

Technical control of nuisances and pollution at the place of work and in the environment of iron and steelworks

Fifth ECSC research programme



Report
EUR 17583 EN

Employment & social affairs



European Commission

Technical control of nuisances and pollution at the place of work and in the environment of iron and steelworks

Fifth ECSC research programme

Summary report of studies completed on 31 May 1994

B. Deckers

Employment & social affairs

Health and safety at work

European Commission
Directorate-General for Employment, Industrial Relations
and Social Affairs
Unit V/F.4

Manuscript completed in 1997

PARL EUROPE. Biblioth.
N.C. eur 17583
CI

Neither the European Commission nor any person acting on behalf of the Commission is responsible for the use which might be made of the following information.

A great deal of additional information on the European Union is available on the Internet. It can be accessed through the Europa server (<http://europa.eu.int>).

Cataloguing data can be found at the end of this publication.

Luxembourg: Office for Official Publications of the European Communities, 1998

ISBN 92-828-2400-4

© European Communities, 1998

Reproduction is authorised provided the source is acknowledged.

Printed in Belgium

SUMMARY

This report takes stock of all the research subsidised by the ECSC under the terms of the 4th and 5th programmes on "Technical control of nuisances at the place of work and in the environment of iron and steelworks" whose final reports were published between the end of 1985 and May 1994. The results of 68 research projects have thus been analysed and the most interesting information of practical use for the European Union steel industry summarised. The report constitutes a follow-up to report EUR 11695 "Fourth ECSC research programme – Technical control of nuisances and pollution at places of work and in the environment of iron and steelworks – Status of research at 31 December 1985" published in 1989, which dealt with 83 research projects subsidised by the ECSC and carried out between 1979 and 1985.

The range of areas dealt with by these research projects is very wide, covering both protection of workers at their places of work and protection of the environment at iron and steelworks. Not only have problems of atmospheric pollution, waste water treatment, and treatment and management of waste been tackled but considerable attention has also been focused on acoustic nuisances and even on protection against ionising radiation which can arise when a radioactive source is introduced undetected through recycled scrap.

The report breaks down the results of the research work by plant: coking plant, ore sintering and pelletisation plant, blast furnaces, melting shops, continuous casting shops, hot rolling mills, pickling lines, cold rolling mills and coating lines.

Research covering an area taking in more than one type of plant has been combined in Chapter 2 entitled "Studies not confined to a specific steel industry workshop".

Of the subjects on which considerable research activity has been focused, the following should be singled out:

- better identification of the risks for workers at their place of work resulting from various atmospheric process emissions. In addition to polycyclic aromatic hydrocarbons, which were studied in coking plants and in blast furnaces and melting shops, other atmospheric pollutants were analysed in terms of the risk to workers. These include inhalable dusts at workstations in blast furnace and melting shops or oil aerosols for which a measuring instrument had to be developed. One study was devoted to emissions into the atmosphere of heavy metal from coking plant and demonstrated that this type of emission was virtually no problem in terms of industrial health;

- reduction of nitrogen oxide emissions from various steel industry workshops.
In order to reduce such emissions the phenomena responsible for the formation of nitrogen oxide molecules first had to be studied in detail.
It proved necessary to use fuel with the lowest possible content of organic nitrogen and at moderate flame temperatures in order to restrict the formation of nitrogen oxide. NO_x emissions were thus reduced significantly by means of suitable burner design and injection of water or steam in the air being burnt. Ways in which nitrogen oxide emissions might be reduced specifically in coke oven heating were studied. Considerable reductions were observed in France and in Germany as a result of a suitable heating system features, such as multi-stage gas and air supply systems or fume recirculation systems;
- reduction of emissions of dust generated pig iron and molten steel by inertisation of the ambient air.
Reductions of between 75 and 90% were obtained at the blast furnace tilting spout, when hot metal was transferred from the submarine ladle and when the converter was charged;
- treatment of steelmaking waste rich in zinc and lead for the purposes of recycling.
A hydrometallurgical process based on acid leaching with depleted hydrochloric pickling liquor was developed, enabling much of the zinc and lead to be extracted from blast furnace sludge. This process was not effective for melting shop sludge. Moreover, the fact that it produces a chlorine brine restricts its use to steelworks by the sea;
- simulation of noise levels in the environment based on an examination of sources of noise in order to deal with and reduce such nuisances. An *in situ* intensity measuring technique was developed whereby the sound power of a source of noise could easily be determined in the presence of other sources of noise.

A simulation model was also developed and tested, enabling the noise level at any point to be assessed accurately (to ± 3 dBA) from the sound power levels of the sources and the geometry and acoustic characteristics of the sites. Acoustic treatment of sources of noise could then be tested before implementation in order to assess their impact on the environment;

- detection of radioactive contamination of scrap on introduction to a steelworks site.
As there is a risk of radioactive components being present in scrap coming into the steelworks (whether due to negligence or by design) it is useful to be able to inspect scrap when it enters the plant. Research work was undertaken to optimise this as an industrial procedure and to obtain the highest possible detection sensitivity;
- analysis of PAH emissions from coking plant.
A key coordinated research project involving Germany, Spain, France and the UK was conducted to select the most suitable sampling and analysis techniques for determining PAH levels in the environment of coking plants.

These were then used to conduct a number of measurement campaigns, which identified the places of work where problems might arise in protecting workers and the most suitable means of protection.

In addition, this also provided a means of determining the scale of total PAH emissions from the main sources in a coking plant;

- olfactory nuisances from coking plant were also studied and the substances chiefly responsible for the nuisances and the main sources of olfactory emissions in coking plants were identified. Indene and naphthalene (two PAHs) are mainly responsible for odour nuisances and the main sources thereof proved to be the gas treatment installations of coking ovens;
- improvement in the treatment of waste water from coking plants. The main focus of the studies was the biological purification of waste water from coking plants. Potential inhibitors were studied and design was improved either by means of cascade reactors, rotating discs or the use of pure oxygen in the reactors. Moreover, the influence of final decantation of the slurries on the quality of effluent was demonstrated and also led to this process being optimised. Studies were also carried out on eliminating these slurries;
- reduction of atmospheric emissions from sintering plants. Ways of reducing emissions of SO₂, NO_x, CO and HC etc. were also studied. First, the process was modified by optimising the thermal functioning of the line, adjusting the mix, using alternative fuels, injecting steam during sintering, and juggling with the index of basicity of the sinter and steelmaking waste being recycled. Second, final purification of fume was studied by means of refining the use of bag filters for dust and the addition of agents upstream to desulphurise the fume. Bag filters certainly proved very effective but caused major pressure drops which need to be reduced by precoating.

It should be noted that a fair number of the research projects were devoted to studying the generation of emissions within the process itself, in order to enable such emissions to be cut out at source rather than merely prevented from being dispersed in the environment by treatment/purification.

The results of this research work thus made a major contribution to reducing the harmful effects of iron and steelworks in the European Union on the environment and on workers' health. The ECSC programme "Technical control of nuisance and pollution at the place of work and in the environment of iron and steelworks" is thus a vital tool in encouraging improved protection of the environment and pooling of information and experience on this matter in the countries of the European Union.

TABLE OF CONTENTS

1.	Introduction	5
2.	Studies not confined to a specific steel industry workshop	7
2.1	Atmospheric emissions	7
2.1.1	<i>Reduction of nitrogen oxide emissions</i>	7
2.1.2	<i>Analysis of pollutants emitted at workstations in terms of the risk to workers' health</i>	13
2.1.2.1.	Emission modelling tests	13
2.1.2.2.	Pollutants at workstations in blast-furnace and melting shops	14
2.1.2.3.	Reduction of emissions caused by drying refractories	16
2.1.2.4.	Oil aerosol emissions	18
2.1.3	<i>Reduction of dust emissions</i>	19
2.1.3.1.	Reduction of blow-off from raw material stockpiles	19
2.1.3.2.	Reduction of dust emissions from molten iron and steel	20
2.2	Waste water treatment	22
2.2.1	<i>Treatment of cooling water to prevent the development of algae</i>	22
2.2.2	<i>Smoothing pollution peaks</i>	23
2.2.3	<i>Removal of cyanides</i>	24
2.3	Management and treatment of waste	26
2.3.1	<i>Waste treatment for upgrading</i>	26
2.3.1.1.	Treatment of sludge and dust containing zind and/or lead	26
2.3.1.2.	Treatment of oily sludges	29
2.3.2	<i>Final waste tipping</i>	30
2.3.3	<i>Decontamination of old lagoons and dumps</i>	34
2.4	Acoustic nuisances	35
2.5	Protection against ionising radiation	40

3.	Coking plants	45
3.1	Atmospheric emissions	45
3.1.1	<i>Reduction of sulphur oxides emissions</i>	45
3.1.2	<i>Reduction of nitrogen oxide emissions</i>	47
3.1.3	<i>Emissions of polycyclic aromatic hydrocarbons</i>	49
3.1.4	<i>Olfactory nuisances</i>	56
3.1.5	<i>Emissions of heavy metals</i>	58
3.2	Treatment of waste water	62
3.2.1	<i>Purification by stripping ammoniacal water</i>	62
3.2.2	<i>Biological purification</i>	63
4.	Sintering and pelletisation	71
4.1	Reduction of atmospheric emissions by means of process modifications	71
4.2	Reduction of atmospheric emissions by end-of-pipe treatment of fume using bag filters	75
5.	Blast furnaces	79
5.1	Treatment of waste water - reduction of cyanide waste	79
6.	Melting shops, continuous casting plant and hot-rolling mills	83
6.1	Atmospheric emissions	83
6.1.1	<i>Energy savings in fume extraction from an electric arc melting shop</i>	83
6.1.2	<i>Scrap preheating in an electric arc melting shop</i>	84
6.2	Treatment of waste water	85
6.3	Management and treatment of waste	85
7.	Pickling lines, cold rolling mills and coating lines	91
7.1	Acid pickling lines	91
7.1.1	<i>Study of the health risks to workers</i>	91
7.1.2	<i>Reduction of nitrogen oxide atmospheric emissions from stainless steel pickling baths</i>	92
7.1.3	<i>Purification of waste water from stainless steel pickling lines</i>	96
7.2	Cold rolling mills	97
7.3	Coating lines	97
7.3.1	<i>Reduction of zinc losses in galvanising lines</i>	97
7.3.2	<i>Purification of waste water from electrogalvanising lines</i>	99
7.3.3	<i>Passivation of coated sheet by treatment without chromic acid</i>	100

8. Conclusion	103
Annex 1 - List of research projects	105
Annex 2 - Research projects dealt with in the various chapters	107

CHAPTER 1

Introduction

This report takes stock of all the research subsidised by the ECSC under the terms of the 4th and 5th programmes on "Technical control of nuisances and pollution at the place of work and in the environment of iron and steelworks" whose final reports were published between the end of 1985 and May 1994. The results of 68 research projects have thus been analysed and the most interesting information of practical use for the European Union steel industry summarised. The report constitutes a follow-up to report EUR 11695 "Fourth ECSC research programme – Technical control of nuisances and pollution at places of work and in the environment of iron and steelworks – Status of research at 31 December 1985" published in 1989, which dealt with 83 research projects subsidised by the ECSC and carried out between 1979 and 1985.

The range of areas dealt with by these research projects is very wide, covering both protection of workers at their places of work and protection of the environment at iron and steelworks. Not only have problems of atmospheric pollution, waste water treatment, and treatment and management of waste been tackled but considerable attention has also been focused on acoustic nuisances and even on protection against ionising radiation which can arise when a radioactive source is introduced undetected through recycled scrap.

It should be noted that a fair number of the research projects were devoted to studying the generation of emissions within the process itself, in order to enable such emissions to be cut out at source rather than merely prevented from being dispersed in the environment by treatment/purification.

The report breaks down the results of the research work by plant: coking plant, ore sintering and pelletisation plant, blast furnaces, melting shops, continuous casting shops, hot rolling mills, pickling lines, cold rolling mills and coating lines. Research covering an area taking in more than one type of plant has been combined in Chapter 2 entitled "Studies not confined to a specific steel industry workshop".

Each chapter deals in turn with aspects relating to atmospheric emissions, discharge of waste water, elimination of waste, acoustic emissions and finally other aspects.

For more information on a given subject, the reader should refer to the final report of the project concerned, references for which are given in a box preceding each summary and are listed in full in Annexes 1 and 2.

CHAPTER 2

Studies not confined to a specific steel industry workshop

2.1 ATMOSPHERIC EMISSIONS

2.1.1 *Reduction of nitrogen oxide emissions*

Pilot study of NO_x emissions from reheating furnaces

Research project 7261-01/407/04 carried out by CSM (Italy)

NO_x emissions cause acid rain, contaminating water and soil, and contributing to forest withering. They are formed at sources of combustion by oxidation of the nitrogen contained in the air and in the fuel. The main compound formed is NO which is converted into NO₂ and far smaller quantities of N₂O in the atmosphere.

The volume of NO_x emissions from steelworks is high and increasingly stringent limits on NO_x emissions are expected in the European Community. At present the *TA Luft* (technical orders on air) in Germany, which restrict NO_x levels in fume to 500 mg/Nm³ (with higher values tolerated if the combustion air is preheated to over 200°C) are the current benchmark. However, these values will be reduced to 350 mg/Nm³ for gas-fired plant and 450 mg/Nm³ for oil-fired plant at the end of 1995 in accordance with European directives and even stricter limits (100 and 150 mg/Nm³ respectively for gas and oil) are being considered.

The Centro Sviluppo Materiali (CSM) has examined the NO_x emissions from an integrated steel plant and has observed that:

- 25% are emitted by the coking plant;
- 55% are emitted in the sintering shop;
- 12% are emitted by reheating furnaces;
- 8% are emitted by power station boilers.

Of the sources of NO_x formed in burner flames a distinction should be made between:

- "thermal NO_x " which results from oxidation of atmospheric nitrogen. This depends essentially on the temperature of the flame (from approximately 1 500°C) and the availability of oxygen. 95% of this is NO;
- "fuel NO_x " which results from oxidation of volatile nitrogen contained in the fuel. This is influenced little by the temperature but depends largely on excess air and local stoichiometry;
- "prompt NO_x ", of which there is certainly less in absolute terms than thermal NO_x and fuel NO_x .

A distinction should be made between the following fuels in terms of NO_x emissions:

- the family of lean gases (blast furnace gas, and steel converter gas possibly enriched by coking oven gas or natural gas) producing NO_x levels in fume close to 100 mg/Nm³, thanks to the low adiabatic flame temperature (approximately 1 900°C);
- the family of high-calorific gases (coking oven gas, natural gas, etc.). The formation of NO_x is strongly influenced by the hydrodynamic design of the burner. Emissions of NO_x can vary by a factor of 10 when the design is modified;
- the family of oil fuels in which "fuel NO_x " accounts for much or most of the NO_x , due to the presence of organic hydrogen compounds. NO_x levels in the fume can be very high (over 600 mg/Nm³).

Further study of nitrogen oxide emissions from steelmaking plants
Research project 7261-01/414/03 carried out by LECES (France)

As mentioned above, the volume of NO_x emissions from steelmaking plants is high. Previous research had shown that between 1 and 3 kg of NO_x were emitted for each tonne of steel produced in non-electrical furnaces (excluding coking plant) and between 0.2 and 0.5 kg for each tonne of steel produced in electric furnaces.

The LECES project first made a fresh inventory of NO_x in the steel industry. Emissions of 1.8 kg of NO_2 equivalent per ton of steel rolled were measured at the SOLLAC-FOS integrated steelworks (with a production of 4 mt/year), of which:

- 24% came from the coking plant
- 58% from sintering
- 2% from blast furnaces

- 9% from reheating furnaces
- 6% from burning of gases in the power station.

Emissions for electric steelmaking were only between 0.2 and 0.3 kg NO₂ equivalent per tonne of rolled steel, depending on the type of furnace.

Subsequently, LECES explored various means of reducing NO_x emission.

- a) Using natural gas instead of coking oven gas was shown to cut NO_x emissions dramatically. The emission factor for coking oven gas is 20 to 30% higher than for natural gas due to the presence of nitrogenated compounds (NH₃, CN-, SCN-) which are converted into NO_x in the fume at a rate varying from 30 to 50%. It would also be possible to reduce the emission factor by decreasing the content of nitrogen compounds in coking oven gas by, for example, desulphurising the gas using the Stretford process, which would also reduce cyanides at the same time.
- b) In sintering, tests modifying the radiant hood ignition furnace showed that a reduction of some 4% in NO_x could be achieved but at the expense of productivity. Closing the bypasses, which led to this reduction, decreased productivity by more than 2%.
- c) The use of low-NO_x burners in furnaces reduced NO_x emissions, as burner design has a major impact on the formation of NO_x. Although the distribution between the central and peripheral air supply does not appear to have a major effect on emission levels, other parameters, such as inducing a swirling movement in the peripheral air supply and varying the air factor (i.e. operating with a deficit rather than an excess of air, or creating staged combustion) enable NO_x emissions to be cut. It thus ought to be possible to reduce emissions from reheating furnaces by 30%, although these only represent 10% of the total nitrogen oxide emissions from the non-electric steelmaking process.
- d) Tests to reduce NO_x emissions from electric arc furnaces have not had any significant effect on NO_x pollution. However, although the use of "airtight" furnaces has not been tested, it should improve the situation, but not by more than 20%.

In conclusion, the LECES study shows that reducing NO_x emissions from steelmaking is no easy matter and a reduction of 10% represents great progress.

Pilot study of nitrogen oxide emission from reheating furnaces
Research project 7261-01/407/04 carried out by CSM (Italy)

This CSM project set itself the target of assessing the formation of "thermal NO_x" from various reheating furnace burners, either roof or wall burners, using natural gas. The influence

of various aspects of burner design and of the control parameters (for gas, primary and secondary air etc.), on NO_x emission was thus determined.

Differences in NO_x emissions of up to a factor of 5 were observed. In particular, the benefits of long rather than short flames for variable burners with secondary air injection were demonstrated (reduction of emissions by a factor of between 3 and 4).

Finally, various mathematical models for simulating the burner flame were tested. Although temperature distribution could be assessed, and hence formation of NO_x in qualitative terms, it is not yet possible to calculate the amount of NO_x formed.

Reduced emission of nitrogen monoxide through the injection of water during the combustion process
--

Research project 7261-01/431/01 carried out by Thyssen (D)
--

Thyssen also examined ways of reducing nitrogen oxide in fume from reheating furnaces. In Germany, NO_x levels must be measured continuously and are limited to 500 mg/Nm^3 . Adding water or water vapour to the combustion air as a cooling agent for the flame was investigated.

First of all, the type of fuel was shown to have a very considerable influence on the amount of NO_x in the fume. When natural gas is used, the NO_x level is only 50% of that generated when coking oven gas is used and when a mixture of blast furnace gas and natural gas is used it is only 20%.

Another parameter which has a marked influence on NO_x emissions is the type of burner used. Various types of burners were thus studied in the laboratory.

- a) The burner where gas is injected at the centre of the burner and the combustion air in the peripheral area by a gas jet proved to produce the highest NO_x levels.
- b) If the flow of peripheral air is inclined at 45° in order to intersect the central gas flow, the flame temperature is lower and the flame longer. The NO_x is reduced by some 40 or 50%.
- c) If a swirl is induced in this peripheral air flow, the temperature of the flame is reduced still more and the NO_x in the fume is only 35% of that produced by the first burner.

The excess air factor also appears to have an influence on the NO_x level. This is highest at an excess air supply of 5% but is only 80% of this figure in stoichiometric combustion without excess air.

Finally, the NO_x in the fume increases exponentially with the preheating temperature of the combustion air, appreciably so from 250°C onwards.

If we consider the various chemical reactions which lead to the formation of nitrogen oxides when gas is burned (coking oven, blast furnace and natural gas), we see that the production of nitrogen oxides is inversely proportional to the water content. With a maximum addition of 300 g of water per Nm^3 of combustion air, it ought theoretically to be possible to reduce NO_x to some 80% of the present levels using coking oven gas and 55% using natural gas etc.

Tests were thus conducted, first in the laboratory and subsequently in an industrial reheating furnace, to establish whether such a reduction can be achieved. In the laboratory the reduction proved to depend largely on the type of burner. With a burner with parallel air and gas flows, a reduction of 50% can be obtained when 60 g of water/ Nm^3 combustion air is injected, but with low- NO_x burners, such as cross-flow burners and, even more so, burners where the peripheral air flow is rotated, such large reductions are impossible. The type of gas used also has a great impact on the reduction rate (which is high for coking oven gas and lower for blast-furnace gas).

Tests were then carried out for 400 hours in an industrial furnace, using coking oven gas injected by parallel-flow burners. One test for one hour demonstrated that adding 50 g of vapour per Nm^3 of combustion air reduced NO_x in the fume by 30%; over the whole period, a reduction of 10% in NO_x emissions was achieved, despite the fact that the vapour injection plant could not be installed throughout the entire furnace. As adding this amount of vapour did not, apparently, cause any increase in fuel consumption, this method could well be applied in industrial furnaces to remedy the situation when the levels of NO_x in the fume temporarily exceed authorised limits. The additional energy costs are, however, $\pm 2.5\%$, including steam production.

Reduction of nitrogen oxide emissions from steel industry power plant
Research project 7261-01/451/04 carried out by CSM (Italy)

Another CSM research project set out to reduce nitrogen oxide emissions from steel industry power stations. These power stations differ from others in that they use several fuels at the same time (fuel oil, natural gas, coking oven gas, blast-furnace gas and steelworks gas), some of which (blast-furnace gas and steelworks gas) are lean fuels.

The NO_x emissions from boilers depend on:

- the type of fuel;
- the calorific power of the fuel;
- the nitrogen content of the fuel.

Emissions are caused principally by "thermal NO_x" formed by the nitrogen in the air being oxidised at temperatures in excess of 1500°C, and "fuel NO_x" formed when the nitrogen in the fuel is oxidised. The "fuel NO_x" can account for most of NO_x emissions when heavy fuel oil or coal is used.

In order to achieve substantial reductions in nitrogen oxide emissions the following parameters must be manipulated:

- the shape of the flame and the burner;
- the fuel mix.

The modifications which could be made to the burners were established through tests on a model using reduced-scale burners.

A first series of tests was carried out on an existing burner (type GAKO Babcock Wilcox) with air preheated to 250°C and a furnace temperature of 1050°C. In this type of burner, the high-calorific fuel is injected at the centre, the lean fuel around the high-calorific fuel and the air at the periphery. NO_x emissions were shown to rise with excess air, with "fuel NO_x" formation when using heavy fuel oil, with flame temperature (this being considerably lower when a lean gas such as blast-furnace gas was being used), and with reduced fuel swirl (axial and tangential angle to the axis of the burner).

Various other types of burner were studied, in particular burners where the combustion air is not only injected at the periphery but also between the central high-calorific fuel flow and the lean fuel flow. The flame stability and NO_x emissions were examined for various angles of fuel injection at the burner exit port, for various proportions of lean blast-furnace gas, for various furnace temperatures and for various excess air levels. It is in particular the lean gas levels and the angle of injection of the fuel to the horizontal which proved to have the greatest influence on NO_x levels in fume. With more than 15% of blast-furnace gas in particular, the NO_x level in fume did not exceed 100 mg/Nm³.

Finally, measurements were made on the burner of an industrial boiler using various fuel mixes and with various excess air supplies, confirming the influence of the parameters determined on the model. The following mathematical correlation was established for this boiler:

$$\begin{aligned}(\text{NO}_x) \text{ mg/Nm}^3 = & 98.66 + 0.20 * (\text{Gcal/h coking oven gas}) \\ & + 0.97 * (\text{Gcal/h fuel oil}) \\ & + 5.86 * (\% \text{O}_2 \text{ in the fume}).\end{aligned}$$

Without major modifications to the combustion apparatus to ensure more effective distribution of the fuel and the combustion air and better regulation of turbulence at the burner exit port, it was not possible to improve boiler performance significantly in terms of NO_x emissions.

2.1.2 *Analysis of pollutants emitted at workstations in terms of the risk to workers' health*

2.1.2.1 Emission modelling tests

Modelling of air pollution at workplaces with a view to developing measuring strategies
Research project 7257-61/402/06 carried out by TNO (NL)

On the basis of several measurements of pollutant concentrations at a given workstation, it is not always easy to predict how high the concentration will be at another time, when the parameters of the operating process have changed.

With this in mind, TNO sought to apply mathematical models to predict pollutant concentrations at a given moment on the basis of:

- the concentration of pollutants measured at other times;
- measurements of operating process parameters and air extraction;
- other measurements which might, under some circumstances, affect pollutant emissions (temperature, pressure, atmospheric conditions etc.).

TNO used the "ARMAX" mathematical models which enable pollutant levels to be predicted at some time in the future from measurements of parameters (pollutant levels, operating parameters and other measurements) available at various times. Obviously, these models require there to be a sound correlation between the pollutant levels and other operating parameters under consideration, which is a prerequisite for determining the correlation coefficients. The difficulty lies *inter alia* in selecting the right parameters.

TNO then attempted to apply this theory by modelling the CO level at a given location in the Hoogovens steelworks, from the following measurements over two 12-hour periods:

- * CO level every 8'
- * dust level every 8'
- * converter status every minute (charging, blowing and pouring)
- * temperature and pressure at various sites in the shop every 5'
- * external atmospheric conditions (wind, rain etc.) every minute.

Modelling was done using the results of the CO level and the number of minutes during which the converter was pouring. Correlation proved to be very weak; in fact, the correlation coefficients varied with the measurement periods selected. Variations in the CO level were difficult to account for in terms of variations in the process parameters.

The conclusion of the study was that application of the ARMAX models used to predict CO level was not worth pursuing and the aim of limiting the number of measurements to be made in a measurement strategy enabling concentrations to be predicted was not achieved.

2.1.2.2 Pollutants at workstations in blast-furnace and melting shops

Characterisation of the health risk caused by the inhalation of particulate matter from pig iron and steel manufacturing processes
--

Research project 7261-04/442/14 carried out by ENSIDESA (ES)
--

When iron and steel are being produced, dust is emitted in the shops occupied by workers.

In order to reduce the effects on both the environment and workers' health, various dedusting systems, called secondary dedusting systems, may be installed. However, they are not always completely effective within workshops and they are not yet installed throughout the industry.

With this in mind, a study was undertaken to attempt to establish what risks were associated with workstations exposed to dust by collecting information on these dusts' properties.

The dusts were gathered at various points in the cast house of a blast furnace (iron notch, iron trough, slag trough and charging area of the hot metal transfer car) and in melting shops.

The study came to the following conclusions:

- Most of the dust collected was respirable dust: the respirable fraction < 6 µm accounted for between 55 and 65% of the total dust collected with a diameter below 21 µm, with microparticles < 0.5 µm accounting for between 12 and 24% of the total.
- The vast majority of the substances the particles contained were iron in the form of iron oxides.

Other metals such as Mn appeared in smaller quantities. Cr, of which much lower quantities were recorded (generally several hundredths of a percentage point) could nevertheless cause problems if they were in an environment where they could be put into a solution in the form of hexavalent Cr.

- Neither silicate compounds nor graphite were found in the respirable particles, which means that there is no risk of silicosis, siderosilicosis or graphitosis.
- Concentrations of PAH (polycyclic aromatic hydrocarbons) were also determined. Although low quantities were detected in the particles, the concentration in the ambient air is higher in relative terms, mainly at the iron notch and the slag trough in blast furnaces. Over 90% of the PAH are in volatile form. This means that equipment designed to prevent dust formation or to filter out dust will have little effect on PAH emissions.

