



Commission of the European Communities

# **industrial health and safety**

## **Fourth ECSC research programme on Technical control of nuisances and pollution at the place of work and in the environment of iron and steelworks**

**Status of research at 31 December 1985**



**Report**

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Directorate-General  
Employment, Social Affairs and Education  
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## INTRODUCTION

The Fourth ECSC Research Programme on "Technical control of nuisances and pollution at the place of work and in the environment of iron and steel works", adopted pursuant to Article 55 of the ECSC Treaty and published in the Official Journal of the European Communities on 13 June 1979, expired in 1984 after running for a period of five years. The 15 million ECU made available had been fully utilized by the end of the programme.

This report is a general review of the 83 research projects subsidized by the Commission.

The research and development work thus fostered in the steelworks, research establishments and universities will have contributed significantly to improving workplaces and the environment of iron and steel plants.

Compared with previous programmes, the work carried out during the fourth programme will have seen a substantial extension of the field of activity. Whereas the second research programme (1967-73) was almost entirely devoted to problems of atmospheric pollution and the third programme (1974-78) extended to the problems of treating waste and liquid effluent, the fourth programme (1979-83) had to take account of technological developments and address new problems. Thanks to greater financial resources, it will have permitted research both in the above-mentioned fields and in the fields of noise, impact evaluation and occupational hygiene. In the same way, it sought to solve certain problems addressed in the research carried out under the three preceding programmes, for which no satisfactory solutions have as yet been found.

Moreover, directives of the European Community and national legislation on the environment are becoming increasingly stringent.

The same observations apply to enforcement of the regulations; indeed the public in the areas concerned are becoming increasingly aware of the latent dangers of pollution.

The fourth programme was inspired by the EEC recommendations, on the following four points in particular:

- a) improving environmental and working conditions;
- b) complying with official requirements;
- c) maintaining the competitiveness of the works and thus safeguarding employment;
- d) conserving raw materials and energy.



The solutions proposed will only be adopted if they involve capital and running costs commensurate with the improvements secured.

It should be noted finally that the increasing attention devoted to research in the field of pollution control is justified by the desire of the citizens of Europe to improve the place of work and hence the health of workers, ensuring also that the positive effect is matched by an improvement in the environment of plants.

The research projects have been grouped for the purposes of this review under the seven headings adopted in the fourth programme. The order in which they are presented corresponds to the traditional sequence of stages in the production of steel.



## CHAPTER 1: COKING PLANTS

"While substantial progress has been made in reducing emissions in new plants, especially during the oven charging and quenching operations, further developments are necessary, and means of improving existing plants must be devised. Particular importance still attaches to the prevention of emissions as a result of leakage and during coke pushing. The need to pay special attention to the treatment of coking plant effluent is as great as ever."

The brief summary of this chapter covers the 23 research projects aimed at improving processes for the treatment of effluent from coking plants so as to minimize the pollution hazard generated by the carbonization industry.

The main agents of pollution are the gases given off during the coking process and the effluent discharged from gas cooling and cleaning plant.

Measures for the control of this pollution are thus concerned with two natural environments, the atmosphere and the aquatic environment; hence the division of the chapter into two sub-chapters: air pollution and water pollution.

Under the latter heading, the research is reviewed in the order in which the anti-pollution treatments are applied.

To sum up, ten projects are concerned with air pollution risks, while thirteen are devoted to the very special field represented by the hazard of water contamination due to the operation of a coking plant.

## 1.1. AIR POLLUTION FROM COKING PLANTS

The Community research projects have shown that in the steel industry coking plants are among the worst sources of air pollution, due to the emission of certain gases whose physiological effect on man is evident from their unpleasant odour but whose noxious consequences are not always known, amongst other things because of the great variation in their concentrations.

The main emissions arising at coking plants are:

- 1) polycyclic aromatic hydrocarbons (PAH)
- 2) benzene hydrocarbons (BTX) which are produced when coal is carbonized to coke
- 3) nitrogen oxides (NO<sub>x</sub>) which, under certain conditions, can accompany any discharge of fumes.

In view of the magnitude of the task, two projects were launched under ECSC sponsorship and with the collaboration of institutes in five countries which have coking plants or are particularly alert to the hazard of pollution from this industry.

The research centred mainly on the measurement, analysis and isolation of gaseous effluent generated in particular during carbonization, coal charging and coke quenching.

The research took place in two stages:

### 1st phase

The first phase consisted in the development and refinement of measurement methods making it possible to determine the different degrees of PAH and BTX concentration at the point of emission, at places of work and in the environment.

The aims pursued by the various research establishments involved were in the first instance geared to harmonizing methods for the sampling, measurement and analysis of pollutants in the coke-producing area.

### 2nd phase

The second phase comprised campaigns of PAH and BTX measurement in coking plants, taking into account the incidence of key parameters such as:

- . design of the plant
- . technical state of the plant
- . extent and nature of the equipment for emission reduction
- . quality of the coal used
- . operating conditions
- . atmospheric conditions.

It was only possible to complete the first phase of the research.

Data on emissions, pollution conditions at places of work and in the vicinity of certain works were gathered, in respect of both PAH and BTX, which enabled valuable lessons to be learned.

#### 1.1.1. POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

PAH are formed in certain natural processes or in the course of activities involving combustion and incomplete pyrolysis or the carbonization of organic substances.

They are found in the volatile products of coal distillation during the coking process; indeed any leakage from coke ovens can cause the discharge to the atmosphere of volatile matter containing PAH and hence constitute a hazard to workers and to people living near the plant.

PAH become fixed to dusts under ambient temperature conditions.

Samples are thus taken by appropriate methods of dust collection, supplemented where appropriate by adsorption processes. The analysis comprises extraction, purification of the extract and gas chromatography on a column.

#### PAH measurement results

##### a) Measurements at points of emission

The measurement results showed that the most serious leaks occurred at the coke oven doors, their intensity varying according to the stage in the coking process.

It was noted that, of the thirty or so PAH detected, only about ten gave rise to a carcinogenicity hazard. These are present at low concentrations in the fumes, and the quantities emitted diminish more or less rapidly over time after the start of the process (PS 346 LECES).

Gas extractors of the older type, without water seals, outside coal charging and coke pushing doors also constitute an important field of research (PS 345 BF).

It was noted that a new type of elastic seal leads to a considerable reduction in leaks at oven doors, compared with conventional rigid seals.

Emissions of gaseous pollutants from modern plants should therefore be considerably reduced.

b) Measurements at places of work

The analysis of individual samples (PS 346 LECES) shows that the most vulnerable workplaces are those located at the top of the battery.

At such workplaces the concentration of benzo(a)pyrene<sub>3</sub> is three to fifty times higher than the recommended maximum (0.15 µg/m<sup>3</sup>).

Wearing a ventilated helmet reduces ambient PAH concentrations by a factor of two.

At the level of the charging cars, it was noted (PS 345 BF) that optimization of the dust removal equipment reduces leaks.

On the coke discharge side, a dry dedusting system fitted with a bag filter gives better results than an older type of device based on a wet cleaning system.

c) Measurements in the environment

The highest PAH values are found at measurement points closest to the coking plant.

The picture which emerges for dusts on the other hand is not altogether the same; the impact zone is located within a radius of about 2000 m, because of the presence of other emitters (PS 346 LECES).

d) Comparison between different collectors in the environment

A comparison between the dust removal and PAH extraction performance of the different sampling devices used by the three research institutes involved showed that the correlation between the four devices tested was low.

LECES (PS 346) assumes that the differences arise in part from the wide variation in particle size limits; this is a characteristic specific to each device.

It is also probable that the proximity of a road gave an additional PAH input, which influenced the measurements.

NSF (342) considers that, as PAH emanating from coking plant gases occur within the respirable dust fraction, whereas those emitted by internal combustion engines are in the non-respirable fraction, the particle size range cut-off should be below 7 µm.

In view of the complexity of the problem and the difficulties of arriving at a unanimous conclusion, it would be worth launching a new Community project for the design of an environmental measuring device which would meet all the requirements and would give reliable and repeatable measurements.

### 1.1.2. HYDROCARBONS: BENZENE, TOLUENE AND XYLENE (BTX)

Benzene, toluene and xylenes (BTX) are contained in the volatile products of coal distillation emitted during the coking process. Any emission from a coke-oven battery or from by-product recovery plants may cause pollution, not only at places of work but also in the environment of the coking plant.

#### Results of BTX measurements

##### a) Measurements at points of emission

The most serious leaks are due to poor gas-tightness around coke-oven battery doors. They vary according to the stage in the coking process and the state of the seals round the doors.

Storage tanks and charging points for coke-oven by-products, such as tars, ammonia and phenol, are major sources of emissions when they are allowed to give off fumes to the open air.

It was noted that low concentrations of benzene, not thought to be very prejudicial to health, predominate.

High concentrations only arise on occasions and for brief periods in certain situations (unfavourable weather conditions and storage locations) (PS 337, BF).

PS 336 - Hoogovens - showed that, in old coke-oven batteries, the main sources are leaks at doors and charging holes.

On the other hand, in newly adapted batteries, leaks are virtually a thing of the past.

##### b) Measurements at places of work

Measurement campaigns carried out at places of work in a coking plant in the Liège steel producing area show that levels detected vary from one workplace to another (PS 431, INIEX).

At the various coke-oven workplaces, BTX concentrations are below the TLV value (10 ppm for benzene, 100 ppm for toluene and xylenes).

On the other hand, in the by-product recovery area, particularly in the benzol plant and around the naphthalene tank, the benzene value is attained.

In the case of the benzol plant, this permissible limit is exceeded from time to time.

In the case of the naphthalene tank, the limit is continuously exceeded.

In these zones, concentrations are thus significantly higher than those prevailing in the coke-oven area (PS 341, INIEX).

Hoogovens (PS 336), on the basis of the results of the measurements carried out, also concludes that, from the occupational hygiene point of view, the hazards of exposure to emissions of benzene, toluene and xylenes from coke ovens are small.

However, precautions need to be taken, chiefly in confined spaces such as tar centrifuge rooms, in which it is advisable to keep a check on concentrations by means of portable personal devices or badges.

#### c) Measurements in the environment

In the immediate vicinity (distance less than 500 m), the impact of gaseous pollutant emissions from the coking plant is probably no greater than that from other sources of hydrocarbon emission.

Motor traffic and by-product recovery and upgrading plants also cause air pollution due to BTX (PS 341, INIEX).

#### d) Conclusions

It emerges from the five research projects on BTX that concentrations of these pollutants at places of work and in the environment are generally below the levels considered acceptable by the legislation of the various countries.

High concentrations harmful to health may arise however when unfavourable conditions coincide:

- no ventilation in areas for the storage or handling of by-products,
- storage tanks venting to the open air,
- unfavourable weather conditions, especially unfavourable wind direction.

#### 1.1.3. NITROGEN OXIDES, NO<sub>x</sub>

Any combustion is accompanied by the emission of smoke and fumes. The latter may under certain conditions contain nitric oxide, NO, which is slowly converted to nitrogen dioxide, NO<sub>2</sub>. As these fumes are considered hazardous to man and nature, the CEC in its fourth research programme included a coordinated project on nitrogen oxides in the iron and steel and coking industries, which involved the collaboration of four research centres in France, Germany and Italy.

The formation of nitrogen oxides in relation to heating conditions in coke ovens - PS 362 CHERCHAR, LECES and CPM, PS 363 BF.

The results of the Community research show that, in the iron and steel industry, the coke oven is practically the biggest NO<sub>x</sub> emitter after ore sintering.

Indeed the trend towards increasing coke-oven productivity, involving a reduction in heating times, tends to increase the temperature at the heating wall.

This trend towards higher temperatures favours the formation of nitrogen oxides.

Measurement campaigns carried out at various coking plants with different designs and operating conditions in several European countries have shown that NO concentrations vary considerably, depending on operating conditions and the technological parameters of the coking plant.

It is thus possible to determine modes of operation for old coking plants and to design ovens for future plants which will minimize discharges.

Techniques for minimizing the emission of nitrogen oxides are based on:

- reduction in maximum temperatures,
- reduction in the availability of reactants, particularly oxygen,
- shortening of periods in which products remain in the hot zones,
- choice of combustion gas.

Certain overseas countries, such as Japan and the USA, where regulations relating to the environment are becoming positively draconian, have already installed plants which are effective in controlling the emission of nitrogen oxides.

The ability of these installations to reduce NO pollution is attributable to:

- new burner designs,
- the type of fuel used,
- modifications to the combustion process (phased combustion, recycling of combustion gases),
- reduction in the temperature at the heating wall,
- treatment of the fumes generated by oven heating,
- reduction in nitrogen oxides present in the fumes by ammonia and a regenerative mobile-bed catalyst,
- electron bombardment of nitrogen oxides in the combustion fumes.

Thus there is still scope for research in this field of pollution abatement.



In view of this, a new coordinated programme of research on nitrogen oxides is being prepared. As far as coke production is concerned, the research will be geared to the following areas:

- . new ovens
- . new coking methods
- . optimization of combustion control
- . presence in the coking plant environment not only of the oxides NO and NO<sub>2</sub>, but also of certain organo-nitrate compounds.

## 1.2. WATER POLLUTION AT COKING PLANTS

The liquid effluent made up of the wastewaters from the coking process constitutes a major hazard to the environment because of its volume and toxicity.

Coking plant effluents contain ammonia, phenols and cyanides, products which are particularly harmful to fauna and flora.

It is imperative that they be treated to neutralize any harmful effects on the aquatic environment before being discharged into the natural environment.

Coking plant wastewaters are considered in the iron and steel industry to be among the most difficult to treat in order to obtain unpolluted effluent which conforms to the discharge standards in force.

Although a great many studies carried out in recent years have led to significant advances in purification techniques, the scale of the problems associated with the treatment of coking plant effluent and the increasing stringency of discharge standards necessitate the continuous improvement of existing technologies and indeed the development of new purification processes.

The first objective of this research is to develop and optimize pretreatment lines in order to bring coking plant effluent to the required degree of purity before discharge to the sewerage system.

In this context the following considerations must be paramount:

- development of reliable, effective and stable treatment processes,
- production of simple flow-sheets aimed at minimizing space occupancy,
- measures to ensure complete safety at places of work,
- reduction of treatment costs to levels acceptable in terms of both capital and operating costs.

