

The CHAIRMAN, in reply, said the opinions expressed by Dr. Hewitt and Mr. Reynolds were quite in accord with his own. With regard to the pollution of rivers, he did not wish to set up any defence on behalf of chemical manufacturers, as they were bound to do all they possibly could to prevent the pollution of streams.

THE RECOVERY OF BY-PRODUCTS FROM COKE OVENS.

BY CHARLES DREYFUS, PH.D.

WITHIN the last twelve or eighteen months there has been a gradual fall in the prices of tar products, and specially of those used in the colour industry, such as benzenes and anthracene.

	Prices.			
	90s Benzene.	50s. Benzene.	Anthracene.	Sulphate.
1891.	s. d.	s. d.	s. d.	£ s. d.
January	4 8	3 6	1 4	10 10 0
December	3 0	2 0	1 2	10 5 0
1892.				
January	2 0	1 8	1 0	10 10 0
July	1 8	1 3½	0 9	10 0 0
September	1 7½	1 3½	0 9	10 0 0
November 1st	1 6½	1 3½	0 9	10 0 0

Most people in this country have been at a loss to account for this shrinkage in values, and various causes have been given as the reasons for it; our old friend, depression in trade, and bad trade in the foreign colour works have been trotted out by even responsible people; but the real reason of such depression—namely, a larger production—has been overlooked. It is to give the real reasons of this great shrinkage in values that I have prepared this paper, and in order that I may not be accused of over-stating the case, I will give you the sources from which my information is drawn: the principal sources of my information are the papers published by my friend Mr. Fritz W. Lürmann, engineer, of Osnabrück, in *Stahl und Eisen*, 4, 1892, and 18, 1892; also a pamphlet published by Mr. Ch. Demanet, C.E., manager of the Havré Colliery, near Mons, and which I owe to the kindness of Messrs. Semet-Solvay, and finally, private information obtained from friends in England and abroad, and which I have the right to use here to-night by permission of such friends.

The real reason of the depression in prices of benzene and anthracene is the large production of tar from the coke ovens abroad, the production of large quantities of benzene from such tar, and more especially from the gas of such coke ovens, and though England has been up to now the greatest producer and exporter of Benzenes and Anthracene, in the future I fear this will not be the case unless the English coke oven proprietors follow the example set to them by their colleagues abroad, and carbonise the whole or part of the "15,000,000 tons* of coal annually coked for the use of our ironworks" in ovens specially constructed for the recovery of the valuable by-products: tar, benzene, and ammonia.

HISTORICAL: PART.—I.

"More than one hundred years ago 'Stauf,' called the 'Kohlenphilosoph,' made a successful attempt to recover

the tar formed in the coking of coal." The ironmasters, engineers, and chemists all over the world have given much time and great attention to the question of coke-oven progress, with special regard to obtain by-products, and their experimental work in this direction extends back 35 years (this Journal, 1884, 601—606; also 1835, 451—452.) "Appolt, Semet, Coppée, and others have constructed ovens which have been for 30 years in very general use in Germany, Belgium, and France, whilst in Great Britain nothing seemed to shake the belief of iron-smelters in the infallibility of the bee-hive ovens. But even on the Continent it was thought that any attempt at condensing tar and ammonia must necessarily be fatal to the quality of the coke. Only quite recently has this belief been thoroughly shaken."

Thus, said Lange, in his second edition of "Coal Tar and Ammonia," edition of 1887, and I can only add my testimony to his, that the coke produced in the ovens where by-products are recovered is now declared to be equal in quality to the coke from bee-hive ovens.