It has also been established that the carcinogenic effect of benzo(a)pyrene increases in the presence of iron oxides.

Analysis and prevention of complex dust contamination in pig iron and steel manufacturing plants
--

Research project 7261-01/446/03 carried out by LECES (F)
--

In the light of the ENSIDESA study, LECES targeted two specific cases:

- dusts containing PAH in workshops such as blast-furnace shops, converter melting shops or electric arc melting shops;
- the possible presence of hexavalent chrome in dusts in plants making stainless steel.

a) Dust laden with PAH (polycyclic aromatic hydrocarbons).

- In blast furnace shops, PAH originates in the taphole clay which comprises between 70 and 85% mineral matter and 15 to 30% of organic binder. In particular when the clay gun is retracted from the iron notch, the remainder of the clay continues to emit vapour until it cools completely.
- Measurements of PAH were conducted in shops with dedusting equipment at the iron notch or serving the whole casting floor. The PAH levels observed were found to be moderate at workstations (below the recommended limit of 150 ng/m³).

PAH are absorbed on very fine particles (< 3 µm) with an iron-based matrix (sometimes on larger particles with high calcium levels). The highest PAH concentrations are obviously encountered near the iron notches.

- In the melting shops (both in oxygen converter and electric arc shops), PAH are emitted either from scrap or when new carbon refractories are preheated.

As in the blast-furnace workshops, PAHs are mainly observed on very fine particles with an iron-based matrix or on larger particles rich in calcium.

The particles containing PAH are mainly found in the area for heating ladles after their refractory lining has been repaired. They are also found in oxygen converters, in casting shops and in secondary metallurgy but not in continuous casting and not on the platforms of electric arc furnaces.

- b) Dust containing chrome in melting shops where stainless steel is produced
- Generally speaking, the measurements taken show that chrome levels at workstations in these shops are relatively low and lower than the limits recommended in France of 0.5 mg/m³.
 - The areas with the highest concentrations of chrome in ambient particles are, in decreasing order of importance, flame cutting of slabs, electric arc and oxygen converter platforms. At these workstations, most of the chrome is found in particles of between 1 and 2 µm and up to 5 µm. In addition, dusts with a diameter < 2 µm contain chrome mostly in the form of Cr VI as do dusts with a diameter in excess of 6 µm. The chrome contained in the intermediate size range of between 3 and 6 µm are, however, mainly in the form of Cr III.

2.1.2.3 Reduction of emissions caused by drying refractories

Study and prevention of emissions from carbon-bonded refractories in iron and steelworks
--

Research project 7261-01/448/03 carried out by LECES (France)

The iron and steel industry uses refractories made from materials (dolomite, magnesium etc.) cold-bonded by organic compounds for converters, ladles, submarine ladle cars etc. This bonding process results in high cold mechanical strength and facilitates handling of the refractories and installation of linings in reaction vessels. These organic binders also permit development of a carbon bond after pyrolysis which has good resistance to corrosion from metals and liquid slag.

Tar and coal pitch are generally used and sometimes organic resins such as urethane, urea-formaldehyde, phenol-formaldehyde etc.

The refractories are heated to high temperatures (1 000 to 1 200° C) to dry them, which can cause emissions of a number of dangerous compounds, depending on the type of binding

agent used: aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, phenols, polycyclic nitrogenated compounds, amines, nitrosamines etc.

The researchers set out to develop a tool to determine the nature and scale of emissions of organic compounds during refractory drying. A pilot furnace was built to simulate industrial drying conditions for various types of refractory. Tests were then carried out both in the pilot furnace and in an industrial furnace in order to quantify emissions of polycyclic aromatic hydrocarbons and phenols. These tests demonstrated the major impact of the drying conditions, and in particular of burner control, on PAH emissions. A slight difference in the burner heating rate and the conditions of oxidation/reduction reduced emissions by a factor of between 30 and 40 for the same refractory. Any inventory of PAH emissions will thus be subject to very considerable uncertainty as the carbon products emitted can be degraded by the action of temperature.

However, the study compared several different refractories under drying conditions as stable as possible and demonstrated the following points:

- Non-tempered pitch-bonded magnesite proved to generate fewer PAH emissions (especially benzo-a-pyrene) than burnt pitch-impregnated magnesite, whereas non-tempered pitch-bonded magnesite produced emissions comparable with those for the tempered version. Tempered pitch-bonded magnesite with anti-oxidants proved to generate very few emissions, like tempered carbon magnesite bonded with a phenol resin of the resol type.
- Coal pitch-impregnated magnesite contained some 0.8% PAH and 0.07% benzo-a-pyrene before drying with no detectable traces remaining after drying.

The PAH originally contained in the bricks was thus emitted during the drying operation, but only 0.07% of the benzo-a-pyrene (BaP) initially present is contained in the emissions.

This means that there is a low rate of BaP emitted compared with the BaP present originally, which indicates very considerable degradation of the hydrocarbons, or transfer to the tar recovered in the lower section of the pilot furnace under the grid supporting the refractory panel.

- A test with tempered magnesite carbon bonded with phenolic resin did not indicate significant emissions of phenols but low emissions of BaP.

The ratio of BaP emissions to BaP present in the bricks was also measured when an industrial ladle was dried in the plant. A figure of 0.07% was also recorded.

We can conclude that rigorous control of the conditions of use of a refractory likely to generate emissions ought to restrict greatly the quantity of pollutants emitted and hence make its use compatible with acceptable conditions of work.



2.1.2.4 Oil aerosol emissions

Development and testing of an apparatus to determine the concentration of oil aerosols
Research project 7257-55/401/01 carried out by the Betriebsforschungsinstitut VDEh (D)

Oil aerosols arise in a large number of technical processes in many areas of production and, inter alia in the metallurgical industry. Oils with various technological properties are used for lubrication and cooling. The toxicological impact of these oil aerosol and vapour emissions is very difficult to assess because of the variety of substances found in them. At workstations the permissible limits are generally 5 mg/m³ for respirable oil aerosols and 20 mg/m³ for total oil aerosols and vapour.

Oil aerosols generated by technical processes generally contain small particles. Blowing compressed air into oil results for example in an average particle diameter of 3 µm whilst vapour condensation gives rise to particles with a diameter of below 2 µm. These particles are therefore in the alveolar range, i.e. are largely trapped in the alveoli in the lungs.

Due to the risks associated with the presence of these aerosols at workstations, it has proved necessary to have an apparatus which can measure the quantity of these aerosols and distinguish between these and other dusts.

As no compact apparatus was available on the market it was decided to develop one.

Various detection techniques were examined (particle counting, scattered-light photometry, fluorescence detection, and detection by infrared light absorption).

The apparatus which was developed comprised an oil particle separator combined with an infrared light absorption detector.

- Oil particles of over 10 µm in diameter are separated by means of mechanical pre-separator;
- subsequently an electrical separator collects all the particles in the alveolar range and dissolves them in an extraction solvent, such as carbon tetrachloride, as carbon tetrachloride does not absorb infrared light;
- finally the concentration of oil in the solution thus prepared is determined by infrared absorption.

This apparatus enables oil aerosols to be measured continuously at workstations. It can also be adapted to determine separately the concentration of oil vapour in the atmosphere. To do this, the oil vapour which is not collected by the separator is absorbed downstream of the separator by silica gel or polymer resin and then dissolved in an extraction solvent (carbon tetrachloride) where the oil concentration can be measured by infrared absorption.

Many measurements taken in the laboratory and at industrial workstations proved this instrument - the OLEmat - to be effective by.

2.1.3 *Reduction of dust emissions*

2.1.3.1 Reduction of blow-off from raw material stockpiles

Reduction of dust blow-off in steelworks, ore and coal stockyards by the use of binding agents.

Research project 7261-03/421/04 carried out by CSM (I)
--

Raw materials stocks (ore, coal and fluxes) can constitute a major source of dust emission into the environment, particularly when the weather is hot, dry and windy and can reach high levels in the summer and in Mediterranean countries.

For this reason the Centro Sviluppo Materiali (CSM) carried out a research project to reduce blow-off from raw materials stockyards. Several ores, a flux (olivine) and several types of coal were analysed from the point of view of their propensity for dust dispersal. Tests were then carried out on these materials to determine whether spraying them with water and with binding agents was effective.

In order to determine dust blow-off propensity, a parameter was defined which was *inter alia* proportional to the percentage of particles below 62 μm and the average density of the material and is inversely proportional to the density of the particle fraction under 62 μm . This parameter thus provides a measure of the overall risk of dust blow-off from a materials stockyard.

Tests were then carried out to determine at what humidity level the risk of dust blow-off was negligible. This "critical humidity" was between 3 and 4% for ore (6% for ore where the average diameter of the particles was high) and between 7 and 8% for coal and fluxes.

Tests were also carried out in the laboratory to verify the rate of humidity loss at various ambient temperatures. As one might expect, this increases with temperature but even at 25° C

is still relatively high. A loss of humidity in the order of 0.2% per hour for ores and 0.4% per hour for coal and fluxes was established.

Finally the strength of the crust formed solely by spraying with water was low or zero for ore and zero for coal and fluxes. This means that dust blow-off cannot be prevented effectively with water.

In order to reduce dust blow-off binding agents must be mixed with the sprayed water. Several binding agents were thus tested in the laboratory first in a static situation to determine the depth of penetration of the film and the strength of the crust formed after drying and then in a dynamic situation under a current of air simulating a wind speed of 50 km/h and an ambient temperature of between 14 and 18° C. These binding agents were effective, especially PAV 50 which comprises 50% polyvinyl acetate and 50% water.

This binding agent was diluted with water to a concentration of between 3 and 6% and a total volume of between 1 and 2 l/m². The binding agent penetrates to a depth of some 1 to 2 cm and, once dry, forms a crust with a fair resistance to breaking. Laboratory tests showed that there was no blow-off even after seven days with a wind blowing at 50 km/hour 10 hours per day. Field trials confirmed the effectiveness of the process.

The CSM then developed a mathematical model to optimise this process for reducing dust blow-offs from raw materials stockyards. This enables both the concentration of the binding agent in the spraying water, the volume of spraying and its frequency to be determined, depending on the physical properties of the materials to be treated.

2.1.3.2 Reduction of dust emissions from molten iron and steel

Reduction of dust emission during metallurgical operations by inertisation of the ambient atmosphere
Research project 7261-01/492/05 carried out by Profil Arbed (L)

During several metallurgical operations such as tapping the blast furnace and transferring hot metal from a submarine ladle or a mixer to a transfer ladle, brown fume is emitted when the hot metal comes into contact with the oxygen in the air.

This brown fume can be controlled or reduced by protecting the hot metal by an atmosphere rich in CO₂ obtained by injecting solid CO₂. The resulting inertisation stops the metal from oxidising and thus dust from being emitted.

Profil Arbed has carried out such inertisation tests at a blast furnace when iron is cast into submarine ladles via a tilting spout and in a melting shop when hot metal is transferred from a submarine ladle to a transfer ladle.

Inertisation is effected by jets injecting solid CO₂ at maximum flow for 30 seconds into the empty ladle and at a reduced rate for the entire period when it is being filled.

Tests in the melting shop showed that inertisation is only effective if applied properly. In particular the operators must abide by the procedure strictly and systematically monitor the state of cleanliness of the ladles if satisfactory results are to be achieved.

Dust analysis shows that only iron oxide dust emissions is reduced, with the emission of graphite particles remaining largely constant. This clearly shows that the technique acts on the actual process of dust generation by oxidation of the molten metal.

A reduction of 88% of dust emission was achieved on the blast furnace tilting spout with a specific consumption of solid CO₂ of between 8 and 10 kg per tonne hot metal using open top ladles (5 kg per tonne hot metal for submarine ladles). The maximum permissible value of 6 mg/m³ of dust for daily exposure of eight hours was complied with at workstations without the corresponding value for CO and CO₂ being exceeded. The cost of the inertisation process was ECU 0.65 per tonne hot metal (including amortisation).

Obviously the inertisation system itself cannot eliminate emissions of dust and organic compounds at the iron notch. Here an extraction and filtration system will have to be installed. It should be noted that emissions of dust at the iron notch are assessed at between 0.04 and 0.1 kg/t hot metal as against 0.2 to 1.6 kg/t hot metal at the tilting spout.

When transferring hot metal from a submarine ladle into a transfer ladle, a reduction of 87% was achieved using an inertisation process similar to that used at the blast furnace tilting spout with a specific consumption of between 2 and 2.4 kg CO₂/tonne of hot metal. The cost was some ECU 0.15 per tonne hot metal (including amortisation).

When the LDAC converter is being charged, there is considerable dust emission which is not captured by primary filtration. The main secondary emissions occur when scrap is being charged into the converter which, at the time, still contains oxygenated liquid slag. By adding a tonne of anthracite to inertise the oxygenated mass and by adjusting the procedure for charging the converter, Profil Arbed was able to reduce secondary emissions by more than 75%.

In addition to its low investment costs, the technique of inertisation has an additional advantage in that it generates far less waste, as the technique is designed to reduce dust generation rather than collect dust.

2.2 WASTE WATER TREATMENT

2.2.1 *Treatment of cooling water to prevent the development of algae*

Testing and pilot- scale development of an ultrasonic system for non-pollutant anti-fouling treatment of cooling water in steelworks
--

Research project 7261-02/435/04 carried out by CSM (I)
--

The spread of living organisms clinging to the walls of cooling water circuits can cause problems due to reduced effective bore of the pipes, reduced thermal transfer in heat exchanges and as a result of corrosion of the surface of piping walls. This is called fouling and is a natural phenomenon occurring on any body immersed in surface water as a result of a deposit of microscopic flora and fauna, leading on to the establishment of microscopic algae and higher organisms.

This problem is generally tackled by using chemical reagents which kill off these organisms. However when the cooling water is disposed of, the residual compounds in the waste are toxic and an environmental hazard. CSM has thus tested an anti-fouling process using an ultrasonic system to destroy the larvae of the organisms and thus avoid any dangerous chemical substances being dumped in the environment.

This study was made for the site of Taranto in Italy where sea water, which can reach a temperature of 28°C in summer, is used for cooling. The first phase of the study was devoted to determining the organisms which were responsible for fouling and how they might spread. This phase which took an entire year mainly identified three organisms: *Serpulidi*, *Balanidi* and *Mitili* which were very widespread, sometimes forming a deposit of between 30 and 60 kg/m².

During Phase 2 of the study these three organisms were subjected to ultrasonic rays at varying power frequencies and for various periods in a laboratory and the rate of mortality amongst the larva was observed during each experiment. At a wattage of 130 W and a frequency of 25 Hz, mortality rates of some 80% after more than 5 seconds of exposure to the ultrasonic waves were achieved.

Phase 3 of the study then set out to assess the effectiveness of a pilot scale system on a test section of 65 cm x 58 cm traversed by the intake water for the main Taranto feed pipe. This test section was equipped with ultrasound generators and test plates to determine the spread of the organisms in the "treated" water. A reference test section not equipped with ultrasound generators enabled the "normal" spread of the organisms in the untreated water to be monitored. After three months of operation the demonstrable effect of the ultrasound was only slight with the spread of organisms being reduced by an average of 26% and a maximum of 44%.

In conclusion, whilst exposure to ultrasound does destroy the larvae of the organisms responsible for fouling, the technique itself is not sufficient to control this phenomena, particularly in systems using large volumes of water with a high density of planktonic biomass. It could perhaps be used in combination with conventional chemical antifouling methods.

2.2.2 *Smoothing pollution peaks*

Smoothing pollution peaks to optimise the functioning of steel industry effluent treatment installations
--

Research project 7261-02/461/03 carried out by IRH (France)

When liquid effluents vary sharply over time (in terms of pollution, concentration, volume and flow, etc.) there is a problem with dimensioning the treatment installations as the cost will be prohibitive if they were designed to cope with peak loads and operation would not be optimal if the flow received was very much lower than maximum flow. This type of problem is mainly encountered in installations for surface treatment of steel plate (pickling, degreasing, tinning, galvanising, etc.) where various effluents with variable flows and types of pollution end up in the same treatment station.

The conventional solution is to provide for damping and homogenisation tanks upstream of the treatment installation to smooth out pollution peaks. However the size of the tanks and the energy needed for mechanical agitation of the effluents in these basins make the installations costly.

However these agitated tanks can be replaced to good effect by hydraulic systems (combinations of tanks) designed more specifically to cope with the dynamics of variation in waste volumes over time, enabling the overall volume of the tanks and, more important, mechanical power for agitation to be reduced for the same output.

The general arrangement for such an installation is to divide the effluent in equal partial flows, convey them to longitudinal non-agitated tanks (piston-flow reactors) of different lengths and, finally, mix the output from each of the longitudinal tanks in a final tank. Under these conditions any concentration peak will be divided into fractions which will leave the reactors (longitudinal tanks) after varying periods of time. In the final stage a perfectly mixed reactor (a tank with mechanical agitation) will smooth out the original residual pollution peaks.

IRH thus devised an installation where the effluent was divided into eight equal partial flows which pass through eight piston-flow reactors before ending up in a perfectly agitated final reactor with a capacity of 10 m³.

Simulations were carried on the basis of both theoretical disruptions and variations in pollution flows measured in a plant factory using real effluents. These showed that, for a given smoothing performance, the buffer tank volume and especially the volume of the tank with agitation could be reduced considerably (by a factor of between 3 and 10).

At the same time IRH examined the relations between titrable acidity/basicity, pH and electrical conductivity and demonstrated that titrable acidity/basicity, which is complex and difficult to determine experimentally, could be calculated from pH and electrical conductivity which could easily be measured on line. This ought to make it possible to facilitate and optimise the control of the operation and management of acid/basic neutralisation installations. In particular it should also be possible at any time to switch the pollutant inflow between various units in the multi-reactor smoothing system and the neutralisation plant proper.

2.2.3 *Removal of cyanides*

Chemical treatment for the specific destruction of cyanides
Research project 7261-02/412/03 carried out by the Institut de Recherches Hydrologiques (F)

The production of raw materials (coke) and the production (in blast furnaces) and processing of metals (in foundries and surface treatment shops) in the steel industry give rise to aqueous effluents containing cyanides in various concentrations. These cyanides are not only a hazard for the aquatic environment due to their toxicity, but may also adversely affect water purification techniques (biological and physical/chemical treatment) and can generate cyanide emissions into the atmosphere.

Removing cyanides in the steel industry thus constitutes a major problem. The IRH first carried out a bibliographical study on the reactivity of cyanides and the main ways they are or might be removed. One conventional method is to oxidise the cyanides chemically with chlorine, but this technique has several drawbacks, such as incomplete oxidation, long reaction times and risks associated with liquid chlorine and some of its toxic derivatives. IRH also studied the literature on other techniques, such as precipitation of cyanides using ferrous sulphates, but mainly concentrated on the high degree of reactivity of cyanides to certain groups of organic substances.

Recent research had shown that cyanides react with formaldehyde (HCOH) to form glyconitrile (OCH_2CN) which remains in solution and is only very slightly toxic.

As the reaction between cyanides and formaldehyde appeared to have potential for the treatment of effluents in the steel industry, it was first studied in detail using synthetic solutions and subsequently using real effluent which contained or could contain high

concentrations of cyanides. Coking plant effluent, blast furnace gas scrubbing effluent and effluent from the treatment of metallic surfaces (copper plating of steel sheet) were all tested in the laboratory to remove cyanides.

During the tests, the parameters (pH, temperature, concentration of formaldehyde with respect to the stoichiometric ratio, concentrations of other pollutants, etc.) were varied in order to examine and optimise destruction of cyanides, the speed of reaction and the residual toxicity of the treated effluent (*Daphnia* tests carried out in accordance with the standardised French method).

The conclusions which can be drawn from the laboratory tests are that:

- optimum pH value for the treatment is between eight and nine;
- temperature has a major influence on the reaction rate: at around 40°C this reaction generally took place in under five minutes;
- in order to achieve a high rate of cyanide removal, it was sufficient to have a slight excess of formaldehyde. However if the solution is impure, parasitic reactions between formaldehyde and other pollutants can make a greater excess necessary.

Treatment of blast furnace gas scrubbing water appears to be the ideal application for this new technique. The purification rate is close to 100% and, irrespective of the initial concentration, the residual concentration can be kept to below 1 mg/l, or 0.2 mg/l. The toxicity of the effluent can thus be reduced by a factor of 20, especially when the stoichiometric ratio is close to 1, as any residual concentration of formaldehyde can have an adverse effect on the residual toxicity, though far less so than the cyanides. The only constraint is that treatment has to be carried out at a pH value of between 8 and 9, whereas the normal pH for such effluent is between 5 and 6. This type of treatment for blast furnace gas scrubbing liquor has been refined for industrial use by CEBEDEAU CRM and IRH (cf. Chapter 5).

Ammoniacal water for coking plant could also be treated though much less effectively than blast furnace gas scrubbing liquor due to the considerable presence of other pollutants such as phenols, which make a large stoichiometric excess of reagents necessary to achieve high rates of cyanide removal, and, even then, the residual toxicity of effluent requires additional treatment. Alternative conventional solutions such as biological treatment therefore seem preferable.

The results of treatment of effluent from electrolytic copper plating of steel sheet with formaldehyde were thoroughly disappointing. Not only were complex cyanides only partially eliminated, but the existence of parasite chemical reactions (dissolving of Cu compounds) increased the toxicity of the effluent instead of reducing it.

2.3 MANAGEMENT AND TREATMENT OF WASTE

2.3.1 *Waste treatment for upgrading*

2.3.1.1 Treatment of sludge and dust containing zinc and/or lead

Study of the possibilities of treating simultaneously steel making waste rich in Zn/Pb and depleted hydrochloric pickling baths
Research Projects No 7261-03/428/02, 7261-03/453/02 and 7261-02/463/02 carried out by CRM and CEBEDEAU (B)

Recycling of blast furnace gas scrubbing and steel making sludges and of dust filtered out of melting shop fumes is prevented by the presence of zinc (0.1 to 6%) and lead (0.05 to 1.5%). This steelmaking waste, which is rich in iron, could easily be recycled in sintering if the concentration of heavy metals, especially Zn, were low, as the blast furnace can only cope with some 120 to 150 gr of Zn per tonne of pig iron.

There are various methods for separating Zn and Pb from this waste:

- physical methods, such as hydrocycloning of blast furnace sludges, which achieve a recycling rate of between 70 and 75% by weight;
- pyrometallurgical or electrothermal methods which are effective but costly, particularly when the concentrations of Zn and Pb are originally low;
- hydrometallurgical methods based on leaching with caustic soda or acid (such as hydrochloric acid).

It was this last avenue which was explored in the CRM/CEBEDEAU research project, using another waste product from integrated steelmaking, namely depleted hydrochloric pickling liquor, as a leaching agent. The basic idea was to try and dissolve selectively the Zn/Pb/alkaline compounds of these steel making wastes in an acid medium, excluding the iron oxides.

The depleted pickling liquor to which the steel making waste containing zinc and/or lead is added is mainly made up of FeCl_2 which first has to be oxidised by, for example, chlorine to form FeCl_3 . Subsequent hydrolysis causes the FeCl_3 to precipitate as goethite (Fe OOH) and the Zn and Pb oxides go into solution as Zn and Pb chlorides. The goethite can then be separated out by means of filtration. The Zn and Pb chlorides can subsequently be recovered by precipitation with caustic soda or lime. The final liquid waste is thus mainly made up of alkaline chloride and alkaline earth brine.

For the first stage in the process, which was to oxidise FeCl_2 from the depleted liquor to form FeCl_3 , the best reaction was obtained using gaseous chlorine at a pH value of between 3 and 3.5.

For the second stage (dissolving Zn and Pb etc.), the best extraction results - whilst maintaining sufficient selectivity vis-à-vis the Fe - were obtained by leaching at pH 2 and 40°C and maintaining a high concentration of chlorine (3 to 6 M) in the leaching environment. The pH value is then stepped up to ± 3.5 to precipitate the ferric iron hydroxides in the form of goethite, which can easily be filtered out. Post chlorination in the precipitation reactor also enables the iron and $\text{Fe}(\text{OH})_2$, which are more difficult to filter out than the goethite, to be recovered.

The extraction yields for blast furnace sludges are as follows:

- between 80 and 99% for Zn;
- between 70 and 95% for Pb

with excellent selectivity in the reaction vis-à-vis iron oxides being maintained. For steel making sludges the yields are low.

The fluctuation in the extraction yields for blast furnace sludges and the low rate of extraction for steelmaking dusts are due to the various mineralogical forms which are present. For Zn, extraction rates are good for ZnO and ZnS, but it was more difficult to dissolve Zn ferrites ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$) and there are more of these in steelmaking dusts. Various ways of dissolving them were examined but no means of selective dissolution vis-à-vis iron oxides could be identified.

The third and final stage, after separation of the goethite precipitate by filtration and successive washing operations, is to extract the Zn and the Pb from the solution. This was easily done in a variety of ways, such as by treatment with caustic soda at a pH value of 10.7 with a yield of over 99% whereby, however, the Pb tends to return to soluble form. Finally lime treatment (pH 8.5) in combination with final treatment with polysulfides was selected.

Zn and Pb hydroxides are obtained by this process. Other techniques can then be used to separate Zn and Pb in metallic form.

The process of acid leaching of residues containing Zn and Pb with depleted hydrochloric pickling liquor can only be envisaged for recycling blast furnace sludges and not for (oxygen or electric) steelmaking dust rich in Zn ferrite. The high concentration of free lime (CaO) in steelmaking dust also increases consumption of the reagent sharply. The rates of yield obtained for blast fire sludges, however, are such that they can be recycled in iron ore sintering.

Finally the liquid waste obtained, which is essentially a chloride brine (with some 16 g/l of chlorides), limits the use of this method to steelworks by the sea where dumping should not be a problem. However, halogenated organic compounds have also been detected in higher

concentrations than normal, which could make it necessary to subject the waste liquor to additional treatment.

Small laboratory pilot unit was built to treat several kilograms per hour of blast furnace gas scrubbing sludge continuously. This has enabled the process to be optimised and an industrial installation with the capacity of 15 000 tonnes per year to be designed.

The cost of such treatment of blast furnace gas scrubbing sludges has been estimated at some 100 to 150 ecus per tonne of treated dry matter, assuming that the installation has a capacity of 15 000 tonnes per year and requires an initial investment in the order of 3 million ecus.

Biological detoxification of steelworks wastes containing heavy metals
Research project 7257-74/404/2 carried out by CEBEDEAU (B)

CEBEDEAU examined another technique, this time using microbial leaching. Such processes are widely used on an industrial scale to extract metals, *inter alia* copper from low-grade ore. CEBEDEAU therefore wished to examine whether these could be applied to blast furnace sludges or mixtures of blast furnace and steel making sludges to extract zinc and lead selectively.

The concentration of zinc and lead in the sludges used for the tests was 0.5 - 1% and 0.1-0.3% respectively.

Microbial leaching processes require good penetration of the percolating agent and a good transfer of oxygen into the material to be treated. The very fine particle size of the sludges to be treated prevents this and the tests thus had to be carried out in air lift reactors in order to obtain sufficient reaction. Natural percolation is not enough if the layer of sludge is more than a few centimetres thick.

Industrial microbial leaching processes also make use of *Thiobacillus* sulpho-oxidising bacteria. It is the sulphuric acid produced by these bacteria which dissolves the metal in an acidic aqueous medium. Unlike copper ores, which are mainly made up of metallic sulphides, steelmaking wastes contained only very little sulphur, so that a sufficient quantity of a material containing sulphur in reduced form (pyrite) has to be added.

Finally, the process requires an acidic pH value (± 3.5) to develop the bacteria, which means that a large quantity of sulphuric acid has to be added to counteract the alkalinity of the sludge.

