 °/o colour removed.
(4.)	6 lbs. Alum Cake, 0·76 lb. Lime per 1,000 galls.	90 °/o colour removed.
(5.)	4·74 lbs. Ferric Chloride, 6·00 lbs. Lime per 1,000 galls.	99·8 °/o colour removed.
(6.)	2·16 lbs. Ferric Chloride, 4·56 lbs. Lime per 1,000 galls.	98 °/o colour removed.
(7.)	0·66 lb. Ferric Chloride, 2·28 lbs. Lime per 1,000 galls.	70 °/o colour removed.

NOTE.—There was a little free HCl along with the Fe_2Cl_6, ferric chloride or perchloride of iron.

(8.)	18·5 lbs. hydrated alumina per 1,000 galls.	60 °/o colour removed.
(9.)	4·12 lbs. Fe_2Cl_6, 12·5 lbs. HCl, 5·0 lbs. Lime per 1,000 galls.	Colour destroyed. The ppt. settles rapidly and perfectly.
(10.)	2·1 lbs. Fe_2Cl_6, 6·25 lbs. HCl, 2·5 lbs. Lime per 1,000 galls.	Colour destroyed. The ppt. settles rapidly and perfectly.
(11.)	1·25 lbs. Fe_2Cl_6, 2 lbs. Lime, 3·75 HCl per 1,000 galls.	Filtrate faintly coloured. Ppt. settled fairly, but left a turbidity in the liquid, which, however, was readily removed by filtration.
(12.)	0·85 lbs. Fe_2Cl_6, 2·5 lbs. HCl, 1·5 lbs. Lime	The ppt. behaved as in No. 11, but the filtrate was distinctly coloured.
(13.)	200 lbs. $CaCl_2$, chloride of calcium, per 1,000 galls.	removed 60 °/o 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, 0·5 lbs. Lime per 1,000 galls.	66 °/o colour removed.
(*b.*)	8 lbs. Ferrous Sulphate per 1,000 galls.	39·3 °/o colour removed.
(*c.*)	12 lbs. Ferrous Sulphate, 0·5 lb. Lime per 1,000 galls.	84·5 °/o colour removed.
(*d.*)	12 lbs. Ferrous Sulphate per 1,000 galls.	78·7 °/o colour removed.
(*e.*)	2·6 lbs. Fl_2Cl_6, (?) Lime per 1,000 galls.	89·4 °/o colour removed.
(*f.*)	8 lbs. Alum, 0·5 lb. Lime per 1,000 galls.	71 °/o colour removed.
(*g.*)	8 lbs. Alum per 1,000 galls.	72·5 °/o colour removed.
(*h.*)	6·5 lbs. Fe_2Cl_6, 5·6 lbs. Lime per 1,000 galls.	95·6 °/o colour removed.
(*i.*)	No. (*h*) with 8 lbs. Copperas per 1,000 galls.	98·9 °/o colour removed.

The ferrous salt was added to destroy the chromate which was left by the ferric salt.

(*j.*)	3·7 lbs. Fe_2Cl_6, 8·0 lbs. Copperas, 2·75 lbs. Lime per 1,000 galls.	96·5 °/o colour removed.
(*k.*)	3·7 lbs. Fe_2Cl_6, 20 lbs. Copperas, 2·75 lbs. Lime per 1,000 galls.	97 °/o colour removed.
(*l.*)	7·4 lbs. Fe_2Cl_6, 4·0 lbs. Copperas, 5·5 lbs. Lime per 1,000 galls.	96·5 °/o colour removed.
(*m.*)	3·7 lbs. Fe_2Cl_6, 2·75 lbs. Lime per 1,000 galls.	92 °/o colour removed.