It also emerged in the course of the research that special attention needs to be devoted to the harmonization of sampling methods and

sample measurement and analysis in order to ensure comparability of results between the various laboratories in the different countries involved in the research.

In this context, twelve research projects specially concerned with this important question were subsidized by the CEC under the fourth programme. Their aim was to secure the maintenance or reinstatement of water purity by the application and strengthening of measures for the control of water pollution and by improvements in knowledge of the phenomena governing changes undergone by the pollutants contained in effluent.

The laboratories in the Community countries which specialize in this field made their contribution to this action and pooled their know-how in order to make their expertise available to coking plant operators.

#### Conventional treatment methods

The present situation is that most coking plants follow a fairly similar procedure for the treatment of effluent from the carbonization of coal, namely:

- tar removal by slow settling and sand filtration,
- removal of volatile pollutants ( $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{HCN}$ ) by steam stripping in an alkaline medium (lime or soda),
- removal of biodegradable pollutants (phenols,  $\text{SCN}$ ,  $\text{CN}$  ...) by biological treatment in fully mixed activated sludge tanks.

Some coking plants form an exception to this pattern, however, by the adoption at the phenol removal stage of pure chemical or physico-chemical processes, as distinct from biological purification, or in combination with it, including for example:

- solvent extraction,
- steam stripping in an acid medium,
- adsorption on activated carbon.

Some coking plants also stand out by their use of finishing treatments:

- aerated lagooning and
- adsorption on activated carbon.

#### 1.2.1. PRETREATMENT IMPROVEMENTS

Apart from the conventional treatments described above, some special techniques have been developed:

Optimization of the ammonia stripping process (volatile and fixed ammonia) by an improvement in processes for tar and oil removal from effluent.

a) Tar separation from ammoniacal liquors by centrifuging

The research undertaken by the CRM - PS 398 - in conjunction with Forges de Clabecq set out to devise a detarring process which would be particularly effective, stable and easy to integrate into existing plants.

Trials conducted for over a year at the Forges de Clabecq coking plant showed that centrifuging was an effective purification technique.

Systematic tests were carried out in order to determine the influence of feedwater flow, counterpressure exerted on delivery, initial tar concentration and temperature on rates of tar removal by centrifuging. Generally speaking, the centrifuge is relatively unaffected by these various parameters, which makes for a high degree of stability in the purification process.

Nevertheless it is essential that the equipment be carefully maintained in order to ensure the efficient operation of the process.

This research subsequently led to the adoption of the process on an industrial scale at the Forges de Clabecq coking plant in Vilvoorde, Belgium.

a) Flotation by air injection with the addition of a demulsifying reagent

CHERCHAR - PS 361, with assistance from the Station Expérimentale de Marienau, for its part conducted experiments on a technique of flotation by air injection with the addition of a demulsifying reagent.

The experiments, which were carried out in a laboratory cell based on the standard type used in ore beneficiation, showed that it was possible to achieve very high suspended solids extraction rates with relatively modest capital and running costs.

In the course of the tests, an extraction rate of 98.5% was achieved from untreated effluent under certain conditions.

The tests made it possible to define the various operating parameters for the process, so that a pilot treatment line could be set up on the site of a coking plant of Houillères du Bassin de Lorraine.

In the course of tests forming part of project PS 361, CHERCHAR noted that it was possible to remove some of the free ammonia by the direct injection of superheated steam into the flotation cell.

As regards stripping proper, the tests confirmed that soda treatment remained the most effective means of extracting total ammonia from effluent. On the other hand, treatment with lime gave rise to deposits and incrustations in the column.

### c) Oil removal from by-product plant effluent

Tests carried out by the CRM - PS 389 - at the Forges de Clabecq coking plant also showed that oil removal from the liquors of by-product recovery plants, prior to discharge into the ammoniacal liquor circuit or immediately prior to steam stripping, may be worth considering as a means of reducing the total burden of organic pollution in coking plant effluent.

Concurrently with the detarring tests, the CRM conducted oil separation tests on oily waters using methods based on:

- coagulation - sedimentation and  
coagulation - air flotation.

Coagulation - air flotation with the aid of aluminium polychloride proved to be the most effective technique, taking account in particular of the problem of sludge removal. Oil removal rates were between 95% and 99.9%.

### d) Organic inhibitors present in carbonization liquors

It was shown that the ease with which any phenolic liquor can be oxidized biochemically is due less to its normal constituents, such as phenol and thiocyanate, than to unidentified inhibiting constituents, usually associated with the BOD and the colouring of a biological effluent.

The BCRA studies - PS 330 - showed that the inhibitors can be removed in a pretreatment by adsorption materials, particularly activated carbon (PAC).

However the research showed that the same improvements could be achieved by the precipitation of the inhibitors with the aid of polyethyleneimine (PEI), a polyelectrolyte specific to oxidized phenols.

## 1.2.2. BIOLOGICAL TREATMENTS

### 1. THE DENITRIFICATION-NITRIFICATION PROCESS

- PS 387 DSM - PS 392 BSC - PS 396 CSM

Up to now research has concentrated on systems for which the biological processes mentioned are carried out in several successive stages. The oxidation of organic products and ammonia requires a supply of oxygen (air), whereas denitrification calls for the addition of a source of biologically degradable carbon.

A major disadvantage of a system involving several separate stages is that it requires settling tanks for the separation of biologically active sludges between the different stages, which gives rise to high capital costs and a high space requirement in the treatment plant.

The DSM - PS 387 - has developed a process for the treatment of chemical plant liquors (3500 m<sup>3</sup>/h) in which the nitrification, denitrification and oxidation of organic products take place as far as possible simultaneously with the aid of active sludges containing both nitrifying and denitrifying bacteria.

After being fed through a non-aerated part and an aerated part of the plant, practically all the substances present on delivery are oxidized by the oxygen derived from nitrates (NO<sub>3</sub> and N<sub>2</sub>) in the first part, while in the second part the ammonia is oxidized to nitrate (nitrification) (NH<sub>4</sub> and NO<sub>3</sub>).

With this aim in view, the DSM in conjunction with the BSC - in projects PS 387 and PS 392 - investigated the possibilities of applying this process on an industrial scale to coking plant effluent in order to facilitate the simultaneous removal of organic matter and nitrogen compounds.

An effluent treatment plant in operation at a BSC works was specially modified for one part to operate in a predenitrification-nitrification mode (pre-DN/N).

The nitrification tanks are aerated at the surface by conventional means, while the liquor in the anaerobic reaction tank is stirred, but not aerated, by a stirring mechanism. The result is a recycling of mixed effluents from the aerated and anaerobic zones of the plant, so that treatment takes place on the basis of a single biological sludge.

The tests carried out on an industrial scale showed that the nitrification and denitrification processes are both easy to achieve.

Nevertheless some problems which arose showed that nitrification is an extremely sensitive biological process, that it is necessary to avoid heavy fluctuations in ammonia concentration and that an appropriate pretreatment of the liquor is indispensable in achieving a uniform yield.

In project PS 396, the DSM experimented on the biological disc technique combined with the denitrification-nitrification process, with the aim of optimizing the process.

A particular type of biomass develops selectively and adheres to the surface of the rotating reactor: aerobic bacteria are carried on the non-immersed aerobic discs, anaerobic bacteria on the immersed biodiscs.

In the first phase of the research, which was devoted to a laboratory study of the process, it was possible to obtain complete nitrification, but only partial pre-denitrification. Future experiments will be aimed at determining the causes of these difficulties.

The second phase will include the completion of a pilot plant to be set up in a steelworks.

## 2. IMPROVEMENT OF CONVENTIONAL PURIFICATION PROCESSES

### a) Use of multi-stage rotating discs

Tests on purification by multi-stage rotating discs - PS 335 CRM - demonstrated major technical advantages over the activated sludge tanks in conventional use.

The pilot-scale tests demonstrated the chief advantage of greater purification stability in treatment by biological discs compared with treatment by activated sludges. Overall, however, the two treatment processes - activated sludges and rotating discs - are likely to result in the same purification rates.

In the future, constant improvements in design and, in particular, the development of perforated discs with increasingly greater specific areas, together with savings in energy and manpower, will be factors which will give rotating biological discs a competitive edge over conventional activated sludge tanks.

### b) Use of oxygen and/or oxygen-enriched air

In project PS 339, the CSM investigated the possibilities of improving the efficiency of the biological treatment of coking plant effluent by the use of oxygen and/or oxygen-enriched air.

The project compares a number of aspects of biological processes using oxygen and oxygen-enriched air (50% O<sub>2</sub> + 50% N<sub>2</sub>) when applied to the purification of ammoniacal liquor in coking plants.

It emerges from the comparison carried out in aeration tanks at two pilot plants that the advantages of the oxygen process are retained and even enhanced when the process is run on oxygen-enriched air.

### c) Combined treatment of coking plant effluent and municipal sewage

The biological treatment of coking plant effluent can be combined with that for domestic sewage. This removes the need for plant operators to undertake costly investment and to train specialized staff.

For combined treatment to be feasible in practice, it is essential that the coking plant effluent be pretreated prior to discharge into the sewage system.

Tests on biological treatability in activated sludge reactors, carried out in the laboratories of CEBEDEAU as part of project PS 335, showed that the plant copes well with temporary overloads caused, for example, by a brief interruption in basic stripping.

Generally speaking, it can be said that the combined biological treatment of coking plant effluent and municipal sewage is a particularly interesting solution from the technical and economic point of view.

As of now, a Belgian coking plant is already linked up to a municipal treatment plant, and several others are preparing to take this step.

#### d) Removal of organic sludges produced during biological treatment

The biological treatment process, particularly that based on activated sludge tanks, generates a bulky and foul-smelling waste: biological sludges.

Project PS 400 - CRM and CEBEDEAU - sets out to optimize the secondary sedimentation of biological coking plant sludges, to test various techniques for tertiary treatment with a view to improving the retention of suspended organic solids prior to discharge of the water into the river and to investigate the final removal of these sludges without pollution transfer.

The first phase in the research is now in progress. The aim is to achieve the standard discharge value, which is generally 60 mg/l.

### 3. ALTERNATIVE ANAEROBIC PROCESS

Anaerobic processes supply a gaseous by-product rich in recoverable energy (a mixture of methane and carbon monoxide) and considerably smaller amounts of secondary sludge (about 10 times less).

Unfortunately the process is slow and considerably more sensitive to disturbances of various origins and has not as yet been applied on an industrial scale.

Work carried out by CEBEDEAU in the course of the research under project PS 393 has made it possible to improve and speed up the anaerobic degradation of phenols.

Several reactor configurations have been investigated with a view to improving and accelerating the process. The novel technique of coupling two reactors together in series has been tried with satisfactory results.



The technique involved a reactor consisting of a fluidized bed of activated carbon followed by a reactor using polyurethane foam.

This system makes it possible, in the most favourable instances, to achieve a yield of 97% in the treatment of undiluted stripped coking plant effluent.

### 1.2.3. TREATMENT BY PHYSICO-CHEMICAL AND CHEMICAL PROCESSES

#### a) Activated carbon

- PS 330, 387, 389, 392

When the physico-chemical adsorption process is used for the removal of phenol from coking plant effluent, the adsorbent used is generally activated carbon.

It has proved to be a stable process relatively immune to the effects of fluctuations in pollution load and effective in phenol and water colour removal.

For this reason many research projects have examined the role of activated carbon in effluent treatment.

However, the complex flow-sheet required and the loss of activated carbon in the regeneration cycle (2-10%) make it an expensive process.

Project PS 315 - BECEWA - highlighted the use of activated carbon with simultaneous treatment by a chemical chlorination process.

The BSC, in a joint project with the DSM, investigated the use of PAC as a source of carbon in the nitrification process (PS 387 and 392).

The tests carried out showed that the addition of PAC improves the denitrification process, making it possible to reduce the oxygen demand by about 90% and achieve 98% thiocyanate removal.

The BSC used active carbon in the first tests to remove inhibitors to phenol degradation (PS 330). The active carbon may show a loss of activity because of clogging due to tars and other inhibitors about which little is known. It is thus essential that preliminary detarring should be efficient (see PS 389).

The BSC is examining the reactivation of PAC as part of project PS 330. The regeneration and recycling of depleted or saturated active carbon are operations which the cost of the product renders indispensable.



b) Adsorbent resins

A new process for phenol removal in a laboratory has been taken up by the CRM (PS 335) with the aim of establishing whether adsorbent resins might be a possible substitute for active carbon.

The tests prompted the conclusion that phenol removal by means of adsorbent resins is not to be recommended for the the treatment of coking plant effluent.

Indeed their adsorption capacities, which are already lower than those of PAC, were further reduced by poisoning during the regeneration cycles and by the accretion of tarry matter and suspended solids.

c) Use of oxygen and/or ozone

The IRH research - PS 358 - set out to investigate the possibilities of using oxygen and/or ozone to achieve:

- the complete purification of ammoniacal liquors in coking plants, or
- a finishing treatment, or
- pretreatment.

Now that the research has been completed, certain conclusions can be drawn:

The use of oxygen alone, at a temperature below 100° C, even in the presence of potential catalysts, is ineffective. On the other hand two approaches do seem technically feasible:

- chemical oxidation by oxygen under pressure in the presence of low-cost catalysts (copper salts);
- chemical oxidation by a mixture of oxygen and ozone at ambient temperature and pressure.

As the technical effectiveness of such a process is burdened by the cost of the necessary ozone, this treatment would only be appropriate in cases in which extremely stringent requirements were imposed in respect of final discharges.

## CHAPTER 2: SINTERING PLANTS

"Despite the considerable achievements in dust collection in sintering plants and associated installations, the use of residues and variations in fuels and ores pose as yet unsolved problems with regard to the effect of these materials on the quantity and composition of the dust and noxious gases emitted. In this context mention should also be made of the cooling of the sinter. Ore pelletization processes also involve some problems of air and water pollution which have not yet been satisfactorily overcome."

This chapter covers eight projects - PS 324, 390, 394, 366, 367, 365, 356 and 368 - aimed at reducing the emission of gaseous pollutants by a modification or an adaptation of the production process which gives rise to them.

Of these eight projects, five devote special study to the sintering process itself in relation to the emission of gaseous pollutants and three are concerned with the optimization of dust extraction installations with a view to increasing their efficiency.