However, even when suitable adjustments were made, the leaching rate was low (40%) Zn and very low for Pb and was mainly due to the initial acidity. It was shown that bacteria do develop, but they do not have any beneficial effect on leaching of Zn and Pb. On the contrary,

the development of the bacteria results in higher leaching of iron, thus reducing the selectivity of the process.

In conclusion we can say that the microbial leaching process is unsuitable for selective extraction of zinc and lead from blast furnace gas scrubbing sludges.

2.3.1.2 Treatment of oily sludges

Treatment of oily sludge by chemical processing and physical separation of the ferrous fraction which can be reincorporated into the steel making cycle

Research project 7261-03/429/04 carried out by the Centro Sviluppo Materiali (I)
--

Two types of waste are obtained from treatment by filtration and decantation of the water used in continuous casting, hot rolling mills and the manufacture of tubular products: coarse scale, which is sufficiently rich in iron and poor in oil to be recycled, and finer sludges with a higher concentration of oil which rules out recycling.

The aim of the research project was to treat the fine sludges which were rich in iron and hydrocarbons in order to reduce their oil and grease content - initially in the order of 15 to 25% - to less than 2% so that they can be recycled through the sintering plant.

The first approach explored the use of de-oiling solutions. Various solutions were tested such as ionic and non-ionic surfactants, alkaline reagents and polyamines, etc. A solution of surfactants to which a wetting agent and an emulsifier from the ethoxylated nonylphenol family were added, proved most effective. Tests were then continued using this solution first in the laboratory and then in a pilot installation in order to fine-tune the method and achieve maximum de-oiling. The researchers managed to reduce the concentration of oil in the sludges to below 2% by treating them at 70°C for one hour at an initial concentration of 10 gr of solution per litre of dry sludge, followed by decantation for 15 minutes. This treatment must be repeated three times and must then be followed by a final filtration of the decantation product in a filter press to reduce the oil content to below 2%. The oily product is separated during decantation. There is no information on the quality of this product in the report.

The second approach examined is hydrocycloning. Hydrocycloning can be used to separate the coarse particles from the fine ones. As the specific surface area (in m^2/cm^3) of the fine particles is greater than of the coarse ones, there is more oil in the fine particle fraction. It was shown that when the coarsest particles, accounting for 25% of the total mass of the sludges, were separated, this fraction contained a concentration of oil of between 3 and 5%.

However, this fraction of 25% was considered too small. Pretreatment before hydrocycloning with a single treatment stage with the deoiling solution used in the first method did not produce better results.

The conclusion is that treatment of sludge containing oil and grease with a de-oiling agent in order to reduce a concentration to less than 2% is technically possible but is a slow and difficult operation. The economic aspects of the treatment were not examined.

2.3.2 *Final waste tipping*

Extension of the research on leaching of iron and steel industry waste to new types of waste
Research project 7257-72/405/03 carried out by the Institut de Recherches Hydrologiques - IRH (F)

Tests and analyses are performed to assess the risk of contaminating the environment when steelmaking waste is dumped. IRH has carried out many of these to:

- evaluate the representativity of these analyses and tests as a basis for assessing the impact of dumping waste on the environment;
- optimise the economics of analyses and tests on steelmaking waste by finding correlations between the parameters. If such correlations can be established, the number of parameters to be analysed can be reduced.

The leaching tests were carried out in accordance with the French *INSA* method, placing the waste in contact with the solution of demineralised water saturated with CO₂ and air for 16 hours, agitating it on a horizontal plane at a frequency of 16 movements per minute, and collecting the leached product by means of a fibre glass filter. During the tests the solid/liquid ratio is normally 100 gr of waste per litre of solution. However, other have been tested.

Analysis of leaching solutions generally shows that there is no direct link between the concentration of elements in the waste and the composition of the leaching solution, which rules out the possibility of forecasting the risk of contamination of the environment by leaching simply by analysing the waste.

Leaching tests can, however, if used carefully, provide information on the behaviour of waste in contact with water and can contribute (usefully rather than conclusively) to forecasting the risks to the environment of leaching from dumped waste. It has thus been shown that:

- one procedure comprising three successive phases of contact with the same solid/liquid ratio of 100 g/l made it possible to assess the soluble fraction in the waste by subtraction and to study how pollutants behaved in the solubilisation process, identifying typical modes of behaviour;
- a procedure comprising a single phase of contact with a solid/liquid ratio of 10 g waste per litre of solution dissolved more pollutants than three contact phases with 100 g/l but did not enable typical behaviour modes to be examined;
- a multiple-purpose leaching procedure could be developed using three successive contact phases with progressively decreasing solid/liquid ratios: 1000 g/l, 100 g/l, and finally 10 g/l. This would enable the immediate pollution peak, resulting from the first contact between the waste and water, to be forecast, the total soluble fraction to be assessed and finally the medium-term leaching effects to be forecast.

The IRH then developed a methodology for assessing variations in steelmaking wastes and by-products in order to find out enough about the characteristics and behaviour of these materials with the minimum number of analysis and thus at the lowest possible cost. This methodology was applied to a large number of steelmaking wastes but, although some correlations were established, the number of parameters which were needed to define a type of waste varies considerably and is generally fairly high, given the independence of many of the parameters. No general tendency could be identified.

The analyses and tests did however confirm the low toxicity of leaching products from electric arc furnace dusts from production of low alloy steels.

Binding of heavy metals in steelworks waste by suitable control of dumping
--

Research project 7261-03/422/03 carried out by LECES (F)
--

More and more stringent standards are being applied for dumping final waste, particularly with regard to the concentration of pollutants in leached products. The same applies to the concentrations of heavy metals, Zn, Pb, Cd, Ni, Cr, etc.

Leaching tests carried out on steel works waste show that release of heavy metals is mainly a result of the initial alkalinity of the product and the resulting pH value. Heavy metals present in a leachate could therefore be bound if they had to pass through a product with antagonistic chemical or physical chemical nature where the reactions accompanying percolation through the deposit neutralise the micropollutant-containing leachate.

The researchers therefore set out to study mixtures or layering of types of steel making waste which do not lead to release of pollutants, especially heavy metals, when dumped.

Steelmaking wastes from which large quantities of heavy metals are leached are mainly sludges from purification of effluent from steel coating lines (electroplating, chromium plating, etc.) and dusts from electric arc furnaces.

By contrast, steel making slag and blast furnace sludges could have properties which are useful in neutralising heavy metals. These were subjected to intensive tests in laboratories and in pilot dumps.

It was discovered the presence of sulphur in steelmaking slag gave it useful properties for binding heavy metals, particularly Zn and Cd, and to a lesser extent, Pb. Under normal percolating conditions, over 90% of these heavy metals are bound very rapidly and irreversibly within the slag. The binding effect on hexavalent chrome is, however, is only slight.

It was also demonstrated that blast furnace sludges were capable of binding hexavalent chromium although less effectively than slag binds Zn and Cd. Blast furnace sludges were shown to be an effective "geochemical barrier" on a pilot scale over a period of some two years where sludge from the purification of coating line effluent and blast furnace sludge were dumped in alternating layers.

Other tests were also carried out to bind heavy metals present in various electric arc steel making dusts using polysulphides in order to obtain a waste product which could be dumped. The polysulphide used was calcium tetrasulphide obtained by boiling sulphur from coking oven gas desulphurisation (flower of sulphur) with milk of lime. The neutralisation reactions were expected to produce virtually insoluble sulphides. The results obtained confirmed that this process is effective with very high abatement rates, sometimes in excess of 99%. However, this was still not enough to comply with the limits for controlled dumping in France, at least for one category of electric arc steel making dust.

The conclusion is that a bottom layer of slag would provide a geochemical barrier for heavy metals both for the disposal of ordinary waste in natural surroundings and for sealed dumping of high-risk wastes.

Retention capacity of Posidonia shale in respect of seepage water containing heavy metals from flue dust dumps

Modelling of migration mechanisms based on laboratory tests and work on site

Research project 7261-03/436/01 carried out by Angewandte Geologie Karlsruhe
(D)

A study carried out by AGK set out to determine migrating speeds for the main heavy metals, especially Zn and Pb, in the subsoil of a dump in order to assess the risks to the environment of dumping steel making wastes.

First of all, the theoretical principles were reiterated showing that the migration of elements can be assessed from:

- adsorption and desorption characteristics of the soil for a given pollutant, characterised by the distribution coefficient K_d between the part adsorbed and the remaining concentration in the percolating water, and by a delaying factor α which represents a measure of the soil's adsorption capacity;
- the convection properties of the soil, i.e. the movement of the pollutant with the rate of flow of underground water, characterised *inter alia* by the permeability coefficient for the soil K_f ;
- soil diffusion properties for each pollutants, determined *inter alia* by the diffusion coefficient D , the tortuosity factor C and the retardation factor D .

The equations governing migration can therefore be used to model a given site, as long as the values for the above parameters are known.

Migration of Zn and Pb in to argillaceous subgrades was determined experimentally underneath several dumps for dusts from scrubbing gas from metallurgical plant, especially the Arbed dump at Esch-Belval in Luxembourg where dumps have been in existence for some 40 years. Boreholes were made which showed that the migration of Zn, Pb and Cd into the subsoil was very slight. After only several centimetres migration ceases in these natural argillaceous subsoils and pollutants are scarcely detected in the percolating water. These experimental results enabled the migration parameters to be determined so that the theoretical models tally with the experimental measurements.

Tests were then carried out in a laboratory to determine the various adsorption, convection and diffusion characteristics of these soils.

Great differences emerged when the characteristics of the soils identified in the laboratory were compared with those identified on site. Adsorption tests in the laboratory produced retardation factors which were much higher than in reality, while the laboratory percolation tests produced retardation factors which were much lower, mainly due to much higher hydraulic gradients used in the laboratory tests.

The conclusion appears to be that an argillaceous layer under dumps for waste containing heavy metals constitutes a highly effective geological barrier to the migration of heavy metals *inter alia* as a result of their adsorption on soil particles.

After some 30 or 40 years, the heavy metals (Zn, Pb and Cd) do not migrate by more than several centimetres. However, this only applies for waste without organic materials, which can give rise to highly complex reactions greatly modifying the migratory characteristics. Heavy metal waste should thus be dumped in sites reserved for this kind of waste. After dumping,

a ceiling layer can be applied from above not only to reduce percolation through the material but also reduce the hydraulic pressure gradient, which in turn will further slow migration into the subsoil.

Migration models can be designed from the equations for the migration of pollutants and the properties of the argillaceous layer.

2.3.3 *Decontamination of old lagoons and dumps*

Physical/chemical treatments of unusable oily sludges
Research project 7261-03/426/03 carried out by the Institut de Recherches Hydrologiques - IRH (F)

In the past a plant dumped all its oils and oily effluent in a lagoon with a surface area of approximately 10 000 m², in accordance with new environmental requirements, must now be decontaminated. At the time of the research project, the lagoon contained a waste which had become stratified in the course of time and which comprised:

- a top liquid phase containing approximately 25% of oil and low-density suspended matter and 75% of water. After treatment by physical/chemical and mechanical means to increase the oil content, the oily phase is eliminated by thermal destruction;
- an intermediate aqueous phase which ought to be able to be disposed of in natural environment, after suitable physical/chemical treatment if the need arises;
- an underlying sludge phase which is highly concentrated and which is only 30 cm thick.

It is the final phase on which treatment tests have been focused, both to reduce as much as possible pollution by percolating water and to obtain a material which can easily be handled. A dozen samples of the waste was first analysed precisely. These contained between 30 and 70% water, 10 and 40% organic hydrocarbons and 3 and 10% of iron, other elements accounting for only between 0.1 and 0.3%.

On average some 30% of the liquid phase could be extracted by spontaneous gravitation separation. The insoluble phase thus obtained was difficult to enrich by mechanical processes (centrifuging or filtration/compression) as laboratory tests showed.

All that remained was chemical treatment. As adding sulphuric acid and mixing with clay did not produce encouraging results, the tests were concentrated on the addition of quick lime, possibly in combination with pozzolana reagent.

In terms of the solubility of the pollutants, the best results were obtained by adding a quantity of quick lime (CaO) not exceeding 50%. If the quantity is higher, the solubility of pollutants (DOC and Pb) increases due to the excess of quick lime. At low quantities of quick lime, the physical state of the oily material is not greatly changed and it is only when the quantity exceeds 20% that the material becomes easy to handle. When the amount of quick lime exceeds 50% the material becomes powdery (but more soluble).

The best compromise between solubility and a physical state which is easy to handle was obtained by treatment with 30% of quick lime and 30% of powdered steel making slag. Under these conditions the amounts of DOC and lead entrained compared with untreated waste are divided by a factor of five and three respectively and the treated material is in a physical state which makes it just possible to handle.

Adding other pozzolanic substances, cement or organic materials which absorb oil (such as sawdust) did not produce better results.

The main finding of this research project was that it was absolutely necessary to make a clear distinction between the two following problems:

- the problem of a solubility of the pollutants when the waste comes in contact with water such as can be simulated by leaching tests in the laboratory;
- the problem of the physical state of the treated waste which determines whether it can be handled and stored.

2.4 ACOUSTIC NUISANCES

Noise from gas transport circuits in the steel industry. An inventory of potential sources of noise and an approach to modelling
Research project 7261-05/445/03 carried out by INRS (F)

INRS carried out measurements of noise levels in France in the vicinity of steel plant showing, of course, that these were high. The areas concerned included blast furnaces, blast furnace stoves, blower rooms, gas pipework, sintering plant, coking plant, oxygen installations and compressors, etc. The study concluded that the main sources are fans and regulating valves where the sound power level frequently exceeds 85 dBA.

All this is known to the steel industry and the research elicited little information which was of generally applicable interest. The values measured were typical of a local situation and depended on the distance from the source.

However, the measurements were taken close to equipment mainly with a view to studying their impact on the workers. No measurements at smoke stack outlets were carried out though these generally constitute the main sources of noise in the environment of steel works.

A bibliographical study of the possibilities of acoustic modelling was then carried out. Various models of equipment presented by various authors were assessed and it was concluded that the very large dimensions of steelmaking plant took it out of the range for which these models have been validated. This was the case for fans, pipework and blowers, etc. The authors therefore concluded that these models needed to be validated by means of additional measurements and some descriptions needed to be expanded. This work could not be carried out under the terms of this research project.

Use of noise prediction techniques to optimise noise abatement in steel shops

Research project 7261-05/444/02 carried out by CEDIA (B)
--

CEDIA and LECES studied modelling of the acoustic levels in large steel works shops in order *inter alia* to examine the acoustic effect of noise abatement equipment and, if necessary, to rationalise the acoustic treatment of a given shop by selecting the equipment with the best cost/benefit ratio.

The following information is required for such simulation exercises:

- the sound power spectrum of each of the sources of noise;
- a geometric model of the area involved;
- sound propagation in the area (attenuation over distance, reflection and absorption by the ground and obstacles, etc.);
- the siting of the workers to be protected.

Traditionally the acoustic power spectrum from a source of noise is determined from the sound power level, which can easily be measured with a sound level meter. However, the sound pressure level is a magnitude which is directly linked to the power emitted by noise sources only in specific cases (in a free field, with the energy flow at right angles to the surface, a single source not disrupted by other sources or by background noise, etc.). The sound power level is calculated as follows:

$$W = \int \vec{I} dS$$

where \vec{I} = acoustic intensity which is proportional to the product of the acoustic pressure for the average speed of air particles

S = the enclosed surface surrounding the source.

In many cases the sound power level calculated from measuring the sound pressure *in situ* produces inaccurate results. This is true of steel making shops with large obstacles where reflections can generate stationary waves and/or other sources can emit interference noise. In theory, acoustic intensity can be determined far more precisely, even in the presence of major sources of interference noise, as long as they are stationary, by means of the product of the acoustic pressure and the gradient of this pressure. The acoustic intensity is measured *in situ* using two sonometers placed face to face some ten mm from each other whose signals are processed in real time by Fourier transform algorithms to obtain a signal proportional to the product of the average acoustic pressure multiplied by the difference in acoustic pressure between the two sonometers. The directional character of intensimetric techniques not only enables sources to be identified but also enables them to be sited better.

The various types of error associated with this measurement were then quantified. By choosing the distance between the two sonometers (10 to 20 mm) and the distance from the source, error can be kept low in the range of normal frequency. This technique for measuring the acoustic intensity was then applied to various items of steelmaking plant including box annealing units and continuous annealing lines for hot rolled coil and an installation for cleaning converter fume in a melting shop. These applications showed that the sound intensity measurement technique was able, in the case of stationary sources, to determine selectively the sound power level emitted by a machine or part of a machine in the presence of other sources of noise in an industrial shop.

Propagation of sound in space was then simulated in a software developed by CEDIA based on the sound ray method. The principle of this method is to distribute all the energy emitted by a source amongst a finite number of fine bundles of energy called "sound rays" going in different directions (up to 30 000 rays can thus be envisaged for a single source). The energy transported by each ray is propagated in a rectilinear fashion until it encounters either a receiver or the wall of the shop where it is reflected in a direction which can be calculated. A ray can thus be monitored until it transports less energy than a predetermined threshold. Monitoring of the propagation of this ray is then abandoned after several dozen reflections.

The errors associated with this simulation method were then evaluated, i.e. systematic sound power level error, sampling error and modelling error.

By carefully choosing the simulation parameters, CEDIA managed to reduce the sum of these errors to a few dBA (3 dBA is quoted in the study). The software enables very accurate sound maps to be drawn and takes account of:

- attenuation of sound over distance;

- attenuation of sound in the air;
- reflection and adsorption by the ground and obstacles.

Sound maps and simulated improvements were then carried out using the software and sound intensity measuring techniques. The applications used included two annealing shops, two rolling mill shops and a continuous annealing shop. These confirmed that the software is a powerful tool for drawing sound maps which accurately represent reality and therefore enable the most suitable modifications or treatments to reduce shop noise levels to be examined.

Control of the acoustical environment in steel works by means of sound intensity measurement and predictive modelling

Research project 7261-05/443/03 carried out by LECES (F)
--

In order to determine the sound power level of a machine, LECES studied in more detail measurement of sound intensity by scanning the plane surfaces surrounding the source instead of single-point measuring, using a technique identical to that used by CEDIA for acoustic sound intensity measurement.

This scanning method enabled measurements to be taken in a far shorter period of time, as the point method required measurements to be taken at a large number of points (> 30). Setting aside the economic aspect of time and hence money, reducing the time taken for measurement mainly made it easier to take the measurements during a period when the machines were functioning stably. By moving the instruments uniformly (to avoid weighting the results in favour of a given part of a machine) and carrying out three successive scanning runs, a high degree of precision can be obtained by the scanning method, generally to within one dBA (3 dBA for difficult environments). Scanning measurement therefore seems well suited to steel making plant, which is characterised by very large sources and proximity with other major sources of noise.

To simulate the noise levels, LECES used software developed by the INRS independently of CEDIA but based on the same principles. The software was simplified to take statistical account of various obstacles in some of the shops. The number of surfaces to be modelled was therefore lower, thus reducing the time taken for inputting the data and for calculation purposes.

A workshop was simulated using the CEDIA software and the LECES software which took statistical account of the obstacles. On comparison, the results matched each other extremely closely, and, in particular, statistical modelling of obstacles produced results which were equivalent to those for modelling all the obstacles separately.

LECES then proceeded to apply the technique of sound intensity measurement combined with simulation in accordance with the sound ray method to various workshops:

- a rail mill;
- a wire rod mill;
- an electric arc melting shop;
- a tinning line;
- a galvanising line.

All these applications demonstrated the power and accuracy of the technique and confirmed CEDIA's conclusions. The simulation method produced values which did not diverge by more than 3 dBA from measurements made *in situ* with a confidence interval of 95%. As was the case for CEDIA, these applications made it possible to work out accurately and fine-tune the most suitable measures to be taken to reduce the noise at workstations to acceptable levels.

Reduction of noise from plasma torches used in continuous casting tundishes

Research project 7261-05/469/04 carried out by the Centro Sviluppo Materiali (I)
--

CSM set out to study of noise where abatement was necessary.

At the continuous casting plant in Aoste (I), the tundish has been equipped with two plasma torches with a capacity of approximately two megawatts, to enable the temperature of the molten steel to be adjusted. This heating system is used intermittently to regulate the temperature precisely and to control more carefully the dynamics of the molten steel in the casting process. However, when the plasma torches are in operation, noise levels in the order of 19 dBA were measured around the tundish, well above the maximum values recommended for workstations by European Directive 86/188/EEC of 12.5.1986.

CSM first measured the initial sound levels at the workstations by CSM before taking any corrective action. The first corrective measure was to place a refractory partition between the area where the molten steel was supplied and the tundish itself in order to screen the tundish area partially from the external environment. A second series of measurements showed that this improvement reduced the noise level by approximately 2 dBA at various workstations.

In order to design other means of reducing noise, a simplified mathematical model was developed to calculate the impact in the environment, and in particular on workstations of a sound source with a given sound power level and located in the tundish.

To apply this mathematical model the tundish had to be modelled (to take account of, for example, its geometry) and the properties (coefficients of adsorption and transmission) of the materials it was made of had to be established. This model was applied to the initial situation. The sound power levels (in watts) of the plasma torch/tundish system was established from measuring the noise at two workstations.

The same procedure was carried out on the basis of noise measurements at three workstations after the first improvement had been carried out (installation of a refractory material partition). The various sound power levels thus calculated proved to be consistent with one another, which enabled the acoustic power spectrum of the plasma torch/tundish system to be determined and the calculation model to be validated.

The effect of various other improvements to reduce the noise level were then simulated, including measures to reduce the acoustic reverberation within the cavity and to increase the acoustic insulating properties of its structure. Two improvements were then carried out, one to close a safety hole on the side of the tundish and another to replace the refractories in the cover by a lighter and more absorbent type of refractory.

Another series of measurements was then carried out to establish the effect of these improvements. Each of them brought an additional abatement of approximately 2 dBA i.e. a total of 4 and 4.5 dBA.

The noise level generated by the plasma torch under these conditions was well below the background noise (75 dBA as against 82 dBA).

The calculation model was once again applied to the whole system after improvement and the sound power level of the plasma torch alone was determined and the validity of the calculation model verified once again.

2.5 PROTECTION AGAINST IONISING RADIATION

Detection of radioactive contamination in steel plant raw materials
Research project 7261-04/467/01 carried out by the Betriebsforschungsinstitut VDEh (D)

The steel industry uses large quantities of scrap as a raw material in producing steel. However, radioactive material can be present in scrap - due to negligence or by design - delivered to a melting shop or a foundry.

Both in the USA and elsewhere, accidents have been reported where radioactive sources enter the melting shop with scrap and are melted in the converter. These materials are not only a

radiation hazard for workers but can also contaminate the steel, gas scrubbing sludge or slag. Such accidents, whilst fortunately infrequent, can result in very considerable expenditure (\$ 4.4 million in the USA in 1983 where a source of 930 GBq of Co 60 was found in the converter) for decontamination and elimination of waste.

In order to prevent such radioactive contamination and to ensure that workers are protected, the Betriebsforschungsinstitut of the VDEh carried out research projects to examine whether radioactive sources in scrap could be detected when they arrive in the lorry at the scrap yard or at the steel plant, and, if so, what detection system would be best.

The study first examines the theoretical aspects of ionising radiation the different forms of radiation (alpha, beta, gamma, neutrons, etc.) and various sources (shielded and non-shielded, etc.). Then it sets out the laws of interaction between ionising radiation and materials, especially the weakening of radiation when it passes through materials, and the effect of radiation when it is absorbed in the human body. The units used for an absorbed dose are then defined and the principles of radioactive protection are then set out.

The German and European standards on permissible radioactive contamination stipulate mass contamination of < 1 Bq/g and surface contamination of < 0.5 Bq/cm² for product not to be considered as radioactive.

Various techniques are available to measure ionising radiation which are based principally on ionisation or scintillation. Ionisation detectors include ionisation chambers, proportional counters and Geiger-Müller counters. Scintillation detectors include those using organic (plastic) scintillants and inorganic (NaI, CsI) scintillants. Scintillation counters are coupled with photomultipliers in order to obtain an electrical signal of sufficient strength. Scintillation counters appear to have very considerable advantages over ionisation counters such as the Geiger counters for detecting radioactive sources in scrap.

Tests were then carried out first in the laboratory and then on site in order to verify the possibility of detecting radioactive sources in scrap.

The laboratory tests show that

- an unshielded source of 240 kBq of cesium 137 can theoretically be detected in a load of scrap at less than 4 m; however, if it is shielded, it is scarcely detectable;
- an unshielded source of Co 60 of 370 kBq (10 μ Ci) could not be detected in practice in a load of scrap on a lorry;
- an unshielded source of 18.5 MBq (500 μ Ci) of Cs 137 was clearly detected in a load of scrap with a density of 800 kg/m³ when the lorry passed the detectors. At maximum sensitivity the detectors can identify a source of 10 MBq of Cs 137 sealed by 2 cm of lead and 5 cm of steel.

In conclusion it seems that not all radioactive sources can be detected with a probability of 100%. It depends on the type of radiation emitted, the intensity and the sealing, etc. However, by installing radioactivity detectors it is possible to reduce the risks involved.

The best detection system proved to be an arrangement of 2 scintillation counters (organic scintillants) placed on opposite sides of the road taken by the lorry transporting the scrap, preferably with measurements being taken while the lorry was moving (at low speeds < 5 km/h) than at a halt.

The study also draws attention to:

- the need, in addition to installing a monitoring system, to provide for training of workers on radioactivity and radio-protection and organisation of measures to be taken if a radioactive source is detected;
- The need to carry out radioactivity monitoring not only at the entry into the steel works but also at the scrap yard and at frontier posts, etc. This would increase the possibility of sources of being detected.

Detection of radioactive sources in steel plant raw materials

Research project 7261-04/468/08 carried out by British Steel Technical (UK)

British Steel also examined the problem of radioactive inspection of scrap and installed 12 detection systems in its steelworks. The systems used are CsI scintillation detectors (diameter 38 mm and length 350 mm), each of which is coupled with a photomultiplier. The aim of this research project was to determine the sensitivity of the detection systems and, if necessary, to optimise them.

Scrap is taken to the steel works either by road or by rail:

- by road, a lorry transports an average of 20 tonnes of scrap measuring 24 m in width, 8 m in length and between 1 and 1.8 m in height (density: 0.6 to 1 tonne/m³);
- by rail, a waggon transports an average of 34 tonnes of scrap measuring 2.4 m in width, 8 m in length and 2 m in height.

As detection sensitivity is mainly determined by the total thickness of scrap between the source and the detector it would be advantageous to place the detector at a point where this dimension is small, e.g. at the place where the scrap is picked up (electromagnet).

Here, however, the environment is not suitable for installing the system and it is difficult to establish where a source of radioactivity has come from.

For this reason the inspection is made when the transport vehicle arrives, preferably by means of several detectors around the vehicle. The vehicle is then moved along the detectors to

obtain maximum detection probability. For a rail waggon, two detectors on each side of it while it is moving at 0.5 m/s are the best arrangement. However, for a lorry, it is best to place detectors above and below the load because it is wider than it is deep. Here, too it is preferable to move the lorry slowly past the detectors (at less than 5 km/h).

Experience has shown that the background signal measured without a load is always higher than the signal measured with a vehicle loaded with scrap which does not contain any radioactive material. The vehicle loaded with scrap thus acts as a shield against natural sources of radiation.

For this reason the alarm threshold must be adjusted to just above the background radiation level measured without a vehicle, in order to optimise sensitivity.

