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DOCUMENTS

AIR POLLUTION BY COKING PLANTS

UNITED NATIONS

ECONOMIC COMMISSION FOR EUROPE

AIR POLLUTION BY COKING PLANTS

UNITED NATIONS
New York, 1968

Plate No.	With dust extractor	Without dust extractor
1	6.97	10.91
2	5.53	6.05
3	3.37	3.94
4	2.53	2.54
5	0.69	1.54
6	0.37	0.68
7	7.05	13.24
8	5.56	11.72
9	30.64	60.87
10	44.88	65.62
11	1.38	3.96
12	0.65	0.67
average:	9.13	15.14

The average dust-fall is of the order of 15 $g/m^2/h$ or 12.5 kg/h (0.3 t/d) for the whole workshop, i.e. about 2 kg/h per screen.

Withdrawal at bottom of coal tower

During coal withdrawal, a fairly substantial discharge of dust occurs; it varies very widely from plant to plant.

Charging

Earlier tests had given the following pollution figures for charging Becker ovens (15-ton chambers, four charging holes, two gas outlets): during the first thirty seconds of each charging operation, dust emission was 420 g; between the end of the first minute and the end of the third half-minute, 410 g; and between the end of the second minute and the end of the fifth half-minute, 180 g.

It is estimated that, from the beginning to the end of the 10-minute charging process, 300 to 600 N m^3/h of gas escapes; if the operation is repeated four times an hour, the average discharge per hour is $\frac{450 \times 10 \times 4}{60}$ = about 300 N m^3/h.

The average pollutant content is as follows:

CO	= 7% by volume;
H_2	= 50% " " ;
CH_4	= 30% " " ;
C_nH_m	= 5% " " ;
Tar (in the vesicular state)	= 100 - 150 g/N m^3
Coal particles	= about 250 g/N m^3.

The average discharge of dust per hour is therefore of the order of 70 kg. It may be much greater where charging is performed dry. The tar discharge would be about half.

One iron and steel works coking plant has carried out a test comprising measurements of air pollution by dust during charging. Such a test, which is difficult to organize and interpret, can show an approximate order of magnitude of pollution in a particular case.

Before oven 36 was charged, ten plates (numbered 1 - 10) were placed in position.

Charging took two minutes; the following weights of dust were deposited on the DIEM plates:

No. of plate	Weight of dust (g)
1	2.55
2	1.89
3	0.62
4	16.13
5	6.59 (plate burnt)
6	19.56
7	2.70
8	44.71
9	10.16
10	7.93
TOTAL	112.84 g

Each plate had a surface area of 10 x 5 = 50 cm^2. Assuming that the plates were arranged in representative fashion, the test would give, for the five-oven battery's surface area alone, i.e. 75 m^2, a pollution of $\frac{113 \times 75}{10 \times 0.0050 \times 1000} = 170$ kg.

Since pollution in fact affects an area far larger th n that of an oven's immediate environs, the above gives an idea of the air pollution produced by one charging operation. It should be noted, however, that most of the coarser dust settles almost at once in the immediate vicinity of the charging holes.

This rudimentary test suggests that the figure of 70 kg/h (or 15 kg per charging operation) assumed in this study is extremely modest.

Carbonization: combustion of gas in risers

- Volume of gas = 40,000 N m^3 (lean gas)
- Volume of waste gases = about 100,000 N m^3
- Analysis of waste gases CO_2 = about 15%
  SO_2 = about 1%
  CO = about 1%

The waste gases entrain very fine particles of C, whose size and weight depend on the efficiency of combustion and on the gas-tightness of the walls between the ovens and the risers. Measurements of waste-gas dust content at one iron and steel works coking plant showed an average of 50 mg/N m^3 or about 5 kg per hour. The dust collected was of extremely small particle size; it should be noted that, on this account, observation of combustion gases at the top of the chimney may lead to erroneous conclusions as to their dust content, because the extremely small particle size might suggest a much larger dust content than the true one. These particles belong to the smoke and vapour family (0.2 - 1 micron in diameter) or to the aerosol family (0.001 - 0.2 micron) rather than to the dust family (1 - 150 microns).

Discharging

Pollution depends on the degree of carbonization of the coke cake and, in particular, of the latter's top end. Gas release varies from a few cubic metres to 20 m^3; the estimated analysis of the gas is as follows:-

Content of: CO = 2% by volume
H_2 = 50% " "
CH_4 = 10% " "
tar = 20 g/N m^3

Coke particles = a minimum of 5 kg per discharging operation

The grain size of these particles is likewise very small (from 10 to 1,000 microns).

The quantity of dust discharged to the atmosphere is thus 20 kg/h for four discharging operations.

Breakdowns of the gas extractor

In such cases, the gas escapes to the flares, and

(a) if combustion is ensured during the breakdown, the waste gases discharged are composed almost entirely of CO_2 and H_2O and accordingly constitute no problem;

(b) if combustion is not ensured, the gas has the same composition as that emitted during charging, but the dust content is very low.

Wet quenching of coke

The quantity of dust discharged to the atmosphere at each quenching operation has been estimated at 5 kg, i.e. 20 kg per hour.