## 2.1. OPTIMIZATION OF THE SINTERING PROCESS AND MEASURES ADVOCATED IN ORDER TO LIMIT NO<sub>x</sub> EMISSIONS

PS 366, 367, 390, 324, 394

Studies of fumes generated in the different plants of a steelworks have shown that the process which produces the heaviest NO<sub>x</sub> emissions is that of iron ore sintering.

### a) Nature of the emissions

The first conclusion of the report on PS 367 - LECES - relates to the nature of the emissions. In fact they occur in the form of NO. This result is important bearing in mind that nitric oxide is less directly toxic than nitrogen dioxide.

A comparison of the NO, NO<sub>2</sub> and NO<sub>x</sub> concentrations encountered with the existing regulations indicates that the situation is satisfactory for the moment. However, in the near future regulations governing the quality of the ambient air in respect of nitrogen oxides may be much more stringent. By then the NO and NO<sub>2</sub> concentrations recorded in this research will probably be at or above, in terms of both averages and point values, the thresholds which will be considered desirable by the public authorities.

### b) Causes of NO<sub>x</sub> emissions and techniques

Extraction tests have shown that the bulk of the NO<sub>x</sub> are produced by the oxidation of nitrogen chemically combined with fuel (PS 366 and 367).

Project PS 366 - CSM - shows that there are two possible approaches to the reduction of NO<sub>x</sub> emissions:

- 1) action affecting the oxidation processes which generate them
- 2) the installation of emission control devices.

In making the choice it should be borne in mind that NO<sub>x</sub> are emitted at relatively low concentrations, since they are diluted by very high gas-flow volumes.

Their removal from gaseous effluent would thus require the installation of complex and costly gas cleaning equipment.

In view of this, it would be appropriate in the first instance to concentrate on measures to reduce the emission of NO<sub>x</sub> within the processes which give rise to them.

In order to limit NO<sub>x</sub> emissions, the CSM - PS 366 - recommends:

- the use of fuel which is low in nitrogen, or
- action on the parameters of the process of NO<sub>x</sub> formation, such as rate of combustion and quantity of free oxygen available.

The CSM - PS 390 - presents the results of tests which established that the production of nitrogen oxides diminishes with:

- 1) a reduction in the content of fixed nitrogen in the fuel
- 2) an increase in the rate of fuel combustion by action on the density of the fuel, its dispersion in the mix, a negative pressure below the grate
- 3) a reduction in percentages of oxygen in the air by recirculating the fumes or by replacing part of the air with argon.

It also notes the negligible role of the ignition phase in the production of nitrogen oxide.

c) Emission of gaseous pollutants, in particular SO<sub>2</sub> and CO

The iron ore sintering process causes the evolution of fumes which contain pollutants, notably SO<sub>2</sub> and CO, derived from the solid and/or gaseous fuels burned.

It was found that the most effective means of reducing the emission of SO<sub>2</sub> is to bind it with slag in the process of pig iron production in the blast furnace.

Project PS 324 MFI looks at ways of blocking or limiting the discharge of pollutants on the sintering strand so that they remain in the sinter and pass into the blast furnace slag.

The tests confirmed that a reduction in the combustion of breeze, which produces the highest percentages of sulphur and carbon in the sinter, leads to a reduction in the emission of SO<sub>2</sub> and CO.

This trend is sustained if the consumption of coke breeze is reduced by a better adjustment of the heat balance.

Tests showed that, for a minimum quantity of coke breeze, a reduction of 25% can be achieved in emissions of SO<sub>2</sub> attributable to its use.

Other tests showed that a further reduction in CO and SO<sub>2</sub> emissions is possible by applying various technological measures, such as:

- reducing the size range of the coke breeze,
- treating the breeze with lime water,
- adding nitrogen to the air.

d) Special case of a sintering line fed with lean ore

Project PS 394 - LECES - sets out to promote techniques for the reduction of gaseous pollutants generated by sintering on a grate fed with iron ore from Lorraine, which has a low Fe content.

Particular attention was devoted to the development of new production processes taking into account their impact in terms of pollution.

Tests on an industrial site made it possible to record discharges of  $\text{SO}_2$  and  $\text{NO}_2$  for a mode of industrial operation serving as a standard.

## 2.2. IMPROVEMENT IN THE OPERATION OF ELECTROSTATIC PRECIPITATORS

Projects PS 365 - LECES - and 356 - CRM - are devoted to improving the operation of the electrostatic precipitators fitted to the dedusting systems of sintering lines.

The performance of these electrostatic precipitators is influenced by a great many factors, such as the operating controls of the devices, but also the characteristics of the gaseous or particulate flows to be treated.

In a first phase, measurement campaigns (PS 365) carried out on a sintering line made it possible to develop a process for the continuous measurement of the efficiency of the electrostatic precipitator and to gain a better knowledge of the state of the dust extractor, studying its operating characteristics in relation to discharges after dust removal.

Subsequently the interactions between the fume emitting plant and its dust extractor were examined and the physico-chemical properties of the dusts passing through the electrostatic precipitator were studied.

### a) Fume conditioning (PS 365)

Tests involving variable quantities of substances for which separation rates are poor, such as alkaline salts and chlorides, demonstrated the effectiveness under certain conditions of fume conditioning by the injection of gaseous  $\text{SO}_3$  before the electrostatic precipitator. During normal sintering operation, this method makes it possible to reduce discharges from electrostatic precipitators by half and to limit their levels to below  $50 \text{ mg/Nm}^3$ .

Nevertheless, when highly resistant salts are present in the dusts in large quantities,  $\text{SO}_3$  becomes ineffective at normal rates of injection. It is possible that other conditioning agents, which do not react with the salts, may improve the separation of these substances by electrostatic precipitators.

### b) Influence of the mode of power supply

Tests have also helped to define the influence of the mode of power supply to the electrostatic precipitator on its efficiency.

According to LECES - PS 365 - operation with suppressed alternating power supply did not lead to any significant increase in the efficiency of the electrostatic precipitator compared with normal operation.

However the planned adaptation of the control device should, according to the authors, make it possible to achieve some improvement.

The CRM on the other hand - PS 356 - has shown that it is possible to achieve significant improvements in this field.

In fact the CRM conducted various tests on the improvement of electrostatic precipitator performance.

These tests showed that the most promising lines of development are:

- optimization of the sequence in which the emitting and receiving electrodes are struck;
- installation of digital controllers making it possible to supply the fields with intermittent current and to achieve a significant reduction in the number of times an arc is struck between the electrodes.

These improvements may lead not only to better extraction performance but also to a considerable saving in energy.

c) Automatic measurement of the dust content of fumes

In the course of the above tests, the CRM - PS 356 - developed an automatic sampling device, the GRAVIDUST.

The operating principle of this device is to collect dusts on a filter by means of a continuous positioning and withdrawal system and to weigh them at regular intervals on an electromagnetic balance with a high resolution (1 mg) and an extended range (400 g), in conformity with standard manual measuring methods.

Systematic comparison tests have shown that this device is a reliable tool for the on-line monitoring of stack dusts and hence for the optimization of dust extractor operation.

d) Special process:

TREATMENT AND DEZINCIFICATION OF LD DUSTS BY THE ADDITION OF CALCIUM CHLORIDE AND DEDUSTING BY A GRAVEL FILTER BED (PS 368, THYSSEN)

The aim of the research is to use more LD dusts in sintering plants as a preliminary step, removing harmful constituents such as zinc, lead and alkaline substances, which tend to disrupt the metallurgical conversion cycle in the blast furnace.

This process takes place in two stages:

- 1) The first consists in the application of a chloridizing treatment by the addition of calcium chloride to the sintering strand at a high temperature in order to convert solid sulphates, sulphides and oxides into volatile chlorides and to remove them from the sinter bed.



The tests showed that the chloridizing treatment is satisfactory, if certain precise conditions are observed.

- 2) The second stage consisted in the development of a dust extraction system based on a gravel filter bed in order to separate metal chlorides from the gases given off and obtain a discharge to the atmosphere which meets the pollution control requirements.

Because of the accumulation of solid deposits at mineralogical points in the circuit, the filtration process has not yet been made to work satisfactorily.

### CHAPTER 3: BLAST FURNACES

"While the blast furnace process itself may be regarded as non-polluting, satisfactory solutions have still to be found for a number of major problems of a secondary nature.

These include the reduction of secondary dust emissions during tapping, the abatement of noise due to changeover of cowpers, burdening of blast furnace and blowing-off, and improvements in the handling of water, dust, slurries and slags."

This chapter covers four research projects - PS 325, 312, 350 and 355 - which address the problem of diffuse emissions, also called secondary fumes, given off during certain phases in pig iron production or during the processing of by-products, such as slag.

Project PS 349 is devoted to problems of noise generated by operations in the blast furnace area.

### 3.1. SECONDARY FUME EMISSION

#### a) Fume characteristics

Secondary fume emissions, which evolve in an uncontrolled manner in blast furnace casting bays and steel melting shops, display particular characteristics: they are not channelled and they vary greatly in flow and composition.

These special features thus preclude the application of conventional and standardized methods of quantification, both for the determination of flows and for sampling.

Dedusting installations are generally designed to absorb maximum peaks in the emission of fumes given off during certain phases in metallurgical processes; their dimensions are thus to a large extent surplus to normal requirements.

It is therefore appropriate, from the point of view of the economy and yield of dedusting plant, to seek means of adjusting the suction performance of the devices to conditions prevailing at a particular time, hence the value of the following projects.

#### b) The formation of fumes

Project PS 325 - LECES - described the main mechanisms involved in the formation of fumes: the emission of gases and dusts chiefly through hydrocarbon cracking or reactions between carbon and hydrogen compounds in the presence of oxygen or a liquid metallic phase.

On the basis of several examples of emissions from various departments of an iron and steel works, it was shown that the flow and temperature of the fumes could be controlled and even reduced by designing each emission point in such a way as to moderate the physico-chemical reactions which generate the fumes and particulate matter, notably by restricting exchanges with oxygen in the air.

#### c) Fume collection

In project PS 325, LECES first developed the equipment necessary for such research, drawing upon the devices used for the measurement of pollutants in a pipeline under specific conditions of fume flow.

#### d) Automatic draught adjustment - PS 312 - MANNESMANN

This project addressed the problem of diffuse fume emissions by setting out to develop a process for the automatic minimization of the volume of fume collected by the secondary dust extractor fitted.

The researchers developed a monitoring and control circuit, operating directly on signals emitted by probes positioned at selected points in the extractor hoods, to be fitted to the devices controlling the extractor fan draught. It was found that varying the speed of the fan made it possible to adjust its draught with maximum speed and efficiency to operating conditions.

Flow tests were carried out on a model.

The model tests revealed that most of the pressure loss occurred, not in the ducting, but in the extractor hoods.

For that reason the work was concentrated on optimizing the shape of the extractor hoods in terms of air flow.

The monitoring and control circuits were successfully applied in real dimensions to a blast furnace casting bay.

e) Zinc-containing pig iron and fumes - PS 350, HOOGOVENS

It was noted that from time to time white vapours appeared during pig iron tapping at the blast furnace. These vapours, which are caused by the presence of zinc, are harmful to the health of casting bay workers and impair visibility in the casting bay. It was also noted that zinc has a disruptive effect on the stability of the process.

On the basis of the data collected, it was noted that:

The permissible quantity of zinc in the blast furnace depends:

- to a considerable extent on gas pressure in the throat;
- to a lesser extent on fluctuations in gas temperature in the throat.

Zinc-containing pig iron arises on tapping at low temperatures, generally below 1400° C. Its production depends critically on the degree of control maintained in the operation of the blast furnace.

The improved pollution control system installed in the casting bay prevented unacceptable conditions from arising during the tapping of pig iron containing zinc.

f) Gaseous sulphur emission during the processing of granulated blast furnace slag - PS 355, FGES

When 75% of slag from the blast furnace is processed into granulated slag, gaseous sulphur, in particular H<sub>2</sub>S and SO<sub>2</sub>, is given off during the water-cooling of the molten slag, which contains 1-2% sulphur. It was noted in the laboratory that a reduction in the emission of gaseous sulphur could be achieved:

- either by eliminating or reducing the quantity of cooling water used,
- or by adding an oxidant or lime water -  $\text{Ca(OH)}_2$  - to the water.

Only the latter option is feasible since, because of the depletion of the deposition surfaces, which has to be compensated by more rapid cooling, wet cooling cannot be dispensed with.

Field tests were carried out on the oxidising process, using  $\text{KMnO}_4$  and  $\text{Ca(OH)}_2$ .

It may be concluded from the research that the cooling oxidants cause a considerable reduction in the emission of  $\text{H}_2\text{S}$  and a slight reduction in that of  $\text{SO}_2$  ( $\text{KMnO}_4$  even seems to increase the formation of  $\text{SO}_2$ ). However  $\text{Ca(OH)}_2$  is more troublesome to handle, and its cooling power is inferior to that of  $\text{KMnO}_4$ .

### **3.2. NOISE IN THE BLAST FURNACE AREA - PS 349, BFI**

The opening and closing of valves in the hot blast stove circuits and in the pipes around the blast furnace throat, operating under top pressure, generate a considerable amount of noise which can reach levels as high as 120-125 dB (A).

The research seeks ways of reducing the noise at its source in preference to expensive pipe insulation measures, the results of which are often of doubtful value.

Measurements were taken to determine sound patterns: pressure, flow rates, acceleration of the air in the pipes under investigation.

All the data were transferred to a test rig equipped with pipes and valves similar to those in use in the industrial situation, so that tests could be performed without disrupting production.

Improvements in noise levels were obtained but were unfortunately accompanied by a greater inertia in the discharging operation.

## CHAPTER 4: MELTING SHOPS

"The remarks on pig iron production also apply here. With certain exceptions, primary dedusting may be regarded as satisfactory, although research may still be carried out to devise techniques which are less costly and cumbersome. Special attention needs to be paid to operations such as the desulphurization of pig iron and the charging and tapping of melting furnaces or converters. It is also essential to carry out further work on noise abatement in electric furnaces. Melting shop slag also needs to be studied with a view to increasing the proportion of waste which can be re-used and to reducing the quantities dumped."

As in the case of the blast furnace area, the main aims of the nine projects devoted to melting shops are:

- 1) The reduction of secondary fume emission (3 projects)
- 2) The control of noise generated by electric furnaces (6 projects)
- 3) We also refer briefly to the problems raised by dust entrained by the fumes given off during the conversion of pig iron to steel.

The four projects in question are merely indicated, as chapter 7 deals with this subject at greater length.