The detection system installed by British Steel enables the following sources to be detected:

- Energy 30 keV
- Unshielded Co 60: 4 MBq (approx. 100 μ Ci)
- Unshielded Cs 137: 30 MBq (approx. 1 mCi)
- Am/Be (neutron source): 3 GBq (approx. 100 mCi)
- Shielded sources: γ dose at a distance of 1 m 0.7 μ Sv/h (0.07 mrem/h).

The sensitivity levels appear equivalent to those reported by the Betriebsforschungsinstitut in Germany.

Increased detection sensitivity can be obtained by equipping the detectors with spectrometers and determining the signal/background level ratio per energy band. With a CsI detector, this is perfectly possible and an increase in sensitivity by a factor of between 2 and 9 can thus be obtained without a major increase in cost. However the size of the scintillator crystal has to be increased to obtain a statistically reliable number of counts (cps).

Finally, British Steel's experience in operating the detectors goes back over 18 years. 15 loads of contaminated scrap have been detected during this period, three of which with major sources of radioactivity.

When an alarm is triggered, a manual inspection with a Geiger counter is carried out to confirm the automatic measurement. The alarm can, in fact, be triggered by natural sources of radioactivity such as those contained in refractories. Few genuinely spurious alarms happen (< 1 a year) and the equipment is regarded as reliable.

CHAPTER 3

Coking plants

3.1 ATMOSPHERIC EMISSIONS

3.1.1 *Reduction of sulphur oxides emissions*

Coke oven gas desulphurisation using multiple alkanolamines

Research project 7261-01/447/06 carried out by Hoogovens IJmuiden (NL)

The gas produced by the Hoogovens coking plant contains some 6 to 7 g of H₂S per Nm³. In order to comply with the standards for SO₂ emissions, the gas must be desulphurised and Hoogovens B.V. uses the Sulfiban system, which cleans the gas with an alkanolamine solution.

The aim of the research was to optimise this desulphurisation installation and to this end a pilot installation was built to vary the parameters and ascertain the effects this had. In particular, the researchers wished to determine whether the monoethanolamine (MEA) could be usefully replaced by a diethanolamine solution (DEA) or triethanolamine (TEA).

The installation comprises equipment for cleaning the gas with an alkanolamine solution, recovering this solution, which now contains H₂S and CO₂, and, stripping it at a temperature of up to 110°C to extract the H₂S and CO₂ and to recover the solution.

A total of 26 tests were carried out and the following interesting conclusions were drawn:

1. The extraction rate for H₂S is much higher with an MEA solution than with a DEA or TEA solution of the same molarity. With MEA a yield of 90% was obtained compared with only 70% for DEA and 55% for TEA, all other parameters being equal. With the MEA it is easy to attain a residual concentration of 600 mg H₂S/Nm³ in the treated gas.

2. By increasing the volume of the scrubbing solution the extraction rate can be increased. The extraction rate for unit of volume treated also increases with the concentration of H₂S in the gas to be treated. The solution/gas volume ratio must be above 1.5.

The effectiveness of the stripping process downstream has a considerable influence on the extraction rate. The alkanolamine used to extract the H₂S must contain as little H₂S and CO₂ as possible and therefore needs to be purified properly before it is used again.

However, the temperature of the solution has an almost negligible effect on the extraction rate. Finally, the ideal concentration of alkanolamine in the scrubbing solution is around two moles for MEA and 2.3 moles for DEA.

3. The tests demonstrated that organic sulphides are not well extracted by the alkanolamine solution (irrespective of whether it is MEA, DEA or TEA). This means that the residual concentration of sulphur in coking oven gas cannot be reduced to a level below 100 to 150 mgS/Nm₃.
4. Other compounds such as CO₂ acids etc. are extracted along with the H₂S. From this point of view the tests proved that TEA is more selective vis-à-vis H₂S than MEA, which gives it an advantage.
5. Consumption of alkanolamines was far higher than expected. The losses (mainly due to chemical reactions) represented a cost factor in the order of 1 ECU per tonne of coke (2.5 to 3 kg of MEA at 15% per 100 Nm³ of gas to be treated). If DEA is used instead of MEA, the cost is almost doubled.
6. The cost of the energy consumed (steam) is in the order of 0.4 ECUs per tonne of coke. Using DEA or TEA instead of MEA ought to reduce the cost, as extraction by stripping is made easier. Using alkanolamines at high temperatures (100°C) corrodes steel. Stainless steel thus has to be used for the high-temperature components of the installation, whereas the low-temperature components (40°C) can be manufactured from carbon steel.
7. The desulphurisation installation should be placed downstream of the gas denaphthalinasation equipment otherwise the naphthaline deposit can clog the installation.

In conclusion, the researchers do not recommend replacing the MEA solution by DEA. However, it might be worth using a TEA solution and a new installation with better selectivity and lower energy costs.

3.1.2 *Reduction of nitrogen oxide emissions*

Emission of nitrogen oxides in coking plants – study of their impact on the environment
Research project 7261-01/408/03 carried out by CPM (F)

Coking plants are a major source of nitrogen oxide emissions (accounting for some 24% of total emissions in the steel industry) and rank second after ore sintering plants.

Most of the nitrogen oxides emitted by coking plants are produced by the oven heating system. The quantities range between 200 and 1 000 g of NO/t coke, depending on the installation, and between 10 and 30 g of NO₂ equivalent/t coke produced by incinerating ammoniacal mist from the liquor still and 10 g NO₂ equivalent/t coke from charging, pushing and quenching the coke.

CPM considered various measures for reducing emissions from the oven heating system, as the concentration of NO in fume:

- increases with the temperature of the combustion fume;
- varies with the excess air. The concentration peaks when the excess is between 40 and 50% but is only half of the maximum value when there is no excess air or when the excess exceeds 80%;
- depends heavily on the design of the oven heating system.

Many NO emissions in the fume from oven heating systems were measured in various coke oven batteries in France with different oven heating systems, including batteries where the air and gas supplies could be adjusted to various admission levels. This confirmed several points which were conducive to low NO_x levels, namely:

- heating systems with higher or multi-stage air and gas feed. A combustion system with a multi-stage air supply and a two-level combustion system enabled emissions of N_x to be kept 20 to 30% lower than those obtained with a system where both air and gas arrive at the base of the flue;
- fume circulation systems;
- the influence of low battery temperatures. Temperatures can be lowered by optimising combustion in the flues, reducing heating imbalances and eliminating hot spots, or by extending the coking time.

It is therefore possible to achieve average levels of 300 mg of NO₂ per m³ of fume (referred to 5% O₂).

The information on the effect of the type of fuel on NO emissions CPM obtained in the course of the study shows that advantages accrue from using rich gases (coking oven gas) rather than lean gases (blast furnaces gases or low-nitrogen coking oven gas). However, as other studies produced results which suggested quite the reverse, these conclusions should be treated with caution.

Finally, the study on the behaviour of NO in the atmosphere demonstrated that, in summer, it is more rapidly converted into NO₂ than in winter. This is probably due to UV rays which produce more ozone in summer. In the presence of ozone, NO + O₃ is converted to NO₂ + O₂.

NO ₂ emissions and associated ambient pollution in connection with the heating of coke ovens
--

Research project 7261-01/411/01 carried out by DMT (D)
--

DMT also studied methods of reducing NO_x from coke oven heating in Germany.

Over the past few years, various coke oven battery manufacturers have developed heating systems to reduce to a minimum the formation of nitrogen oxides. The main design modification has been to provide for multi-stage air supply for combustion. Previously only two suppliers had adopted the multi-stage system (Didier and Still) and now Koppers and Otto have also added an additional air supply at mid-flue height.

DMT has shown that, given equal oven size, the design modifications have enabled the NO₂ formed in ovens 4 m high to be reduced by 50 to 65%, limiting nitrogen oxide emissions (expressed as NO₂ equivalent) to less than 200 g/t of coal as against 400-600 g/t of coal with the older design.

NO_x emissions from large dimension ovens, with greater oven width and higher wall temperatures, are also higher, peaking at some 300 g/t of coal with the new combustion system design.

One element with a major influence on the formation of nitrogen oxides is the longitudinal conicity of the ovens. The oven width must increase from the pusher side to the coke side in order to make it easier to push the coke. In order for the coke to be carbonised evenly throughout the length of the oven, the temperature must be higher on the coke side than the pusher side, and the increase in temperature, which varies from 40 to 70°C, can cause differences of 40% in the quantity of nitrogen oxides formed.

DMT also studied the effects on of nitrogen oxide emissions of using different fuel gases. As the German regulations limit NO_x concentrations in fume to 500 mg/Nm^3 , it was these levels which were compared. This is not a logical approach since the volume of fume produced varies greatly from one fuel gas to another. If the concentration of NO_x is much lower when a mixture of blast furnace gas and coking plant gas rather than coking plant gas or a mixture of coking plant and melting shop gas is used, one cannot draw any conclusions with respect to the total quantity of NO_x emitted per tonne of coal treated. However, a relationship between the concentration of inert elements (CO_2 and N_2) in the fuel gas and the quantity of NO_2 emitted was observed.

Finally the researchers set out to examine the influence of coking plant operation on concentrations of NO and NO_2 in the environment. At a distance of between 500 and 2 000 m, measurements showed that the concentration of NO rose on average by only 5-6 ppb. The increase in NO_2 is much lower.

3.1.3 Emissions of polycyclic aromatic hydrocarbons

Emission of polycyclic aromatic hydrocarbons (PAH) into the atmosphere is a health hazard for coking plant workers and local residents, due to the carcinogenic nature of some PAH. For this reason the *TA-Luft* (technical instructions on the quality of air) in Germany has specified permissible limits for both emission and ground level concentration around coking plants:

- emission limit: the sum of benzo(a)pyrene (BaP) and dibenzo(a, h)anthracene (if the mass flow is $> 0.5 \text{ g/h}$): $100 \mu\text{g/m}^3$;
- ground level concentration limit: benzo(a)pyrene (BaP): 5 ng/m^3 .

The limits applicable in Germany for BaP concentrations at places of work are $2 \mu\text{g/m}^3$ (and $5 \mu\text{g/m}^3$ for coke oven batteries).

A coordinated research project was undertaken jointly by CPL (UK), ENSIDESA (Spain), DMT (Germany) and LECES (France).

The aim of the research was to:

- establish whether various sampling and analyses techniques provided consistent figures for the concentration of PAH in the atmosphere;
- establish whether PAH concentrations inside and in the vicinity of coking plants compared with the limit values mentioned above.

As regards the sampling techniques, the various instruments available proved to supply comparable results as long as there was no risk of evaporation of PAH. This was virtually non-existent at temperatures below 50°C for PAH with more than four cycles. If evaporation can take place, sampling should be done by filtration followed by adsorption. The sampler

developed by the Institute of Occupational Medicine in Edinburgh was also tested and proved effective.

Air pollution in coking plants
Measurement of polycyclic aromatic hydrocarbons (PAH) in the atmosphere within the environs and in the neighbourhood of coke works (Phase II)
Research project 7261-04/424/08 carried out by CPL (UK)

In this coordinated research project, CPL (Coal Products Limited UK) set out to:

1. Test the sampler developed by the Institute of Occupational Medicine (IOM) Edinburgh.
2. Develop a mathematical model to determine the change in PAH concentrations as a function of distance from coking plants.
3. Carry out measurements of PAH concentrations in the environment of coking plant in order to verify the sampler and mathematical model.

The measurements of PAH resulted in several conclusions confirming that the sampler developed by the IOM was suitable:

- the "light" PAH, i.e. up to four cycles, very largely appeared in gaseous form, mainly when the sampling flow was high. At molecular weights above pyrene, they appeared solely in particulate form.
- Only particles smaller than $7 \mu\text{m}$ contain PAH.

It is therefore important to collect not only the respirable dust but also the gaseous phase downstream of the filter if one wishes to detect all the PAH. Filtration is sufficient if only the concentrations of benzo(a)pyrene are to be determined.

This highlighted the possibilities and limitations of other samplers (Hexhlet which only collects dust with particle size smaller than $7 \mu\text{m}$ and the Anderson cascade impactor).

The representative character of benzo(a)pyrene as an indicator of total PAH was also demonstrated with various samplers.

Finally, the results obtained using the four different IOM samplers are thoroughly consistent, which indicates clearly the representative character of this sampler.

The CPL has also developed a mathematical model demonstrating that the concentration of PAH should vary with the distance from the coke oven battery in accordance with the following formula:

$$C(x) = a \cdot x^{-3/2}$$

This model could not, however, be validated by sufficient measurements in the field. Nevertheless, they did show that, at distance of between 1 and 3 km from the battery, only background levels of PAH were detected.

Study of the criteria which determine occupational exposure to PAH in coking plants. Characterisation and quantification of the risk factors.

Research project 7261-01/440/14 carried out by ENSIDESA (E)

ENSIDESA focused on the measurement of PAH at workstations in coking plants which can have harmful effects on health of workers. It also tested the sampling instrument for PAH developed by the Institute of Occupational Medicine (IOM) in Edinburgh.

ENSIDESA set out to measure first 10 and then 31 PAH using the method recommended by NIOSH 5515. Six of these are acknowledged to be potentially carcinogenic (benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a, h) anthracene and indeno(1,2,3-c,d) pyrene).

What is more, their carcinogenic effect can be increased by the presence of other substances such as monocyclic aromatic hydrocarbons (benzene, toluene and xylene) or iron oxides. Finally, in order to have a carcinogenic affect by being inhaled at workstations, these substances must take the form of particles which can enter the bronchial alveoli and be retained there, i.e. small particles (< 3 µm).

It was therefore established that PAH emitted by coking plants into the atmosphere appear in both particulate and volatile form:

- the volatile fraction only comprises "light" PAH up to and including pyrene. None of the particularly carcinogenic substances figure amongst the lighter PAH; the carcinogens have at molecular weights higher than pyrene. In terms of mass, this volatile fraction is, however, the larger of the two. Some 90% of the volatiles are collected by the IOM sampler, and 60 to 70% by conventional instruments.
- The particulate fraction mainly comprises the "heavy" PAH, especially fluoranthene and pyrene. Some 40% of the particulate fraction are PAH which are acknowledged to be potentially carcinogenic. The size distribution of these

particles, shows that the vast majority of them are small, and hence can be retained by the bronchial alveoli.

More than 90% are in fact smaller than 9 μm , over 75% < 3.7 μm , and over 40% < 1 μm .

The concentrations of benzo(a)pyrene (BaP) measured at the top of the batteries are in the region of 20 to 50 $\mu\text{g}/\text{m}^3$. The concentration of BaP and total concentration of particulate PAH (Σ of the 31 types analysed) correlated well, with the BaP accounting for 7.2 of the total (10% with the IOM Edinburgh sampler). An even better correlation was discovered between the concentration of BaP and the total concentration of carcinogenic PAH, BaP accounting for 23%, with a regression coefficient of 0.979.

Concentrations of monocyclic aromatic hydrocarbons were also measured. Benzene accounted for over 50%, with concentrations in the ambient air of up to 0.4 mg/m^3 at the top of the batteries, peaking at between 4 and 12 mg/m^3 near the benzol extraction installations. The relationship between BTX and PAH is unmistakable: the greater the polycyclic volatile fraction, the higher the concentration of benzene.

Measurements showed the concentration of iron oxides, which is likely to increase the carcinogenic effect of PAH, to account for between 0.05 and 3% of the total mass of the particles. However, it should be borne in mind that these iron oxides originate from the melting shop and the blast furnaces on a site alongside the coking plant.

These tests carried out using the sampling instrument developed by the IOM in Edinburgh were positive and confirmed CPL's conclusions. More PAH were collected by this sampler than by conventional ones, mainly the volatile fraction. ENSIDESA points out some defects in the instrument, including a problem with stabilising the sampling flow and with handling due to its cumbersome design and weight.

ENSIDESA concludes the study by indicating that there is a real risk of pulmonary deposit of carcinogenic agents for coking plant workers due to PAH emissions and that biological tests could be carried out by measuring urinary BaP. BaP can in fact be taken as a biological marker of exposure to PAH, in view of the excellent correlation between BaP and total potentially carcinogenic PAH.

<p>Pollution in coking plants – Measurement of polycyclic aromatic hydrocarbons in the atmosphere within the environs and in the neighbourhood of coke works (Phase II)</p>

<p>Research project 7261-04/425/03 carried out by LECES (F)</p>

In this coordinated research project, LECES set out to:

- Define a method for determining PAH and other aromatic families (including nitro PAH) by sampling and laboratory analysis and *in situ* analysis.
- Measure emissions from several coking plants, at workstations and in the environment, during charging and pushing and from leakage at doors.

LECES selected a method for analysing PAH which was a slightly simplified version of the AFNOR standard, in view of the high concentrations measured in coking plant emissions, and a method for analysing nitro PAH presented in 1984 by R. Campbell and M. Lee.

For analysing PAH absorbed on particles, a LAMMA (Laser Microprobe Mass Analysis) microprobe enabled positive or negative ion mass spectra to be determined from materials ionised by impact laser. Particles were analysed *in situ* with this instrument to determine the concentrations of PAH, including very heavy PAH (atomic mass of > 280) which cannot be detected by gas-phase chromatography.

The LAMMA microprobe also proved effective in selective and specific detection of nitrated polyaromatic compounds, especially in the low concentrations likely to be encountered in samples from coking plants.

Emission measurements were then made:

a) Of leakages from doors

Several types of door were tested (including a new door with a semi-rigid metallic seal) in various environments (before/after cleaning of the jamb at an old/new coking plant).

These tests showed the effect of cleaning the jamb (reducing emissions by 60 to 70%), the type of door etc.

During the first four hours of coking time emissions at the door are as follows:

200 to 400 mg of PAH in the volatile fraction at a new coking plant (10 to 20 times higher at an old coking plant);

1.5 to 5 mg of PAH absorbed on dust.

b) During charging

Dust levels of up to 25 mg/m³ are observed during charging, obviously leading to a wide range of concentrations.

At an old coking plant, average concentrations of benzo(a)pyrene of 25 µg/m³ are observed regularly.

At new plant the concentration is lower (between 2 and 11 $\mu\text{g}/\text{m}^3$) but still considerably higher than the limit recommended in France of 0.15 $\mu\text{g}/\text{m}^3$ for workstations.

c) At workstations

At the top of the battery average concentrations of benzo(a)pyrene of over 10 $\mu\text{g}/\text{m}^3$ are observed regularly and can be as high as between 50 and 70 $\mu\text{g}/\text{m}^3$ (mainly at coking plants with high dust levels).

Analysis of the dusts shows that PAH are mainly found in the size fraction between 1 and 5 μm .

However, the tests did not identify any nitro-PAH in the atmosphere at the top of the battery. Operators at lower levels (coke guide, coke car, etc.) work in an environment where the concentration of PAH is lower and varies from 0.1 to 5 $\mu\text{g}/\text{m}^3$.

There was no evidence that the filter and activated carbon air purification systems in the cabin of a larry car were effective. Concentrations downstream were not always lower than concentrations upstream of the purification system!

Concentrations of benzo(a)pyrene in such a cabin, although considerably lower than outside the cabin, are still above the recommended value of 0.15 $\mu\text{g}/\text{m}^3$ in France.

d) In the neighbourhood of the works

At a distance of 200 m from a battery in the direction of the prevailing winds, LECES finds concentrations of between 0.2 and 0.3 $\mu\text{g}/\text{m}^3$ of benzo(a)pyrene, which is still higher than the recommended value for ambient air at work.

Finally, a comparison of the results obtained with a French sampler and those obtained with the instrument developed by the IOM in Edinburgh shown the results to correlate well both for dust and benzo(a)pyrene as long as the concentrations are not too low.

Pollution in coking plants – Measurement of polycyclic aromatic hydrocarbons in the atmosphere within the environs and in the neighbourhood of coke works (Phase II)
--

Research project 7261-04/423/01 carried out by DMT (D)
--

DMT also measured PAH concentrations in and around coking plants. Its conclusions tally with those of the other partners in the coordinated research project.

Gas-phase chromatography provided results comparable with HPLC (high-performance liquid-phase chromatography) when the samples were analysed.

As HPLC is faster, this was the technique which was adopted to pursue the research project.

The measurements carried out by DMT at German coking plants showed that there were BaP emissions:

- at the oven doors:
 - of 5 mg/t coke for a new coking plant with large-capacity ovens and doors with sealing membranes;
 - 55 mg/t coke, i.e. 10 times as much at an old coking plant;
- at the charging ports:
 - 12 mg/t coke at a new coking plant;
 - 270 mg/t coke i.e. 20 times as much for an old coking plant;
- at the ascension pipe valves:
 - 0.3 mg/t coke at a new coking plant with liquid seals;
 - 33 mg/t coke i.e. 100 times as much at an old coking plant;
- at the heating flues:
 - < 1 mg/t coke;
 - < 1 $\mu\text{g}/\text{m}^3$;
- at the quenching towers:
 - 2 mg/t coke at a new coking plant;
 - 60 mg/t coke at an old coking plant.

Detailed measurements of ground level concentrations showed that at workstations on the upper part of the coking ovens there were BaP concentrations of between 1 and 10 $\mu\text{g}/\text{m}^3$ which exceeded the authorised limits.

At other levels, these limit values were generally not exceeded. Moreover, the climate-controlled cabins proved to offer a protection factor of around five. These values measured at workstations of an old coking plant are no different from those at a new one.

As the limit values at some workstations had been exceeded, DMT assessed the protection afforded by wearing a mask. All the masks tested proved effective. It is easy to reduce the

amount of PAH inhaled to below the limit values if masks are worn during the charging periods when PAH levels are high, i.e. approximately 20% of the time.

Finally, ground level concentration measurements were taken 300 to 400 m away from the installation both near a new coking plant with large capacity ovens and near an old coking plant. The increase for PAH is some 10 ng/m³ for a new coking plant and can be as high as an average of 35 ng/m³ around an old coking plant in the direction of the prevailing winds. Where there is no coking plant the background concentration is between 3 and 6 ng/m³.

3.1.4 Olfactory nuisances

Odour nuisance in the iron and steel and coking industries
Research project 7261-01/409/02 carried out by the Société Belge de Filtration (B)

In order to combat the olfactory nuisances generated by coking plants, the Société Belge de Filtration carried out a large series of measurements of the concentrations of the main volatile compounds likely to be responsible for such nuisances at different points in various coking plants.

On the basis of the concentrations and the olfactory perception thresholds for various chemical compounds it is possible to calculate the odour intensity from the following formula:

$$(p\ OU)_i = \log \frac{C_i}{d_i}$$

where C_i is the concentration of the compound
 d_i is the olfactory perception threshold of the compound
and the total odour intensity is $\sum (pOU)_i$.

The 69 compounds analysed were divided into eight families: BTEX, PAH, phenols, alkanes, ammoniac, other nitrous compounds, hydrogen sulphide and other sulphur compounds.

This study clearly showed the origin of these olfactory nuisances:

- a) It is principally indene and naphthalene (two PAHs) which are responsible for these odours, followed by BTEX (isopropylbenzene, trimethylbenzene, ethylbenzene and xylene) and hydrogen sulphide. The other compounds cause hardly any olfactory nuisance or none at all.

- b) Although olfactory nuisances had coke ovens (in the ambient air, during charging and pushing) is caused by the emission of volatile gases, the study showed that similar amounts of odiferous compounds are emitted into the atmosphere in the form of dust.
Reducing dust levels will therefore contribute largely to reducing olfactory nuisances emitted during the operations of charging and pushing in coke ovens.
- c) But the most interesting point is that the study showed the vast majority (96% at one coke works) of the olfactory nuisances from old coking plants to come from the installation for treatment of gases from the coking ovens: open reservoirs, vents from closed reservoirs, drip pots, various leaks etc. The biological purification systems for waste water do not cause olfactory nuisances.
Olfactory emissions during charging are of the same magnitude as during pushing, whilst olfactory levels in the air around coking ovens are much lower, especially on recent batteries where sealing is better on the oven doors, levelling doors and charging holes.

The study then presents the most effective techniques for reducing olfactory nuisances:

- Olfactory emissions are most easily precluded at the installation for treating coke oven gas. This can be done by guiding the emissions responsible for odours (from reservoir vents etc.) to the collecting mains.
- The most effective method of reducing olfactory emissions on charging is aspiration at the tar cleaning tube, possibly combined with sequential charging of coal in the ovens.
- It is most difficult to reduce olfactory nuisances on pushing. Even the Minister Stein type of dust collection system which is being used more and more widely is of limited use in reducing olfactory nuisances. The only effective means seems to be to rely on the skill of the coking operative who must ensure that the charge is coked as thoroughly as possible.
- Around coke ovens it is the sealing of the equipment which keeps olfactory emissions down. Good sealing can partly be obtained by investments (in liquid seals on ascension pipes and automatic systems for cleaning doors etc.) but also and above all by meticulous operation and careful maintenance of the equipment.

Investigation, inventory and control of odiferous pollutants in the steel and carbonisation industries – Phase B (control)
Research project 7257-71/403/08 carried out by BCRA Scientific and Technical Services Ltd (UK)

The BCRA mainly concentrated on losses from coking oven doors during coking. These can lead to the release of gas which can greatly increase the odours from a coking plant. The other main sources of odours from coking plants, namely leakage from charging holes during coking or leakage from ascension pipes, were not studied as effective solutions for controlling such emissions already exist in the industry.

A technique for measuring the sealing quality of doors was developed in order to assess the effectiveness of solutions for reducing leakage. On the basis of leakage observed at 20 m, the sealing quality of the doors is defined between a range of 0 (no visible leaks) and 4. Leakage from some doors was also quantified by placing a hood all around the door enabling the volume of the leakage and dust, as well as H₂S and odours to be measured accurately. Correlations between various parameters – quality of seal, and volume of dust leakage, H₂S and odours - were also established in this way. The dust volumes measured were around 1 g/t coke.

The maximum distance – d max – at which the odour is perceptible can be calculated from the odour volume E, expressed in m³/s by the following formula:

$$d \text{ max} = (a.E)^{0.6}$$

where a is between 0.7 and 7 with an average value of 2.2.

The sealing on the doors at four coking plants were thus examined and ways of improving it developed and tested. Most of these catered very specifically for the type of door the coking ovens were equipped with. However, it must be said that merely by reviewing the operation, cleaning and maintenance programmes in detail, two of the coking plants were able to reduce the emissions at doors by 90% and 80% respectively without any design modifications.

In particular the frequency and care deployed in cleaning the door jambs was crucial. Whilst no improvement was produced by increasing cleaning to more than once in five cycles, reducing it to once every 27 cycles can result in doubling or tripling of leakage.

Tests were also carried out on injecting a sealing product between the door and the jamb. The product used, sodium silicate, reduced significantly the leakage observed and may hence be considered to be an effective interim solution.

3.1.5 Emissions of heavy metals

In order to ascertain whether emissions of heavy metals are likely to cause problems during the process of coking coal, a coordinated research project was carried out jointly by CRM (B), CPL (UK), DMT (D) and LECES (F).

Coking plant pollution – Balance and fate of heavy metals during the process of coal carbonisation
--

Research project 7261-04/419/03 carried out by LECES (F) 7261-04/418/02 carried out by CRM (B)

The first aim of the project was to find a better process for analysing concentrations of heavy metals in samples (of coal, coke, tar and coking liqueur). Several techniques for putting the samples into solution were tested (dissolving in HCl, HNO₃ and H₂O, dissolving in a sulphuric/nitric medium and dissolving after ashing at 500°C for 24 hours and fusion with LiBO₂ and the results compared between the laboratories (LECES, CRM, CPL and DMT). The best results proved to be obtained by the method which eliminated all the carbon.