Tests carried out at Margam in the United Kingdom suggest that dust emission from the quenching tower is about 2 kg per quenching operation (use of discs greased with a silicone lubricant).

The figure of 10 kg for four quenching operations per hour may therefore be assumed.

Evaluation of dust emissions at a coking plant not equipped against pollution

Even if some sources of pollution (screening, etc.,) are disregarded and even though such an evaluation entails many un ertainties, it is in our view nevertheless of interest to set down the hourly quantities of dust discharged to the atmosphere by a coking plant with a daily coal throughput of 1,000 - 1,200 t; the figures will at least reveal, very roughly, the orders of magnitude involved.

Unloading	20 kg/h
Handling	12.5 "
Other handling sectors	12.5 "
Combustion of gas in risers	5.0 "
Oven charging	70.0 "
Oven discharging	20.0 "
Coke quenching	10.0 "
TOTAL	150.0 kg/h,
or about 3.6 tons per day.	

D. ITALY

Types of pollutants discharged by coking plants

The pollutants discharged by coking plants are as follows:

(a) Coal and coke dust, which may be released during:

(i) coal handling (loading and unloading operations at coal stores; crushing; conveyance to ovens);

(ii) oven-charging operations;

(iii) oven-discharging operations;

(iv) wet quenching of coke;

(v) coke handling.

(b) The pollutants contained in the gases which may be released:

(i) during oven-charging;

(ii) by the ascension pipes in the event of accidental stoppage of the extractors.

These pollutants are mainly:

(i) carbon monoxide;

(ii) hydrogen sulphide;

(iii) tarry-substances.

(c) The gases and vapour discharged in the wet quenching of coke, i.e. principally:

(i) sulphur dioxide;

(ii) ammonia;

(iii) cyanides;

(iv) phenols.

(d) The various pollutants discharged during heating of the ovens with gas. The principal such pollutants are:

(i) sulphur dioxide (only if the gas is not purified);

(ii) carbon monoxide.

Quantities of pollutants discharged by coking plants

After analysis of samples collected at places where the phenomenon is most marked, it can be affirmed with reasonable accuracy that the quantities of pollutants discharged are as follows:

(a) Coal and coke dust:

(i) Coal dust is discharged when the coal is unloaded at the stores; the quantity depends on the moisture content of the coal and on

atmospheric conditions. In the most unfavourable cases, the unloading of about 300 tons of coal per hour produces approximately 10-15 kg/h of dust, i.e. less than 0.005 per cent. In any case, this dust consists of rather large particles which resettle within a short distance of the place of discharge.

(ii) The coal dust released during oven-charging may be estimated at less than 1 kg per charging operation of 15 - 20 tons, i,e. at about 0.005 per cent. In this case also, the dust normally resettles within a short distance of the place of release.

(iii) The quantity of coke dust released during oven-discharging is about 2 kg per 10 - 15 tons of coke.
Here, too, the dimensions of the dust particles are such that the particles resettle within a short distance of the place of release.

(iv) The dust released in the wet quenching of coke is entrained by the water vapour produced during the operation and is rendered considerably heavier by droplets of condensation water; it likewise resettles within a short distance of the place of release.

(v) The quantity of dust discharged during coke handling (particularly crushing and screening) is reduced to a minimum by the installation of special dust-arresting and dust-recovery systems at the places where such dust is formed.

(b) Pollutants contained in gas:

The quantity of first gases released during oven-charging does not exceed 20-30 m^3 per 15 - 20 tons of coal.

These gases usually contain only traces of CO and small quantities of H_2S; they also entrain tarry substances (about 5 g/m^3).

In any case, the quantities are to all intents and purposes negligible.

(c) The pollutants released during wet coke quenching, i.e. sulphur dioxide and traces of ammonia, cyanides and phenols, are so insignificant in quantity that their presence is scarcely noticed, since they readily disperse in the atmosphere.

(d) The pollutants released during heating of the ovens with gas are of only limited importance, since:

(i) if gas produced by synthetic ammonia plants or purified coke-oven gas is used, no sulphur dioxide is formed, as the gas contains no hydrogen sulphide;

(ii) if blast furnace gas is used, traces of sulphur dioxide are found;

(iii) carbon monoxide is produced only accidentally, and hence in tiny quantities insufficient to cause pollution, particularly as coking-plant chimneys are fairly tall (70-80 m) to ensure complete dispersion in the atmosphere.

E. POLAND

(a) Introduction

Not all of the pollutants discharged to the air by coking and coke-oven by-product plants are measured to determine their content in the plant environment. Atmospheric concentrations of the following substances discharged by such plants are measured:

- coal and coke dust;
- suspended bitumens;
- phenol and cresols;
- benzole and its homologues;
- carbon monoxide;
- ammonia;
- hydrogen sulphide;
- sulphur dioxide.

These substances are singled out for quantitative determination because they account for a high percentage of the total discharges or because they are extremely harmful or offensive.

The availability of quick and reliable methods of measurement is therefore of great importance. The substances listed above are acknowledged to be representative of three categories of harmful discharges by coking plants: dust, hydrocarbons and toxic gases.

(b) Methods for the quantitative determination of pollutants discharged to the air

(i) Methods for determining dust content in the atmosphere

In the coke and coke by-product industry, three methods for determining the dust content of air are applied concurrently: weighing, konometry and sedimentation.