#### 4.1. SECONDARY FUME EMISSION

##### a) The optimization of filtering devices

The aim of project PS 352 - BSC - is to determine the optimum combination of certain filter parameters, devoting particular attention to the study of materials used in the manufacture of bag filters, fume flow-rates and bag cleaning methods.

For this purpose the BSC carried out a series of industrial-scale tests on a compartment of a large-size bag filter in order to determine the optimum conditions for the filtering of gases from an electric arc furnace.

Four different bag filter fabrics were tested, namely:

- 1) a woven terylene,
- 2) a less expensive knitted seamless polyester,
- 3) a polyester felt, already tested by LECES,
- 4) a PTFE lined on one side with a very expensive polyester felt.

The fabrics were tested with different cleaning methods and varying the parameters: frequency of cleaning, amplitude of vibrations, flow-rate of cleaning air etc.

The following conclusions can be drawn from this very extensive series of tests:

- The lowest energy consumption was achieved by cleaning the bags more frequently and for longer periods.
- A combination of the two methods of cleaning by shaking and counterdraughting proved to be very effective.
- Fitting the most expensive fabric quality (PTFE) (4) to all compartments of the dedusting plant gave a better flow/load ratio.



b) Devices for the extraction of fumes and dust from an automatic flame-cutting plant for cutting up iron and steel skulls

- PS 370 MW and BFI

The usual technique applied in cutting up iron and steel skulls requires the operation of the flame torch by hand.

The Company MW planned to instal a centralized unit for automatic cutting.

The BFI was asked to examine conditions of fume and dust extraction on a reduced-scale model and to design a configuration for the plant which would ensure the most favourable working conditions and safety arrangements for the employees.

The installation of television cameras and a system of mirrors would improve visibility, particularly in longitudinal cutting operations. After a series of experiments on different variants, a system was finally devised for extraction through a channel laid below floor level. The carriage was fitted with side cladding in order to reduce air turbulence.

Air from the outside is fed in through apertures appropriately arranged along the entire length of the roof. Valves control and direct the flow of air in such a way that efficient fume extraction is assured and the supervisor always has a clear view of the cutting carriage.

c) Magnetic filtering of electric furnace fume cleaning liquors

- PS 386, CSM

Fumes from an electric arc furnace are cleaned in a dedusting plant using a wet process.

The concentration of solids in the cleaning liquor may vary from 100 to 2000 g/m<sup>3</sup>, depending on the phase in progress. In the usual way, this liquor is conveyed to a flocculation plant which reduces the content to 30-50 g/m<sup>3</sup>.

The aim is to reduce suspended solids to 10-15 g/m<sup>3</sup> by magnetic filtration.

A variety of filters tested gave interesting results. Filtering time was reduced and sedimentation speed improved. The clogging of filters, due to significant quantities of oil in the liquor, was counteracted by counter-flow cleaning with lukewarm water accompanied by air blowing.

A comparison of the final costs of the two systems shows that there is no great difference between magnetic filtration and a conventional clarifier. In the case of magnetic filtration, however, the work involved in removing the sludge deposited on the bottom of the thickener is simplified.

Because of residual magnetization, the solids separated by the magnetic filter coagulate readily and settle on the bottom of the thickener, thus forming a sludge which contains up to 70% by weight of solids.

This particular property of the separated solids considerably eases subsequent handling operations. Moreover the space required for the magnetic clarifying plant is five times less than that for a conventional plant. This is a factor which cannot be overlooked in view of the increasingly stringent constraints on space availability.

## **4.2. NOISE ABATEMENT IN MELTING SHOPS**

### Motivation

Increases in furnace power, sought after for obvious reasons of productivity, lead to an increase in the pulses which generate noise.

The noise emitted by high-power furnaces reaches levels of 100 dB (A) and sometimes more, such values being considerably in excess of the recommended standards.

The design of shops sometimes promotes sound propagation. Few studies have been undertaken or measures tried with a view to reducing the volume of noise or its propagation.

This noise is a source of considerable discomfort to employees working close to the points of emission. It is also a source of irritation to residents of neighbourhoods close to iron and steel works.

The reduction of disturbance due to sound emission is limited to the application of two series of measures: either the installation of anti-noise screens, cowlings or hoods; or technological modifications effected at the source of the noise.

The first solution is often the one adopted, although it is not always very effective and it may cause inconvenience by impeding access for maintenance or free passage for furnace charging and tapping operations.

Hence the need to promote research into noise abatement with the primary aim of reducing the noise at its source.

## Research programme

Under the fourth programme, work on the problem of noise nuisance was continued and extended by the implementation of six research projects, including:

- four projects on electric arc furnaces, and
- two projects on furnaces using plasma burners.

Results obtained from the application to industrial furnaces of solutions found appropriate for laboratory furnaces were often disappointing, hence project PS 328 proposed by LECES for alternating current furnaces.

The new furnaces, for which direct current has been selected, represent a solution which would improve the stability of the arc and hence attenuate the noise, while at the same time offering an advantage from the metallurgical point of view.

IRSID set out to investigate noise in direct current furnaces (PS 348). The BFI (PS 374) and BSC (PS 331) sought to evaluate the same advantages and to devise solutions involving the use of plasma gas burners in melting furnaces.

On the other hand, PS 375 - FIAT - followed a different approach to noise abatement by experimenting on the use of sound insulation materials in enclosure hoods, using the plasma gun as a means of additional heating, while the BFI (PS 379) studied optimum conditions for the extraction of fumes and the use of sound absorbing materials.

### 4.2.1. ELECTRIC FURNACES OPERATING ON ALTERNATING CURRENT

- PS 328, LECES and IRSID

The aim of the research is, in the first phase, to demonstrate the links between arc noise and electrical parameters. In the second phase, various procedures for the reduction of arc noise will be tested on production furnaces.

#### a) Conditions for the striking of the arc

It was shown that gains in sound attenuation could be achieved if the conditions under which arcs are struck were improved. Tests were carried out, amongst other things on the use of doped-core electrodes. However the analysis of measurements carried out on a 60 t furnace using normal and doped electrodes showed that doping had little effect.

b) Influence of the electric control system

A measurement campaign was also carried out on a 100 t UHP furnace in order to determine the influence of the type of electric control on sound pressure. These tests showed that phase by phase electronic control, balancing each phase independently of the other two, did not offer any significant gains in sound attenuation compared with conventional impedance control.

c) Influence of operating parameters

Flows of acoustic energy, in particular those emitted by leaks through the slag door during the initial period of melting when the intensity of sound emission is greatest, were evaluated on a 60 t furnace with the aid of a noise meter. The influence of various operating parameters, such as charging characteristics, on the level of sound emissions and, more especially, the impact of the thermal state of the charge were studied experimentally.

The results obtained, for a basket of similar composition, did not show any marked difference in the level of sound emission between operation with and operation without scrap preheating. On the other hand, differences in excess of 5 dB(A) during melting were observed when the nature of the charge was modified, particularly by altering the size range of the scrap particles.

4.2.2. ELECTRIC FURNACES OPERATING ON DIRECT CURRENT - PS 348, IRSID

The work carried out under the previous research (PS 289) showed that the substitution of direct current for three-phase current, while retaining the three-point arrangement of the electrodes, led to a reduction in sound pressure by about 5 dB (A). In order to optimize operation still further and to reduce fluctuations in the electric power supplying the arc, which determines the noise emission, the following programme of modifications was devised:

- an electrode in the hearth of the furnace to ensure that the current is returned through the bath;
- replacement of the three graphite electrodes necessary for three-phase power supply by a single electrode;
- better control of the power supply;
- introduction of self-smoothing devices in the secondary circuit in order to limit fluctuations in intensity;
- installation of special doped electrodes;
- more accurate positioning of electrodes.

The modifications produced an improvement of 5 dB (A) in relation to the direct current furnace with three electrodes (95 dB (A)) and a reduction of 10 dB (A) in relation to the alternating current furnace (100 dB (A)).

This gain can be explained by a reduction in overall electrical disturbance due to the replacement of the three electrodes by a single electrode, hence a single arc instead of three, and better sealing of the furnace.

The fitting of doped electrodes did not have any significant effect on the sound level.

The measures taken to reduce the level of sound produced by the arc were relatively ineffective because the arcs of industrial furnaces, in contrast to those of laboratory furnaces, are subject to a variety of disruptive effects due to the charging of the bath, scrap movements, displacement of the arc etc, which may reduce or cancel out their efficiency.

The researchers devised a mathematical interpretation to explain the discrepancies in noise levels obtained, which would also serve as a forecasting basis for the application of other remedies.

#### 4.2.3. FURNACES WITH PLASMA BURNERS

##### a) Technological characteristics

A technological improvement for the future consists in the use of plasma burners for the production of steel.

In this process, the graphite electrodes are replaced by cylindrical metal vessels incorporating a thoriated tungsten bar as a cathode (negative pole) and a ring concentric to the electrode (positive pole).

All around the cathode a "plasma" gas is injected which crosses the arc and, after attaining a very high temperature, escapes through the nozzle of the anode. If the positive pole is transferred from the ring to a material located outside the burner, a "transferred" arc can develop.

"Transferred arc" plasma burners have a high capacity and offer good output rates.

##### b) Advantages sought

This new technology, though costly because of the high degree of material wear and the cost of the inert gas argon, should offer a number of advantages, including a reduction in noise and dust levels and the moderation of feedback effects on the electrical circuit.

### c) Results obtained

Project PS 374 - BFI - first describes the current status of the technology of furnaces using plasma burners, then goes on to evaluate the sound and particulate emissions generated by the various types of burner.

In addition to electrical and acoustic parameters and the characteristics of the plasma gases injected, movements of the plasma arc are recorded with the aid of a high-speed camera with simultaneous measurement of the lengths and variations in length of the arc. The sound emissions fall within the following bands:

- minimum 80
- mean 90-100
- maximum 130-135 dB (A).

They depend to a large extent on the flow-rate of the plasma gas, determined by the speed of exit of the gas, on the design of the burner and tuyeres and, to a lesser extent, on the electrical characteristics.

#### 4.2.4. Enclosure hoods - PS 375, FIAT, Turin

FIAT is experimenting on the installation of an enclosure hood to provide sound insulation for a 150 t electric arc furnace.

FIAT's first approach was aimed at the more effective collection of fumes given off during the operational melting phase.

Consequently the initial project provided for the installation of simple corrugated plates. It was subsequently modified by the fitting of sound insulation panels.

The main problems in execution were those associated with furnace operation. It was necessary to provide movable side panels which could be withdrawn by powered gearwheels to allow the charging, tapping and maintenance of the furnace.

The hood is fitted with retractable doors as a precaution against explosions.

The acoustic panels were mounted elastically on the supporting frame to take account of expansions and vibrations transmitted through the air and through furnace components.

An additional treatment, consisting in the projection of a visco-elastic material onto the outer surface of the sheets, was necessary.

The results were convincing. Reductions of 10-18 dB (A) were measured with respect to the sound levels obtaining before the installation of the hood, which had been in the range of 90 to 100 dB (A) and over.

#### 4.2.5. OPTIMIZATION OF DUST EXTRACTION FACILITIES IN STEELPLANTS

Project PS 373 - BFI - first gives an account of the present situation with regard to the technical modifications which have been applied in the industry to provide acoustic separation between furnace bays and adjoining bays. It also examines the advantages and disadvantages offered by furnace cowlings. The disadvantages are poor access and the restriction of space needed for the transport of materials and maintenance. The scope for the application of these measures to old plants is limited, and they require a radically different approach to the design of new melting shops.

Various systems were reviewed and analysed from the point of view of acoustic performance and dust collection. For three furnaces of recent construction (1981), these arrangements made it possible to achieve a reduction in noise level of 12-15 dB (A), with mean measured values of the order of 90 dB (A) and even 85 dB (A), depending on the extent of the measures applied.

It was also found that the extraction of fumes and dust could be improved by a better distribution of the volumes of gas extracted in relation to the operations being carried out. In view of the results obtained and the experience gained, new measures for improvements to cowlings were taken on a production furnace.

It was found that the use of sound-absorbing materials to line the cowlings panels made it possible to reduce emission of noise to the melting shop bay by about 19 dB (A).

A difficult problem to solve was that of the clogging or reduction of vital furnace openings, i.e. the charging door, the openings in the roof for the electrodes, the seal between the furnace lid and hearth and, generally speaking, between fixed and movable parts.

Tests are continuing to bring about improvements in this direction.

The relation between power consumption and sound level was also analysed.

d) Use of plasma as a means of additional heating in electric arc furnaces

Project PS 331 - BSC - addressed the same problem of noise reduction in the field of plasma guns by investigating their use as an additional means of heating in electric arc furnaces.

Indeed, according to information from the Freital steelplant in East Germany, which uses a plasma furnace for the production of high-alloy stainless steels, the process of melting under plasma is carried out at sound levels below 80 dB (A).

The aim is to investigate applications of this technique for the mass production of non-alloy or low-alloy carbon steels.

Experiments were carried out in a furnace with a capacity of 500 kg and a power rating of 1.5 MW.

The plasma burner is mounted on a pivoting carriage so that the arc, which can attain a length of 850 mm, can be positioned at will.

A plasma burner with an output of 2.8 MW was tested. Noise levels of between 90 and 97 dB (A) were measured, depending on the power supplied to the burner and the stability of the arc. Although less intense than the noise generated by the arc of a conventional electric furnace, it was of uneven quality, so that detailed spectral analyses were necessary to determine it.

The operators were affected by ultraviolet radiation, so that it is clearly essential to take strict safety precautions during the operation of the furnace.

#### **4.3. DUST IN MELTING SHOPS**

Special attention was devoted to the presence of heavy metals (Cr, Pb, Zn, Ni) contained in electric steelplant dusts. There were several reasons for this:

- a) These elements constitute a potential pollution hazard to the ecosystem when steelmaking waste is dumped.
- b) Certain of them are valuable elements and it should be possible to extract and recycle them.
- c) If this were done, less waste would be dumped and the pollution hazard would be reduced accordingly.



- 1) For these reasons research, starting at the laboratory stage and leading through to that of industrial applications, was launched in order to determine more precisely the real risk arising (PS 384 - CREUSOT-LOIRE).
- 2) The separation of zinc and lead from their host products was successfully achieved, thanks to a treatment based on a process of leaching in an alkaline medium (PS 385 - CEBEDEAU). Thus zinc can be recovered and recycled.
- 3) Other tests were undertaken with the aim of improving the yield of treatments carried out on zinc and lead compounds with a view to their extraction.