For this reason the methods for putting products into solution for analysis by atomic absorption mainly provided for initial removal of carbon. Finally, sample preparation protocols were agreed upon between the laboratories in order to obtain representative and reproducible results from analysis.

- For Be, Pb, Cr, Ni, Zn, Cu, Co, Mn and Tl contained in coal and coke: ashing at 500°C for 24 hours (550°C for 72 hours for tar) followed by fusion with lithium borate (1 000°C for 20 minutes) followed by treatment with HNO₃.
- For samples of water and for As, Mn, V, Tl and Se contained in coal and coke: treatment with acid (Hcl/HNO₃).
- For Cd: treatment with acid (HCl).

The heavy metals were then measured by atomic absorption spectrometry. A round robin test was carried out to confirm the representatively and reproducibility and hence the soundness of the methods used.

CRM also examined a method of analysis which did not require the sample to be put into solution called the Glow Discharge Mass Spectrometry (GDMS) method. Here a surface was bombarded by Argon⁺ ions. These tear away particles of metal from the surface which are then re-excited in the form of M⁺ ionic gas. When the values obtained by the GDMS method and by the atomic absorption spectrometry method after putting the sample in solution were compared, they were found to tally well with one another.

The research project then set out to determine the concentrations of heavy metals in dust emitted at various locations in coking plants. The concentrations measured in the ambient air (of As, Be, Cd, Co, Cu, Ni, Cr, Pb, V and Zn) were, in most cases, lower than 0.2 µg/m³, except for the volatile elements Pb and Zn, for which concentrations of between 1 and 3 µ/gm³ were detected. These values are some 200 to 5 000 lower than the recommended limits for exposure at work in France.

Heavy metals should therefore not pose an industrial health problem in coking.

A mass balance sheet drawn up for the coal charged and the coke produced showed that some:

about 100% of the Be, Co, Cu, Ni, Cr and Zn was in the coke;

about 50% of the Cd and Pb was in the coke;

and only some 15% of the V was in the coke.

The research project finally went on to establish the concentration of heavy metals in coking plant soil. It was mainly the first 30 cm of the soil which was sampled.

Over the whole area of the site (approximately 10 ha), average concentrations of heavy metals did not generally exceed the Dutch guide values B (the threshold for more intensive investigation). The values for Pb and Zn, the volatile elements in and tracers of steelmaking activity, were the highest compared with the Dutch guide values (on average 20 to 40% higher than the B values but always lower than the C values). High concentrations of zirconium (average value of over 1.5 mg/g over the entire site) were observed, its impact being felt above all in the vicinity of the coking oven batteries and the coal stockyard, which means that this element must be a marker for the type of coal used.

Coking plant pollution – Balance and fate of heavy metals during the process of coal carbonisation
--

Research project 7261-04/420/08 carried out by CPL (UK)

CPL's share in the coordinated research project was mainly to concentrate on:

- the method for determining the concentrations of heavy metals in coal, coke, tar and coking plant liquor;
- the mass balance sheet for heavy metals in feedstock (coal) and output materials (coke, tar and liquid effluent).

The study showed that a mass balance sheet can be drawn up for heavy metals with relatively accurate determination of the concentration of heavy metals in samples of coal, coke, tar and effluent. Only the cadmium balance sheet is incomplete, perhaps due to the low concentrations vis-à-vis the detection limit.

The distribution of heavy metals between coke, tar and effluents shows that:

- the elements with a high melting point are almost exclusively concentrated in the coke. This is the case with Co, Ni, Cr, V and Mn. 4% of the Be and the Zn, 6% of the As and 8% of the Cd are found in the tar. Less than 0.5% of these elements are in the effluent;
- the elements with a low melting point are, by contrast, found in large quantities in the tar: 20% of the Hg and 53% of Pb.
Some 1% of these elements are also found in liquid effluents.

Chimney emissions of heavy metals proved non-detectable and hence negligible.

However, high concentrations of heavy metals were detected in particles from coke-quenching facilities, especially Cr (0.2 to 0.3%), Ni (0.1%) and Pb and Zn (0.06%). The CPL study showed that 300 mg Cu/t coke, 200 mg Ni/t coke and 90 mg Pb and Zn/t coke were emitted at the coke quenching facilities. Very little Be, Cd and V (<1 mg/t coke) were found.

Preparation of balance sheets for trace elements in coking plant material flows

Research project 7261-04/417/01 carried out by DMT (D)
--

Under the terms of the coordinated research project, DMT first set out to develop and verify the technique for measuring trace elements in coal, coke, tar and waste liquor. The trace elements comprise heavy metals (Pb, Cd, Hg etc.), light metals (such as Be), and semi-metallic elements (such as As). The measurement techniques were verified by comparison tests between the four participating laboratories.

A mass balance sheet was always prepared for the elements entering the coking plant (coal) and leaving it (coke, tar and waste liquid). This shows that Be, As, Co, Ni, Sb, Cr, Cu, V and Mn stay in the coke whereas large quantities (between 20 and 25%) of Cd, Hg, Tl, Pb and Zn are found in the tar. The quantity found in the liquor does not play any part in the balance sheet, coal, coke and tar being the only significant vectors. The mass balance sheet proved satisfactory for many of the substances but less so for others such as Mn and Zn.

DMT also focused on emissions from the quenching tower. Sampling instruments were placed at the outlets of three quenching towers which measured fairly low concentrations of dusts – between 15 and 47 g total dust/t coke produced and some 10 g fine dust/t coke. The conclusions differed from those of CPL in that emissions of metals (Pb, Cr, Cu, Mn, Ni, V, Zn and As) from this source were very low, in the order of 20 mg Zn/t coke, 4 mg Cu/t coke, 4 mg Ni/t coke and 7 mg Cr/t coke. At a coking plant producing 3.5 MT of coke per year emissions at the quenching tower of only 19 g/h of trace elements was measured and virtually all the values were found to be within the limits of the *TA Luft* (technical instructions on the quality of air).

Measurements carried out at various workstations showed that these elements were not a safety hazard at all. The values measured were in fact, lower by several orders of magnitude than the limit values except for Pb, where the maximum value measured was 10% of the limit value. This confirms the conclusions of LECES.

Measures of the ground level concentrations carried out 300 m from the coking plant also showed that there was no additional load of heavy load of metals in the environment.

3.2 TREATMENT OF WASTE WATER

3.2.1. *Purification by stripping ammoniacal water*

Development of an automatic control system for ammonia stills for coking plant liquor
Research project 7257-18/406/08 carried out by British Steel plc (UK)

In order to ensure that ammoniacal nitrogen in coking plant liqueur is purified sufficiently a still is generally used which is made up of two parts. In the first part free ammonia contained in the effluent is extracted by steam stripping and in the second part the effluent which only contains fixed ammonium is treated with caustic soda to bring the pH value up to 12, releasing the ammonia which can then be steam stripped. The efficiency of this method depends both on the temperature of the liquor (and correct regulating of the vapour flow) and a sufficiently large volume of caustic soda.

Purification by this method is expensive, accounting for over half the overall costs for treating coking plant waste water, mainly due to the consumption of caustic soda.

For this reason British Steel installed an automatic regulating system water for injection of steam and caustic soda injection into the still at its Scunthorpe coking plant. The following continuous measurements were used as input data for the regulation system:

- volume of effluents to be treated;
- volume of vapour and caustic soda injected;
- pH of the outlet liquor;
- ammonia concentration on the outlet liquor.

The ammonia level was measured continuously by means of an instrument developed in a previous ECSC research project (7257-18/333/08) which can be used to measure the total concentration of (free and fixed) ammonium in an effluent.

The regulation system first of all ensures that any change in the volume of effluents to be treated is followed immediately by a commensurate change in the volumes of steam and caustic soda injected. Then when the total ammonium concentration or the pH in the outlet liquor is no longer within a range, the regulation system first corrects the injection of caustic soda, and if this has no effect, steam injection. The decision to regulate the injection of caustic soda before steam was based on operating experience.

After the parameters have been changed, a time lag of one half-hour is provided for to stabilise the system before any further changes are made.

With this automatic system, British Steel was able to achieve a reduction of 15% in the consumption of caustic soda as well as more reliable purification (lower probability of the limits for ammonia waste being exceeded. However attention was drawn to the importance of maintenance and periodic calibration of the measuring instruments.

3.2.2 *Biological purification*

Improving the stability and performance of biological treatment facilities for coking plant effluent
--

Research project 7261-02/434/03 carried out by IRH and LSGC (F) and by CRM, CEBEDEAU and SIDMAR (B)

Coking plant effluent undergoes a series of treatments before it complies with standards. These are generally filtration to remove tar, caustic soda and steam stripping to extract ammonia compounds and other volatile pollutants and finally biological treatment using activated aerobic sludge to remove biodegradable materials such as phenols, thiocyanates etc. The biological treatment also reduces ammonia levels in the liquor by nitrification followed by denitrification to obtain the nitrogen burden in the form of N₂.

As regulations governing the disposal of coking plant effluent are becoming more and more stringent it was thought useful to identify more precisely the toxic and inhibitive effect which certain substances present in coking plant effluent could have on the efficiency of activated sludge treatment to remove biodegradable substances. The study also set out to optimise the efficiency of biological purification stations for coking plant effluents in terms of both design and operation.

However, before starting the study proper, it quickly became clear that there were serious problems involved in identifying organic micropollutants in coking plant effluents.

For this reason the researchers first compiled protocols to obtain representative and reproducible results of analysis for polycyclic aromatic hydrocarbons, monocyclic aromatic hydrocarbons and absorbable halogenated organic compounds contained in coking plant effluent. Round robin tests showed that the analytical methods which had been developed were sound. A high-speed chromatographic method was also developed as an overall means of analysing coking plant effluent.

In order to determine the substances likely to inhibit the effectiveness of activated sludge in the biological purification station, variability of the influent was studied systematically at two industrial coking plants, one of which was the Sidmar plant, for over two years. The following parameters were monitored: temperature, pH, Cl^- , DOCs, NH_4^+ , SCN^- , $\text{S}_2\text{O}_3^{2-}$, phenols, matter in suspension and chromatographic profiles (for a period of six months). The parameters which proved to vary most sharply were phenols, NH_4^+ and $\text{S}_2\text{O}_3^{2-}$ (σ in the same order of magnitude as the average value). Correlations between these variations were also investigated.

The study then showed that neither organic micropollutants nor inorganic micropollutants (heavy metals and associated metallic compounds) were responsible for inhibiting the activated sludge. It was mainly the macropollutants sulphur, cyanide and free ammonia to which the microorganisms proved sensitive. pH value had an indirect inhibiting effect due to the fact that when the pH value was higher than 9, ammoniacal nitrogen appeared more frequently in the form of free ammonia NH_3 , which has a considerably greater inhibiting effect than fixed ammonium NH_4^+ .

It was chiefly the thiocyanate (SCN^-) rather than the phenol purification biomasses which are sensitive to these pollutants and threshold values were defined: $\text{pH} < 8.5$, $\text{N-NH}_3 < 10 \text{ mg/l}$, sulphides $< 1 \text{ mg/l}$ and cyanides $< 1.5 \text{ mg/l}$ as the maximum permissible concentrations in the effluent entering the biological purification stage. Biomass activity is, however, not disrupted by fixed ammonium (N-NH_4) or by phenols up to values of 500 and 300 mg/l respectively.

The disruptions observed in industrial biological purification reaction vessels can therefore essentially be linked to dysfunctions in treatment upstream. The study led the researchers to recommend a first chemical treatment phase, such as the addition of a ferric salt (Fe III) which would attenuate the crucial inhibiting effect of sulphides and cyanides and would ensure that tar was removed.

In order to forecast the inhibiting effects when coking plant purification stations using activated sludge were in operation, a test was carried out with the Toxiguard instrument, a commercially available activated sludge respirometer. This test was inconclusive. However on-line monitoring of temperature, pH value and matter in suspension enabled the researchers, on the basis of the existing correlations, to retain 71% the information on the variability of the macropollutants. If one adds the parameters DOCs, $\text{S}_2\text{O}_3^{2-}$ and fixed NH_4^+ , it is 91% of the information which is kept.

Finally the researchers set out to optimise the design of the biological purification station. By designing the reactor as a series of biological tanks in cascade form, it was microorganisms could be developed selectively in each tank and multi-stage feed increased the effectiveness of biological treatment, especially for thiocyanates and COD and in terms of better operating stability. The improvement process was based on a detailed study of the kinetics and modelling of biological purification. This has been applied on an industrial scale at the Sidmar cooking plant which uses four biological reaction vessels in series with multistage influent and dilution water flows and is one of the most efficient in the world.

Extraction of ammoniacal nitrogen from coking plant effluent using rotating biological discs and simultaneous extraction of organic pollutants
--

Research project 7257-15/396/04 carried out by CSM (I)
--

CSM studied a single-phase biological treatment method for coking plant effluent by means of pre-denitrification and nitrification using biological rotating discs. The aim of such an integrated method is to dispense with stripping and vapour combustion installations upstream of the biological treatment, hence eliminating pollution of the air by NO_x and SO_2 . This method was first tested in a laboratory and then in a pilot unit which had a treatment capacity of some 25 l/hour of coking effluent.

The biological treatment comprised aerobic nitrification of ammoniacal nitrogen to form a nitrate.

The liquid from this treatment process is then recirculated (at a rate of 3 to 5) to the head of the treatment unit where the oxygen in the nitrates is used to oxidise the organic carbonated compounds contained in the effluent. The nitrogen is finally emitted in the form of N_2 during this phase of denitrification.

During the biological treatment the rotating discs support the biomass. During denitrification, they are not in contact with the air, whilst in the nitrification stage only 35% of their surface is immersed, the remainder in being contact with the air.

This technique provides for:

- selective development of various types of biomass on the surface of the discs during the denitrification and nitrification stages;
- little transfer of sludge: it is mainly the nitrogenated liquid which is transferred;
- the sludges which detach themselves from the discs are very easily settled which means that only a small sedimentation tank is required;

- no foam being formed;
- very low energy consumption (with the discs rotating at low speeds).

In order to prevent inhibition of the biomass:

- the pH value of the water must be monitored on entry and during the denitrification and nitrification stages, and regulated to between 7.5 and 7.7 on entry with H_2SO_4 , and, in the aerobic section, with $NaHCO_3$;
- the effluent must be diluted on entry by a factor of approximately 10 when all the effluent from the coking plant (ammoniacal and gas scrubbing liquor) is to be treated. This is necessary to keep the concentration of N - NH_4 lower than 800 mg/l which is regarded as the inhibition threshold.

With the effluent diluted to such an extent, additional organic carbon is required at the pre-denitrification stage. This is supplied by a solution of methyl alcohol and sugar (to prevent the methyl alcohol from becoming volatile). During the nitrification stage, the additional inorganic carbon required is supplied by the $NaHCO_3$ which is also used to control the pH value at the same time.

Under these conditions and with a recirculation rate of 3, purification yields of 95% for ammoniacal nitrogen and nitrate with loads of N - NH_3 of between 1 and 3 g/m² per day can be obtained. At a recirculation rate of 5, these yields have been achieved with a load of over than 5 g/m² per day.

These tests demonstrated that purification of sulphides, cyanides and phenols is not a problem.

It is, however, worth asking whether a rate of dilution of 10 is acceptable. Nevertheless, the method is equally applicable to other types of coking effluent such as the liquid from the ammonia still, where the concentration of ammoniacal nitrogen is far lower.

Investigation of the technical and economic benefits associated with the use of pure oxygen in the biological treatment of carbonisation effluents
--

Research project 7261-02/416/08 and 7261-02/452/08 carried out by Monckton Coke & Chemical Co Ltd (UK)
--

One way of improving the quality of effluent leaving biological treatment plant and reducing the costs of such treatment is inject pure oxygen instead of using the usual mechanical aeration systems to ensure that oxygen is supplied to the process. The research carried out by Monckton Coke & Chemical Co Ltd studied the advantages which might accrue from injecting pure oxygen in terms of both purification efficiency and economy.

The first phase of the research set out to evaluate over a period of 18 months the effectiveness and cost of biological treatment with pure oxygen injection at the Royston coking works in the UK. The effluent comes from the free and fixed ammonia stills at a rate of between 8 and 10 m³/hour and is normally diluted by a factor of two to ensure that the organic load is not too high at the entry to the biological treatment stage.

With a residence time of between 24 and 36 hours in the aeration tank the following biological purification yields were obtained:

- +/- 90% for COD
- > 99% for phenols
- > 99% for sulphocyanides.

The installation operated stably with few dysfunctions.

At the same time as the industrial biological purification station was operating with pure oxygen injection, an installation with mechanical aeration was used in a laboratory to purify the same effluents as those entering the industrial station. The aim was to compare pure oxygen injection and mechanical aeration in biological purification systems.

The results provided no evidence of any advantages accruing from pure oxygen injection:

- in terms of residence time in the aeration tank to produce stable purification;
- in terms of eliminating sludge to be dumped (or at least a reduction of the quantity);
- in operational cost terms. Whilst consumption of electrical energy is similar, pure oxygen injection does enable savings to be made on anti-foaming products and on heating the effluent in winter, but, on the other hand, gives rise to additional costs resulting from the consumption of oxygen.

As far as purification efficiency is concerned only a slight increase in the reduction of COD (in the order of between 2 and 3%) was observed when oxygen was supplied by injection.

The research was pursued to refine the comparison by including biological purification of effluent from another coking plant (Sluiskil in the Netherlands). This additional research was carried out in the laboratory on parallel purification lines, identical except in respect of the oxygen supply.

- It was shown that neither the pH value in the aeration tank nor the system for supplying oxygen (by injection or mechanical aeration) had any systematic influence on purification efficiency.
- The same applied as regards the quantity of suspended solids in the effluent after treatment.

- Only the maximum biological load seemed higher in the case of pure oxygen injection. In fact when the residence time in the aeration tank was reduced, there was a very considerable decrease in the nitrification of ammoniacal nitrogen in the case of mechanical aeration which is not the case when pure oxygen is injected. Purification efficiency as regards COD, phenols and sulphocyanides is however not influenced.

It could thus be shown that biological treatment with pure oxygen injection can cope with organic loads of up to at least 0.3 kg COD per m³/hour without the influent having to be diluted before entry into the biological treatment installation.

In conclusion, the research has not demonstrated any conclusive technical advantages of pure oxygen injection over mechanical aeration in supplying oxygen for biological treatment of coking plant effluent. Any decision to use pure oxygen will therefore be taken on the basis of financial criteria, taking into account both the investment costs and running costs.

Elimination of organic sludges produced during biological purification of coking plant effluent
Research project 7257-15/400/02 carried out by CRM (B)

When waste water is treated biologically, sludge forms in the purification tanks. It is very important to separate the sludge from the waste water:

- any waste sludge will involve waste BOD (biological oxygen demand): 1 mg of sludge from the biological treatment is equivalent to between 0.3 and 0.6 mg of BOD (BOD – five days);
- limits for suspended solids (< 60 mg/l in Belgium) and biological oxygen demand – five days (< 100 mg/l in Belgium) are generally specified for waste water disposal from coking plant.

For this reason water containing sludge from biological treatment tanks for coking plant effluent are conveyed to a secondary settling tanks. The study therefore focused on optimising the operation of this secondary settling tank – tank design, dimensioning, age of the sludges treated etc. After very intensive bibliographical study, the design favoured by the researchers was for deep circular tanks with central reflocculation wells for the sludge and a sludge age of \pm 20 days for a biological treatment installation without nitrification and with a hydraulic residence time of 24 hours and a recycling rate of 1:1. Even with this optimised tank, the residual liquor from the coking plant did not always comply with the limits with respect to solids in suspension (between 80 and 125 mg/l when measured, whereas the limit is 60 mg/l).

Techniques for tertiary purification of the liqueur were then explored. After various possibilities were examined, the choice fell on fixed or fluid-bed filtration of the water which still contained too much sludge. The best results were obtained by filtering the liqueur from secondary sedimentation through a double layer of anthracite and sand. However, with this method, the filtration yields were not more than 40 or 50% under stable conditions and far less when biological purification was disrupted. When this happened, the sludge did not settle properly in the secondary sedimentation tank and tertiary filtration could not remedy this. The researchers were not able to develop a more effective system.

The sludge separated from the purified liqueur contains only $\pm 1\%$ of solid matter. Further treatment is required to obtain a sludge which can be shovelled. The first stage of treating the sludge comprises gravity thickening which can increase the concentration of dry matter to between 3 and 5% without any problem after some 15 days of storage. However, as a concentration of dry matter of over 15% is required to obtain a sludge which can be handled by shovel, possibilities of subsequent treatment were examined.

At this stage the sludges still contained a significant proportion of degradable matter. Aerobic treatment to increase degradation did not prove effective, and the additional degradation hoped for was slight (around 20%), slow and difficult to obtain.

All that remained was to dehydrate the sludge, either mechanically (filter press, draining etc.) or naturally. Although a mechanical process can be applied at a comparable cost, CRM concentrated on natural dehydration. A covered drying bed was devised and the sludge was mixed with a polyelectrolyte (2.5 kg/tonne of dry matter of *Röhm Rohaflox KF 370*) to improve drainability. Under these conditions handleable sludge was readily obtained and the drying capacity was in excess of 1 000 kg of dry matter per m² per year.

Finally, the sludge so obtained can be recycled in coking ovens by mixing it with the coal. The dehydrated sludge is spread on the ground coal by a reciprocating pump before the coal is conveyed to the tower. The amount of sludge is negligible (0.01% by weight).

The entire treatment for the sludge costs in the order of 0.06 ECU per tonne of coke.

CHAPTER 4

Sintering and pelletisation

4.1 REDUCTION OF ATMOSPHERIC EMISSIONS BY MEANS OF PROCESS MODIFICATIONS

Minimisation of emissions of gaseous pollutants by thermal optimisation of grate sintering

Research project 7257-21/394/03 carried out by LECES (F)

Iron ore sintering is one of the major sources of emissions of sulphur compounds (SO_2 , H_2SO_4), nitrogen compounds (NO and NO_2) and carbon compounds (CO and CO_2) in the steelmaking process. Emissions of F⁻ and Cl⁻ and gaseous organic compounds are also regenerated.

The sintering process generates fume in which 150 to 180 mg/Nm³ (0.25 to 0.36 kg/t sinter) of sulphur have been measured when high-grade ore is used and up to 1200 mg/Nm³ of sulphur (2.5 kg/t sinter) when low-grade Lorraine ore is used.

The aim of the LECES research project was to minimise gaseous pollutant emissions by optimising the thermal operation of the sintering strand without considering processes for abating pollutants by treating raw materials or fume.

The first avenue explored was to predry the ore mix. Evaporating the water contained or adjusted to the raw materials consumes 20 to 30% of the total energy consumed in sintering. If predrying is carried out using a more economically auxiliary source of energy such as the sensible heat currently lost in the gaseous waste from the blast furnace stoves, substantial savings in solid fuel will result. At constant productivity SO_2 waste were thus reduced to 40% by drying for a period of 2 minutes with hot air at a temperature of between 325 and 530°C and CO emissions were also reduced by nearly 50% by drying for a period of 20 minutes. However, NO rejects did not vary to any significant degree. Another avenue explored was to replace part of the solid fuel used for sintering by a gaseous fuel with a low sulphur content, increasing the surface of the ignition hood and commensurate consumption of gas. Increasing the rate of coverage by between 5 and 25% in this manner led to a reduction of SO_2 and CO waste in the order of 30 to 40%, without any major change in NO_x waste. However, there is a loss of productivity in the strand.

Increasing the bed depth from 47 to 52 cm and accordingly reducing the speed of the strand from 3.6 to 3 m per minute reduces productivity but improves the yield of the solid fuel. These measures enable SO₂ emissions (calculated for constant productivity) to be reduced by 10%. However, still on the basis of constant productivity, there is an increase in NO_x emissions of 5% and no significant variation in CO emissions.

Optimum wetting of the mix also enables the yield of the solid fuel to be improved whilst maintaining satisfactory production in terms of quality and quantity. By increasing wetting from 11.5 to 13% for Lorraine ores, reductions of 10% in SO₂ and NO emissions and 23% in CO emissions were obtained.

SO₂ waste in sintering fume is largely determined by the index of basicity of the sinter mix. The partition coefficient of sulphur between the fume and the sintered material is 80% in the fume when the index of basicity is 1.35 and 10% when it is 3.4.

SO₂ emissions can thus be reduced by some 70% by producing sintered material with an index basicity of 3.4. In this case, the sulphur would be removed in the blast furnace slag instead of being emitted in the sintering fume. This would mean that the operating point of the blast furnace would have to be adjusted, as the index basicity of the sintered material is generally kept very low to prevent alkalines from being introduced into the blast furnace.

Cl⁻ and F⁻ emissions in sintering fume were also studied. These mainly depend on the contents of Cl⁻ and F⁻ in the raw materials. Values of 12 mg Cl⁻/Nm³ and 2 mg F⁻/Nm³ have been measured in high-grade ores and 48 mg Cl⁻/Nm³ and 4 mg F⁻/Nm³ when using low-grade Lorraine ores. In order to keep emissions of Cl⁻ low, adding Cl⁻ to the mix must be avoided, in particular CaCl₂ which is sometimes added to eliminate alkalines and zinc when using alkaline ores.

Finally, recycling of steelmaking waste containing waste oil from rolling mills is an increase of unburnt products in the sintering fume. Measurements have revealed the presence of 610 mg/Nm³ CH₄ equivalent of total HC, including 443 mg CH₄/Nm³ dry weight and 14 mg HC/Nm³ in the form of condensables at 2°C. This means that waste with a high concentration of iron but containing organic compounds should be deoiled before being recycled in sintering.

Effect of the operational parameters of iron ore sintering plants on emissions of sulphur and nitrogen oxides into the atmosphere

Research project 7261-01/410/02 carried out by CRM (B)
--

CRM carried out a laboratory study on the influence of the following production parameters on SO₂ and NO_x emissions from sintering plant:

- sintering temperature (production of sintered material at low temperatures by reducing the fuel yield;
- type of fuel;
- addition to the mix of potential catalysts;
- oxygen potential and partial recycling of the fumes.

First of all, it was observed that the concentration of NO_x in sintering fume drops significantly when the coke rate is increased. Increasing the amount of coke per tonne of sintered material from 55 to 65 kg reduces concentrations of NO_x by some 30%. This is probably due to the increase in CO which reduces the NO to $1/2 \text{N}_2 + \text{CO}_2$. No significant results were observed as regards the concentration of SO_2 in the sintering fume.

Fuel type can influence the NO_x emissions. 30 to 40% of the nitrogen introduced with the fuel is actually emitted in the form of nitrogen oxides. Specific NO_x emissions therefore increase with the concentration of N in the fuel. The same phenomenon is observed for SO_2 emissions, but here the quantity of sulphur emitted in the fume represents between 80 and 110% of the sulphur entering the process with the fuel (sulphur also being present in the other mix components).

Various catalysts for decomposing NO_x (or materials inhibiting their formation) were added to the bed. Adding an ilmenite ore Fe O.TiO_2 (with 30% of TiO_2) or sludge of Fe (OH)_3 had no effect on NO_x emissions. Only a highly hydrated Robe River ore (with 10% water of crystallisation, with addition of 10% of this ore in the raw mix) led to a significant reduction in NO_x emissions of between 15 and 20% without any major change in productivity and sintered material quality.

Finally, variations in the content of oxygen in the fuel gas have no significant influence on NO_x emissions. However, injection of 5% of CO into the combustion air reduces NO_x emissions by between 10 and 20%. This CO is burnt up completely during the sintering process, resulting in an increase in the coke combustion speed for the same coke rate.