(*n.*) No. (*m*) with 8 lbs. $FeSO_4 . 7 H_2O$ 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 °/o 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. $CaCl_2$, 1·5 lbs. Fe_2Cl_6, 11·0 lbs. SO_3 per 1,000 galls. (neutral iron sol.)	Filters slowly. Filtrate coloured blue.
(*q.*)	5 lbs. $CaCl_2$, 1·5 lbs. Fe_2Cl_6 per 1,000 galls. (neutral iron sol.)	Similar to (*p.*)

(*r.*)	5 lbs. $CaCl_2$ 1·5 lbs. Fe_2Cl_6 with 3·0 lbs. HCl (Acid solution of iron.) } per 1,000 galls.	Filters clear. Filtrate slightly yellow.
(*s.*)	5 lbs. $CaCl_2$ 1·5 lbs. Fe_2Cl_6 2·0 lbs. HCl } per 1,000 galls. (neutral iron sol.)	Filtrate blue and turbid.
(*t.*)	5 lbs. $CaCl_2$ 1·5 lbs. Fe_2Cl_6 3·0 lbs. HCl } per 1,000 galls. (neutral iron sol.)	Filtrate coloured; not very clear.
(*u.*)	5 lbs. $CaCl_2$ 3 lbs. HCl } per 1,000 galls.	
	To the filtrate from the foregoing— 2 lbs. Fe_2Cl_6 (neutral) per 1,000 galls. ? Lime (till faintly alkaline).	The filtrate from the iron was good.
(*v.*)	5 lbs. $CaCl_2$ 4 lbs. SO_3, sulphuric acid calculated as anhydride. } per 1,000 galls.	Filtrate slightly alkaline.
(*w.*)	5 lbs. $CaCl_2$ 20 lbs. SO_3 } per 1,000 galls.	Filtrate slightly turbid.

Mixture of polluted liquids from Woollen Mills.

20 lbs. sulph. acid 4·12 lbs. Fe_2Cl_6 12 lbs. CaO	per 1,000 galls.	Filtrate colourless.
20 lbs. sulph. acid 0·82 lb. Fe_2Cl_6 5·0 lbs. CaO	per 1,000 galls.	Filtrate colourless.
lbs .O. V. 0·41 lb. Fe_2Cl_6 4·0 lbs. CaO	per 1,000 galls.	Filtrate slightly coloured.
5 lbs. $CaCl_2$ 8¼ lbs. Fe_2Cl_6 CaO	per 1,000 galls.	Colourless.
2·5 lbs. $CaCl_2$ 2·1 lbs. Fe_2Cl_6 6·6 lbs. HCl ? CaO	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_2O_3 per 1,000 galls.	Equivalent of Fe_2O_3.	% of Colour removed.	Lbs. Chemicals per 1,000 galls.	Fe_2O_3 per 1,000 galls.	Equivalent of Al_2O_3.	% of Colour removed.
17·5 lbs. cake	Lbs. 2·4	Lbs. 3·8	—	10 lbs. ferric chloride	Lbs. 3·8	Lbs. 2·4	
4·6 lbs. lime	—	—	99	4 lbs. lime	—		98·4
10 lbs. cake	1·4	2·17	—	5 lbs. ferric chloride	1·9	1·225	—
2·3 lbs. lime	—	—	95·8	2·6 lbs. lime	—	—	84·0
5 lbs. cake	0·7	1·085	—	3 lbs. ferric chloride	1·14	0·735	—
2 lbs. lime	—	—	88	1·6 lbs. lime	—	—	75·6
4 lbs. cake	0·56	0·868	—				
3·5 lbs. lime	—	—	82				
3 lbs. cake	0·42	0·651	—				
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_2, BaS, CaS, and H_2O_2.

BaO_2 gave the best result; then came BaS, soda waste, H_2O_2 and CaS. This arrangement is according to the immediate effect. The H_2O_2 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
	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 incandesence if care were not taken to turn over the heap during the interval. In this manner the temperature rarely exceeds 90° (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° (C) into polysulphide and sulphate.

After this first lixivation 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
	99·85

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 oxidées).

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
	100

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 binoxide, 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 binoxide 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° to 14° 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 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
	£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
					157 06
Off Sulphate of Soda - -	39	0	21	49/	96·01
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*l.* 10*s.*	7*l.* 0*s.*	1*l.* 10*s.*
Sulphur - -	3*l.* 5*s.*	6*l.* 10*s.*	3*l.* 5*s.*

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° to 8° 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 1½ 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 3¼ 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 ½ 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 ⅔ 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 ⅓ 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 8½° Twaddell.