Indeed it was shown that the yield from these processes was increased if they could be applied to preconcentrates.

However, mechanical operations involving screening or magnetic separation or a combination of them gave relatively disappointing results.

Only the attrition process made it possible to obtain a product rich in iron and low in lead and zinc which could thus be recycled in the steel melting shop (PS 359 CRVM).

- 4) A recent technological advance based on the plasma arc melting process has enabled dusts entrained by smoke and fumes from electric arc furnaces to be recovered by the chemical reduction of the metal oxides they contain (PS 388 BSC).

Sections 3 and 4 of chapter 7 give a more detailed account of this research.



## CHAPTER 5: ROLLING MILLS

"In addition to the familiar sources of pollution mentioned in the third programme and requiring special measures to prevent air and water pollution, i.e. those associated with re-heating furnaces, flame scarfing, grinding and pickling, research should also cover certain secondary sources, such as oil mists at certain types of rolling stand.

Hot-rolling mills account for a considerable proportion of steelworks effluent. The techniques for treating this effluent must be further developed and fundamental principles must be established for the design of water treatment plants. No satisfactory solution has yet been found for the treatment of oily sludges from rolling mills or oily mill scale, and further research is required in this area."

The ten research projects covered by Chapter 5 are mainly devoted to two problems raised by rolling operations.

- 1) Effluent, consisting either of wastewater from cooling circuits or of spent liquors from the passivation of sheet and plate.
- 2) Noise generated by rolling and product handling operations and its propagation in adjoining bays.

## 5.1. EFFLUENT TREATMENT

### Effluent properties

Water for the cooling circuits of plant in an iron and steel works has to be chemically conditioned in order to combat phenomena such as limescale, corrosion and biological incrustations.

The effluent from rolling mills in particular is in addition contaminated with oils, greases and chemical solvents, all of which are essential to the proper functioning of the plant but are taken up by circulating or cooling water.

Coated products, such as tinned or galvanized sheet and plate, are given passivating treatments in order to improve the final properties of these products.

The work taken on by those involved in this research covered:

- a) the elimination of oil and grease (PS 310 - IRH), 5.1.1.
- b) the separation of magnetizable solid particles present in the effluent (PS 338 - CSM), 5.1.2.
- c) the testing of special non-polluting formulations for cooling circuits (PS 308 - IRH), 5.1.3.
- d) the treatment of chromic wastes in order to obtain discharges containing non-polluting compounds (PS 383 - CEBEDEAU), 5.1.4.
- e) non-polluting passivation processes without chromates (PS 395 - CSM), 5.1.5.
- f) the use of electrochemical sensors in order to measure the concentration of pickling baths (PS 398 - IRSID), 5.1.4.

The application of these projects is expected to yield a great many advantages:

- g) the elimination of nitrogen oxides produced by mixed pickling baths, 5.1.7.
  - the elimination of surface water pollution,
  - the recovery of high-value products,
  - the recycling of treated water.

#### 5.1.1. THE REMOVAL OF OIL AND GREASE - PS 310, IRH

The filtering process makes use of the sand bed technique. This particular method is used to "precondition" the filter bed before a filtering cycle is carried out. Preconditioning consists in injecting reagents into the filter, before the filtering operation takes place, which become fixed to it, radically altering the subsequent behaviour of the filter bed.

An automatic pilot plant has been designed, developed and constructed and set up at an industrial site.

Once the plant had been put into operation, the optimum conditions were determined in the course of extended trials and defined with a view to operating the plant for a period of several months.

The results and performances achieved confirmed the predictions of the laboratory tests. Provided the procedure for cleaning the filter was satisfactory, the performance of the plant was stable over time, and no irreversible clogging of the filter bed was observed.

The results of this work should make it possible to develop the process for industrial use.

### 5.1.2. EXTRACTION OF SOLIDS

#### HIGH-GRADIENT MAGNETIC CLARIFICATION - PS 338, CSM

The high-gradient magnetic separation (HGMS) technique, already employed for a number of years in the industry for the beneficiation of magnetic or magnetizable minerals or, conversely, for the removal of magnetic or magnetizable impurities from industrial products and minerals shows promise as a technique for the future in the purification of treatment liquors and sludge-containing effluents.

The HGMS process is not only competitive in relation to conventional systems but also takes up much less space (1/5 of the space normally occupied), consumes the same amount of energy or less and produces sludges which are easier to handle. It does not require the addition of expensive flocculants. It is an automatic process and enables savings to be made on the capital cost of sludge thickeners located downline, as their surface area can be reduced.

The results of the first preliminary experiments carried out on effluent from hot rolling mills were very encouraging.

### 5.1.3. TREATMENT OF COOLING WATER

#### a) Conditioning formulations for cooling circuit water without impact on the environment - PS 308, IRH

If such formulations which are both effective and without danger to the environment are to be used industrially, it is necessary to demonstrate that they are consistently effective over a period of time by long-term trials in pilot circuits simulating industrial conditions and to compare the results with the performances of commercial formulations in current use.

Two types of circuit were chosen to cover those in actual operation in the iron and steel industry:

- completely closed circuits,
- semi-closed circuits with an atmospheric coolant.

In view of the number of formulations to be tested and the duration of the tests, four pilot circuits of the first type and six of the second type were constructed. Different qualities of water were tested.

The results as a whole showed that it is technically possible to define conditioning formulations for cooling water circuits, both hermetically sealed and closed (with make-up and bleed) using an atmospheric coolant, which display high efficiency and have little or no impact on the environment.

#### 5.1.4. TREATMENT OF CHROMIC WASTES - PS 383, CEBEDEAU

The most widely used method for the purification of industrial effluent containing chromates consists in a reduction of the chromium from the hexavalent to the trivalent state. However this treatment is not normally achieved with 100% efficiency. Highly toxic chemical products are discharged into the natural environment.

Moreover this process, which consists in converting (by reduction) a high-value product (CrVI) then discharging it in a less toxic form (CrIII), is not very satisfactory. The system also has the disadvantage of producing sludges which have to be treated.

In an initial phase, the proposed study undertakes a critical and comparative examination of all the existing treatment methods.

In a second phase, it experiments with methods which appear likely to meet the objectives of the research adequately.

CEBEDEAU carried out successive experiments on:

- 1) the process of recovering hexavalent chromium by the precipitation of a salt which is not readily soluble,
- 2) the process of recovering and recycling the effluent by REVERSE OSMOSIS.

A pilot plant is being set up.

The present status of the research does not permit any conclusions as to the effectiveness and economy of these different processes.

a) New processes for passivation in baths without chromates  
- PS 395, CSM

The aim of the research is to study the feasibility of obtaining formulations for the passivation of galvanized or tinned sheet containing passivating agents other than chromates which would be economically competitive with conventional treatments. The substitute baths envisaged will involve experimental work on the application of extremely fine surface layers with a phosphate, tungsten, molybdenum or manganese base. The setting up of a circulation cell will make it possible to reproduce the exact operating conditions and hence to modify them in such a way as to optimize the process.

The products will be subjected to technical tests in order to evaluate their properties, their resistance to chemical agents and their behaviour in relation to subsequent operations.

b) Study and application of electrochemical sensors with a view to reducing pollution caused by acid pickling - PS 398, IRSID

The use of electrochemical sensors should make it possible to achieve a reduction in the pollution rate by optimizing all the treatment facilities, thereby obtaining a better surface condition in the products and an increase in acid yields, hence "clean" pickling.

The aim is in fact to replace the present system, which requires samples to be taken and sent to the laboratory, hence a delay before the results are obtained, by a system of on-line analysis. This involves criteria of automatic operation, continuous in situ analysis and resistance to the industrial environment. This work is thus devoted to much the same area of research as that covered by the BSC in project PS 333.

The first experimental studies consisted in determining the characteristics of different selective electrodes and different sensors, in testing them in the laboratory and in making a selection.

c) Removal of nitrogen oxides produced in mixed-acid pickling baths  
- PS 397, KFI and BFI

During the pickling of high-alloy special steel sheet or plate in mixed-acid baths containing nitric acid and hydrofluoric acid, nitrogen oxides are formed which must be extracted in order to protect workers and the environment. In the present state of the art, these fumes are discharged to the atmosphere through relatively inefficient absorption systems.

Under this project it is intended to develop new treatment processes through the experimental stage to their application in an existing pickling plant.

## 5.2. STEELWORKS NOISE

### Motivation

Plant and equipment in an iron and steel works generate a considerable amount of noise. The movement of machines and transport appliances, especially in machining and merchant bar finishing shops and shot-blasting facilities emit high noise levels.

The design of workshops sometimes facilitates the propagation of noise. Few studies or experiments have been carried out on the attenuation of noise or its propagation during handling operations on transfer lines.

However three research projects are devoted to this. Two of the projects were suggested by BFI - PS 326 and 353 - and another by the BSC - PS 378.

This is a recent field, as it did not feature in the previous research programme.

### 5.2.1. SOUND PROPAGATION IN HIGH-ROOFED WORKSHOPS IN THE IRON AND STEEL INDUSTRY - PS 326, BFI

The project investigates the propagation of sound in high-roofed bays in iron and steel works, such as rolling mills and merchant bar finishing shops.

The BFI research extended the study of sound propagation to its reflection from separating partitions and from the walls and ceilings, taking into account the transversal or parallel disposition of the bays.

A technique for the calculation of sound propagation parameters in workshops having rectilinear dimensions was devised in the form of a computer program.

This program calculates the acoustic distribution within the workshops and presents it in the form of noise maps.

The predictive calculation of sound levels in the bays of a works represents an important step towards a more exact formulation of noise control problems in workplace areas and towards the evaluation of noise nuisance in the vicinity of the works.

The research is based in particular on the information contained in documents drawn up on the initiative of the Federal Ministry of Research and Technology in Germany.

However these recommendations are limited to stationary sources of noise in very long bays, in which the noise is propagated along the length of the building.



The noise maps plotted make it possible to locate the major source of noise among a number of others, which can be of great value in pinpointing the origin of serious nuisances. The researchers did not content themselves with theoretical calculations, but tested the calculations on industrial plants using very sophisticated anti-noise devices.

#### 5.2.2. NOISE ABATEMENT AND MEASURES TAKEN TO ACHIEVE IT

##### a) Modification of handling operations - PS 353, BFI

Project PS 353 studies the scope for noise abatement in a merchant bar machining and finishing shop, where the machines used are among the noisiest installations in a works.

The aim of the research is to develop a comprehensive noise reduction project which not only draws upon all the technical measures currently known in the field of the design and technology of the equipment, but also rethinks the flow of materials and sequencing of operations, with due regard to the application of essential safety arrangements.

Measures which it was found could be applied immediately included the sound insulation of points of impact between mill products and transport appliances.

A new handling device was designed to perform a sequence of operations consisting in the collection, assembly, storage, transfer and stacking of section mill products with a minimum of noise.

Its construction and installation in a production system is in progress.

##### b) Modification of charging and transfer skids - PS 378, BSC

Most beam and section mills use skids made of rail steel for the lateral transfer of products on cooling and charging banks and for transfer between roller conveyor lines.

Their main disadvantage with regard to the environment is the nuisance created by the sliding/skating friction due to the movement of the section along the skids, which makes the section vibrate, emitting a noise which can reach levels as high as 125 dB (A).

In an initial phase, auxiliary materials with more favourable static and kinetic characteristics than rail steel were tested.

Four auxiliary materials were selected from a whole range of samples. Their selection took account of the ease with which they could be applied to long skid lengths.

Three methods for the application of the materials to the rails were tested and investigated at the same time.

The conclusion was reached that, generally speaking, the vibrations and noise generated in the audible frequency range depend more on the mass and shape of the product than on the configuration of the skids on the rolling mill banks and that they increase slightly with the speed of transfer.

The test results showed that the friction characteristics of composite rails were more favourable than those of conventional solid steel skids.

## CHAPTER 6: MEASUREMENT

"Measurement of pollution played a major part in the last three programmes. The fourth programme seems likely to focus on the following points:

- development of measurement techniques, especially for continuous measurement;
- adaptation of existing techniques to the particular needs of the iron and steel industry;
- harmonization of sampling, measurement and analysis procedures to ensure comparability of results."

Concern centred on the joint development of examination methods and the codification of operations with the aim of ensuring the accuracy and comparability of measurements from the laboratories of the different countries.

This chapter also presents the main characteristics of measurement and sampling devices developed by specialists in the course of work to devise methods for the measurement and detection of effluents.

The presentation of new equipment, developed on the strength of basic research, highlights the practical direction of this research.

## 6.1. MEASUREMENT OF ATMOSPHERIC POLLUTION IN THE IRON AND STEEL INDUSTRY

### a) Measurement strategies

In order to obtain comparable results in the determination of levels of dust and gas pollution at workplaces, it is important to harmonize not only sampling and analysis methods but also, and especially, to adopt a uniform measurement strategy.

While recent work dealing with industrial hygiene problems in polluted workplaces has shown a trend towards the standardization of techniques for the sampling and analysis of fibrous dusts, sampling methods sometimes differ in their duration and frequency, which makes any comparison of measurement results difficult, if not impossible.

For reasons of efficiency and economy, the strategy adopted should be to secure significant measurements of pollution levels at every workplace with the aid of a limited number of measurements, appropriately scaled over a period of time. The research carried out under projects PS 402 - TNO - and PS 316 - CEBEDEAU - pursues this objective.

### b) Mathematical model - PS 402, TNO

The previous research showed that, if the mean concentration was close to a maximum value, the measurement volume necessary to undertake an industrial hygiene assessment with the aid of a mathematical model may be reduced to a fraction of that which would be required to reach the same conclusions departing from measurement operations based on statistics.

For that reason, TNO proposed the study of workplaces displaying other similar characteristics. This is the aim of project PS 402.

### c) Treatment programme - PS 316, CEBEDEAU

The aim of project PS 316, entrusted to CEBEDEAU, was to establish a research methodology in the field of industrial hygiene. For that purpose, CEBEDEAU designed and constructed a sampling unit able to measure the concentration of gaseous or solid pollutants over relatively short sampling times and simultaneously to record micro-climatic data and technical details relating to the workplace.

The shorter sampling time makes it easier to follow the trend in concentration and hence to pinpoint sequences of industrial operations in which the heaviest emissions are generated.