CRM thus concludes that the potential for reducing SO_2 and NO_x emissions at source is low. The scope for manoeuvre is slight and there is a risk of improvement being made to the detriment of productivity and/or the quality of the sintered material.

Reduction of CO, NO_x and SO_2 emissions from sintering plants by modifying the charging and process parameters

Research project 7261-01/450/04 carried out by CSM (I)
--

CSM then conducted laboratory studies of the effects on CO, NO_x and SO₂ emissions of adding catalytic agents to the mixture used for sintering and adding steam during sintering. The effects of these additions on productivity, oxidation of the sintered material and the fuel requirements were also studied.

The catalysts for coke combustion which were added were copper nitrate, manganese nitrate and cobalt nitrate, the quantity ranging from 1 to 2 gr per kg of coke. This increased the speed of coke combustion, increasing productivity by between 2.3 to 4.6% (depending on the permeability of the bed) when an addition of 2 g/kg was made. However, adding the catalysts had no significant effects on CO, NO_x and SO₂ emissions. Some 36 to 40% of the nitrogen contained in the coke was found in the form of NO_x in the fume.

Other tests were carried out injecting steam at 180°C during the sintering process. The best results were obtained by injecting between 30 and 36 kg of steam per tonne of sintered material for 5 minutes, starting steam injection 7 minutes after ignition.

Injecting the steam:

- increased productivity by between 5 and 8% (depending on the permeability of the bed);
- reduced oxidation of the sintered material (increasing the content of FeO by between 0.5 and 1%);
- reduced the coke combustion ratio (CO) from 13 to 20% (CO + CO₂);
- reduced specific emissions of CO by 25% and of NO_x by 12.3%;

had no significant effect on SO₂ levels in the fume.

Due to the injection of steam, the formation of CO₂ from CO is accelerated ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ and $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$), releasing more energy and resulting in more rapid combustion of the coke.

The results obtained from these laboratory tests suggest that it would be useful to test steam injection on an industrial installation to determine the extent of the reduction of emissions and the costs of investment and operation.

4.2 REDUCTION OF ATMOSPHERIC EMISSIONS BY END-OF-PIPE TREATMENT OF FUME USING BAG FILTERS

Research into the use of bag filters to reduce particulate and gaseous pollutants in process fumes from iron ore sintering plants
Phase A

Research project 7261-01/432/03 carried out by LECES (F)

Iron ore sintering plants are considerable sources of atmospheric pollutants, accounting for up to 40% of the atmospheric pollution from an integrated steel plant. In order to reduce dust emissions, these plants are equipped with installations for treating fume (generally electrostatic precipitators). Despite this equipment, the fume still has concentrations of:

- between 100 and 200 mg/Nm³ dust
- between 150 to 800 and 1250 to 2300 mg/Nm³ of SO₂
- between 150 to 500 and 600 to 1500 mg/Nm³ of NO_x (as NO₂).

In order to achieve higher rates of abatement, the research project set out to assess the possibilities of using bag filters instead of electrostatic precipitators to capture the dusts and acid aerosols in the sintering fume.

In order to do this, the fume to be treatment was first analysed in full. The following characteristics were determined for an industrial installation:

- Temperature : 100 to 130°C (up to 220°C when the strand is halted)
- Gas :
 - O₂ 15 ... 18.7% volume
 - CO₂ 5 ... 7.2% volume
 - SO₂ 0.027 ... 0.037% volume
 - NO 0.024 ... 0.032% volume
 - Cl₂ 2 mg/Nm³
- Dust:
 - 640 mg/Nm³ (total dust before filtration)
 - 20% <10 µm
 - low content of Fe (1%)
 - high content of alkalines Na and K (23%)
 - contains the vast majority of Pb (0.07%), Cd (0.005%) and Hg (0.001%) present in the total dusts.

- 60% <10 μm <200 μm .
 - high concentration of Fe (44%) and Si + Ca (25%)
- 20% >200 μm .
 - same composition as the fraction between 10 and 200 μm .

Some 2 000 Nm³/h - part of the sintering fume from this industrial installation - were conveyed to a pilot bag filter installation for a period of 18 months, to test various filtration media; in particular gas fibre weave and teflon felt which is much more expensive but highly resistant to acids and which permits filtration rates of between 70 and 140 m/h, double that of glass fibre.

These tests produced the following results:

- a) Due to the temperatures involved and the mechanical resistance required, only filtration media made of glass or teflon fibre can be used.
- b) The bag filter ensures that almost all of the dust is removed (residual concentration being between 1 and 1.5 mg/Nm³). Moreover, it is highly effective in filtering acid aerosols (containing Cl⁻ and F⁻ compounds) and volatile organic compounds.
- c) However, the pressure drop occasioned by the bag filters soon proved unacceptable. The threshold of 200 mm WG considered acceptable is exceeded even at low velocities (35 m/h) and with offline compressed air backblowing for 40 seconds every 7 minutes (as on-line cleaning results in an even more rapid increase in pressure losses). The threshold of 200 mm WG, which was regarded as an acceptable value, is considerably higher than the 20 to 40 mm WG pressure drop of an electrostatic precipitator, and therefore require considerably higher ventilation performance for extraction.

The fineness and the composition of the dusts forming the "filter cake" clinging to the bags are considered responsible for the rapid blinding effect. The average diameter of the dusts was measured at 9 μm , the maximum being below 50 μm , and the particles are rich in alkalines and chlorides, together with organic compounds, which increase the adhesive quality and reduce permeability. With the means deployed at present (compressed air at a pressure of between 5 and 6 bars), cleaning is only effective in eliminating the coarsest dust particles from the "cake" with the very fine clinging particles still remaining.

In order to cope with this phenomenon, tests were carried out injecting slate line upstream of the filter to precoat it. At an injection rate of 35 mg/Nm³ of Ca (OH)₂, a two-month test showed that the pressure drop never exceeded 200 mm WG at a velocity of 55 m/h with cleaning only every four hours without any loss of filtration efficiency. These tests still need to be continued with other filtration media.

The coarsest of the dusts recovered from the bag filters can readily be recycled in the sintering process. The finer dusts have a high alkaline concentration which might prevent such

recycling. If this is the case they need to be disposed of in a Class 1 tip due to the leachates they will produce.

On conclusion of this first phase of the study, bag filters do not yet appear to be a feasible means of collecting dust in sintering plant fume on an industrial scale due to the blinding which results in too great a pressure drop. However, periodic precoating of the bags promise a reduction in the pressure drops which could make the technique industrially viable.

Use of bag filtration to reduce particulate and gaseous pollutants in process fumes
from iron ore sintering plants
Phase B

Research project 7261-01/455/03 carried out by LECES (F)

Phase B of the research project then examined desulphurisation of sintering fume by adding a desulphurising agent - also acting as a precoating agent - upstream of the bag filter, in which case dry or semi-dry technology must be used.

In order to do this a bibliographical study of various desulphurisation techniques was first carried out. Although wet processes using calcium (limestone or slaked lime) were the most widely used in iron ore sintering and resulted in high levels of purification, the study was mainly focused on semi-dry or dry processes. Amongst these, the slaked lime process with simultaneous injection of water to reduce the fume temperature to 20°C above the dew point (a process applied *inter alia* by LURGI) and the sodium (Na HCO₃) process, which has an efficiency rate of over 90% with a near-stoichiometric ratio and a residence time in the order of two seconds (SOLVAY process), were chosen. The latter also had a slight denitrogenation effect.

A pilot desulphurisation/dedusting installation with a capacity of between 1 000 and 1 500 Nm³/h was constructed, comprising a preseparator for dusts of large particle size, a system for injecting the reagent, a reactor and finally a bag filter (glass fibre and P 84 bags). Tests were first carried out on a sample representing the sinter fume as a whole and then on a sample representing wind box fume which had the highest concentrations of SO₂. The wind boxes are located just before and at the burn-through point. Various measurements were carried out before two boxes accounting for 70% of SO₂ emissions, and three boxes accounting for 85% of such emissions were selected.

The conclusions from these tests showed that a dry or semi-dry desulphurisation technique can be applied upstream of a bag filter to treat sintering fume as a whole and the fume from the wind boxes which are responsible for most of the SO₂ emission.

- The methods tested produced high dedusting rates (<10 mg/Nm³) with acceptable pressure drops (±150 mm WG at velocities of between 50 and 100 m/h).



- The NaHCO_3 process resulted in a high rate of desulphurisation (80 to 90%) with a stoichiometric consumption of 2 Na/S in the order of between 1 and 1.2. The reaction is very rapid and the size of the reactor may thus be reduced (residence time of 2 seconds). Between 30 and 40% of the nitrogen is also removed at the same time. It should be noted that 2/3 of the desulphurisation process takes place in the bag filter and only 1/3 in the reactor upwind.
- The Ca(OH)_2 process also produces high desulphurisation rates, as long as the fumes are wetted to bring down their temperature to between 20 and 30°C above the dew point. The efficiency of the desulphurisation process is highly sensitive to this difference in temperature but is relatively insensitive to the ratio Ca/S in the desulphurising agent between 1 and 1.5 and to the residence time between 3 and 10 seconds.
- The NaHCO_3 is three times as expensive as the Ca(OH)_2 . However, the investment costs are lower for the NaHCO_3 process as the reactor is smaller.
- Finally, we should not forget the problem of waste. Desulphurisation products account for between 60 and 80% of the solids recovered from the filters.

With the NaHCO_3 process, the desulphurisation product Na_2SO_4 is soluble and can therefore be separated from the dust fairly easily. With the Ca(OH)_2 process, the desulphurisation products could be recycled immediately as long as the excess sulphur is compatible with the blast furnace operating parameters.

Tests will have to be carried out on a larger pilot unit (with a capacity of between 20 000 and 50 000 m^3/h) to test the process industrially before looking at an industrial application.

CHAPTER 5

Blast furnaces

5.1 TREATMENT OF WASTE WATER - REDUCTION OF CYANIDE WASTE

Chemical treatment for the specific destruction of cyanides

Research project 7261-02/413/02 carried out by CEBEDEAU-CRM (B)
Research project 7261-02/460/02 carried out by CRM (B)

The first part of the research project was devoted to studying cyanide emissions from blast furnaces during both daily operation and blow-down. A bibliographic study clearly showed that formation of cyanides in blast furnaces is connected with the presence of alkaline materials in the stock, essentially in the form of potassium and sodium silicates. At a temperature of some 1 500°C, at the base of the blast furnace, a small portion of these alkaline substances evaporate and are swirled up by the gas to condense in the central part of the blast furnace in the bosh to form alkaline cyanides which are then oxidised as carbonates at the top of the shaft in the presence of CO₂. Under stable conditions therefore few of the cyanides escape from the blast furnace despite the fact that there are large quantities of them.

Environmental problems arise when the cyanide compounds migrate to the blast furnace top and then are found in the gas scrubbing water. This water can then not be disposed of until it has undergone special treatment. This can happen when the conditions of operation of the blast furnaces are unstable and during blow-down.

Two periods of unstable operating conditions in a blast furnace with the emergence of several peaks of cyanides in the gas scrubbing liquor (up to 40 mg/l) were analysed in detail. The cyanide concentrations were correlated with wall temperatures and temperatures of the gas at the furnace top, suggesting that cyanide emission is linked with major slips and/or to the formation of gas bypasses caused by falling scaffolding.

The quantity of cyanides emitted through the scrubbing liquor can be very large. Over a period of 20 hours when there were major slips in a blast furnace, the quantity of cyanides captured in the gas scrubbing liquor was put at 2 t. Such cyanide emissions are generally accompanied by an increase in emissions of other substances such as Zn.

During blow-down, when the level of the stock has dropped by approximately 10 m (\pm 40% of the useful height) in the blast furnace and the zone of oxidation of alkaline cyanides to form carbonates has thus completely disappeared, there is a sharp increase in cyanide levels

in the scrubbing water which can be as high as 240 mg/l, representing several tonnes of cyanides. Maximum cyanide emissions occur at between 60 and 80% of the working height. These cyanide emissions are accompanied by alkalines and other substances such as Cr.

However, during daily operation cyanide emissions are generally zero or at least negligible.

In order to prevent cyanide emissions during a blow-down, alkaline "washing" of the furnace before the blow-down can be effective. In a furnace where alkalines have been very largely eliminated before the blow-down by reducing the index basicity of the slag, cyanide emissions were restricted to several hundred kilogrammes of cyanide.

Two techniques were tested for removing cyanides in gas scrubbing water, one with potassium caroate and the other with formaldehyde and oxygenated water. Both techniques proved effective (with a residual concentration of < 1 mg/l of CN⁻) but the second was far more economical (ECU 3.75/tonne of cyanide removed as against 62.5).

For this reason the researchers focused on the formaldehyde treatment devised by IRH (ECSC research project 7261/02/412/03 cf. Chapter 2, paragraph 2.2.3) which appeared particularly suitable for blast furnaces. The cyanide liquor is mixed with the formaldehyde which leads to the formation of glyconitrile, a cyanhydrin. The pH value of the gas scrubbing water is generally around 9, the optimum pH value for this reaction, which takes place very rapidly (between several minutes and several hours).

The analytical problems were first studied, the aim being to demonstrate that the technique for analysing the cyanides in the treated water, which contained glyconitrile and formaldehyde, did not rerelease cyanides which had previously been converted into glyconitriles. This led to several measurement techniques being ruled out and the direct colorimetric technique being selected.

As formaldehyde was being used polarography or iron chromatography was selected to monitor cyanides in the water after treatment.

Subsequently, various secondary reactions were studied to ensure that after treatment, cyanides or ammoniac cannot be released either in the reaction medium or in the natural environment (after disposal in rivers). These secondary reactions proved to be slow and neither cyanides nor ammonia were released at pH values of under 10.

Finally, an ecotoxicity study on the treated water - already carried out by IRH using a standardised French test (*Daphnia* test) - was pursued using bacteria, protozoa and fish (*Brachydanio serio*). The results confirmed that the residual toxicity of the treated water was much lower and was largely due to excess reagent (formaldehyde). In order to treat blast-furnace gas-scrubbing water, a suitable method for automatic control of the reagent is therefore needed. 83% of the products of the reaction proved to be biodegradable, with glyconitrile degrading slowly and excess formaldehyde fast.

In conclusion the study confirmed that blast-furnace gas-scrubbing water containing cyanides could be treated effectively with formaldehyde to obtain residual cyanide levels lower than 1 mg/l.

Optimisation of formaldehyde treatment to remove cyanide from blast-furnace scrubbing water
Research project 7261-02/459/03 carried out by the Institut de Recherches Hydrologiques (F)

The previous research project demonstrated the need for a suitable method of automatic control of the cyanide removal reagent (formaldehyde) to avoid not only additional costs but also an increase in the toxicity of the effluent.

IRH therefore studied several systems for detecting cyanides and/or formaldehyde which could be used continuously in an automatic control system with a sufficiently short response time.

The first method, comprising gas-phase transfer of cyanide and formaldehyde through a liquid/gas permeation cell was not satisfactory. Sensitivity was too low to detect cyanide and much higher for formaldehyde but with too long a response time.

A second technique, comprising based liquid-phase transfer of residual cyanide and formaldehyde through a microporous membrane and electrochemical detection using a gold electrode, however, appeared sufficiently sensitive. An acceptable response time was obtained (in the order of 20 minutes) when the effluent was passed into a dynamic circulation cell comprising a microporous teflon membrane and by capturing the cyanide and/or formaldehyde passing through the membrane in a buffer solution with a pH value of 9. However, difficulties arose in obtaining microporous teflon tubes. Moreover, interference is very high if sulphides are present. As sulphides accompany cyanides during blast-furnace blow-down, it remains possible to use the device as a rapid overall detector of cyanides in a process control unit.

A third technique was developed with a microreactor which can be used in a sampling and measurement loop and which is capable of completing the CN⁻/formaldehyde reaction ensuring that there is an excess of only one of the reagents. This can then be measured using an analytical measurement device (polarography or colorimetry etc.) or a more general device (potentiometry etc.). The excess of one of the reagents (cyanide or formaldehyde) can then be measured by comparison with the stoichiometric value. This technique seemed the most promising means of conducting automatic and continuous process control.

A design for a two-stage automatic process control system was then mapped out, the idea being to treat the gas scrubbing water in a closed circuit by injecting formaldehyde at a ratio lower than the stoichiometric conditions and at the existing pH value of the water, i.e. 5 or 6. As the system incorporates a settling tank, it can take advantage of the long reaction time,

but efficiency is limited to some 10 to 20 mg of CN⁻/l as the pH value of the water is too low. The majority (some 90%) of the CN would thus be treated. The excess of reagents vis-à-vis the stoichiometric value could then be determined by a microreactor as above. Then the pH value of the quantity bled from the gas scrubbing circuit could be adjusted to about 9 (the ideal value for the formaldehyde/CN⁻ reaction) and then formaldehyde could be added (adjusted) until the stoichiometric ratio of 1.2 was reached. Under these conditions the reaction between the residual CN⁻ and the formaldehyde is very rapid and CN⁻ levels ≤ 1 mg/l can be expected in the effluents to be discarded.

CHAPTER 6

Melting shops, continuous casting plant and hot-rolling mills

6.1 ATMOSPHERIC EMISSIONS

6.1.1 *Energy savings in fume extraction from an electric arc melting shop*

Energy savings through improvements in fume control methods for melting shop extraction systems

Research project 7261-01/430/08 carried out by British Steel (UK)

Fume (primary and secondary emissions and ladle metallurgy emissions) extraction systems for electric arc furnaces use large amounts of power for the fans. At the British Steel plant concerned, fume is extracted by a battery of four fans installed in parallel on the main offtake duct upstream of the bag filters.

In order to save energy, a regulation system was designed to start up the fans sequentially by signals which reflect the potential fume emissions. One of the four fans was also equipped with a variable speed system.

For secondary emissions, the signal for dust emissions is given by an obscuration meter in the roof of the electric arc melting shop. The signal triggers opening and closing of the dampers for extracting secondary fume and the damper control signal governs the speed of the variable-speed fan.

In order to prevent too much dust from escaping from the shop to the atmosphere when this automatic regulation system is used, a second obscuration meter was placed on the roof outside the shop for the purposes of control.

This regulation system produced savings of some 30% of the energy required to extract fumes from the shop which fell from 26.5 to 18.7 kWh/t of steel produced.

6.1.2 Scrap preheating in an electric arc melting shop

Technical control of nuisances and pollution caused by scrap preheating techniques in electric arc melting shops
--

Research project 7261-01/415/03 carried out by LECES (F)
--

The total energy contained in fume from an electric arc furnace can be between 80 and 180 kWh/t steel, which represents 15 to 35% of the energy introduced into the furnace. The fume leaves the furnace at a temperature of between 500 to 800°C. Advantages could therefore accrue from using the energy contained in this fume to preheat scrap before it is charged.

Using the preheater also produces a savings of electrical energy of between 10 and 50 kWh/t and a reduction of between 5 and 10 minutes, i.e. between 6 and 15% of processing time.

The aim of the research project was to examine the impact of preheating of scrap on primary and secondary emissions from an electric arc furnace on the quality of air in the shop and on odour and sound emissions from the furnace.

The research was based on information obtained from the operation of two electric arc furnaces, one of 60 t - 45 MVA the other 150 t - 85 MVA.

The total energy contained in the fume from the furnace, i.e. between 80 and 180 kWh/t steel, can vary greatly depending on the type of scrap used. Thermal emissions also vary considerably in time during one steel-making operation, with peaks exceeding the average value at the extraction point under the hood of the furnace by a factor of between 2 and 3. The fumes give up some 20% of their energy to the cooling water in the ducts before leaving the post-combustion chamber and afterwards, if there is no preheating unit, they lose another 20% of their energy to the cooling water in the cooled ducts downstream and another 30 to 50% in the ducts and cooling equipment further downstream until they enter the smoke stack.

Generally, fume used for preheating is sampled as it leaves the post-combustion chamber. It was verified that there is no risk of a gas explosion here, as the levels of CO and H₂ were already insignificant at the entry to the post-combustion chamber (as long, of course, that the post-combustion air injection system functions correctly, ensuring that the level of O₂ is >12%).

Once the fume has passed through the scrap, the amount of dust contained in the fume can decrease as a result of the filtration effect of these scrap. Between 200 and 300 kg/h of dust are thus captured, but between 50 and 230 kg/h are subsequently released again. However, when the preheated scrap is charged, there is an increase in dust emission on charging of between 10 and 35%.

During preheating, organic compounds are emitted. Cold scrap produces some 15 g/t steel condensed organic compounds but when it is preheated total organic emissions rise to between 450 and 900 g/t steel, depending on the type of scrap used. Phthalates, esters and oxiranes are found amongst the pollutants, as a result of boiling and vaporisation mechanisms acting on grease and oily deposits.

These organic compounds are mainly deposited on the filtering elements, causing considerably greater and irreversible blinding of the filter bags when the scrap is heated. The dedusting equipment, which is generally designed to operate with a pressure drop of between 120 and 100 mm WG, is subject to a pressure drop which can be in excess of 300 mm WG. Moreover, condensation of these compounds downstream of the dust-collecting plant can cause flow problems with the dust is conveyed to the hopper, and possibly the risk of fire.

At the smoke stack there are still between 300 and 1 000 mg/Nm³ of organic compounds in the gaseous phase, approximately 30% of which can be condensed when the temperature is reduced to 2% (when the scrap is not preheated this is only between 30 and 50 mg/Nm³). Measurements have also shown that PAH (some tens of µg/Nm³) and benzene (500 µg/Nm³) are also present.

Once the scrap has been preheated, dust is emitted when it is transferred to the furnace and subsequently when partly burnt impurities ignite. Here another 0.2 to 1.5 kg of volatile organic compounds are emitted per tonne of steel, depending on the type of scrap used.

Finally, odour emissions to the atmosphere increase by a factor of 2 to 3 as a result of preheating, and a theoretical study on the dispersion of the gases into the atmosphere has shown that the perception threshold for odours can be exceeded at a distance ranging between 0.6 and over 15 kg depending on the type of scrap used and the atmospheric conditions.

However, preheating scrap does not have any significant influence on acoustic emissions from the furnace or the quality of air inside the shop.

In order to examine the problems linked with major emissions of organic compounds during preheating, some plants have made provision for partial or total recycling of preheating fume before directing it towards a post-combustion chamber for the VOCs to be destroyed. Recycling has not yet been demonstrated to be effective. However, total recycling does reduce the thermal flow of fume to the preheating unit by some 60% due to a commensurate decrease in the temperature of preheating fume (a reduction by 180°C and the volume of the fume.

6.2 TREATMENT OF WASTE WATER

Token entry

6.3 MANAGEMENT AND TREATMENT OF WASTE

Manufacturing stainless steel produces Cr, especially Cr⁺⁶, in waste water and in the waste during several phases of production:

- in the melting shop in the dust from the electric furnace and AOD converter (Argon, Oxygen and Decarburisation);
- in the scale formed in continuing casting and in hot-rolling mills;
- in pickling, in depleted liquor and in rising water.

The quantity of dust produced by the electric arc furnace and the AOD converter is between 10 and 15 kg per tonne of steel. The Cr content fluctuates widely in electric arc smelting (between 0 and 10%) and is between 15 and 25% for an AOD converter. Small quantities of nickel are produced by electric arc smelting and larger quantities in an AOD converter (between 2 and 7%). These elements always appear in the form of oxides.

The scale from continuous casting and hot-rolling mills comprises thermodynamically highly stable oxides and hence hold no danger for the environment. It contains some 20 to 30% of Cr oxides and 0 to 6% of Ni oxides.

Hexavalent chrome is highly soluble in water which means it can very easily be absorbed by cellular tissue. As Cr can have very harmful - i.e. carcinogenic - effects on some cells, it is highly toxic and the levels which can be tolerated in the air and in the water are very low. Trivalent chrome, however, is less soluble in water and hence less directly toxic.

Recycling of steel industry wastes containing chromium
Research project 7261-03/439/03 carried out by LECES (F)

The waste from plant producing stainless steels (dust from electric furnaces and AOD converters, millings and rolling mill scale) contain chrome which makes the waste dangerous or toxic. In some Member States it is forbidden to dump such waste and in others it must be dumped at controlled disposal facilities which are insulated from underground water and are therefore expensive.

The aim of the LECES research project is to take stock of the techniques available for recycling waste containing chrome, examining recycling by pyrometallurgical means and exploring the possibilities afforded by hydrometallurgical treatment.

A bibliographical study was carried out on the various pyrometallurgical treatments which have undergone a large range of pilot tests. These processes generally involve the following stages:

- preparation of the waste by pelletisation or compacting using cement or a press etc. possibly adding coke or coal dust as a reducing agent;

- reduction/fusion of the prepared waste in a furnace (electric furnace or plasma torch furnace).

The Bureau of Mines, Thyssen, Inmetco, Nisshin and Scandust methods were thus examined, some of which are currently being applied in industry (Nisshin and Scandust).

The conclusions to be drawn are that Fe and Ni can effectively be reduced in an electric furnace. In the case of chrome, reducing agents (such as FeSi) and a flux might have to be added to lessen its absorption in the slag. The high temperatures generated by plasma torches enable the Scandust procedure to recover chromium effectively even without a powerful reducing agent.

The study also showed that metals contained in waste can be recovered in a normal electric arc furnace used in production at the plant, which keeps investments to a minimum. The operating costs are around ECU 100 per tonne of waste treated (1990). Other installations such as Inmetco, Nisshin and Scandust have specific shops with high treatment capacities (between 20 and 70 kT/year) but the investment costs are high (between ECU 25 and 40 million in 1990).

Some tests for hydrometallurgical treatment of wastes containing chromium have also been carried out. These showed that Cr can be leached by oxidation in an acid medium with an extraction yield of some 60% but the problem of simultaneous dissolution of metallic cations associated with chromites (Ca^{++} , Mg^{++} , Zn^{++} , Al^{3+} etc.) remained unsolved.

Preliminary alkaline roasting at 800°C made it possible to convert chromium oxides into soluble alkaline chromates. The Cr can then be leached out simply with deionised water and extraction yields can be as high as 50% or even higher. The chrome can then be extracted from the leached product by electro dialysis.

However, tests for extracting Cr in an oxidising alkaline medium showed very low extraction yields (approximately 2%).

Another approach is to detoxify the dusts without extracting the Cr but merely by fixing it. Several tests were thus carried out with polysulphides obtained from lime and sulphur (residues from desulphurisation of coking plant gas). This technique reduces the hexavalent chrome to the (less toxic) trivalent chrome which, moreover, is trapped by the formation of an insoluble associated sulphide. The leaching rate in an AOD converter dust went from 150 mg Cr VI/kg before treatment to 10 mg Cr III/kg after treatment.

Prevention of pollution from aqueous solutions generated by the manufacture and processing of stainless steel
Research project 7261-03/438/03 carried out by Ugine (F)

Ugine also looked at recycling metals contained in these dusts in an electric furnace. To do this, they first had to form "blocks" which could be charged and then ensure that they could be reduced in such an environment. Ugine thus carried out several fusion tests in a laboratory with several mixtures of iron and converter dust and scale agglomerates. The main conclusions from these tests confirm LECES's view that:

- recovery by reduction is more efficient for nickel than for chromium;
- carbon does not seem to be the most effective reducing agent;
- adding FeSi sharply increases the reduction yield, indicating that Si has a powerful reducing effect. However, this resulted in considerable wear to the hearths;
- the rate of reduction to the metallic state seemed to be highly dependent on particle size. Particles larger than 5 mm produced reduction rates which were markedly higher.