Containing:—		Lbs.
Sulphur as hyposulphite of lime	-	1·015
„ sulphate of lime -	-	·712
„ sulphides of calcium	-	53·569
Total sulphur	-	55·296

Manganese used 10 lbs., containing 68 per cent. MnO_2 (Dunlop's recovered black oxide).

Oxidized liquors:—

421·8 gallons of 4½° Twaddell.

(The specific gravity varied from 1° in the beginning to 6½° at the end of the whole experiment.)

Containing:—		Lbs.
Sulphur as hyposulphite, CaS_2O_3	-	34·377
„ sulphite, $CaSO_3$ -	-	1·350
„ sulphate, $CaSO_4$ -	-	·506
Total sulphur	-	36·233

No Sulphide.

Precipitate :—

It weighed wet 52 lbs., and contained :—

		Lbs.
Sulphur as sulphate $CaSO_4$ - -		1·235
„ sulphide MnS - -		1·940
„ free sulphur - -		15·140
		18·315
		Lbs.
Total sulphur started with - -		55·296
„ at finish of experiment in solution	Lbs. 36·233	
„ at finish of experiment in precipitate	18·315	
		54·518

0·648 lbs. lost.

This loss occurs by evolution of H_2S, 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°/₀
In precipitate - -	33·18
Lost - - - -	1·17°/₀
	100·00

In the precipitate there exists—

As available sulphur, say for melting out for sale - - -	27·3°/₀
As sulphide - - -	3·64°/₀

Lime :—

The lime CaO in the yellow liquor was equal to 43·9 lbs. CaO, and the CaO in oxidized liquor amounted to 37·2 lbs. The difference = 6·7 lbs. 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. CaO = 15·26 per cent. of the CaO in original liquor. Say that the lime equals two equivalents of sulphur $\frac{6{\cdot}7 \times 32}{28} = 7{\cdot}66$ lbs. sulphur. Then, as total sulphur precipitated was equal to 18·315 lbs., and the sulphur equal to loss of CaO in liquor was equal to 7·66 lbs., we have $\frac{7{\cdot}66 \text{ lbs.} \times 100}{18{\cdot}315 \text{ lbs.}} = 41{\cdot}8$ 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 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.)

MnO, protoxide of manganese, added to the solution without air, the CaS_2 is not decomposed.

If MnO_2 or any oxide above 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 H_2S 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.