The reduction in sampling times also makes it possible to draw up stratified sampling plans, even in the case of sporadic emissions, and hence to calculate the most probable weighted mean concentration over an eight-hour period, but also the minimum and maximum possible concentrations.

This approach has the advantage of being relatively simple and hence easy to use by the safety engineers responsible for industrial hygiene.

#### d) Sampling and measurement of sulphuric aerosols - PS 318, LECES

The iron and steel industry is one of the sources of this type of pollutant. Responsibilities for the total output of pollution at a steel industry site have never been clearly defined.

This research has helped to bring about a better understanding of the origin and behaviour of this pollutant, to identify the main steelworks emitters and to evaluate the impact of their discharge on the environment.

The first part of the report deals with the measurement of sulphuric aerosols at the point of emission by a method known as "controlled condensation" in conjunction with ion exchange chromatography, then presents the results obtained in iron ore sintering and in reheating furnaces.

The second part studies facilities for the measurement of the various sulphur compounds (total sulphur, total sulphates, soluble sulphates, sulphuric aerosol) in the environment.

Statistical processing of the results of measurements carried out in the environment of an iron and steel complex provided the basic data needed for an investigation of the sources of sulphur compounds in the ambient air and mechanisms governing the changes which they undergo.

## **6.2. METHODS AND EQUIPMENT FOR THE MEASUREMENT OF DUST**

### Motivation

This heading covers research aimed at improving operations for the measurement of quantities of dust present in a flow of gas. The dusts contained in gas flows, in particular silica, constitute a serious hazard to health.

Two projects - PS 321 BFI and PS 343 TNO - investigate dust extraction operations and the influence of external phenomena. Two other projects- PS 314 CEBEDEAU and PS 334 BSC - provide for experiments to determine free silica and crystalline silica levels.

Project PS 369 - BCIRA - aims to select a cristobalite sample for use as a standard in the analysis of contents of this crystalline silica allotrope in airborne dusts.

a) Sampling operations

The research sets out to codify sampling techniques used in the measurement of "total" dust concentrations at places of work the aim being to ensure the accuracy and comparability of measurements.

It is not enough just to measure the particle size distribution of the dust; it is also absolutely essential to make chemical analyses of certain pollutant particles and to determine the occurrence of their constituents in the size distribution.

Various types of sampling device were investigated in previous research (see LECEPS PS 261 and UCL PS 272) on the reliability and comparability of measurements. Two disruptive phenomena come into play:

- 1) the rate of air-flow at the point of sampling,
- 2) chemical modification.

Indeed some samplers in use separate the dust by means of a filter through which an entraining gas passes, and this can give rise to chemical reactions between the gas sampled and the separated dust.

Projects PS 321 and 343 both set themselves the basic objective of investigating devices which would make it possible to obtain error-free results and samples which give an absolutely faithful representation of the source materials. It should also be mentioned that methods for sampling fine dusts are based on three techniques:

- a) filtration,
- b) gravity separation,
- c) electrostatic precipitation.

Electrostatic precipitation is by far the least sensitive to chemical changes.

b) Techniques for sampling and dust separation - PS 321 BFI

The BFI has designed and produced a sampling device based on the electrostatic precipitator technique.

The purpose of this design is to collect and extract dusts contained in gaseous effluents which are identical to the source particles and have not undergone chemical change.

The device consists essentially of an assembly of tubular filters fitted with a stepped diameter high-voltage electrode.

This two-stage filter design yielded separation results in the particle size range of 0.1-1  $\mu\text{m}$  with a high gas flow and low corona effects, superior to those obtained with the conventional single-stage tubular electrostatic precipitator.

The research presents the separation yields determined experimentally, analyses the results, then compares them with those obtained on the basis of various other theories of electrostatic separation.

c) Sampling of total dust- PS 343, TNO

The mass of the particles when subjected to gravitational forces and their inertia in motion can disturb dust flows in sampling operations.

The influence of air currents and, in particular, horizontal air movements, such as arise at workplaces inside buildings, may have unexpected consequences.

The combination of these two disruptive phenomena can distort the measurement results.

Photographs showing particle trajectories, taken under different conditions and with parameters varied (dimension, speed of air currents, diameter of suction tubes, sampling frequency), supply valuable information on the consequences for the sampling results.

This work led to the development of a personal sampler, which can be worn by workers and is insensitive to the disturbances referred to above.

d) Determination of respirable dust and free silica levels

- PS 314, CEBEDEAU and GHFAB

The aim of this project is to devise a simple, fast and specific method for the determination of respirable free silica levels and the content of fine dust in the air at workplaces in iron and steel works. The object is to make available to the various laboratories involved a method which will guarantee absolutely comparable results.

In order to achieve this objective it was first necessary to design and make a new sampler for respirable dust.

In order to take account of the criteria and recommendations put forward by industrial hygiene specialists, the researchers incorporated into the sampling system a cyclone which can be used either in a fixed installation or in a personal sampling device carried or worn by an individual worker moving around an area.

e) Determination of crystalline silica in respirable dust

- PS 334, BSC

The aim of this research is to devise a method for the quantitative determination of crystalline silica in respirable dust by means of infra-red absorption spectrometry.

This work was carried out on dust samples collected from filters used in personal respirable dust samplers.

Efforts centred on the direct method for reasons of economy, time and ease of analysis.

The filter (as received) is presented directly to the infra-red beam without an intervening stage of specimen preparation.

The problem of spectral interference in "real samples" prompted the investigation of materials, normally present in dust samples from melting shop environments, which can have an influence on the quantitative determination of crystalline silica. In particular, iron oxide and amorphous silica were examined in detail and their effect on samples containing crystalline silica was evaluated.

Comparative work on the technique of X-ray diffraction developed for the determination of quartz gave an acceptable correlation.

f) Analysis of the cristobalite content of airborne dusts

- PS 369, BCIRA

Cristobalite is present in the atmospheres of workshops in which siliceous refractories are processed.

Respirable particles of airborne quartz and of cristobalite constitute hazards to health. Much is known about quartz but less about cristobalite.

The properties of 16 different samples of cristobalite were investigated in order to determine which one might serve as a standard for the analysis by X-ray diffraction and infra-red absorption of dusts suspended in the air.



### **6.3. MEASUREMENT OF GASEOUS POLLUTANTS**

#### Motivation

Techniques to deal with the impact of gaseous pollutants depend on the detection and quantification of the most toxic gases from the point of view human health, in particular:

- carbon monoxide (CO) and
- sulphur dioxide (SO<sub>2</sub>).

The research is geared mainly to the improvement of sampling methods and to the determination of concentrations of these gases.

These pollutants have serious effects on the health of workers. Even low doses of CO can have irreversible, even fatal consequences (PS 357, BSC). SO<sub>2</sub> can cause respiratory complaints leading to cardio-vascular disorders (PS 318) LECES.

#### a) Detection and measurement of carbon monoxide - PS 357, BSC

The aim of this project is to improve the prevention of acute, sometimes fatal respiratory failure due to gas poisoning by carbon monoxide (CO) in the iron and steel industry, particularly the foundry sector.

Progress achieved in sensing technology has led to the development of CO monitoring devices which are small enough to be worn or carried by a person.

Twelve monitoring devices of this kind were investigated, two of them fitted with semiconductor sensors and ten with electrochemical sensors, with the aim of determining whether they are suitable for use in the iron and steel industry.

One electrochemical sensor of a kind fitted to two of the monitoring devices was considered most suitable, from the point of view of its performance, cost and service life, for use in CO monitoring devices of such small dimensions.

### **6.4. MEASUREMENT OF SECONDARY FUMES**

#### a) Characteristics

The secondary fumes given off in a random fashion in the casting bays of blast furnace and steelmaking shops display special characteristics of their own: they are not channelled and they vary greatly in flow and composition.

These characteristics thus preclude conventional and standardized methods of quantification, with regard to both determination of flows and methods of sampling.

b) Fume collection - PS 325, LECES

This research made it possible to define a practical methodology to deal with the problem of collecting diffuse emissions in the iron and steel industry.

The equipment required for such research is based upon that used for the measurement of pollutants in ducts and piping and has to be adapted to the special flow conditions of the fumes:

- isokineticism is achieved with the aid of sampling probes fitted with funnel-shaped nozzles to allow for the lower flow-rates arising. The sampling probe should be cooled, where appropriate, depending on the temperature of the fumes;
- flow-rates are measured with the aid of rotary-vane anemometers, protected against prolonged heat exposure, or by sturdy mechanical probes, such as a microventuri, when the temperature is too high;
- the pattern of flow of the fumes and the order of magnitude of the flow-rate can be determined with the aid of simple cinematographic equipment.

c) Device for the collection and analysis of fumes - PS 366, CSM

In the context of project PS 366, which deals with ways of limiting quantities of NO<sub>x</sub> emitted, the CSM has developed a system for the collection, conditioning and analysis of fumes, avoiding water condensation and supplying continuous measurements of the various pollutants without solubility losses.

d) Gravimetric measurement of the dust content of fumes

- PS 356, CRM

In order to achieve real weighing of the dust content of gaseous effluents on the basis of a gravimetric method, the CRM has developed a device which it calls GRAVIDUST.

This device collects the dust on a filter by means of a continuous positioning and withdrawal system, then weighs it at regular intervals on an electromagnetic balance.

A computer link-up made it possible to automate all the handling operations and calculations.

The GRAVIDUST was first tested in the laboratory, then fitted to a sintering line dedusting fan whose operation it monitors and controls with the aim of achieving constant optimum yield.

Comparative tests were carried out to verify the performance of the device (see also section 2.5).

e) Measurement of dust and gas concentration in the atmosphere using laser beams - PS 329, ITALSIDER Taranto

The measurement of the concentration of gaseous pollutants and particles in the air at workplaces or in the vicinity of works can be achieved by exploiting the property of laser beams by which they are reflected differently depending on the substance penetrated.

The laser machine which measures the particle concentration is based on the principle that the particle intercepted by the light beam diffuses a quantity of light linked to its diameter.

The determination of the diameter is effected by an electrical signal which is proportional to the quantity of light diffused.

The device was linked up to a minicomputer enabling the data to be monitored and processed. The tests carried out and results obtained made it possible to verify the accuracy and sensitivity of the system and the validity of the methodology used.

f) Devices for the continuous remote monitoring of waste gases from steelmaking processes - PS 351, BSC Rotherham

The aim of this project is to develop, refine and calibrate devices for the measurement of waste gases, in particular from electric arc furnaces.

The special feature of these devices is that they measure the parameters of composition, moisture content and temperature in an open area continuously without the need for an intermediate stage of sample collection, as required by conventional instrumentation.

The research was pursued concurrently on three different techniques, resulting in the development of four measurement devices.

These devices were assembled together to form a compact block which is easy to instal at the intake to a dedusting plant downline from an electric arc furnace. Further successive refinements were carried out in order to correct hysteresis errors due to dust deposition, high temperatures and inadequate sealing. After correction and calibration with conventional measuring instruments, this device operated satisfactorily.

## 6.5. AQUEOUS EFFLUENT ANALYSIS

### a) Criteria used for analysis

A certain number of projects under the third programme were aimed at the development of analysis techniques and the refinement of detection devices to secure greater efficiency in the determination of the properties of effluent and consequently in the monitoring of pollution phenomena.

Isolated samplings and analyses of effluent are of little value because the operation of workstations may vary between two sampling operations, and discharges exceeding the permissible levels may occur. The real solution to this problem is to be found in the continuous analysis of effluent at a specific point, which makes it possible to detect in advance situations in which the unsatisfactory operation of effluent treatment stations could give rise to discharges at variance with the standards imposed.

These devices must also be designed to withstand the hostile and corrosive environment of an iron and steel works.

What is needed is a method of on-line analysis to replace the present system, which requires a sample to be collected and sent to the laboratory, giving rise to a certain delay before the results are obtained.

The method has to meet criteria of "automaticity", continuous in situ analysis and resistance to the industrial environment.

Projects PS 333 - BSC - and PS 398 - IRSID - concentrate on this aspect, the first being concerned in particular with the detection of pollution in coking plant effluent and the second with the monitoring of acid pickling liquors.

### b) Continuous measurement and monitoring devices - PS 333, BSC

The BSC's Teesside Laboratories in Middlesbrough, as part of project PS 333, developed devices to meet these specific needs, taking particular account of the criteria of continuous operation and monitoring, low maintenance requirement and increased resistance to corrosion. In outline, each instrument consists of the following three modules:

- 1) precipitation filtering and cleaning element,
- 2) pumping and mixing element and cell with sensing probe,
- 3) amplification, recording and processing equipment.

After the inevitable start-up adjustments, the prototype devices tested at an industrial site gave satisfactory results.

The devices were used successfully, in particular to determine ammonia levels in the two stripping processes using lime and soda.

c) Electrochemical sensors to reduce pollution caused by acid pickling - PS 398, IRSID

Present monitoring methods on finishing lines (pickling baths, surface treatment baths, dedusting and rinsing liquors) do not take account of the fact that the solutions to be analysed are often mixtures of acids or metals, more or less in the state of complexes, in thermodynamic equilibrium.

Any changes caused in the initial medium by the analysis may alter this equilibrium.

The use of electrochemical sensors should make it possible to achieve a reduction in the pollution rate by the optimization of all the treatment installations, thereby ensuring better surface quality in the finished products and an increase in acid yield, resulting in "clean" pickling.

The first experimental studies consisted in determining the properties of the various selective electrodes and sensors, testing them in the laboratory and making a first selection.

d) Detection of oily aerosols - PS 401, BFI

Motivation

The mineral oils used in a plant are transported not only by water circuits, but also through the air in the form of aerosols, where they have extremely harmful effects on the human organism. The process whereby oils age as a result of their use can give rise to the production of chemical substances with carcinogenic properties. It is therefore necessary and worthwhile to be able rapidly to detect emissions and increases in the concentration of oil mists at workplaces.

Objective

The BFI - PS 306 - had developed a device which detects mineral oils on the surface of a water body and is based on fluorescence induced by ultra-violet light. The researchers plan to use the experience gained in this field in order to construct a device which can detect very fine aerosol particles.

## 6.6. HARMONIZATION OF SAMPLING METHODS

The main focus of the chapter on measurement concerned the harmonization of sampling methods and measurement procedures with the aim of securing comparability of the results obtained.