The French first, and the Germans afterwards, took up this question, and it has made slow but sure progress with them. The plant for the recovery of tar, benzenes, and sulphate of ammonia is not simple, and requires the greatest attention. The fear was entertained that by the introduction of these methods the coalowners would have to add chemical works to their mines; this plant increases considerably the primary cost of the coke ovens; then again, the coal-mine owners did not know what a ready market existed for the disposal of the by-products. The value of the recovery of the by-products has become clearer and clearer within the last 10 years, and the greatest praises are due to Mr. Hüssener and Dr. Otto for their efforts in that direction. This latter gentleman has erected, for account of his own firm, as well as for others, a great number of Hoffmann-Otto ovens. These ovens are now at work over seven years, and the installation is so carefully planned that they give everywhere the greatest satisfaction.

II.—PROGRESS MADE IN THE ERECTION OF SUCH OVENS.

The Hoffmann-Otto coke ovens exist now in the greatest number in Germany; they are the ovens worked in connection with Siemens regenerators. The following figures will show how this extension has taken place:—

	Ovens at Work.	Ovens in Construction.
1884	40	120
1885	210	140
1889	605	..
1892	1,205	..

Of these 1,205 ovens there are at work:—

	Ovens.
1. In the Ruhr district	470
2. In Upper Silesia	705
3. In the Saar district	30
	1,205

The firm of Dr. C. Otto and Co., of Dahlhausen, undertakes the construction of a group of 60 Hoffmann-Otto ovens with the necessary machinery and appliances for the recovery of the by-products (of which steam engines, gas exhausters, ventilators, and pumps are in duplicate) for the sum of 700,000 marks (about 36,000*l.*), of which about 15,000*l.* are for the ovens themselves, and 21,000*l.* for the condensation plant of by-products.

One Hoffmann-Otto oven can be charged with 6½ tons of coal, and requires 48 hours to work off; therefore in one

* See Lecture by Sir Lowthian Bell delivered at the Autumn meeting of the Iron and Steel Institute this year.

year the following amount of coal is coked, and by-products recovered :—

—	One Hoffmann-Otto Oven.	A Group of 60 Ovens.
1. In the Ruhr district	Tons, 1,125	Tons, 67,500
2. In Upper Silesia.....	1,170	70,200
3. In the Saar district	960	57,600

The yield from the dry coal is :—

—	Coke.	Tar.	Sulphate of Ammonia.
1. In the Ruhr district	Per Cent. 75-77	Per Cent. 2-3-3	Per Cent. 1-1-1-2
2. In Upper Silesia.....	65-70	4-4-5	1-0-1-15
3. In the Saar district.....	63-72	4-4-3	0-8-0-9

One ton of dry coal yields therefore an average of about 14½ cwt. of coke, 10 gallons of tar, and 25 lb. of sulphate of ammonia.

One Otto oven produces, therefore, per annum an average of 820 tons of coke, 44 tons of tar, and 13½ tons sulphate of ammonia.

The production, use, and surplus gas is per day and per oven :—

—	Production.	Use.	Surplus.
1. In the Ruhr district.....	Cub. M. 1,000	Cub. M. 600	Cub. M. 400
2. In Upper Silesia.....	1,150	650	500
3. In the Saar district.....	1,000	600	400

It is reckoned that every 100 cubic metres of this surplus gas replaces 87·5 kilos. (about 1½ cwt.) of coal in the heating of boilers. The saving in coal by the surplus gas for a group of 60 Hoffmann-Otto ovens is :—

—	Per Day.	Per Annum.
1. In the Ruhr district.....	Tons, 21	Tons, 7,560
2. In Upper Silesia.....	26½	9,458
3. In the Saar district.....	21	7,569

Of this surplus must be deducted one-third for use by the condensing plant.

II.—SEMET-SOLVAY COKE OVENS.

I come now to another system of coke ovens, which are in use in Belgium, in France, in Germany, and in one works only in England.