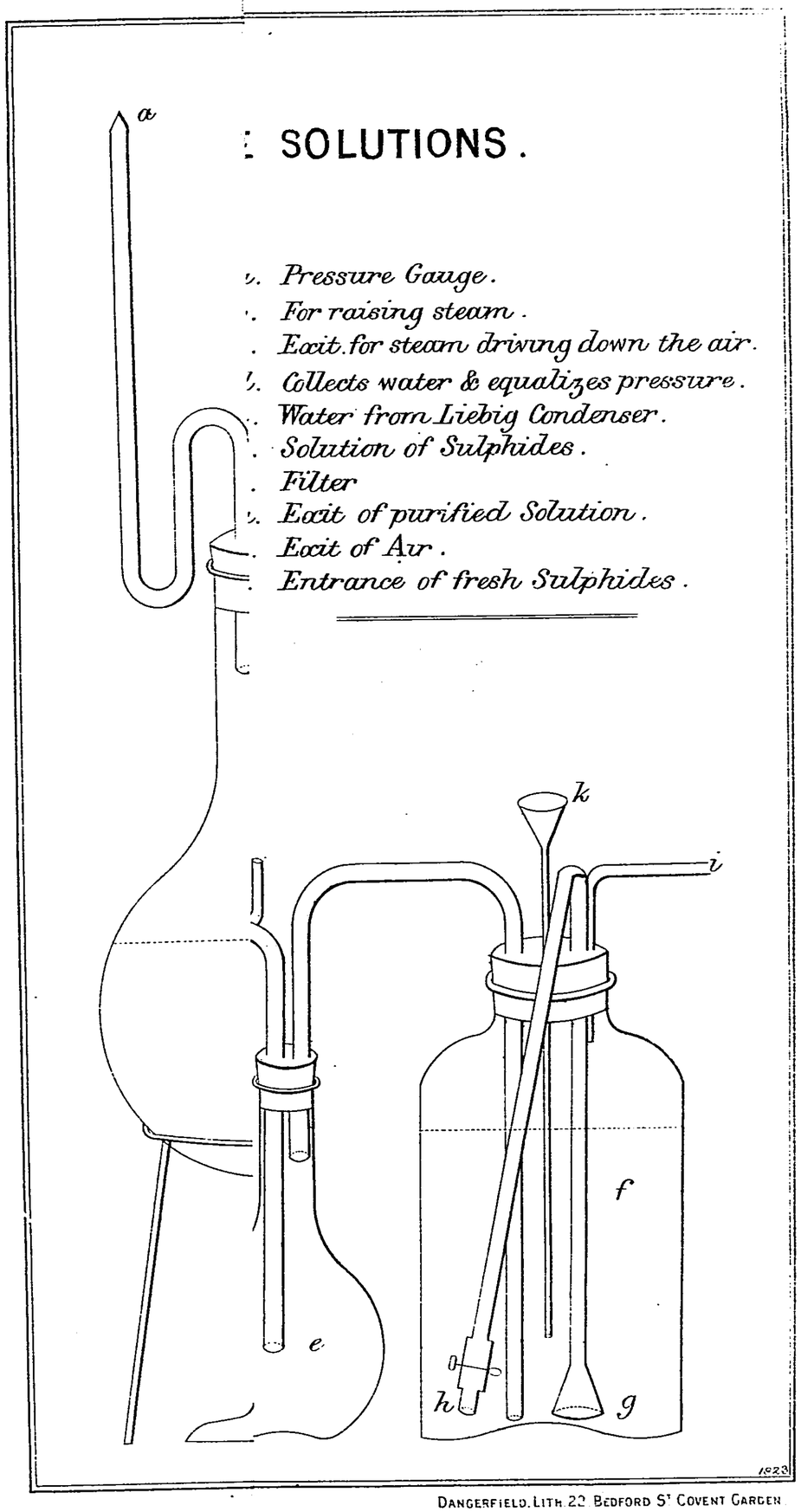
He also spoke of applying the process to the oxidizing of manganese in the Weldon process, and in oxidizing sulphur liquors in soda works, a purpose also laid down in my report.

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."