In this context several research projects were launched at Community level, so that the research on a single topic could be entrusted to the laboratories of five different countries with priority given to the harmonization and codification of sampling and measurement operations.

The projects in question are briefly indicated here with a note of the chapters in which the reports are examined in more detail.

### a) Measurement of PAH and BTX

Two research topics were launched by the ECSC with the collaboration of institutes in the five countries which have coking plants or are alive to the hazards of the pollution generated by this industry.

The subjects of the research are:

The measurement and definition of:

- 1) polycyclic aromatic hydrocarbons (PAH)
- 2) benzenic hydrocarbons (BTX)

The following institutes collaborated in these two major groups of projects:

<u>in the first group</u> (PAH):	. LECES	(F)	PS 346
	. BF	(D)	PS 345
	. NSF	(GB)	PS 342

<u>in the second group</u> (BTX):	. LECES	(F)	PS 332
	. BF	(D)	PS 337
	. NSF	(GB)	PS 340
	. INIEX	(B)	PS 3341
	. HOOGOVENS	(NL)	PS 336

The first phase of the research consisted in developing and refining measurement methods which will make it possible to determine the different degrees of concentration of PAH and BTX in emissions at workplaces and in the environment. The research made it possible to coordinate methods at international level in order to ensure comparability of results.

These topics are examined in more detail in Chapter 1 (Coking plants, 1.1 and 1.2).

There are grounds for some reservations with regard to the various sensors used for the measurement of PAH concentrations in the environment.

The comparison of measurement results led the project leaders to conclude that correlation between the four devices tested was poor.

A new programme must be devised with the aim of developing a reliable device.

b) The measurement of nitrogen oxides (NO<sub>x</sub>)

In its fourth research programme, the CEC introduced a coordinated topic on nitrogen oxides in the iron and steel industry and at coke works with the collaboration of four research centres. With regard to coke ovens (see Chapter 1: Coking Plants, section 1.1.3), the research on NO<sub>x</sub> was conducted jointly by the SEM at Marienau in France (PS 362) and the BFI at Essen in Germany (PS 363).

Measurements carried out at the same time and jointly by the two partners on the same ovens made it possible to coordinate the measurement methods and obtain good comparability of results.

In Chapter 7 (section 7.1), we give an account of the research pursued jointly by two research centres, LECES (PS 367) and CSM (PS 366), on the topic: means of limiting the quantities of NO<sub>x</sub> emitted in the iron and steel industry.

Olfactory pollutants

The coking and steel industries are a source of fairly extensive olfactory nuisance. The ECSC, aware of this problem, at the beginning of 1982 launched a Community research project with the collaboration of research institutes in three countries:

- . for Belgium: SBF - PS 382,
- . for France: LECES (coordinator) - PS 381,
- . for the United Kingdom: BCRA - PS 380.

In the course of a great many exchanges, the partners were able to compare and harmonize their sampling methods and analysis techniques and to cross-check their results.

Comparability tests undertaken between different partners on the same site provided confirmation of the reliability of the measuring instruments used.

The results of this research are presented in more detail in Chapter 7.





## CHAPTER 7: GENERAL PROBLEMS AND AREAS OF OVERLAP

- Reduction of emissions of fine dust and gaseous pollutants such as F, NO<sub>x</sub>, SO<sub>2</sub> and malodorous substances such as H<sub>2</sub>S, mercaptans, etc.;
- reduction of pollution caused by the storage and handling of waste products in the form of dusts and slurries;
- treatment, processing and recycling of waste from iron and steel production and from air and water cleaning plant;
- development of suitable dumping techniques for the disposal of waste resulting from the production of pig iron and steel;
- detection and assessment of the effects of pig iron and steel production on the environment,
- measures to reduce the volume and degree of contamination of effluent;
- reduction of energy requirements and costs of gas cleaning, effluent treatment and recycling;
- precautions against the hazards of inhaling toxic gases and dusts, e.g. silicosis-producing dusts emitted when handling certain refractories or abrasives;
- reduction of the noise produced by certain plant in the iron and steel industry and development of suitable low-cost means of noise abatement to protect both employees and the environment;
- reduction of the noise produced by transport equipment used in the iron and steel industry, to protect employees from excessive noise and vibrations and to prevent noise in populated areas;
- replacement of cleaning agents and adjuvants, which can cause damage to health or to the environment.

This chapter covers 24 research projects dealing with general problems of pollution associated with all the activities of an integrated iron and steel works. They seek to pinpoint the sources (emission) and examine the impact of the pollution on man and the environment (immission). Finally they address problems of waste management and auditory and olfactory nuisance arising from steel industry activities.

## 7.1. REDUCTION OF GASEOUS POLLUTANTS CONTAINING NITROGEN OXIDES (NO<sub>x</sub>)

### Motivation

As we saw in relation to atmospheric pollution at coking plants, nitrogen oxides can have serious effects on the health of workers and on the environment, especially when, under certain conditions, they are subjected to high temperatures and high degrees of humidity.

It is thus essential to reduce such emissions as far as possible or to control their concentrations in treatment facilities.

### Topics

The work done previously on nitrogen oxides (PS 226, 250, 295 and 297) served as a basis for the research carried out jointly by two research centres, LECES (PS 367) and CSM (PS 366), on the scope for controlling the quantities of NO<sub>x</sub> emitted.

The CSM (PS 390) also investigated the formation of nitrogen oxides in relation to the operating parameters of sintering plants.

Two recent projects are worth mentioning, the results of which have not yet been published:

Project PS 394: "Minimization of emissions of gaseous pollutants by optimum heat control during grate sintering", suggested by LECES in this field, which sets out to study the quality of sinter produced from Lorraine iron ore in relation to measures to reduce the emission of gaseous pollutants, including NO<sub>x</sub>.

The Company KRUPP, of Düsseldorf, is conducting a project (PS 397) to investigate means of eliminating the nitrogen oxides emitted by mixed pickling baths.

- PS 367, LECES -

#### a) Measurement

LECES concerned itself with the measurement aspect of the two projects, PS 366 (CSM) and PS 367 (LECES), conducted at Community level. In this context:

- a) for the continuous automatic analysis of NO and NO<sub>2</sub>, LECES devised a device for the analysis of nitrogen oxides by chemiluminescence, which is now being marketed throughout the world.
- b) for the sequential manual analysis of NO and NO<sub>2</sub>, LECES adopted a method of sampling and analysis, the "daily manual method", developed by INSERM in France.

- c) for the measurement of nitrogen oxides at the point of emission, a sampling and conditioning line (dedusting, drying) adjusted to this type of effluent was set up.

This systematic measurement campaign contributed to the optimization of the sequence of measurements applied and led to a significant improvement in measurement accuracy, despite certain difficulties.

b) Systematic recording

The systematic measurements recorded showed that, of all the plants in an iron and steel works, sintering lines are the heaviest producers of  $\text{NO}_x$ .

From the results obtained, it seems that the presence of nitrogen combined chemically with a fuel accounts for a high proportion of the nitric oxide emitted, particularly in iron ore sintering and in reheating furnaces.

c) Measurements in the vicinity of an iron and steel works

The report assesses six months' experience of a system for the day-to-day monitoring of nitrogen oxides set up in a French steelmaking area. A comparison of concentrations of  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{NO}_x$  recorded with the regulations in force revealed a satisfactory picture to begin with.

Research into the mechanisms of air pollution by nitrogen oxides in a steelmaking area showed that these are highly complex processes. Further research will be needed to refine the results.

- PS 366, CSM -

Measurements of fumes in iron and steel plants confirmed that, as in the case of project PS 367, sintering lines produce the heaviest emissions of  $\text{NO}_x$  (325-470 g  $\text{NO}_x$  per t of sinter).

Their removal from gaseous effluents, in view of their highly dilute state, would require the installation of complex and costly treatment facilities. It therefore makes more sense first to investigate ways of reducing  $\text{NO}_x$  emissions at source by acting on the processes which generate them.

In the case of sintering plants, tests showed that the  $\text{NO}_x$  arise mainly from the oxidation of nitrogen in coke. Possible remedies would therefore be:

- either to use a fuel with a low nitrogen content,
- or to alter the parameters of the formation of  $\text{NO}_x$ , such as rate of combustion and quantity of free oxygen available.

In the case of other plants, such as thermal power plants and steelmaking furnaces fitted with burners, the strategy would be to develop burners generating low NO<sub>x</sub> emissions.

## **7.2. REDUCTION OF EMISSIONS OF MALODOROUS SUBSTANCES**

### Olfactory pollutants

The coking and iron and steel industries are a source of considerable olfactory nuisance, which may also be due to the presence of toxic substances. A Community research initiative was launched with the collaboration of research centres in three countries:

- . for Belgium: SBF - PS 382,
- . for France: LECES (coordinator) - PS 381,
- . for the United Kingdom: BCRA - PS 380.

In the course of a great many exchanges, the partners were able to compare and harmonize their sampling methods and analysis techniques and to cross-check their results.

### Measurement methods

For the physico-chemical identification of odoriferous compounds, analysis techniques were used based on gas chromatography (HCP6), together with computer-aided mass spectrometry (CAMS).

In order to measure the concentration of the odoriferous mixture and the intensity of the odours present in an atmosphere, a novel technique was applied: "olfactometry", which involves the human olfactory system.

It consists in measuring the intensity of the odour of a gaseous effluent by determining the factor by which it has to be diluted in order to reduce the odour to the threshold of perception.

In order to determine the impact of odoriferous emissions on the environment, the BCRA investigated the theory of dispersion which enables odour propagation to be predicted mathematically under variable weather conditions (PS 380).

### Measurement results

The first phase in the research programme was devoted to drawing up an inventory of pollution sources, to measuring odour intensity and to defining the physico-chemical properties of the products responsible for the odour. Comparability tests between different partners at the same sites confirmed the reliability of the measuring instruments used.

The development of the analysis techniques and the knowledge gained made it possible to pass on to the investigation of means of prevention by way of abatement techniques and modifications to production processes.

### **7.3. REDUCTION OF POLLUTION CAUSED BY WASTE DISPOSAL**

#### Motivation

The iron and steel industry generates considerable amounts of waste of various kinds in the course of steel production. They include sludges and dusts separated from the water used for cooling blast furnaces, electric steelplants and rolling mills and effluent from blast furnace gas cleaning plants, which give rise to grave ecological problems due to the presence of heavy metals, such as zinc, lead, chromium and nickel.

Two possible solutions are available for the disposal of these wastes, having regard to the potential hazard of pollution posed by them:

- either disposal by dumping,
- or the recovery and upgrading of the metals contained in the sludges and dusts.

Dumping is not without its adverse effects on the natural and human environment.

These are the problems that LECES (PS 344), IRH (PS 379) and CREUSOT-LOIRE (PS 384) set out to investigate with the aim of gaining a better understanding of the phenomena involved and of eliminating or, at least, mitigating the noxious and sometimes disastrous consequences of these phenomena.

#### THE POLLUTANTS FLUORINE, ZINC AND LEAD - PS 344, LECES

LECES investigated the consequences of the action of natural phenomena on the materials of which a particularly large tip (area 200 ha, height 120 m) of considerable age (80 years) is made up and the spread of pollutants to the water table and to fauna and flora.

The researchers sought to determine the impact on the environment not only of past iron and steel making activities but also of the present-day industry and to simulate the effects of the dumping of iron and steel industry waste in the future.

Their research concentrated first and foremost on the behaviour of three pollutants: fluorine, zinc and lead.

With the object of investigating the real impact of certain waste, two pilot tips were set up with a unit capacity of about 50 m<sup>3</sup> and the behaviour of certain pollutants in the soil and groundwater below them was observed and monitored.

The results obtained show that the soil acts as an effective geochemical barrier to heavy metals such as lead and zinc, severely restricting the migration of these metals to the water table.

The many studies carried out as part of this project show that levels of fluorine, lead and zinc do not give grounds for concern.

#### THE LEACHING OF STEELWORKS WASTE - PS 379, IRH

The application of the results of project PS 291 to the framing of a policy on the management and possible commercial exploitation of waste calls for a knowledge of variations in the behaviour of co-products, depending on their origin (nature of processes and production methods) and the period in which they were produced.

The first results obtained on a certain number of wastes show to what extent the composition of these materials and the leachates derived from them varies. The analysis of leaching solutions confirms that there is no direct relation between the concentration of elements in a waste and the composition of the leaching solution. Generally speaking, in the case of the wastes studied, the entrainment of potentially toxic elements by leaching is very low, as is the overall toxicity of the leachates. This confirms the harmless nature of the blast furnace and steelmaking slags sold and extensively used, notably, in road construction.

#### HEAVY METALS CONTAINED IN ELECTRIC STEELPLANT DUSTS - PS 384, CREUSOT-LOIRE

The presence of heavy metals (Cr, Pb, Zn, Ni) in electric steelplant dusts disposed of by dumping constitutes a potential medium- or long-term pollution hazard to groundwater and the ecosystem. In view of the volume of such waste dumped annually, a three-stage study was undertaken at the Creusot Works of the Company CREUSOT-LOIRE.

- a) Laboratory studies
- b) In situ pilot studies
- c) Industrial-scale study

This work was carried out with the assistance of five specialized laboratories, each concerned with a particular problem.

## LEACHING OF FOUNDRY SANDS - PS 327, CREUSOT-LOIRE

In the foundry industry, very large quantities of waste sand used to make casting moulds and cores have to be routinely disposed of by dumping. This sand, for which mineral or organic binders are used, can give rise to major environmental pollution.

On the basis of extensive sampling of industrial sands, representing the most common and the most noxious situations arising in foundry practice, research workers at the Firminy Laboratory of CREUSOT-LOIRE set out to define the pollution hazard generated by the dumping of such sands.

The results obtained as a whole show that, in fact, foundry sands give rise to cyanide and phenol concentrations in leaching solutions which are well within acceptable limits for normal dumping practice. There is thus no need to impose a requirement that special disposal facilities be set up for them.

### **7.4. TREATMENT, PROCESSING AND RECYCLING OF IRON AND STEEL PRODUCTION WASTE**

The presence of heavy elements such as iron, zinc, lead, chromium and nickel in dumped waste from iron and steel production poses a hazard of pollution due to groundwater contamination by the percolation of rainwater through tips or sludge ponds.

These observations explain why considerable efforts have been deployed in recent years in most industrial countries to devise and apply reliable processes designed to recover, upgrade and recycle metals whose presence can disturb and contaminate the natural environment.