The first ovens of this system were built in 1882 by Mr. Semet, at the Bellevue Pit, No. 2, belonging to the Ouest Mons Colliery Co., with a small set of six ovens, which were worked on trial for about one year. Since then the experiments have been carried out by the Solvay Co., with a set of 25 ovens erected close to the Havre Colliery. Finally, the Bois du Luc Co. have taken up on their own account the working of this plant, which has now been greatly enlarged; the Semet-Solvay system has thus entered definitely into industrial practice. The following are the ovens at work of this system :—

103 ovens at	Havré, near Mons.
26 "	Seraing (Société John Cockerill).
25 "	Ghlin (Société des Charbonnages du Nord du Fleury).
24 "	Ruhrort (Société Phoenix).
39 "	Northwich (Britannia, Mond, and Co.)
205 ovens.	

There are in construction this year the following ovens of this system :—

50 ovens at	Drocourt (at Henin Liétard, France).
15 "	Syracuse (Solvay Process Co.).
24 "	Ruhrort (Société Phoenix).
20 "	Seraing (Société John Cockerill).
25 "	Jemeppe, near Liège (Charbonnages des Kessales).
140 ovens.	

From the fact that the Phoenix Co. and the Société John Cockerill are erecting a second set of these ovens, I would conclude that the system gives full satisfaction. The construction of the Semet-Solvay ovens permits of a stronger formation of the covering masonry, a very high temperature can be attained, and good coke can be obtained from poor coal.

The cost of the oven itself, with fittings, steam ram, rails for the same, &c., can be estimated at 160*l.* per oven. This figure is not high, considering the large production of coke, which amounts to 100 tons per month per oven. To this estimate must be added the cost of the apparatus for the recovery of the by-products, which is about 100*l.* per oven. Each oven takes a charge of 4 tons of coal, and the coking is finished in 22 hours; the yield of coke is a maximum, and corresponds to the theoretical yield owing to the air tightness of the ovens.

At the Havré works, with coal containing 16 to 17 per cent. of volatile matter, the yield of coke averages 81 per cent.; in this figure are not included small coke and breeze. The coke is absolutely the same as that produced in ovens of the ordinary type; the by-products vary in quantity, according to the nature of the coal used. At Havré, where poor coal is used, the average yields are :—sulphate of ammonia, 13½ lb. per ton of coal used, and 31 lb. of tar. Through the kindness of Mr. Mond, Mr. Gustav Jarmay, managing director of the Northwich works, has communicated to me the following figures of the average yield of by-products obtained in the Semet-Solvay ovens in use at Northwich :—"For the last half-year we have recovered ammonia equal to 12 kilos. (27 lb.) sulphate per ton of coal, and 40 kilos. (88 lb.) of tar per ton. Our ovens are the oldest type of Semet-Solvay, and at present are out of repair, as we intend to replace them by the new type of Semet-Solvay ovens, and we quite expect that the yield of ammonia and tar will be better after the alterations."

III.—EXTRACTION OF BENZENE FROM THE GAS OF COKE OVENS.

It is now about three years ago, that besides tar and ammonia, benzole was directly recovered from the gas of these ovens. The plant for this process has been devised by Mr. Frank Brunk, C.E., of Dortmund. The process is kept a secret, but my friend, Mr. George E. Davis, and others who have studied this question years ago, will know probably what that secret consists of. So much, however, is known that between 3 kilos. (7 lb.) and 7 kilos. (16 lb.) of 90 per cent. benzene are recovered from the gas of one ton of coal coked. The quantity varies, of course, according to the nature of the coal; these figures offer nothing abnormal when it is known that 12½ kilos. (27½ lb.) of 90s benzene can easily be obtained from the gas of one ton of good coal, distilled in an ordinary gasworks retort. (See *Lunge*, page 31.)