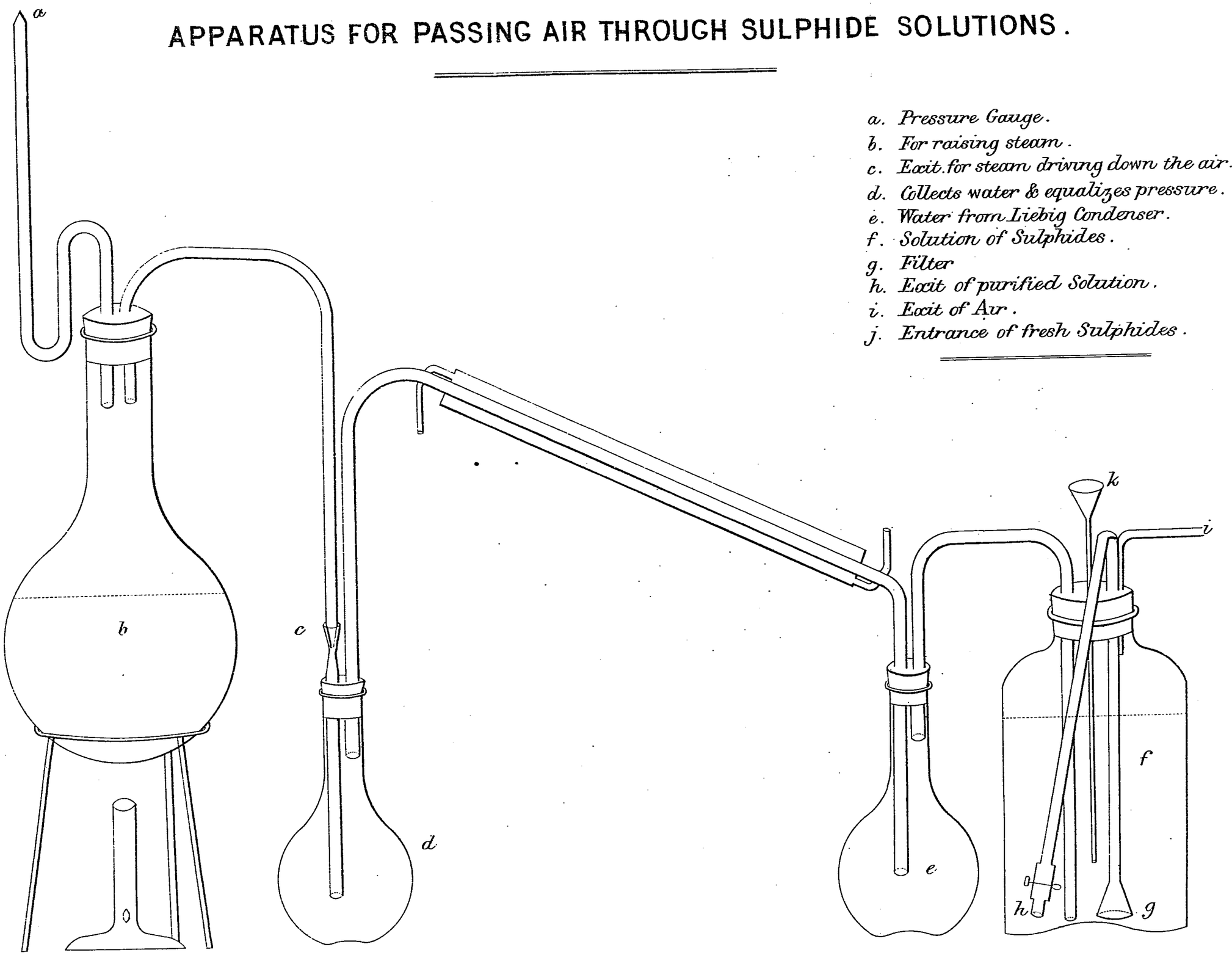
Complete recovery of Sulphur and Lime from Tank-waste.

"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



DANGERFIELD. LITH. 22 BEDFORD ST COVENT GARDEN

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.

1923

DANGERFIELD, LITH. 22, BEDFORD ST COVENT GARDEN.

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:—

$$\text{"I. } CaS + MgCl_2 + H_2O = CaCl_2 + MgO + H_2S$$

(calcium carbonate not being acted upon by $MgCl_2$).

"(*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 H_2S to the action of carbonic acid, by which calcium carbonate and magnesium chloride are formed, thus:—

$$\text{"II. } MgO + CaCl_2 + CO_2 = MgCl_2 + CaCO_3.$$

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 $CaCl_2$ liquor is drawn off. Of course the action of CO_2 can only recover as much $CaCO_3$ as corresponds to the $MgCl_2$ employed.

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

$$\text{"III. } 2H_2S + SO_2 = S_3 + {}_2H_2O.$$

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 H_2S and 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 $CaCl_2$ or $MgCl_2$ equivalent to the total sulphur is required.

"The greatest impediment to the application of the mutual decomposition of H_2S and 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 $MgCl_2$ 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 $MgCl_2$, or, inversely, the $MgCl_2$ 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 H_2S 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 SO_2 in the decomposers over and above that corresponding to the arriving H_2S, 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.

APPENDIX.

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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REPORT

TO

THE LOCAL GOVERNMENT BOARD

BY

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

ONE OF THE INSPECTORS UNDER THE ACT.

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

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