The principal method used for determining the dust content of the air quantitatively is weighing, a method which has been standardized.

It consists in passing an air sample through a glass-fibre or cotton-fibre filter. About 2 g of glass fibre or 0.5 g of cotton-fibre is placed in a cylindrical absorption bottle 25 mm in diameter. The air is passed through the bottle at 10 - 20 litres per minute, and the volume insufflated is so regulated, by experiment, that the quantity

of dust deposited in the bottle is not less than 6 mg. The minimum quantity of dust detectable in the air by this method is 1 mg per m^3 of air. The results are converted into mg/Nm^3.

In addition to weighing, the konometer method using the Zeiss konometer is employed. The result is expressed as the number of dust particles contained in 1 cm^3 of the air sampled, separate figures being supplied for particles less than 5 microns and more than 5 microns in diameter respectively.

The third method used in coking plants for measuring the quantities of dust is sedimentation; it involves placing, at suitable points in the coking plant, receptacles at the bottom of which dust and aerosols are deposited from the surrounding air.

After a month, the dust which has accumulated in the receptacles is weighed, and the quantity of dust deposited during one month per m^2 of plant floor area is calculated. The dust collected is analysed to determine its content of bituminous substances soluble in benzole, of combustible substances and of ash. If there are other sources of dust formation outside the coking plant, the content of substances coming from those sources is likewise determined. Although expressed in g per m^2 and per month, the results obtained by this method show the mean statistical level of dust concentration in the air of the district considered. The application of this method is therefore recommended for the purpose of statistical verification of the mean level of air pollution by coking plants.

(ii) Method of determining the quantity of bitumen in suspension in the air

The quantitative determination of bitumen suspended in the air has not yet been standardized. In the coke industry the use is recommended of a method in which the air sample is passed into an absorption device made of filter paper, the bitumen deposited in the filter then being dissolved in benzole. The quantity of bitumen in the solution obtained is determined by comparison with a standard sample, using the fluorescence method. The air is passed through the filter at 10 - 20 litres per hour, and its volume is regulated experimentally in the light of local conditions.

The result is converted into mg/Nm^3 on the basis of the quantity of air insufflated and the quantity of bitumen deposited.

(iii) Method of determining the benzole-vapour content in the air

The content of benzole vapours in the air is determined by a colorimetric method in conformity with standard PN-62/3-04033.

The principle is as follows: the benzole is converted into m-dinitrobenzene and is then made to react with methyl ethyl ketone and potassium hydroxide. A violet-pink coloration is obtained, which is compared with the standard sample.

The air sample is passed into two communicating wash bottles each containing 2 ml of nitrating solution (20 g of ammonium nitrate and 200 ml of sulphuric acid). The quantity of air insufflated is 0.2-0.5 litre, at the rate of 10 litres per hour. A solution of caustic potash and a solution of methyl ethyl ketone are then added successively.

When the contents have settled, the layer of acetone is poured off and its colour compared with that of the standard sample. The result is expressed as mg of benzole per litre of air, the latter being referred to its volume in normal conditions.

(iv) Method of determining the phenol-vapour and cresol-vapour content in the air

The phenol and cresol vapours discharged to the air by and near coking plants are measured by the general colorimetric method based on the reaction of diazotized p-nitroaniline with a phenol or cresol solution, the coloration obtained being then compared with the standard sample. Since these substances may be discharged separately in some industries, two different standards for the quantitative determination of these vapours in the air have been established, i.e. standard PN-56/3-04040 for phenol and standard PN-62/3-04079 for cresols.

In coking plants, these two substances are generally discharged at the same time and they are therefore determined simultaneously by means of appropriate standard samples.

The air sample is passed into two communicating wash bottles, each containing 10 ml of a 10-per-cent solution of sodium carbonate; the quantity of air insufflated is about 5 litres and the rate of insufflation 20 litres per minute.

Solutions of p-nitroaniline, of sodium nitrite and of sodium carbonate are added one after the other to the solution contained in the bottles, and the coloration obtained is then compared with the standard sample. The result is expressed in mg per litre.

(v) Determination of the carbon monoxide content in the air

The quantitative determination of carbon monoxide content in the air is carried out by means of indicator tubes filled with silica gel satured with palladium chloride and ammonium molybdate. The air is hand-pumped into the tubes in a volume which may be 0.1 or 1.0 litre, according to the degree of concentration of the carbon monoxide

it contains. In the presence of carbon monoxide, a green coloration appears, which is compared with the standard sample. The result is shown in mg per litre or as a percentage. Although this method has not been standardized, its use is recommended for all branches of industry.

(vi) Method of determining the ammonia content in the air

The quantity of ammonia contained in the air is determined by a colorimetric method using Nessler's solution, which is added to an ammonia solution. The coloration obtained is then compared with the set of standard samples. This standardized method is described in standard PN-55/3-04041.

The air sample is insufflated into two communicating wash bottles, each containing 10 ml of an 0.01-N sulphuric acid solution. The volume of air insufflated depends on the degree of ammonia concentration in the air and ranges from 2 to 5 litres, at a rate of 60 litres per hour. Nessler's solution is added simultaneously to samples of the solution contained in the bottles and to the set of standard samples, and the coloration is then compared. The result is expressed in mg of ammonia per litre of air analyzed, converted to a standardized volume.