It is stated that the cost of erecting the benzene recovery plant is 250*l.* per oven (the Brunk system). Taking the present coke ovens as 1,205 (I have been informed there are now 1,350 Hoffmann-Otto ovens at work in Germany only, and that more are in course of construction). The quantity of coal these 1,205 ovens

can coke per annum is 1,382,400 tons: taking only the minimum yield of 3 kilos. of benzene per ton of coal, the yield in benzene, from the gas alone, would be 4,147,200 kilos., or over 1,000,000 gallons. I do not think there is quite as much as this quantity produced in Germany from coke ovens as yet; all the ovens not being arranged to recover the benzene from the gas, but I believe if we take Belgium and Germany together, there is not less than 1,000,000 gallons of benzene, and principally 90s quality, produced at present already from coke ovens alone; there is no doubt that this production of by-products is on the increase, because the Semet-Solvay system of ovens can be put down at a moderate figure, including the recovery of all by-products, tar, ammonia, and the extraction of the benzene from the gas. The cost of an oven, including all, would be about 260*l.*; the by-products, after deducting supplementary costs, yield 72*l.* per annum as net profit (this does not include the extra profit from the extraction of the benzene from the gas).

The recovery of by-products is not only of importance to the tar and colour industries, but it is of enormous value to agriculture. If we take into consideration the great profits realised in this industry (notwithstanding the lower prices now ruling), and which on tar and ammonia alone are over 40 per cent. on the cost of the plant, as we will show later on: if we add to this the profits on the benzene from the gas, we come to the conclusion that this recovery of by-products from coke ovens must go on increasingly. The demand for sulphate of ammonia and for tar is such that all the coke ovens in Germany, and even in England, if they were to recover their products, would find a ready sale for them. The actual daily consumption of pitch in Westphalia alone is 150 tons, which would take already the tar of 3,000 ovens.

Sulphate of ammonia is a valuable manure; in Germany the consumption of nitrogen containing manures has been as follows:—

—	1887.	1888.	1889.	1890.
Sulphate of ammonia . . .	Tons, 33,805	Tons, 35,561	Tons, 33,535	Tons, 33,788
Nitrate of soda	101,610	250,182	320,820	330,346
Guano	71,880	68,261	51,062	46,144

If all the nitrogen in the above manures could be replaced by sulphate of ammonia it would mean that 285,000 tons of sulphate of ammonia would be required. The total quantity of sulphate of ammonia produced till now per annum from coke ovens is only 17,500 tons, and if all existing ovens in Germany were to recover by-products, the total annual production of sulphate of ammonia would only be 120,000 tons.

If we take the price of tar at 10*s.* per ton; of sulphate of ammonia at 10*s.* per cwt.; then the yearly income from a group of 60 Otto ovens would be:—

—	For Tar.	For Sulphate.	Total.
1. In the Ruhr district.	£ 930	£ 7,800	£ 8,730
2. In Upper Silesia . . .	1,500	8,100	9,600
3. In the Saar district .	1,200	4,920	6,120

This would give for one Otto oven a gross income of:—

1. In the Ruhr district	£ 145
2. In Upper Silesia	165
3. In the Saar district	102

From the above have to be deducted general expenses and sulphuric acid used for sulphate making, which are estimated at 50*l.* per oven, leaving therefore a net profit of over 100*l.* for by-products per oven, not including benzene.

There existed in 1892 in Germany, 16,047 coke ovens, of which 15,726 were at work; there are, therefore, at present barely 10 per cent. fitted up for the recovery of

by-products. It is estimated that the production of coke in Germany was, in 1891, 7,700,000 tons; if the whole of this coke had been produced in ovens fitted up for the recovery of by-products, Mr. Lürmann estimates the net profit from tar and ammonia alone (without taking into account either the benzene or the extra gas useful for other heating purposes) at 1,440,000*l.*

I would put the matter in a different way to prove how profitable this industry would be to this country. The best coke ovens without recovery of by-products give 60 tons of coke per month, according to information which I consider reliable. Suppose that the construction of such an oven costs 80*l.*; therefore the capital required for putting up ordinary ovens producing 100 tons of coke per month, would be, without recovery of by-products, 133*l.* 6*s.* 5*d.* for the Semet-Solvay oven, with recovery of by-products, the cost is 260*l.* for 100 tons coke produced per month, 126*l.* 13*s.* 7*d.* more capital is expended; these 100 tons of coke yield in by-products, after deducting supplementary cost, 6*l.* per month, or 72*l.* per annum, which is 57 per cent. of the additional capital spent for the same production. If to this we were to add the extra available gas of which one-half is sufficient for heating the ovens, and the benzene contained in the gas which can be extracted at very small cost, then these figures would come out still more favourably.