If recycling in an electric furnace is not totally justified in economic terms, the fact that the non-reduced chromium is in a stapher form in slag than in dust and no longer contains Cr^{+6} is a plus for the environment.

The behaviour of toxic metals during the plasma smelting of stainless steelmaking dust and development of viable disposal practices

Research project 7261-03/437/08 carried out by British Steel Technical (UK)

During a research project completed by British Steel Technical in 1985, a technology had been tested to recover metals present in waste from melting shops producing stainless steels. This was a furnace using a mechanically rotated plasma electrode. The substances to be treated were mixed with a suitable reducing agent such as coke or coal and transported pneumatically into the plasma arc using supply tubes arranged around the furnace roof. The metallic oxides were reduced chemically both in the plasma arc and in the metallic bath.

Following this, British Steel installed a plasma torch furnace to treat all the dust - 8 kT/year - from the production of 400 kT/year of stainless steel at its Sheffield plant. The technology for the furnace was developed by Tetronics R & D Company (Faringdon - UK). Reduction was carried out by adding 17% of anthracite to 83% of dust.

After replacing the original tungsten electrodes, with which there were problems, by graphite ones, the furnace could be run at full capacity.

The objective of this study was thus to analyse the recycling of metal in the furnace in the metal, slag and dust phases.

Recycling tests were carried out with dust from bag filters from the melting shop (EAF/AOD dust) and from plasma torch cutting in a rolling mill.

Generally speaking the results of the tests showed that:

- Cr, Ni and Mo were mainly found in the metal phase (over 90% of the Ni and the Mo and approximately 2/3 of the Cr);
- some of the Cr is also found in the slag (between 10 and 20%);
- Zn, Pb and Cd are found in the dust (between 70 and 90% according to the tests).

The tests with a mixture of dust from the furnace and the rolling mills gave the best separation rates.

The dust extracted from the recycling furnace was also used for recycling tests to enrich their metal content. Recovery of Cr, Ni, Mo, Mn and Pb was good but the tests showed that Zn enrichment was much lower than the theory had led the researchers to expect. The dusts were used for leaching tests to assess their behaviour when dumped and showed that they might be an environmental hazard and that special precautions were necessary.

However, the leaching tests on slag showed that it should not cause any environmental problems when dumped. Its properties from the point of view of recycling in road building were not assessed.

CHAPTER 7

Pickling lines, cold rolling mills and coating lines

7.1 ACID PICKLING LINES

7.1.1 *Study of the health risks to workers*

Acid mists at workstations on pickling and coating lines
Study of the sampling of acid mists in order to assess their impact on exposed personnel and to study exposures of personnel in different types of process

Research project 7261-04/465/08 carried out by British Steel (UK)

The possible link between laryngeal cancer and exposure to acid mists prompted the researchers to look more closely at the risks associated with exposure and determining the concentrations in such acid mists in the atmosphere at various workstations. It is important to determine the dimensions of the acid droplets forming the mist as well as the acid concentration as these influence acid retention when they are inhaled.

British Steel therefore set out first to assess various sampling methods and then carried out a sampling campaign on its sheet steel pickling and coating lines using various acids (chromic acid, sodium dichromat, HF, H₂SO₄ and HCl). The campaign included sampling of both fixed points and the ambient air inhaled by line operators.

An atmospheric sampling instrument was selected on the basis of the study of sampling techniques for acid mists which established precisely the volume sampled at a great variety of pressure drops.

Next the filter carriers filters were selected for each type of acid whose concentration is to be determined (Cr⁺⁶, HCl, H₂SO₄ and HF).

Droplet size was determined, with the benefit of previous experience, by a technique for determining chromic acid fallout using thin layer chromatographic plates. This technique was used during the project and proved also capable of determining the quantity of chromic acid in the ambient air. There was a correlation of virtually 1 with a confidence margin of 95% when the results obtained with this technique were compared with those from conventional techniques. This therefore enables the concentration of Cr⁺⁶ in the ambient air to be determined easily, quickly and economically.

The sampling campaign of ambient air was carried out at a large number of operating lines including:

- hydrofluoric, hydrochloric and sulphuric acid pickling lines;
- electrolytic tinning lines (sodium dichromate or chromic acid passivation);
- electrochrome coated steel lines;
- electrolytic galvanisation lines (with a sulphuric acid electrolytic bath);
- hot dip galvanisation lines (chromic acid passivation);
- organic coating lines with chromic acid chemical pretreatment.

The results of this campaign showed that the exposure limits for workers were very largely abided by for line operators both vis-à-vis hexavalent chrome and HCl and H₂SO₄, with the exception of the chemical pretreatment section of an organic coating line. At this site faulty design of the covers led to high levels of chromic acid exceeding the permissible exposure limits. This design had to be modified.

Designing installations to comply with the permissible exposure limits for hydrofluoric acid is more difficult.

Sampling acid mists at fixed points identified spots with high concentrations though these levels did not exceed permissible exposure limits except in the case of hydrofluoric acid.

In conclusion, the study showed that exposure of operators at various workstations on pickling and coating lines is not generally a problem except for exposure to hydrofluoric acid, where installation design to achieve the required level of protection is proving more of a problem.

7.1.2 *Reduction of nitrogen oxide atmospheric emissions from stainless steel pickling baths*

Elimination of nitrogenous waste gases from mixed-acid pickling baths
Research project 7257-54/397/01 carried out by Krupp Stahl (D)

After hot processing of stainless steel, mechanical descaling followed by chemical pickling is required, and after cold processing electrochemical pickling followed by chemical pickling, to remove oxide layers with high levels of chromium.

Chemical pickling is carried out with a solution of nitric acid (between 10 and 25%) and hydrofluoric acid (between 1 and 4%).

The reaction of Fe, Cr and Ni with nitric acid produces metallic nitrates which are dissolved and releases NO which reacts with the oxygen in the air to produce NO₂. Other nitrogen oxides are also released.

In order to restrict NO_x emissions, the gaseous effluent from the Krupp Stahl pickling baths is cleaned with water but, since NO is not readily soluble in water, concentrations of NO_x in scrubbed effluent exceed the values authorised in Germany (750 ppm).

Krupp Stahl therefore examined the effect of injecting the deoxidising agent into the pickling baths, the aim being to convert the nitrites created within the bath itself immediately into nitrates and hence to preclude the development of nitrogen oxides when they are formed. Krupp Stahl chose urea (CO (NH₂)₂) as a deoxidising agent which converts nitrogen oxide into N₂, CO₂ and H₂O.

After carrying out tests in the laboratory which verified the feasibility of the process and its effectiveness in reducing NO_x, Krupp Stahl built an installation to inject urea into industrial pickling baths.

The volume of urea injected is automatically adjusted for the level of NO_x measured in the gaseous effluents in order to limit the concentration of NO_x in the effluent to 750 and 400 ppm respectively.

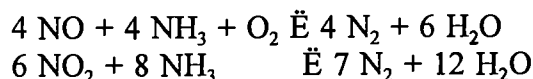
The tests showed that the technique for injecting varying quantities of urea varying between several l/h to 60 l/h does enable the emission values to be complied with, resulting in a reduction of between 55 and 70% of nitrogen oxide emissions. However, the urea causes side-effects including:

- an increase in ammonium levels in the waste water: from 50 mg/l to between 120 and 190 mg/l of N-NH₄⁺. By contrast, the nitrite content is reduced from 60 mg/l to between 15 and 30 mg/l;
- an increase in the consumption of nitric acid solution by between 20 and 50% and hydrofluoric acid by between 75 and 120%, with the urea actually consuming some of the pickling solution directly.

As Krupp Stahl does not have an installation for removing ammonium from waste water, the technique has not been applied to normal operations.

Other avenues were then explored:

- Additional purification of gaseous effluents containing nitrogen oxides using the following catalytic reaction:



However, this reaction requires a minimum temperature of 350°C. The purification system comprises preseparator for hydrofluoric acid and aerosols, an air/air heat exchanger to recover the calories from the purified air, a natural gas boiler and finally a reactor with a catalyst converting nitrogen oxides and ammonia into nitrogen and water. An automatic system controls the amount of ammonia injected, depending on the levels of NO_x in the purified effluent.

- Replacing nitric acid by other pickling products to prevent formation of nitrogen oxides, was keeping pickling time sufficiently short (1 to 1.5 minutes).

A preliminary study showed that pickling in successive baths with only hydrofluoric acid in the first bath and a mixture of nitric and hydrofluoric acids in subsequent baths should reduce NO_x emissions by 65%.

Using hydrogen peroxide (oxygenated water - H₂O₂) as a method of deoxidisation in the second pickling bath was also tested.

However, these avenues could not be explored exhaustively due to lack of time.

Elimination of pollution and utilisation of waste products from the pickling of stainless steel
Research project 7261-03/427/03 carried out by Ugine (F)

Ugine has developed a pickling process called UG-3P, using a bath of hydrogen peroxide plus hydrofluoric acid. Nitric acid is replaced by nitrogen peroxide, which prevents nitrogen oxide emissions and pollution of aqueous effluent by nitrogenous compounds.

The pickling solutions are passed continuously through settling tanks for recycling and the sediment must be treated before being disposed of. The first stage of treatment is to dissolve the sludge in water, which can easily be done at 50°C.

The most simple treatment of the waste solution thus obtained is to induce total precipitation of the metal hydroxides (Fe, Ni and Cr) and of the fluorine using lime. The effluent obtained complies with the permissible limits for waste water disposal and the precipitate is a waste product which cannot be leached by rain water or only very little. This treatment process is thus effective from the environmental point of view, is very cheap but does not enable either the metals or the fluorine contained in the waste solutions to be recycled.

This project thus set out to study other techniques for recycling the by-product, first by carrying out a bibliographical study and subsequently by laboratory tests. The techniques studied covered:

a) Chemical methods:

- solvent extraction;
- separation by ion-exchange resins;
- dialysis separation;
- distillation separation;
- selective precipitation of metals, (using soda, phosphoric acid, sodium carbonate, potassium, ammoniac and sodium benzoate).

b) Electrochemical methods:

- electrolysis;
- electrodialysis;
- electro-electrodialysis.

Several of these methods proved to have a very low yield following the formation of highly stable complexes (Fe F_3 , Fe F_2^+ , Fe F^{++} and their equivalents for chrome), which the reactions induced by these methods could not break down. Moreover, separation of metals by cationic resin was of little interest as the resin very quickly became saturated. The most promising technique seems to be separation by distillation, decomplexing of the fluorides by concentrated sulphuric acid. This technique enables the hydrofluoric acid to be recycled but its pay back is put at five years. The study therefore concludes that recycling by-products can only be countenanced for environmental reasons but not for economic ones.

Design and installation of electrochemical sensors intended to reduce pollution caused by acid pickling

Research project 7257-62/398/03 carried out by Creusot-Loire Industrie (F)
--

Creusot Loire investigated another means of reducing nitrogen oxide emissions by optimising the pickling capacity of the baths and thus reducing to a minimum depleted baths and the resulting effluent. To do so the balance within the solution, whereby the following ions and molecules:

HF , F^- , NO_3^- , H^+ , Fe^{+++} , Cr^{+++} , FeF^{2+} , FeF_2^+ , FeF_3 , $(\text{HF})_2$, HF_2^- , ...

within the solution has to be controlled on line.

Ultimate analysis of these baths provide correct results in the laboratory but are not always capable of use on-line, which induces a time delay between sampling and analysis.

The research thus focused on sensors which can be used for continuous monitoring of pickling baths.

A bibliographical study was first carried out to study the collectors which could be used. First of all the new ISFET collectors using field-effect transistor electrodes, which combine integrated circuit technology and ion-sensitive electrodes were examined. They seemed highly promising in theory but the research showed their life to be very short. So far they have not been applied in industry. As a result, in the current state of the art, the researchers could not envisage using them. However, the bibliographical study identified the possibility of using ion-sensitive electrode collectors comprising a crystalline membrane and a glass membrane.

Experimental tests were then carried out on different sensors with ion-sensitive electrodes for the following ions: H^+ , F^- , NO_3^- , Cl^- , SO_4^{2-} , Na^+ , Ca^{2+} , on sensors to measure the oxidation/reduction potential and on conductimetric collectors.

All the sensors sensitive to H^+ ions examined led to problems in the pickling baths for stainless steels. It was decided that it would be more useful to measure conductivity, as variations in electric conductivity being largely due to a variation in the concentration of H^+ ions in solution.

There are also problems with the sensors sensitive to NO_3^- ions and SO_4^{2-} ions.

However, satisfactory results were obtained for the Cl^- , Na^+ , and Ca^{2+} ions and for measuring oxidation/reduction potential and electric conductivity.

It was shown that all the pickling reactions corresponded with oxidised metal/solution reactions and that therefore one of the prime parameters to be measured was the oxidation/reduction potential.

Measuring electrical conductivity also offers many advantages in determining accurately how much acid needs to be added to pickling baths and during neutralisation.

Creusot Loire finally developed a multielectrode electrochemical sensor and a mobile on-line bath monitoring unit.

7.1.3 Purification of waste water from stainless steel pickling lines

Prevention of pollution from aqueous solutions generated by the manufacture and processing of stainless steel
Research project 7261-03/438/03 carried out by Ugine (F)

Hexavalent chrome is highly soluble in water and can easily be absorbed by cell tissues. It is highly toxic and the concentrations permitted in the air and water very low, as chrome can

be very harmful - or carcinogenic - in certain cells. Trivalent chrome, however, is less soluble in water and less directly toxic.

Recycled water from pickling lines - either electrolytic or chemical - contain hexavalent chrome and other heavy metals (Cr^{+3} , Ni, etc.) which must be eliminated as far as possible. Uguine investigated the mechanisms for forming Cr^{+6} in order to assess the possibilities of eliminating Cr^{+6} by modifying the process. However, during the course of the project only treatment of effluent to remove Cr^{+6} was considered.

Such treatments included reduction of Cr^{+6} and Cr^{+3} by Fe^{++} which was examined in both an acid medium (of particular interest to plant with a supply of FeSO_4) and alkaline medium (which has the advantage of precluding acidification by H_2SO_4 and enables Cr^{+6} to be reduced to Cr^{+3} simultaneously with precipitation of Fe and Cr hydroxides). Other treatments enabling Cr^{+6} to be separated (without reduction) were also examined, and included chemical extraction, especially treatment with ion-exchange resins.

The latter technique involves two in-series treatment stages, first with a cation-exchange resin to extract Fe, Ni and ammonium cations and then to extract CrO_7^- and SO_4^- anions. Various resins available on the market were tested with the effluent to be treated and finally two of them (*Lewatit SP 112* from Bayer (Germany) for the cations and *Duolite - A 368* from Dia-Prosium (France) for the anions). This treatment keeps concentrations in the water within the levels permitted by the regulations and enables the Fe^{++} , Ni^{++} , ammonium⁺ anions and the CrO_7^- and SO_4^- cations to be recovered separately.

7.2 COLD ROLLING MILLS

Token entry

7.3 COATING LINES

7.3.1 *Reduction of zinc losses in galvanising lines*

Study and development of means of recovering and recycling waste from electrogalvanising lines
--

Research project 7261-03/464/04 carried out by the Centro Sviluppo Materiali (I)
--

When 4 500 t of sludge used to treat waste water from the Ilva electrogalvanising lines in Turin were dumped in 1989, the 450 t of zinc they contained were lost. In 1991 the quantity was reduced to 270 t by reducing accidental losses.

In order to reduce the quantity lost still further CSM carried out a study pursuing two different approaches:

- recycling of water within the installation;
- recovery of the Zn contained in the sludge at the purification station.

Material loss was reduced very simply by replenishing liquid lost (*inter alia* by evaporation) from degreasing baths, electrolytic cleaning, pickling and electrogalvanising baths not with fresh water but with water drawn from the rinsing baths downstream of the treatment bath. 15 l/h per hour had to be replenished in each bath and this simple system enabled 21 t of degreasing solution, 10 t of H₂SO₄ and between 50 and 100 t of zinc to be recovered each year.

After complete dehydration, the purification station sludge contains between 40 and 50% ZnO and 40 and 50% calcium sulphate, the remaining 10 to 12% being other metallic oxides.

Recovery of the Zn contained in this sludge is prevented by the presence of calcium sulphate which is undesirable for the majority of applications for recycling/upgrading zinc. The origin of the calcium sulphate was thus investigated.

The electrogalvanising bath is made up of a Zn sulphate electrolyte generated by sulphuric acid attack of metallic zinc. The depleted baths and other waste water therefore contain Zn sulphate which is precipitated with milk of lime, the precipitation solution pH value being regulated to 9.4 by the addition of soda. Research showed that effective precipitation of Zn could be achieved without adding milk of lime, and that the alkaline and acidic waste could be mixed to save some of the soda required to regulate the pH. The waste is treated with soda alone, to which a flocculant (*AN 971*) is added. Zeolite is also added upstream of filter press to reduce the concentration of water in the sludge, increasing the mass of the sludge by less than 1% without jeopardising the possibility of recovering Zn.

The quantity of sludge produced annually is lower due to the fact that lime is no longer used and due to improved flocculation and improved dehydration at the filter press.

The sludge thus obtained can be dissolved in sulphuric acid and then recycled in the process. 1 ml of sulphuric acid at a concentration of 96% or 3 ml at a concentration of 50% is sufficient to dissolve between 5 and 10 g of sludge from the filter press. The deferrisation unit in the electrogalvanising line which retains the iron content is no obstacle to recovering the sludge. The Zn present in the sludge is reutilised in the electrogalvanising line process.

7.3.2 *Purification of waste water from electrogalvanising lines*

Removal of heavy metals from industrial scrubbing water, with particular attention to removing zinc and nitrite ions
Research project 7261-02/433/04 carried out by Lavezzari SpA (I)

The effluent from electrogalvanising and phosphatation/passivation lines has high concentrations of zinc. Some waste water also contains Cr^{+6} and nitrites. The Italian standards for disposal of such effluent restrict concentrations of Zn, Cr^{+6} and nitrites to 0.5 mg/l, 0.2 mg/l and 0.6 mg/l, which are difficult to achieve by normal purification methods.

Lavezzari therefore studied other methods of purifying waste water from these lines. Before the research commenced, its purification system comprised several stages:

- reduction of Cr^{+6} chromate by adding sodium bisulphite to obtain a pH value of 3 (using hydrochloric acid);
- coagulation by adding milk of lime which renders the metals insoluble by forming hydroxides;
- flocculation by adding a polyelectrolyte;
- sedimentation;
- filtration with a sand filter and an activated charcoal filter to remove the mineral oils;
- demineralisation on cationic resin to eliminate residual metals;
- correction of the pH values;
- dehydration of the sludge using a filter press.

First of all, the chromates reduced effectively by the ACTIMAG system which reduces the Cr^{+6} and Cr^{+3} using metallic iron exposed to an external magnetic field. This system has a number of advantages - it is easy to use, there is no sulphite in the discarded effluent and less milk of lime is required to coagulate the metal.

Tests subsequently showed that it was feasible to recover Zn from waste water by ionic exchange with resin. Two types of resin were tested with waste water containing 500 mg/l of Zn. The specific maximum capacity was 16 g of Zn per litre of resin with good selectivity (less than 3% of Fe compared with the Zn collected).

Various procedures were studied to remove nitrites by oxidation including the use of oxygenated water, sodium hypochlorite and ozone. The ozone treatment finally proved the most effective and the most economical and produced levels of nitrites lower than 0.6 mg/l.

Zn removal from the effluent was studied very intensively and showed that, in theory, treatment with milk of lime produces a minimum residual concentration of Zn in the effluent if treatment is carried out at a pH value of 9.5. However, the residual concentration in practice was still as high as 1 mg/l, although theory would lead one to expect values lower by a factor of between 10 and 100. In order to enable the level to be reduced to less than 0.5 mg/l (the limit specified in the regulations), LAVEZZARI tested an additional organic additive, a dithiocarbimide solution called NOOR "soda salt".

Levels lower than the statutory limit of 0.5 mg/l were achieved by adding between 2 and 4 mg/l of this salt which also improved the settling rate of the flocculants. However, the *Daphnia* ecotoxicity test shows that the toxicity of the effluent is increased as a result.

LAVEZZARI also tested an automatic analysis instrument for the concentration of Zn in waste water. This instrument, the SERES 2000, has a measurement cycle of 15 minutes and seems to be satisfactory.

Finally, leaching tests were carried out on purification sludges to establish whether this waste was dangerous. However, the tests carried out were not the standardised ones used in other countries and it is difficult to assess the results. All the same, the sludge from the treatment with the NOOR soda salt contains only half the concentration of zinc specified for toxic waste.

7.3.3 *Passivation of coated sheet by treatment without chromic acid*

New passivation processes for tinned sheet and thin galvanised sheet using baths not containing chromates. Feasibility study
--

Research project 7257-15/395/04 carried out by CSM (I)
--

Some coated products such as tinned sheet and thin galvanised sheet are passivated during manufacture. This is done in baths containing solutions based on chromic acid and its derivatives. The chromates they contain are formed from hexavalent chrome which is well known to be toxic and dangerous so CSM looked for replacements which were less toxic but offered comparable passivation performance with that obtained using chromates.

As replacement products CSM examined molybdates and tungstates which form subgroup VIB of the periodic table together with chromates, these three acids being relatively strong acids which ought to have similar chemical properties.

The concentration of the solutions used for the tests was 0.1 M/l at pH 4 and a temperature of 40°C, which is similar to those now used in industrial chromate solutions and therefore ought to be suitable for use in existing industrial lines.

The oxidation capability of the surface layers obtained by molybdate and tungstate treatment was assessed by means of the Britton test (a test of anodic oxidation at constant current). This test, which was developed for bichromates, only provides a qualitative and not quantitative results. However, to assess the passivation layer obtained, detailed examinations of the surface layers obtained by this treatment were carried out using X-ray photoelectron spectroscopy. These showed that a molybdate solution did not produce any detectable passivation film. The quantity of molybdenum - either oxide or metallic form - is practically zero. The film obtained with a tungstate solution is close to that obtained with a bichromate solution.

Other tests were then carried out to identify better the properties of the surface layer obtained:

- Varnishability test which showed decreasing wet adhesion for chromate, tungstate and finally molybdate baths respectively.
- Exposure in a mist chamber (ASTM 417).
- Test for resistance to sulphuration, which produced results which were substantially poorer for tungstates and molybdates than for bichromates.
- Electrochemical test for resistance to corrosion by measuring the polarisation resistance. Here too, corrosion resistance declined with the use of bichromates, tungstates and molybdates respectively.

In conclusion, the feasibility study showed that a solution of molybdate could not be used for passivation and that a tungstate solution was superior to a molybdate one and produced a passivating layer on tinned sheet under test conditions which might enable it to replace bichromates, albeit with substantially inferior properties. No economic comparison of the solutions was carried out.

CHAPTER 8

Conclusion

The fifth ECSC research programme on "Technical control of nuisances and pollution at places of work and in the environment of iron and steelworks" of which 68 research projects are summarised in this report, covers a period of research between 1985 and 1994. The results of all this industry-based research work, a fair amount of which has been applied directly in industry, is now at the disposal of the entire European steel industry as a result of the subsidies granted by the ECSC. Moreover, many of the research projects are also of interest to other sectors of industry, which gives the programme a wider compass.

This research work has made a substantial contribution to reducing the adverse effects of steelmaking in the European Union on our environment and on workers' health. Much has been achieved, in terms of both identifying the effects emissions have and devising techniques for reducing or eliminating them, and potential users are now free to take advantage of this as a result of the ECSC programme. However, it is still necessary for information to be distributed effectively and this is one of the aims of publishing this report.

The programme is thus an essential tool for encouraging improved environmental protection and pooling of information and experience in this field in the European Union.

ANNEX 1

LIST OF RESEARCH PROJECT

PROJECT No	ORGANISATION	COUNTRY	CHAPTER
394	LECES	F	4.1.a
395	CSM	I	7.3.c
396	CSM	I	3.2.c
397	KRUPP STAHL	D	7.1.b
398	CREUSOT-LOIRE	F	7.1.d
400	CRM	B	3.2.f
401	VDEh	D	2.1.2.e
402	TNO	NL	2.1.2.a
403	BCRA	GB	3.1.4.b
404	CEBEDEAU	B	2.3.1.d
405	IRH	F	2.3.2.a
406	BRITISH STEEL	GB	3.2.a
407	CSM	I	2.1.1.a
408	CPM	GB	3.1.2.a
409	SBF	B	3.1.4.a
410	CRM	B	4.1.b
411	DMT	D	3.1.2.b
412	IRH	F	2.2.c
413	CEBEDEAU	B	5.1.a
414	LECES	F	2.1.1.b
415	LECES	F	6.1.b
416	MONCKTON	GB	3.2.d
417	DMT	D	3.1.5.d
418	CRM	B	3.1.5.b
419	LECES	F	3.1.5.a
420	CPL	GB	3.1.5.c
421	CSM	I	2.1.3.a
422	LECES	F	2.3.2.b
423	DMT	D	3.1.3.d
424	CPL	GB	3.1.3.a
425	LECES	F	3.1.3.c
426	IRH	F	2.3.3.a

427	UGINE	F	7.1.c
428	CRM	B	2.3.1.b
429	CSM	I	2.3.1.e
430	BRITISH STEEL	GB	6.1.a
431	THYSSEN	D	2.1.1.c
432	LECES	F	4.2.a
433	LAVEZZARI	I	7.3.b434 IRH F3.2.b
435	CSM	I	2.2.a
436	AGK	D	2.3.2.c
437	BRITISH STEEL	GB	6.3.c
438	UGINE	F	6.3.b et 7.1.e
439	LECES	F	6.3.a
440	ENSIDESA	E	3.1.3.b
442	ENSIDESA	E	2.1.2.b
443	LECES	F	2.4.c
444	CEDIA	B	2.4.b
445	INRS	F	2.4.a
446	LECES	F	2.1.2.c
447	HOOGOVENS	NL	3.1.1.a
448	LECES	F	2.1.2.d
450	CSM	I	4.1.c
451	CSM	I	2.1.1.d
452	MONCKTON	GB	3.2.ce
453	CEBEDEAU	B	2.3.1.a
455	LECES	F	4.2.b
459	IRH	F	5.1.c
460	CRM	B	5.1.b
461	IRH	F	2.2.b
463	CRM	B	2.3.1.c
464	CSM	I	7.3.a
465	BRITISH STEEL	GB	7.1.a
467	VDEh	D	2.5.a
468	BRITISH STEEL	GB	2.5.b
469	CSM	I	2.4.d
492	ARBED	L	2.1.3.b

<p style="text-align: center;">ANNEX 2</p> <p style="text-align: center;">RESEARCH PROJECTS DEALT WITH IN THE VARIOUS CHAPTERS</p>
--

1. Introduction

2. Studies not confined to a specific steel industry workshop

2.1 ATMOSPHERIC EMISSIONS

2.1.1 *Reduction of nitrogen oxide emissions*

- a) Pilot furnace study of nitrogen oxide emissions from reheating furnaces in the steel industry and ways of reducing them in the ECSC industries (Centro Sviluppo Materiali - 7261-01/407/04)/
- b) Further study of nitrogen oxide emissions from steelmaking plants (LECES - 7261-01/414/03).
- c) Reduced emission of nitrogen monoxide through the injection of water during the combustion process (Thyssen Stahl AG - 7261-01/431/01).
- d) Reduction of nitrogen oxide emissions from steel industry power plant (CSM - 7261-01/451/04).