(vii) Method of determining the hydrogen sulphide content in the air

The content of hydrogen sulphide in the air is determined by the standardized method PN-56/3-04042. This method basically consists in fixing the hydrogen sulphide in a solution of sodium arsenate and ammonium carbonate, the solution then being treated with acidified silver nitrate.

The brownish yellow coloration obtained by this reaction is compared with the standard samples.

In this analysis, 4-5 litres of the air sample are insufflated at the rate of 30-40 litres per hour into three absorption bottles in succession, each containing 10 ml of absorptive solution.

The contents of each bottle are analysed separately by the addition of silver nitrate and starch solutions.

At the same time, sets of standard samples are prepared with a view to comparing their coloration with that of the samples obtained.

The concentration of hydrogen sulphide in the air sample is calculated on the basis of the quantity of that substance contained in the samples taken from the bottles and of the volume of air insufflated, converted to a standardized volume. The result is expressed in mg of hydrogen sulphide per litre of air.

(viii) Method of determining the sulphur dioxide content in the air

The analytical method used to determine the content of sulphur dioxide in the air essentially consists in acidifying this dioxide so as to obtain sulphuric acid and then determining the quantity of acid with barium chloride, using the turbidimetric method. This standardized method is described in standard PN-55/3-04039.

In order to absorb and acidify the sulphur dioxide simultaneously, a 5 per cent solution of potassium chloride is used. The air sample is passed into two absorption bottles in succession, each containing 10 ml of absorptive solution. The volume of air insufflated is 10-15 litres and the rate of insufflation 30 litres per hour. Solutions of hydrochloric acid and of barium chloride are added to the absorptive solution one after the other. These reagents are added simultaneously to the solution being studied and to the standard solution, their degree of turbidity then being compared. The concentration of sulphur dioxide is calculated in mg per litre from the quantity of sulphur dioxide determined and the standardized volume of air insufflated.

(c) Measurement of pollutants

Air pollution is a phenomenon incidental to virtually all technical operations and processes carried out at a coking plant. In most cases, however, it is on so small a scale as to have no marked effect on total atmospheric pollution.

On the whole, only the coke ovens constitute a source of pollutants having a decisive effect on total pollution of the atmosphere.

In the coke-oven department, the following sources of pollution may be distinguished:

- oven charging;
- the coking cycle proper;
- coke discharging and quenching; and
- firing of the battery.

Determination of the precise nature and absolute magnitude of the pollutant discharge presents a very difficult problem, which often cannot be solved by direct measurements. Data on the quantitative aspect of the discharge are only rarely obtained by direct measurement; in most cases, use is made of data obtained indirectly - from the input-output balance, for example - and it is sometimes necessary to resort to rough estimations.

These circumstances have a particular bearing on the accuracy with which the amount of pollutant discharge is determined, and it must be said that even an estimation of its order of magnitude is not always reliable.

(d) Determination of the nature and quantity of pollutants discharged by the coke-oven department

(i) Air pollution during charging of coking chambers

Measurements made near several coke-oven batteries show that the quantity of crude gas released during charging fluctuates between 1.46 and 2.35 kg of gas per ton of wet charge. Calculations which take charging times into account yield an average figure of 2.24 kg per ton of charge for the Polish coke industry as a whole. However, this figure is not an indicator of the discharge to the atmosphere, because part of the crude gas released burns, thereby adding a large quantity of soot to the various components of the crude gas. It is estimated that only 25 per cent of the gas released is discharged to the atmosphere unburnt; 50 per cent of the gas released undergoes incomplete combustion in which the carbon from all the compounds containing carbon and hydrogen separates out in the form of soot; the remaining 25 per cent burns, giving off soot formed from the heavy hydrocarbons. Apart from this, the gas emerging from the coking chambers entrains fine coal dust from the charge, and graphite deposited in the ascension pipes and under the crown of the chambers. Measurements show that the quantity of entrained dust varies considerably - from 35 g/Nm^3 to about 400 g/Nm^3, depending on the charging system, on the moisture content and degree of crushing at the charge, on the design of the coking chambers and on their degree of wear. The average figure for Polish coking plants in the aggregate is 85 g/Nm^3 or 0.183 kg per ton of charge.

Disregarding the water vapour and the inert or neutral gases contained in the crude gas or formed during its combustion, the composition of the noxious substances and foreign bodies discharged to the atmosphere is as follows:

- constituents of the crude gas:	
tar, combustible gases, heavy hydrocarbons, toxic gases	0.2430 kg/t
- dust:	
entrained by the crude gas	0.0340 kg/t
solid products of incomplete combustion (aerosols)	0.4040 kg/t
mechanically-entrained dust	0.1830 kg/t

These substances constitute the aggregate pollution (formed during charging), amounting to 0.9 kg/t of charge used.

(ii) Discharge of pollutants to the atmosphere during the complete coking cycle

During the coking cycle, coke gas is discharged to the atmosphere through interstices in the brickwork and through the coking chamber doors.