These figures apply to the poor coal used at Havré; in England, where better coal is available, better results are obtained, which can be tabulated as follows:—

—	Sulphate of Ammonia.	Tar.
Per ton of coal in England	Lb. 27	Lb. 88
" " Belgium	13½	81

The available gas in England would be larger also than in Belgium, our coal being so much richer in volatile matter.

Let us suppose that the 15,000,000 tons of coal which are coked per annum in England were treated in ovens of the Semet-Solvay type for recovery of by-products, we should obtain sulphate of ammonia, 180,000 tons, and in tar, 130,000,000 gallons; we should have surplus gas available, equivalent to one-fifth of the total coal consumed, and benzene from gas in such quantity that I fear to mention the figure.

The Board of Trade returns for 1890 (the last issued), give the quantity of coal used for gas making as 10,242,317 tons. This applies to authorised companies, but as there still are a large number of others, it is probable that the above total would reach 11,000,000 tons. If instead of the present system of working, gas were produced for sale by Semet-Solvay ovens, the coke could be used for metallurgical purposes, and the gas could be produced much cheaper than at present. If, finally, all the coal used in factories, works, and houses for heating purposes, and for the production of power, were coked, the gas and the coke produced would be available for heating and lighting purposes; we would do away with fogs and smoky towns, and the cost would be less than at present. I throw these suggestions out and they merit the consideration of all thinking men whether politicians, sanitarians, engineers, chemists, or manufacturers.

If we in England, using annually such an enormous amount of coal, were to recover the by-products, our profits would be great, our agriculture and industry would greatly benefit by the progress, and our towns would have a bright and clear atmosphere, where it would be a pleasure to live, and I hope the time will come when this progress which I foresee will be an accomplished fact.

Newcastle Section.

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Dr. J. T. Dunn, The School, Gateshead.

SESSION 1892-93.

Notices of Papers and Communications for the Meetings to be sent to the Local Secretary.

Meeting held in the Durham College of Science,
Newcastle, on Thursday, November 10th, 1892.

MR. ALFRED ALLHUSEN IN THE CHAIR.

Professor BEDSON made an informal communication, giving an account of some work undertaken by Mr. W. McConnell and himself on the gases enclosed in coal and coal-dust. The coal broken up into small pieces, and enclosed in an exhausted vessel, was heated to 100° C. for over 100 hours, and gave off gases amounting to 10 or 11 times its volume (about 300 cubic feet per ton), of which about one-sixth was marsh-gas. After this treatment the coal, crushed to dust, was similarly heated for 26 hours, and gave off more gas (nearly 20 cubic feet per ton), of which 18 per cent. consisted of marsh-gas and its homologues; analysis showed that members of the series at least as high as propane, C_3H_8 , were present. The experiments seem to show that the coal parts more easily with the lighter hydrocarbons than with the higher homologues.

ON THE PART PLAYED BY CALCIUM CHLORIDE IN THE WELDON PROCESS.

BY G. LUNGE.