2.1.2 *Analysis of pollutants emitted at workstations in terms of the risk to workers' health.*

- a) Modelling of air pollution at workplaces with a view to developing measurement strategies (TNO - 7257-61/402/06).
- b) Characterisation of the health risk caused by the inhalation of particulate matter from iron and steel manufacturing processes (ENSIDESA - 7261-04/442/14).
- c) Analysis and prevention of complex dust contamination in iron and steel manufacturing plants (LECES - 7261-01/446/03).

- d) Study and prevention of emissions from carbon-bonded refractories in iron and steelworks (LECES - 7261-01/448/03).
- e) Development and testing of an apparatus for determining the concentration of oil aerosols (VDEh - 7257-55/401/01).

2.1.3 *Reduction of dust emissions*

- a) Reduction of dust blowoff in steelworks ore and coal stockyards by the use of binding agents (Centro Sviluppo Materiali - 7261-03/421/04).
- b) Reduction of dust emission during metallurgical operations by inertisation of the ambient atmosphere (ARBED - 7261-01/492/05).

2.2 WASTE WATER TREATMENT

- a) Testing and pilot scale development of an ultrasonic system for non-pollutant antifouling treatment of cooling water in steelworks (Centro Sviluppo Materiali - 7261-02/435/04).
- b) Smoothing pollution peaks to optimise the functioning of steel industry effluent treatment installations (IRH - 7261-02/461/03).
- c) Chemical treatment for the specific destruction of cyanides (IRH - 7261-02/412/03).

2.3 MANAGEMENT AND TREATMENT OF WASTE

2.3.1 *Waste treatment for upgrading*

- a) Study of the dissolution of low-soluble zinc and lead compounds in waste generated by the steel production cycle (CEBEDEAU - 7261-03/453/02).
- b) Study of the possibilities of treating simultaneously steelmaking waste rich in Zn/Pb and depleted hydrochloric pickling baths (CRM - 7261-03/428/02).
- c) Study of the possibilities of simultaneous treatment of steelmaking waste rich in Zn/Pb and depleted hydrochloric pickling baths - Phase II (CRM - 7261-01/463/02).
- d) Biological detoxification of steelworks wastes containing heavy metals (CEBEDEAU - 7257-74/404/02).

- e) Treatment of oily sludge by chemical processing and physical separation of the ferrous fraction which can be reincorporated into the steelmaking cycle (Centro Sviluppo Materiali - 7261-03/429/04).

2.3.2 *Final waste tipping*

- a) Extension of the research on leaching of iron and steel industry waste to new types of waste (IRH - 7257-72/405/03).
- b) Binding of heavy metals in steelworks waste by suitable control of dumping (LECES - 7261-03/422/03).
- c) Retention capacity of Posidonia shale in respect of seepage water containing heavy metals from flue dust dumps (modelling of migration mechanisms based on laboratory tests and work on site) (AGK - 7261-03/436/01).

2.3.3 *Decontamination of old lagoons and dumps*

- a) Physical/chemical treatments of unusable oily sludges (IRH - 7261-03/426/03).

2.4 ACOUSTIC NUISANCES

- a) Noise from gas transport circuits in the steel industry. Inventory of potential sources of noise and an approach to modelling (INRS - 7261-05/445/03).
- b) Use of noise prediction techniques to optimise noise abatement in steel shops (CEDIA - 7261-05/444/02).
- c) Control of acoustical environment in steelworks by means of sound intensity measurement and predictive modelling (LECES - 7261-05/443/03).
- d) Reduction of noise from plasma torches used in continuous casting tundishes (Centro Sviluppo Materiali - 7261-05/469/04).

2.5 PROTECTION AGAINST IONISING RADIATION

- a) Detection of radioactive contamination in steel plant raw materials (VDEh - 7261-04/467/01).
- b) Detection of radioactive sources in steel plant raw materials (British Steel - 7261-04/468/08).

3. Coking plant

3.1 ATMOSPHERIC EMISSIONS

3.1.1 *Reduction of sulphur oxide emissions*

- a) Coke oven gas desulphurisation using multiple alkanolomines (Hoogovens - 7261-01/447/06).

3.1.2 *Reduction of nitrogen oxide emissions*

- a) Emission of nitrogen oxides in coking plants. Study of their impact on the environment (CPM - 7261-01/408/03).
- b) NO_x emissions and associated ambient pollution in connection with the heating of coke ovens (DMT - 7261-01/411/01).

3.1.3 *Emissions of polycyclic aromatic hydrocarbons*

- a) Pollution in coking plants (measurement of polycyclic aromatic hydrocarbons in the atmosphere within the environs and in the neighbourhood of coke works - Phase II (CPL - 7261-04/424/08).
- b) Study of the criteria which determine occupational exposure to PAH in coking plants. Characterisation and quantification of the risk factors (ENSIDESSA - 7261-04/440/14).
- c) Pollution in coking plants - measurement of polycyclic aromatic hydrocarbons in the atmosphere within the environs and in the neighbourhood of coke works - Phase II (LECES - 7261-04/425/03).
- d) Pollution in coking plants - measurement of polycyclic aromatic hydrocarbons in the atmosphere within the environs and in the neighbourhood of coke works - Phase II (DMT - 7261-04/423/01).

3.1.4 *Olfactory nuisances*

- a) Odour nuisance in the iron, steel and coking industries. Study of methods of prevention and control and techniques (SBF - 7261-01/409/02).

- b) Investigation, inventory and control of odiferous pollutants in the steel and carbonisation industries (BCRA Scientific and Technical Services Ltd - 7257-71/403/08).

3.1.5 Emissions of heavy metals

- a) Coking plant pollution - balance and fate of heavy metals during the process of coal carbonisation (LECES - 7261-04/419/03).
- b) Coking plant pollution - balance and fate of heavy metals during the process of coal carbonisation (CRM - 7261-04/418/02).
- c) Coking plant pollution - balance and fate of heavy metals during the process of coal carbonisation (CPL - 7261-04/420/08).
- d) Preparation of balance sheets for trace elements in coking plant material flows (DMT - 7261-04/417/01).

3.2 TREATMENT OF WASTE WATER

- a) Development of an automatic control system for an ammonia stills for coking plant liquor (BRITISH STEEL plc - 7257-18/406/08).
- b) Improving the stability and performance of biological treatment facilities for coking plant effluent (IRH - 7261-02/434/03).
- c) Extraction of ammoniacal nitrogen from coking plant liquor using rotating biological discs and simultaneous extraction of organic pollutants (pre-denitrification and nitrification) (CSM - 7257-15/396/04).
- d) Investigation of the technical and economic benefits associated with the use of pure oxygen in the biological treatment of carbonisation effluents (Monckton Coke & Chemical Co. Ltd - 7261-02/416/08).
- e) Further investigation of the technical and economic benefits associated with the use of pure oxygen in the biological treatment of carbonisation effluents (Monckton Coke & Chemical Co. Ltd - 7261-02/452/08).
- f) Removal of organic sludges produced in the biological purification of coking plant liquor (CRM - 7257-15/400/02).

4. Sintering and pelletisation

4.1 REDUCTION OF ATMOSPHERIC EMISSIONS BY MEANS OF PROCESS MODIFICATIONS

- a) Minimisation of gaseous pollutant emissions by thermal optimisation of grate sintering (LECES - 7257-21/394/03).
- b) Effect of the operational parameters of iron ore sintering plants on emissions of sulphur and nitrogen oxides into the atmosphere (CRM - 7261-01/410/02).
- c) Reduction of CO, NO_x and SO₂ emissions from sintering plants by modifying the charging and process parameters (Centro Sviluppo Materiali - 7261-01/450/04).

4.2 REDUCTION OF ATMOSPHERIC EMISSIONS BY END-OF-PIPE TREATMENT OF FUME USING BAG FILTER

- a) Research into the use of bag filters to reduce particulate and gaseous pollutants in the process fumes from iron ore sintering plants - Phase A (LECES - 7261-01/432/03).
- b) Use of bag filters to reduce particulate and gaseous pollutants in the process fume from ore sintering plants - Phase B (LECES - 7261-01/455/03).

5. Blast furnaces

5.1 TREATMENT OF WASTE WATER - REDUCTION OF CYANIDE WASTE

- a) Chemical treatment for the specific destruction of cyanides (CEBEDEAU-CRM - 7261-02/413/02).
- b) Study of blast furnace cyanide emissions during daily operation and blow down (CRM - 7261-02/460/02).
- c) Optimisation of formaldehyde treatment to remove cyanide from blast furnace scrubbing water (IRH - 7261-02/459/03).

6. Melting shops, continuous casting plant and hot-rolling mills

6.1 ATMOSPHERIC EMISSIONS

- a) Energy savings through improvements in fume control methods for melting shop extraction systems (BRITISH STEEL - 7261-01/430/08).
- b) Technical control of nuisances and pollution caused by scrap preheating techniques in electric arc melting shops (LECES - 7261-01/415/03).

6.2 TREATMENT OF WASTE WATER

Token entry

6.3 MANAGEMENT AND TREATMENT OF WASTE

- a) Recycling of steel industry wastes containing chromium (LECES - 7261-03/439/03).
- b) Prevention of pollution from aqueous solutions generated by the manufacture and processing of stainless steel (UGINE - 7261-03/438/03).
- c) The behaviour of toxic metals during the plasmas melting of stainless steelmaking dust and development of viable disposal practices (BRITISH STEEL - 7261-03/437/08).

7. Pickling lines, cold rolling mills and coating lines

7.1 ACID PICKLING LINES

- a) Study of the sampling of acid mists in order to assess their impact on exposed personnel and to study exposures of personnel in different types of process (BRITISH STEEL - 7261-04/465/08).
- b) Elimination of nitrogenous waste gases from mixed-acid pickling baths (KRUPP STAHL - 7257-54/397/01).
- c) Elimination of pollution and utilisation of waste products from the pickling of stainless steel (UGINE - 7261-03/427/03).

- d) Design and installation of electrochemical sensors intended to reduce pollution caused by acid pickling (CREUSOT-LOIRE - 7257-62/398/03).
- e) Prevention of pollution from aqueous solutions generated by the manufacture and processing of stainless steel (UGINE - 7261-03/438/03).

7.2 COLD ROLLING MILLS

Token entry.

7.3 COATING LINES

- a) Study and development of means of recovering and recycling waste from electrogalvanising lines (CSM - 7261-03/464/04).
- b) Removal of heavy metals from industrial scrubbing water with particular attention to the removal of zinc and nitrite ions (LAVEZZARI SpA - 7261-02/433/04).
- c) New passivation processes for tinned sheet and thin galvanised sheet using baths not containing chromates - feasibility study (CSM - 7257-15/395/04).



CORDIS

The Community Research and Development Information Service

Your European R&D Information Source

CORDIS represents a central source of information crucial for any organisation - be it industry, small and medium-sized enterprises, research organisations or universities - wishing to participate in the exploitation of research results, participate in EU funded science and technology programmes and/or seek partnerships.

CORDIS makes information available to the public through a collection of databases. The databases cover research programmes and projects from their preparatory stages through to their execution and final publication of results. A daily news service provides up-to-date information on EU research activities including calls for proposals, events, publications and tenders as well as progress and results of research and development programmes. A partner search facility allows users to register their own details on the database as well as search for potential partners. Other databases cover Commission documents, contact information and relevant publications as well as acronyms and abbreviations.

By becoming a user of CORDIS you have the possibility to:

- Identify opportunities to manufacture and market new products
- Identify partnerships for research and development
- Identify major players in research projects
- Review research completed and in progress in areas of your interest

The databases - nine in total - are accessible on-line free of charge. As a user-friendly aid for on-line searching, Watch-CORDIS, a Windows-based interface, is available on request. The databases are also available on a CD-ROM. The current databases are:

News (English, German and French version) - Results -
Partners - Projects - Programmes - Publications -
Acronyms - Comdocuments - Contacts

CORDIS on World Wide Web

The CORDIS service was extended in September 1994 to include the CORDIS World Wide Web (WWW) server on Internet. This service provides information on CORDIS and the CORDIS databases, various software products, which can be downloaded (including the above mentioned Watch-CORDIS) and the possibility of downloading full text-documents including the work programmes and information packages for all the research programmes in the Fourth Framework and calls for proposals.

The CORDIS WWW service can be accessed on the Internet using browser software (e.g. Netscape) and the address is: <http://www.cordis.lu/>

The CORDIS News database can be accessed through the WWW.

Contact details for further Information

If you would like further information on the CORDIS services, publications and products, please contact the CORDIS Help Desk :

CORDIS Customer Service
B.P. 2373
L-1023 Luxembourg

Telephone: +352-401162-240
Fax: +352-401162-248
E-mail: helpdesk@cordis.lu
WWW: <http://www.cordis.lu/>

European Commission

EUR 17583 — Technical control of nuisances and pollution at the place of work and in the environment of iron and steelworks — Fifth ECSC research programme — Summary report of studies completed on 31 May 1994

B. Deckers

Luxembourg: Office for Official Publications of the European Communities

1998 — VI, 114 pp. — 21 x 29.7 cm

ISBN 92-828-2400-4

Price (excluding VAT) in Luxembourg: ECU 13.50

This report takes stock of all the research work subsidised by the ECSC under the terms of the fourth and fifth programmes on 'Technical control of nuisances and pollution at the place of work and in the environment of iron and steelworks' whose final reports were published between the end of 1985 and May 1994. The results of 68 research projects have thus been analysed and the most interesting information of practical use for the European steel industry summarised.

The range of areas dealt with by these research projects is very wide, covering both protection of workers at their places of work and protection of the environment at iron and steelworks. Not only problems of atmospheric pollution, waste water treatment, treatment and management of waste have been tackled but considerable attention has been focused on acoustic nuisances and even on protection against ionising radiation which can arise when a radioactive source is introduced undetected through recycled scrap.

Of the subjects on which considerable research activity has been focused, the following should be singled out:

- better identification of the risks for workers at their place of work resulting from various atmospheric emissions from the processes, in particular at coking plants;
- reduction of nitrogen oxide emissions from various steel plants;
- reduction of emissions of dust generated by pig iron and molten steel by inertisation of the ambient air;
- treatment of steelmaking sound power levels in the environment;
- detection of radioactive contamination of scrap on introduction to steelworks sites;
- improvement in treatment of waste water from coking plants.

The results of this research work thus made a major contribution to reducing the impact of iron and steelworks in the European Union on the environment and the health of workers.

BELGIQUE/BELGIË

Moniteur belge/Belgisch Staatsblad
Rue de Louvain 40-42/Leuvenseweg 40-42
B-1000 Bruxelles/Brussel
Tél. (32-2) 552 22 11
Fax (32-2) 511 01 84

Jean De Lannoy
Avenue du Roi 202/Koningslaan 202
B-1060 Bruxelles/Brussel
Tél. (32-2) 538 51 69
Fax (32-2) 538 08 41
E-mail: jean.de.lannoy@infoboard.be
URL: http://www.jean-de-lannoy.be

Librairie européenne/Europese Boekhandel
Rue de la Loi 244/Wetstraat 244
B-1040 Bruxelles/Brussel
Tél. (32-2) 295 26 39
Fax (32-2) 735 08 60

DANMARK

J. H. Schultz Information A/S
Herstedvang 10-12
DK-2620 Albertslund
Tlf. (45) 43 63 23 00
Fax (45) 43 63 19 69
E-mail: schultz@schultz.dk
URL: http://www.schultz.dk

DEUTSCHLAND

Bundesanzeiger Verlag
Breite Straße 78-80
Postfach 10 05 34
D-50667 Köln
Tel. (49-221) 20 29-0
Fax (49-221) 202 92 78
E-mail: vertrieb@bundesanzeiger.de
URL: http://www.bundesanzeiger.de

ΕΛΛΑΔΑ/GREECE

G. C. Eleftheroudakis SA
International Bookstore
Panepistimiou 17
GR-10564 Athina
Tel. (30-1) 331 41 80/1/2/3
Fax (30-1) 323 98 21
E-mail: elebooks@netor.gr

ESPAÑA

Mundi Prensa Libros, SA
Castelló, 37
E-28001 Madrid
Tel. (34-1) 431 33 99
Fax (34-1) 575 39 98
E-mail: libreria@mundiprensa.es
URL: http://www.mundiprensa.es

Boletín Oficial del Estado

Trafalgar, 27
E-28010 Madrid
Tel. (34-1) 538 21 11 (Libros/
384 17 15 (Suscripciones))
Fax (34-1) 538 21 21 (Libros/
384 17 14 (Suscripciones))
E-mail: webmaster@boe.es
URL: http://www.boe.es

FRANCE

Journal officiel
Service des publications des CE
26, rue Desaix
F-75727 Paris Cedex 15
Tél. (33) 140 58 77 01/31
Fax (33) 140 58 77 00

IRELAND

Government Supplies Agency
Publications Section
4-5 Harcourt Road
Dublin 2
Tel. (353-1) 661 31 11
Fax (353-1) 475 27 60

ITALIA

Licosa SpA
Via Duca di Calabria, 1/1
Casella postale 552
I-50125 Firenze
Tel. (39-55) 64 54 15
Fax (39-55) 64 12 57
E-mail: licosa@ftbcc.it
URL: http://www.ftbcc.it/licosa

LUXEMBOURG

Messageries du livre SARL
5, rue Raiffeisen
L-2411 Luxembourg
Tél. (352) 40 10 20
Fax (352) 49 06 61
E-mail: mdl@pt.lu

Abonnements:

Messageries Paul Kraus
11, rue Christophe Plantin
L-2339 Luxembourg
Tél. (352) 49 98 88-8
Fax (352) 49 98 88-444
E-mail: mpk@pt.lu
URL: http://www.mpk.lu

NEDERLAND

SDU Servicecentrum Uitgevers
Extieme Fondsen
Postbus 20014
2500 EA Den Haag
Tel. (31-70) 378 98 80
Fax (31-70) 378 97 83
E-mail: sdu@sdu.nl
URL: http://www.sdu.nl

ÖSTERREICH

**Manz'sche Verlags- und
Universitätsbuchhandlung GmbH**
Siebenbrunnengasse 21
Postfach 1
A-1050 Wien
Tel. (43-1) 53 16 13 34/40
Fax (43-1) 53 16 13 39
E-mail: auslieferung@manz.co.at
URL: http://www.austria.EU.net:81/manz

PORTUGAL

Imprensa Nacional-Casa da Moeda, EP
Rua Marquês de Sá da Bandeira, 16 A
P-1050 Lisboa Codex
Tel. (351-1) 353 03 99
Fax (351-1) 353 02 94, 384 01 32

Distribuidora de Livros Bertrand Ld.ª
Rua das Terras dos Vales, 4/A
Apartado 60037
P-2701 Amadora Codex
Tel. (351-1) 495 90 50, 495 87 87
Fax (351-1) 496 02 55

SUOMI/FINLAND

**Akatteenin Kirjakauppa/Akademiska
Bokhandeln**
Pohjoisesplanadi 39/
Norra esplanaden 39
PL/PB 128
FIN-00101 Helsinki/Helsingfors
P./tfn (358-9) 121 41
F./fax (358-9) 121 44 35
E-mail: akatilaus@stockmann.mailnet.fi
URL: http://booknet.cultnet.fi/aka/index.htm

SVERIGE

BTJ AB
Traktorvägen 11
S-221 82 Lund
Tfn (46-46) 18 00 00
Fax (46-46) 30 79 47
E-post: btjeu-pub@btj.se
URL: http://www.btj.se/media/eu

UNITED KINGDOM

**The Stationery Office Ltd
International Sales Agency**
51 Nine Elms Lane
London SW8 5DR
Tel. (44-171) 873 90 90
Fax (44-171) 873 84 63
E-mail: jill.speed@theso.co.uk
URL: http://www.the-stationery-office.co.uk

ÍSLAND

Bokabud Larusar Blöndal
Skólavörðustíg, 2
IS-101 Reykjavík
Tel. (354) 551 56 50
Fax (354) 552 55 60

NORGE

NIC Info A/S
Ostenjoveien 18
Boks 6512 Etterstad
N-0606 Oslo
Tel. (47-22) 97 45 00
Fax (47-22) 97 45 45

SCHWEIZ/SUISSE/SVIZZERA

OSEC
Stampfenbachstraße 85
CH-8035 Zürich
Tel. (41-1) 365 53 15
Fax (41-1) 365 54 11
E-mail: oleimbacher@osec.ch
URL: http://www.osec.ch

BÁLGARIJA

Europress-Euromedia Ltd
59, Bld Vitosha
BG-1000 Sofia
Tel. (359-2) 980 37 66
Fax (359-2) 980 42 30

ČESKÁ REPUBLIKA

NIS CR — prodejna
Konviktská 5
CZ-113 57 Praha 1
Tel. (420-2) 24 22 94 33, 24 23 09 07
Fax (420-2) 24 22 94 33
E-mail: nkposp@dec.nis.cz
URL: http://www.nis.cz

CYPRUS

Cyprus Chamber of Commerce & Industry
Griva-Digeni 38 & Deligiorgi 3
Mail orders:
PO Box 1455
CY-1509 Nicosia
Tel. (357-2) 44 95 00, 46 23 12
Fax (357-2) 36 10 44
E-mail: cy1691_eic_cyprus@vans.infonet.com

MAGYARORSZÁG

Euro Info Service
Európa Ház
Margitsziget
PO Box 475
H-1396 Budapest 62
Tel. (36-1) 111 60 61, 111 62 16
Fax (36-1) 302 50 35
E-mail: euroinfo@mail.mataw.hu
URL: http://www.euroinfo.hu/index.htm

MALTA

Miller Distributors Ltd
Malta International Airport
PO Box 25
LQA 05 Malta
Tel. (356) 66 44 88
Fax (356) 67 67 99

POLSKA

Ars Polona
Krakowskie Przedmiescie 7
Skr. pocztowa 1001
PL-00-950 Warszawa
Tel. (48-22) 826 12 01
Fax (48-22) 826 62 40, 826 53 34, 826 86 73
E-mail: ars_pol@bevy.hsn.com.pl

ROMÂNIA

Euromedia
Str. G-ral Berthelot Nr 41
RO-70749 Bucuresti
Tel. (40-1) 210 44 01, 614 06 64
Fax (40-1) 210 44 01, 312 96 46

SLOVAKIA

**Slovak Centre of Scientific and Technical
Information**
Námestie slobody 19
SK-81223 Bratislava 1
Tel. (421-7) 531 83 64
Fax (421-7) 531 83 64
E-mail: europ@tb1.stk.stuba.sk

SLOVENIA

Gospodarski Vestnik
Zalozniska skupina d.d.
Dunajska cesta 5
SLO-1000 Ljubljana
Tel. (386) 611 33 03 54
Fax (386) 611 33 91 28
E-mail: belicid@gvestnik.si
URL: http://www.gvestnik.si

TÜRKIYE

Dünya Infotel AS
İstiklal Cad. No: 469
TR-80050 Tünel-Istanbul
Tel. (90-212) 251 91 96
Fax (90-212) 251 91 97

AUSTRALIA

Hunter Publications
PO Box 404
3167 Abbotsford, Victoria
Tel. (61-3) 94 17 53 61
Fax (61-3) 94 17 51 54

CANADA

Subscriptions only/Uniquement abonnements:
Renouf Publishing Co. Ltd
5369 Chemin Canotek Road Unit 1
K1J 9J3 Ottawa, Ontario
Tel. (1-613) 745 26 65
Fax (1-613) 745 76 60
E-mail: renouf@fox.nstn.ca
URL: http://www.renoufbooks.com

EGYPT

The Middle East Observer
41, Sherif Street
Cairo
Tel. (20-2) 393 97 32
Fax (20-2) 393 97 32

HRVATSKA

Mediatrade Ltd
Pavla Hatza 1
HR-10000 Zagreb
Tel. (385-1) 43 03 92
Fax (385-1) 43 03 92

INDIA

EBIC India
3rd Floor, Y. B. Chavan Centre
Gen. J. Bhosale Marg.
400 021 Mumbai
Tel. (91-22) 282 60 64
Fax (91-22) 285 45 64
E-mail: ebic@glasbm01.vsnl.net.in

ISRAËL

ROY International
17, Shimon Hatarssi Street
PO Box 13056
61130 Tel Aviv
Tel. (972-3) 546 14 23
Fax (972-3) 546 14 42
E-mail: royil@netvision.net.il

Sub-agent for the Palestinian Authority:

Index Information Services
PO Box 19502
Jerusalem
Tel. (972-2) 627 16 34
Fax (972-2) 627 12 19

JAPAN

PSI-Japan
Asahi Sanbancho Plaza #206
7-1 Sanbancho, Chiyoda-ku
Tokyo 102
Tel. (81-3) 32 34 69 21
Fax (81-3) 32 34 69 15
E-mail: psijapan@gol.com
URL: http://www.psi-japan.com

MALAYSIA

EBIC Malaysia
Level 7, Wisma Hong Leong
18 Jalan Perak
50450 Kuala Lumpur
Tel. (60-3) 262 62 98
Fax (60-3) 262 61 98
E-mail: ebic-kl@mol.net.my

PHILIPPINES

EBIC Philippines
19th Floor, PS Bank Tower Sen.
Gil J. Puyat Ave. cor. Tindalo St.
Makati City
Metro Manila
Tel. (63-2) 759 66 80
Fax (63-2) 759 66 90
E-mail: eccpcom@globe.com.ph

RUSSIA

CCEC
60-letiya Oktyabrya Av. 9
117312 Moscow
Tel. (70-95) 135 52 27
Fax (70-95) 135 52 27

SOUTH AFRICA

Safto
5th Floor Export House,
CNR Maude & West Streets
PO Box 782 706
2146 Sandton
Tel. (27-11) 883 37 37
Fax (27-11) 883 65 69

SOUTH KOREA

Kyowa Book Company
1 F1, Phygung Hwa Bldg
411-2 Hap Jeong Dong, Mapo Ku
121-220 Seoul
Tel. (82-2) 322 67 80/1
Fax (82-2) 322 67 82
E-mail: kyowa2@ktnet.co.kr.

THAÏLANDE

EBIC Thailand
Vaniasa Building 8th Floor
29 Soi Chidlom
Ploenchit
10330 Bangkok
Tel. (66-2) 655 06 27
Fax (66-2) 655 06 28
E-mail: ebicbkk@ksc15.th.com

UNITED STATES OF AMERICA

Berman Associates
4611-F Assembly Drive
MD20706 Lanham
Tel. (800) 274 44 47 (toll free telephone)
Fax (800) 865 34 50 (toll free fax)
E-mail: query@berman.com
URL: http://www.berman.com

**ANDERE LÄNDER/OTHER COUNTRIES/
AUTRES PAYS**

Bitte wenden Sie sich an ein Büro Ihrer
Wahl / Please contact the sales office of
your choice / Veuillez vous adresser au
bureau de vente de votre choix



NOTICE TO THE READER

Information on European Commission publications in the areas of research and innovation can be obtained from:

◆ **CORDIS, the Community R & D Information Service**

For more information, contact:

CORDIS Customer Service, BP 2373, L-1023 Luxembourg

Tel. (352) 40 11 62-240; fax (352) 40 11 62-248; e-mail: helpdesk@cordis.lu

or visit the website at <http://www.cordis.lu/>

◆ **Euroabstracts**

The European Commission's periodical on research publications, issued every two months.

For more information, contact:

RTD help desk, European Commission, DG XIII, L-2920 Luxembourg

Fax (352) 43 01-32084; e-mail: rtd-helpdesk@lux.dg13.cec.be

Price (excluding VAT) in Luxembourg: ECU 13.50



OFFICE FOR OFFICIAL PUBLICATIONS
OF THE EUROPEAN COMMUNITIES

L-2985 Luxembourg

ISBN 92-828-2400-4



9 789282 824009 >