This discharge occurs mainly in the initial phase of coking, when the pressure in the chambers is relatively high. The volume discharged depends not only on the condition of the ceramic block and of the battery's metal fittings, but also on the pressure in the collecting main.

Since the quantity of crude gas discharged cannot be determined by direct measurements, it is assessed from the losses shown by the balance sheet. According to the degree of wear of the battery, crude gas losses in the balance range from 1.5 to 8 per cent of the total quantity of gas produced.

For Polish coking plants in the aggregate, these losses average 5.5 per cent. Some of the crude gas seeps from the chambers into the heating system, where it burns; as an average for all the coking plants, this infiltration constitutes 6 per cent of the gas used for battery heating.

Since gas-firing accounts, on the average, for 55 per cent of the total of crude gas produced, it may be assumed that, of the balance-sheet total of crude gas losses, (5.5 per cent), 3.5 per cent enters the heating system, the remaining 2 per cent being discharged direct to the atmosphere. Assuming the output of crude gas to represent 30 per cent of the wet charge, direct losses to the atmosphere per ton of charge are:

$$1000 \times 0.3 \times 0.02 = 6 \text{ kg per ton of charge}$$

This figure comprises both losses during charging and losses during the coking cycle.

Losses of crude gas through leaks therefore amount to 6 - 2.24 = 3.76 kg/t of charge.

On the basis of the average composition of the crude gas, in which the water vapour and the neutral gases are disregarded, the following figures are obtained for pollutant discharge to the atmosphere:

- coal dust	0.0590 kg/t
- tar	0.3490 kg/t
- heavy hydrocarbons	0.1390 kg/t
- combustible gases (hydrocarbons of the aliphatic series)	1.000 kg/t
- noxious gases	0.0910 kg/t

The above components together account for the pollution of the atmosphere during the coking cycle, this pollution amounting to roughly 1.9 kg/t of charge.

(iii) Air pollution during discharging and quenching of coke

The character of the air pollution caused by coke discharging and quenching may vary according to the level to which coke preparation is carried. If that level is high, only coke dust will be released, but if it is low, the dust will be accompanied by certain constituents of the crude gas.

The coke dust discharged to the atmosphere during coke discharging and quenching consists of relatively large particles. Most of the dust therefore settles close to the battery, but the rest pollutes the atmosphere even at quite considerable distances from the coking plant.

The crude gas constituents discharged from incompletely prepared coke burn partially in the quenching car, forming a thick, black smoke. During actual quenching, they are discharged to the atmosphere in the form of brown vapours, contributing considerably to air pollution through their wide dispersal.

In determining the magnitude of dust release during coke discharging and quenching, account is taken only of the finest coke dust and of the aerosols associated with incompletely prepared coke.

Since direct measurement of dust release during discharging and quenching is virtually impossible, a preliminary estimate is made on the basis of comparative measurements of such effects of that release as the deposition of dust or the dust content of the air at a given amount. coke discharge

The finest coke dust is discharged to the atmosphere in a quantity of about 0.205 kg per ton of coke, representing 0.205 x 0.7 = 0.143 kg per ton of useful charge, a figure which is independent of the degree of carbonization. The discharge of constituents of the crude gas is estimated at about 20 per cent of the quantity released during oven charging. This estimate applies, of course, to coking plants where the coke discharged is for some reason incompletely carbonized. According to preliminary estimates, the maximum proportion of coke incompletely carbonized can be put at 30 per cent; the indicators of pollutant discharge for the industry as a whole are therefore as follows:

- dust (aerosols): 0.621 x 0.2 x 0.3 = 0.037 kg per ton of charge;
- constituents of the crude gas: 0.279 x 0.2 x 0.3 = 0.017 kg per ton of charge.

Air pollution occurring where coke is quenched with effluents is a problem apart. The pollutants entrained by the water evaporate or decompose on contact with the hot coke and are discharged to the atmosphere with the water vapour. In such a case, the character of the discharge depends on the substances contained in the effluents used.

The quantity and nature of the pollutants discharged to the atmosphere where coke is quenched with waste waters has been investigated at one coking plant, and it seems possible to regard the results obtained as being representative of other coking plants using waste waters for this purpose. The nature of the pollutants discharged to the atmosphere has been determined by analysis of the condensate from the vapours escaping from the quenching tower, while the quantity discharged has been calculated both by direct measurement and from the balance-sheet of the pollution due to coke-quenching. The following amounts per ton of charge have been computed:

- phenol	0.158 kg/t
- naphthalene	0.028 kg/t
- ammonia	0.114 kg/t
- hydrogen sulphide	0.077 kg/t
- hydrocyanic acid	0.0095 kg/t
- tar compounds	0.010 kg/t
- chlorine compounds (Cl^-)	0.028 kg/t
- sulphur compounds (SO_4^{--})	0.072 kg/t

If it is assumed that about 50 per cent of all the industrial coke produced in the country is quenched with waste waters, the total atmospheric pollution associated with coke discharging and quenching is found to have more or less the same composition for all Polish coke-oven plants, as computed per ton of charge:

- coke dust	0.143 kg/t
- coal dust	0.037 kg/t
- crude gas	0.017 kg/t
- hydrocarbons (heavy)	0.098 kg/t
- noxious gases	0.100 kg/t
- inorganic anions	0.100 kg/t
Total:	0.490 kg/t

(iv) Pollutant discharge during firing of the battery

Certain quantities of dust and sulphur dioxide are discharged to the atmosphere as pollutants from the chimneys of coke-oven batteries.