THE late Walter Weldon knew very well that the presence of considerable quantities of calcium chloride is essential to the recovery of manganese peroxide by his celebrated process. No doubt a good many observations had been made on that point in various works with which he was in communication, and probably many others have been made since his time, but they seem to have remained buried in the works' note books, and never to have been utilised for deriving distinct quantitative rules therefrom. The only quantitative statement on the amount of calcium chloride required for the Weldon process which I know of is that which I have received from Mr. Schaffner, of Aussig, and which is found in my "Sulphuric Acid and Alkali," viz., that there ought to be from 2 to 2½ molecules of calcium chloride present for each molecule of $MnCl_2$. I thought it therefore advisable to investigate this question as far as possible, and this I have done with the assistance of Mr. B. Zahorsky. I shall now give a short description of our results.

The most natural explanation of the auxiliary part of calcium chloride is this, that it serves as a solvent for the

lime, which is so essential for the Weldon process. It is well known that lime is more soluble in hot chloride of calcium solution than in water, undoubtedly owing to the formation of an oxychloride. Crystallised calcium oxychloride has the formula $3CaO, CaCl_2, 15H_2O$, recently confirmed by Mr. Zahorsky, who found that no other crystallised oxychloride can be obtained. Quantitative statements on the solubility of lime in $CaCl_2$ solution have only once been published (by Post, in "Berichte," 1879, 1541), but they are extremely fragmentary, since only four observations were made, and the concentration of the solution was merely established by the hydrometer. We therefore commenced by making more complete observations on the solubility of CaO in $CaCl_2$ solutions of various strengths and at different temperatures, of which the following is a synopsis:—

SOLUBILITY of LIME in Solutions of Calcium Chloride (expressed in grammes of CaO per 100 cc. of $CaCl_2$ solution).

Liquid.	Temperature in Degrees C.				
	20°	40°	60°	80°	100°
Pure water.	0·1374	0·1162	0·1026	0·0815	0·0654
5 per cent. $CaCl_2$	0·1370	0·1160	0·1020	0·0806	0·0606
10 " "	0·1661	0·1419	0·1313	0·1328	0·1389
15 " "	0·1093	0·1781	0·1706	0·1796	0·1842
20 " "	0·1857*	0·2249	0·2204	0·2205	0·2325
25 " "	0·1661*	0·3020*	0·2989	0·3261	0·3714
30 " "	0·1636*	0·3684*	0·3634	0·4112	0·4922

In the cases marked with an asterisk a precipitate of calcium oxychloride was formed which removed some $CaCl_2$ from the solution.

We notice that the solubility of CaO in solutions containing up to 10 per cent. $CaCl_2$ at the ordinary or a slightly raised temperature does not differ very much from that in pure water, no doubt because no oxychloride is formed up to that point. At higher temperatures the presence of $CaCl_2$ increases the solubility of CaO , and this takes place proportionately with the quantity of $CaCl_2$, except where the phenomenon is complicated by a precipitation of solid oxychloride. Otherwise from 40° C. upwards the concentration of the solution has more effect than a rise of the temperature.

Apart from CaO , a solution of calcium chloride can also dissolve protoxide and peroxide of manganese, and we shall have to refer to this later on.

After this preliminary work it was our task to construct an apparatus in which the part played by calcium chloride in the Weldon process might be experimentally studied in the laboratory under conditions sufficiently resembling those of actual practice. That this is no easy task is best proved by the fact that Weldon himself did not succeed in getting any satisfactory results so long as he worked on a laboratory or even on a semi-grand scale; and it is also proved by the complete failure of Post to establish a process even remotely similar to that carried on on the large scale. The task was, however, successfully accomplished, as we shall see, by means of the resources of our technical laboratory, which has indeed been expressly constructed with a view to similar investigations.

We possess a blowing-engine driven by steam-power, with a network of pipes and taps for distributing the compressed air in the laboratory. With one of these taps I connected a circular iron vessel, from which three vertical glass tubes carried the air to the bottom of tall glass cylinders (40 cm. high) placed in a large common water-bath, heated to 55°—60° C. The ends of the glass tubes were provided with many small perforations in order to divide the stream of air into many bubbles, and at the same time to thoroughly stir the mass, just as in a Weldon oxidiser. As it was important