The discharge of dust may be disregarded here because its quantity is very small, being about 0.005 kg/t of charge; but the firing of coke-oven batteries with a gas not freed of sulphur causes considerable air pollution by sulphur dioxide.

The quantity of sulphur dioxide released per ton of charge is calculated from the average output of gas per ton of wet charge, from the quantity of gas consumed for heating the battery and from the average hydrogen sulphide content of the gas. The relevant figures are as follows:

- output of gas — 300 Nm^3/t
- consumption of gas — 55% = 165 Nm^3/t
- hydrogen-sulphide content of the gas — 7 g/Nm^3

The quantity of sulphur dioxide released per ton of charge is:

$$165 \times 0.007 \times \frac{64}{34} = 2.171 \text{ kg/t.}$$

(v) Comparison

Table 1 below compares the nature and quantities of pollutants discharged to the atmosphere by coke-ovens.

The table shows separately, in kg per ton of charge utilized, the quantities released by the various technical operations and also the total discharge in kg/t. The last column shows the corresponding annual discharge, as computed from the annual wet throughput (18.5 million t).

Table 1

Table 1

Nature and extent of atmospheric pollution caused by coke-oven batteries

Serial No.	Pollutant	Chemical formula	Discharge in kg/t of charge					Annual discharge t/year
			Charging of chambers	Coking cycle	Discharging and quenching	Firing	Total	
1	Coal (coke) dust		0.621	0.059	0.182	0.005	0.867	16,039
2.	Tar		0.104	0.349	0.010	-	0.463	8,565
3	Methane and homologues	C_nH_{2n+2}	0.103	0.676	-	-	0.779	14,411
4	Ethylene and homologues	C_nH_{2n}	0.015	0.102	-	-	0.117	2,164
5	Acetylene	C_2H_2	0.001	0.006	-	-	0.007	129
6	Carbon monoxide	CO	0.037	0.252	0.005	0.001	0.295	5,457
7	Benzene	C_6H_6	0.015	0.087	-	-	0.162	1,887
8	Naphtalene	$C_{10}H_8$	0.005	0.034	0.014	-	0.053	980
9	Phenol	C_6H_5OH	0.006	0.010	0.079	-	0.095	1,757
10	Pyridine	C_5H_5N	0.061	0.006	-	-	0.007	129
11	Ammonia	NH_3	0.008	0.027	0.057	-	0.092	1,702
12	Hydrogen sulphide	SH_2	0.012	0.047	0.038	-	0.097	1,794
13	Hydrocyanic acid	HCN	0.001	0.003	0.005	-	0.009	166
14	Oxides of nitrogen	NO	0.013	0.006	-	-	0.019	351
15	Sulphur dioxide	SO_2	0.011	0.001	-	2.171	2.183	40,385
16	Carbon disulphide	CS_2	-	0.001	-	-	0.001	18
17	Chlorine	Cl_2	0.001	0.003	-	-	0.004	74
18	Chlorides	Cl^-	-	-	0.028	-	0.028	518
19	Sulphates	SO_4	-	-	0.072	-	0.072	1,332
Total:			0.96	1.45	0.49	2.17	5.29	

F. FEDERAL REPUBLIC OF GERMANY

It is particularly difficult to determine and reduce emissions of pollutants in coking plants, because such emissions are essentially intermittent and uncontrolled. They are caused mainly by the dust released during coke-oven charging, coke-cake discharging and coke quenching, and thus necessarily depend on the design and mode of operation of the coke ovens. With an average carbonizing time of twenty hours, pollutants consisting mainly of dust are emitted during the charging of the coke ovens and, after completion of carbonization, during coke-cake discharging and coke quenching, i.e. for only about ten minutes in all. The only source of permanent pollutant discharge in a coking plant is the firing of coke ovens, if gases containing hydrogen sulphide are used for this purpose. The volume of SO_2 discharged to the atmosphere depends on the nature of the heating gas used. Table 2 shows the quantities of SO_2 which may be released; it should be noted in this connexion that release of SO_2 during coke-oven firing depends on the nature of the heating gas employed.

Table 2

Approximate figures for the discharge of SO_2 during the coking of 1 ton of coking coal

Heating gas used	Calorific value (net) kcal/Nm^3	Heating requirement per t of coal (10% H_2O) Nm^3	Content of gas in (a) sulphur dioxide (b) organically combined sulphur g/Nm^3	Discharge of SO_2 per t of coal kg
Coke-oven gas				
1. without partial elimination of sulphur	4200	130	(a) 5 - 13 (b) 0.5-1.3	1.3-3.5
2. with partial elimination of sulphur	4200	130	(a) 1.5-5 (b) 0.2-0.6	0.4-1.3
Producer gas	1100	500	(a) 1-2 (b) 0	
Blast-furnace gas	830-1070	670-520	traces	traces
Mine gas (methane)	8400-9000	160- 90	0	0
Recovered synthesis gas	5100-5500	110-100	0	0

G. UNITED KINGDOM

(a) Methods of measurement

The methods described below should be regarded as merely tentative; the data obtained are subject to possible errors of unknown magnitude.

Smoke

The emission of smoke on the charging of ovens is estimated visually, the mass emission factor (M.E.F.) being determined.

The difficult task of devising a method for estimating the quantity of smoke emitted during this operation was undertaken by a Joint Working Group of the British Coking Industry Association and the Alkali Inspectorate. The problem is a complex one, for some account must be taken of the volume and density of clouds which may rise from the leveller door, the charge-holes, or the charging-car hoppers, or simultaneously from any of these openings. A method was evolved which is based on the techniques used in the realm of work study. The density of the smoke was classified by visual observation in five categories, designated D0, D1, D2, D3 and D4 respectively, and the duration of the emission of smoke in each of these categories during any charging operation could be accurately timed by means of a split-finger decimal-minute stop watch. The total duration of the emission in each of the categories was designated as S0, S1, S2, S3, S4 minutes respectively, and the mass emission factor was defined as follows, smoke of density D1 being ignored:

$$M.E.F. = S2 + 2\,(S3) + 3\,(S4),$$

To assist in determining the appropriate category, the smoke densities were given the following tentative definitions:

D0: no smoke -unavoidable, translucent wisps of smoke;

D1: negligible smoke - smoke which issued from one or more outlets but became translucent within about one foot of the outlet;

D2: slight smoke - smoke which became translucent some four feet from the outlet;

D3: moderate smoke - smoke which obscured the bottom half of the charging car or issued from the tops of hoppers in a dense mass which was quite opaque;

D4: heavy smoke - smoke which obscured at least 75 per cent of the charging car.

It was suggested that observations should be made from a standard position forty feet from the charging car on the leeward side when the wind strength was not in excess of force 6.

It is not, however, possible to apply this technique accurately from a written description, and in order to establish a consistent standard of assessment, the British Coke Research Association holds training courses at which personnel from different plants compare their own observations with those of an instructor who himself participated in the initial work of the Joint Group.

The conversion of M.E.F. to weight of smoke is a development of the British Coke Research Association, which has a fully-equipped coke-oven and by-product plant for large-scale experiments on the coking process. Charging is "off the main", and most of the smoke emitted is normally burned in a special flare pipe. Experiments were carried out in which the whole of the gas and smoke produced during charging were emitted to the atmosphere without combustion and assessed by the M.E.F. method described above. On completion of charging, the oven was put "on the main" in the usual way, and simultaneously measurements of the volume of gas evolved were commenced, using the gas meter which is part of the normal equipment and which measures the gas after it has been washed for benzole and ammonia and the tar precipitated. Readings were taken every three minutes during the next half-hour. A correction factor was applied to bring the volumes to standard temperature and pressure. A graph of the rate of gas production was then plotted against time, and this gave a straight line. To obtain the rate of production during charging, the line was extrapolated backwards to the commencement of charging. In other experiments at this plant, the amounts of tar and other products had been determined, and the amount of tar associated with the volume of gas evolved during the charging period could therefore be calculated. This weight of tar was then equated to the smoke measurement, it being assumed that the visible smoke consisted largely of tarry particles and dust particles. From these observations it was concluded that one unit of M.E.F. was approximately equivalent to 100 cu. ft. (2.8 m^3) of gas or 0.85 - 0.9 lb (0.39 - 0.41 kg) of tar. Thus the M.E.F. can now be related to weight of smoke.

Emission of smoke, dust and grit on pushing of ovens

The emission of dust and grit was measured by erecting a framework of rods supporting greased plates spaced at intervals and holding this over the rising column of pollution as an oven was pushed. The total collected weight found from a series of pushes gave an average weight for the area of the plates, and this, adjusted to the total cross-sectional area of the rising column, gave the total emissions of dust and grit per push. To this was added the weight of smoke measured by the application of the M.E.F. method, already described, to oven discharging. In that way, a figure for the total pollution due to smoke, dust and grit was obtained.

Emission of grit on quenching

Several methods of measurement were used, the more reliable results being obtained as follows. On a fine day with light wind, Petri dishes were set out, suitably separated, at ground level or in some cases at about three feet (0.9 m) above ground level, to catch the grit. A study of the deposition pattern was made to determine roughly the area of important fall-out. The area of the Petri dishes was multiplied by the area of deposition to give a factor for the calculation of the total weight of grit. A more direct method involved the suspension of a number of greased plates over the top of a quenching tower, the weight of grit collected per quench being multiplied by the ratio of the area of the cross-section of the tower at the point of measurement to the area of the plates. A specially-designed cyclone probe was also used to collect grit at the top of the tower. The disadvantage of this latter method was the small area presented by the probe, so that many observations had to be made, the cross-sectional area of the tower being sub-divided into twenty-seven smaller areas for the individual determinations.

Emission of moisture on quenching

For the determination of moisture, only one direct method was used, the drizzle being collected at ground level in Petri dishes (set out as previously described) and weighed. An indirect semi-quantitive method was also used, water-sensitive paper being employed and the weight of water being estimated from the amount of coverage by water droplets. The paper, which normally darkened on development, remained white over the area covered by droplets.

Emission of grit from screening of coke

This pollution is composed mainly of large particles, which readily settle in the area of the screens. The weight was estimated from the amounts of material collected on a network of trays or Petri dishes set out in a manner similar to that used for the studies on quenching.

(b) Noxious gases

(i) Sulphur dioxide. Air is passed through a bubbler containing hydrogen peroxide and the resultant acidity determined. This apparatus is frequently used in conjunction with the filter-paper method for estimating smoke, the bubbler being inserted between the filter paper and gas-meter.

This method is given in British Standard 1747, part 3.

(ii) Oxides of nitrogen. Nitrogen dioxide can be measured by drawing air through bubblers with sinters, the Saltzman solution[1/] being used. Nitric oxide is then oxidized by acid potassium permanganate to nitrogen dioxide prior to absorption in further bubblers.

(iii) Carbon monoxide. This is measured by the length of stain developed on a silica-gel column impregnated with palladium compound and through which a known volume of air has been passed.

(iv) Hydrogen sulphide. This can be estimated by the production of a stain by passing a known volume of air through filter paper impregnated with silver nitrate. The stain is fixed with sodium thiosulphate solution and then measured optically.

(v) Sulphur trioxide. This can be estimated by the acidity developed on a filter paper through which a known volume of air has been drawn.

(c) (c) Quantity and variety of noxious substances emitted by a coking plant

The following information is intended to be indicative of average practice in the United Kingdom and relates to a theoretical plant producing 1 million tons of coke per annum.

1/ Naphthylethylenediamine dihydrochloride plus sulphanilic acid in acetic acid.

(i) Charging of ovens (with the main connected)

It is estimated that smoke emission varies from 36 kg per day under good conditions to 270 kg per day under poor conditions, with an average of 160 kg per day. These figures are based on the determination of the M.E.F. (mass emission factor) values, as previously reported.

(ii) Pushing of ovens

The total emission of grit, dust and smoke is estimated to be of the order of 1 ton per day.

(iii) Quenching

The average grit emission on quenching is estimated to be about 225 kg per day without grit arrestors. This figure is probably reduced to the order of 45 to 70 kg per day when grit arrestors are fitted in the quenching tower.

The amount of moisture emitted as drizzle from the quenching tower varies widely, but an average figure might be of the order of 5 tons per day without arrestors, and of 0.5 ton per day when arrestors are fitted.

(iv) Cutting and screening coke

It is estimated that grit production on cutting and screening coke is of the order of 225 kg per day.

(v) Size range of particles from quenching and screening

The size range varies from less than 7 microns to over 100 microns. However, at some coking plants the largest fraction may lie within a narrower size range, say 8 to 80 microns, which makes the arrestment of grit less efficient. For an average coking plant it is believed that the efficiency of grit arrestors would vary from 60 per cent to 90 per cent, depending on the type of arrestor used.

(vi) Sulphur dioxide

It is possible that the underfiring gas might produce a sulphur-dioxide emission of up to 20 tons per day.

LOVAKIA

dized methods are prescribed for the measurement of air pollution. The
alyses are made:

t content of the air is determined by passing a given quantity of air
mbrane filter and then measuring the excess weight.

and its salts are recovered by introducing sulphuric acid into a
easured quantity (1-3 litres) of polluted air; the substance causing the
tion observed after the addition of Nessler's solution is then identified
ry.

zole from the air is absorbed in a nitrating mixture, and the
zene produced is identified by polarization.

nol from the air is absorbed by introduction into the alkali. After the
$K_3Fe(CN)_6$ and of amino-4 antipyrine, the substance which has produced the
on observed is identified by colorimetry.

luted with hydrogen sulphide is introduced into a zinc acetate solution.
p-aminodimethylaniline and $FeCl_3$ is then added, and the origin of the
ion observed is determined by colorimetry.

luted with carbon disulphide is passed through cotton wool impregnated
tate and a bath consisting of a diethylamine and copper acetate solution.
ration is produced, whose origin is determined by colorimetry.

on monoxide is determined either by an infra-red analyzer or through
es filled with silica gel to which palladium sulphate, ammonium
sulphuric acid have been added. In the presence of CO, the yellow
s film changes to green and then to blue; the coloration observed is
st a graduated scale.

reproduced below exemplify air pollution measurements carried out at
ants.

tities shown below of dust and gas discharged to the air by a coking
gross output of about 2 million tons are based on calculations or on
It has been assumed that this output will be achieved after all the
scribed below have been carried out:

t emitted by dust extractors, the dust content
the air to be de-dusted being assumed to be
mg/m^3 — 0.5 t per day

t emitted during coal handling in the
paration shed — 0.1 - 0.25 t per day

:r day

:r day

:r day

day

:r day

1 1964 at a
cment was
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1964

Stity
Wg/m^3
M
mg/m^3
5 mg/m^3
T/m^3
2-0.06%
Dg/m^3
1%
L-0.06%
S and over
mg/m^3
C0 mg/m^3
F0 mg/m^3
T2 mg/m^3
5 mg/m^3
A mg/m^3
F mg/m^3
40 mg/m^3
F20 mg/m^3
mg/m^3