#### PROCESSES FOR THE REMOVAL OF ZINC AND LEAD

In project PS 313, CEBEDEAU investigated all processes for the extraction of zinc and lead from iron and steel by-products.

Briefly, these are:

##### 1) PYROMETALLURGICAL PROCESSES, including:

###### 1.1. Chloridizing:

The volatility of the chlorides of zinc and lead is exploited to isolate these elements by the addition of  $\text{CaCl}_2$  prior to sintering. Project PS 368 - THYSSEN - deals with this process.

## 1.2. Reduction in a rotary kiln:

In these processes the elements Zn and Pb are volatilized by reduction in the presence of carbon (coke, lignite or anthracite) at temperatures in the range of 950-1100° C.

## 2) HYDROMETALLURGICAL PROCESSES

These consist in leaching in an alkaline medium with the solution of zinc and lead to the state of sodium zincate and plumbate. On the basis of the good results achieved, a pilot plant was constructed and prepared for tests on a semi-industrial scale.

It was found that the prospects offered by the treatment process studied were sufficiently promising to justify the extension of the study to similar wastes, in particular the residual dusts generated in the melting of small scrap in electric furnaces.

## 3) PHYSICAL METHODS

A third group of purification processes makes use of physical separation methods by which the dusts are preconcentrated to give higher contents of zinc and lead. This stage of beneficiation provides raw materials better suited to the chemical processes listed above.

Methods include:

### 3.1. Screening and cycloning:

These are grading processes which depend on the particle size of products.

### 3.2. Magnetic separation

This operation consists in the separation of suspended solids contained in a fluid into magnetic and non-magnetic elements through the use of powerful magnets whose effect on the magnetic elements is to divert them as they fall.

The CVRM, as part of project PS 359, has made a comparative study of these physical methods for the extraction of zinc and lead.

## TREATMENT OF ELECTRIC ARC FURNACE DUSTS - PS 385, CEBEDEAU

Project PS 313 showed that the prospects offered by the caustic soda process for the treatment of blast furnace sludges were sufficiently promising to justify the extension of the research to the treatment of residual dusts from the melting of small scrap in an electric furnace.



The dusts thus obtained are generally rich in zinc-bearing compounds (+ 20% Zn), and the recycling of this metal constitutes a viable source of supply.

To sum up, overall yields from leaching were on average 56.5% for zinc and 73.5% for lead. The purification process proved to be efficient. The results obtained were significant. A reasonable quantity of zinc was thus recovered and fed into the processing cycle.

#### UPGRADING BY PHYSICAL MEANS OF CLARIFICATION SLUDGES FROM BLAST FURNACE GASES AND STEELPLANT DUST - PS 359, CVRM

Research into dry and wet processes had shown that their yield could be improved if they were applied to zinc and lead preconcentrates.

The aim of this project is to supplement the initial research (PS 317) by the investigation of other physical treatment processes, mainly magnetic separation.

This work was carried out with the cooperation of four major iron and steel research centres.

The efficiency of magnetic separation is directly linked to the mineralogical composition of the dust and hence, chiefly, to phases containing lead and zinc.

In certain cases in which zinc and lead are incorporated into poorly organized phases, concentration by magnetic methods is impossible.

Magnetic separation applied directly to unsorted material gave slightly less favourable results than those obtained from grading to 36  $\mu\text{m}$  but enabled more iron to be removed.

Magnetic separation tests carried out on graded products do not generally make for any significant change in contents.

Attrition made it possible to improve results and obtain a ferromagnetic product rich in iron (60.2% Fe) and practically free from lead and zinc (0.04% Pb and 0.58% Zn), hence perfectly suitable for recycling in steel melting shops.

#### PROCESSES FOR THE UPGRADING OF WASTE FROM STAINLESS STEEL MANUFACTURE

Project PS 388 takes up the two main topics of PS 307, which are:

- 1) removal of oil from machining scrap and millscale, and
- 2) the recovery of waste from electric arc furnace fumes.

- PS 388, BSC

a) Oil removal process

It has been found in practice that the recovery and recycling of stainless steel production waste requires the prior extraction of water and oil.

The maximum hydrocarbon content tolerated in briquettes of such material charged to an electric arc furnace is 2%.

As part of project PS 388, therefore, the BSC conducted tests on the extraction of oil prior to the charging of recovered waste.

Various processes were tested:

1) Briquetting:

No press made it possible to reduce the liquid included to less than 6%.

2) Chemical de-oiling:

As the economic viability of this process is not proven, the researchers looked at a third process.

3) Thermal de-oiling:

The qualities of the oil recovered remained good. However an economic assessment prompted the conclusion that the operating and running costs of a de-oiling plant would exceed the value of the oil recovered, so that this route was also abandoned.

b) Process for the recovery of waste from electric arc furnace fumes

The technology of the furnace makes use of a mechanically rotating plasma electrode which emits a conical arc in a sealed enclosure.

The substances obtained as finished products are mixed with an appropriate reducing agent, such as coke or coal, and transported pneumatically to the region of the plasma arc by means of feed tubes arranged around the roof of the furnace.

The chemical reduction of the metal oxides takes place both in the plasma arc and in the metal bath.

## **7.5. EFFECTS OF PIG IRON AND STEEL PRODUCTION ON THE ENVIRONMENT**

The iron and steel and carbonization industries discharge a certain quantity of pollutants into the atmosphere, despite the elaborate pollution control equipment which has been installed in recent years.

Nevertheless there are other sources of identical pollution, varying in concentration according to the site. These consist of motor vehicle exhausts and the combustion gases from industrial and domestic heating installations.

It is thus essential to have a means of estimating the share of each emitter in responsibility for the pollution as a whole, when several potential pollutant emitters are present on an industrial or urban site.

Apart from the problem of pollutant origin, this research also covers the following areas:

- migration of the pollutant and changes undergone by it during transport,
- the energy policy of the works, with particular reference to SO<sub>2</sub> levels,
- application of prevention measures,
- verification of abatement rates following the installation of pollution control equipment.

Three projects dealt with this problem:

- project PS 347, conducted by LECES, which devoted special attention to gaseous pollutants,
- project PS 391, conducted by the BRGM in conjunction with LECES, which focused on the investigation of dust sources,
- project PS 372, carried out by INIEX, also concerned with the determination of dust origins.

a) Research into the sources of atmospheric pollution in an industrial environment - PS 347, LECES

The LECES research first set out to determine the ideal tracer which would reveal and localize the gaseous pollutant. The choice was finally in favour of a method of tracing by the injection of a chemical compound of an inert gas: SF<sub>6</sub>.

The work, intended to establish the responsibility of the emitter in respect of a given pollutant, required the deployment of considerable technical, analytical and data processing resources.

It was found from the results obtained in the course of a number of tracing campaigns, conducted under different weather conditions, that responsibility was very difficult to prove in the case of a highly unstable atmosphere, whereas in the case of atmospheres subject to little disturbance - the more stable the better - it is easier to pinpoint the responsibility of one or more emitters in a complex industrial environment.

b) Determining the origin of dusts in an iron and steel environment

- PS 391, BRGM

The quantification of pollutants in relation to one another, if it is to be capable of extrapolation to different steelmaking complexes, requires a total inventory of the characteristics of particulate emissions.

The result of such an inventory shows that concepts such as "morphology" (specific or angular) and "texture" (homogeneous or multiphase) are dominant selective characteristics which are not revealed by overall analysis techniques (chemical or X-ray). The demonstration of these characteristics, associated with the specific chemistry of particles, opens up prospects for automatic quantification by means of a recent technological development, achieved at the conclusion of this research programme: a direct electronic link between a scanning electron microscope and an image analyser, which bypasses the intermediate stage of taking photographs.

This work will make a major contribution to the improvement of knowledge involved in:

- 1) pinpointing the responsibility of the different emitters for total environmental pollution in the vicinity of a steelmaking site,
- 2) determining the impact of these polluters on the ecosystem.
- c) Development of methods for determining the origin of dusts in the environment of iron and steel works and quantifying the responsibility of the principal emitters - PS 372, INIEX

The purpose of the present research is to gain a better understanding of the problem of a correlation between emission and immission of dusts, in both physical and chemical terms, by studying the characteristics of the dusts emitted at source and those deposited in the environment of the plant, and to evaluate the relative importance of emitters in respect of both respirable and settling dusts.

As the collection of these two types of dust is governed by different physical principles, the retrieval of the "tracer" elements in the environment required the setting up of a system of deposit gauges for the sampling of settling dusts and volume collectors for the sampling of suspended dusts.

In order to analyse dusts deposited in the environment, a system of sampling and analysis instruments was set up at different distances within the works and outside.

The many results obtained were analysed and then statistically evaluated.

## **7.6. MEASURES TO REDUCE THE VOLUME AND DEGREE OF CONTAMINATION OF EFFLUENT**

The previous programmes had already drawn attention to the harmfulness of effluents.

Even so, despite the successes and improvements achieved through that work, the problems addressed could not be said to have been finally solved:

- On the one hand regulations on environmentally relevant discharges are becoming increasingly stringent and their enforcement increasingly strict.
- On the other hand economic problems associated with the steel industry's struggle for survival have obliged management to reconsider solutions already applied, with a view to reducing capital and maintenance costs.

With regard to effluent quality, a distinction can be made between that originating in coking plants and that discharged from cooling and circulating water systems in iron and steel plants.

a) Coking plant effluent

Processes specifically applied for the treatment of coking plant effluent contaminated with ammonia, phenol etc. were discussed at length in the chapter on coking plants in this report.

b) Steelworks effluent

The conditioning agents added to water used in the cooling circuits of iron and steel plants and passivating agents used for tinned or galvanized plate have a feature in common: they are generally chromium-based.

Seven projects were put forward to deal with different aspects of this field:

- 1) The IRH (PS 308) worked out some formulations for cooling water conditioning agents which would enable those based on chromates to be replaced by less polluting products.

All the many tests carried out show that it is technically possible to define formulations for the conditioning of cooling circuit water which show both good efficiency and low or zero impact on the environment.

- 2) CEBEDEAU (PS 383) set out to convert chromic wastes into a non-toxic or less toxic product.

The research, after undertaking a critical comparative examination of all existing methods, set out in a second stage to experiment on processes which seem likely effectively to meet the three objectives of the research: non-toxicity, efficiency and economy.

- 3) The CSM (PS 395) set out to experiment on passivation treatments for rolled steel in baths containing passivating agents other than chromates.

Applications of thin films based on phosphate, tungsten, molybdenum and manganese were tested in succession.

- 4) IRSID (PS 398) attempted to develop and test the use of electrochemical sensors for the measurement of pickling bath concentrations.

The use of electrochemical sensors should make it possible to achieve a reduction in the rate of pollution by optimizing the treatment plant as a whole, resulting in "clean" pickling.

- 5) The CSM has developed devices for the extraction of magnetic particles from fume cleaning liquors.

Almost all cooling waters, treatment effluent and wastewaters from iron and steel plants contain suspended solids. Many of these solids are magnetic or magnetizable. Hence the proposal of the CSM to purify the sludges by extracting the magnetic fraction in order to recover materials of value and to upgrade them.

The subjects of these projects are:

- 1) the extraction of magnetizable solids by electromagnets (PS 338).
- 2) the magnetic filtration of dedusting sludges from electric steelplants (PS 386).

The high-gradient magnetic separation (HGMS) technique is not only competitive compared with traditional systems but is also significantly more economic in terms of space occupancy. It does not require the addition of expensive flocculants.

- 6) The process of oily water filtration (PS 310, IRH) is also worth mentioning.

This particular filtering process involves the "pre-conditioning" of the filter bed before a filtration cycle commences.

It offers a number of advantages, in particular:

- removal of oil and grease
- high yield
- reduction of circulating volume and recycling of spent water after treatment.

## 7.7. REDUCTION OF NOISE PRODUCED BY CERTAIN PLANTS IN THE IRON AND STEEL INDUSTRY

The reduction of nuisance due to noise is limited to the application of two series of measures:

- the installation of anti-noise screens or the fitting of hoods or cowlings;
- technological modifications applied at the source of the noise.

Of the twelve research projects devoted to noise abatement:

- 1) six are concerned with electric arc and plasma gas furnaces;
- 2) one - PS 326 - investigates the propagation of noise in high-roofed workshops in the steel industry, such as those housing rolling mills and merchant bar finishing lines (BFI);
- 3) one - PS 376 - examines the scope for reducing noise emitted in the course of welding and flame-cutting operations, in particular in continuous casting plants (ILFA);
- 4) one - PS 349 - is concerned with the reduction of noise from gas pipes and the operation of valves during the bleeding and charging of blast furnaces (BFI);
- 5) the same Company - as part of project PS 353 - conducted a study aimed at reducing noise in merchant bar finishing shops (BFI);
- 6) the Company EDW Buderus - PS 354 - is investigating the changes necessary to reduce noise generated by plants for the shot-blasting of narrow strip.

### a) Welding and flame cutting plants - PS 376, ILFA

The use of welding and flame-cutting equipment generates sound pressure levels which can be as high as 120 dB (A). The generation of ultrasound accompanying this noise causes considerable discomfort to workers.

Special attention was devoted to:

- 1) the parameters defining the jet of flame and gas from the burner (position, angle, gas pressure);
- 2) the arrangement of the burners in relation to the slabs to be cut;



- 3) the separation of the various noise sources. It is noted that electric arc furnaces and the various cutting installations are housed in a single workshop with no acoustic separation between them;
- 4) secondary sound insulation, in order to provide and increase protection for the workforce and the environment.

a) Blasting plant for narrow strip - PS 354, Edelstahlwerke BUDERUS

Noise emission in plants for the shot-blasting of narrow strip falls within the range of 95 to 105 dB (A) and is therefore a major source of nuisance to workers and the environment.

For this reason, the Technical Committee of the Company EDW Buderus in Wetzlar, in conjunction with the TÜV in Essen (PS 354), devised an anti-noise cabin consisting of steel sections panelled on the inside with special perforated partitions for sound-proofing filled with fire-retardant glass wool, the outer cladding consisting of trough-rib profile steel sheet.

The access doors fitted in these walls are surrounded by an airtight rubber seal. The joints between wall sections are filled with a sound-proofing foam. The openings for the entry and exit of strip through the housing are fitted with seals incorporating a slit.

In order to achieve further reductions in noise nuisance, the normal shock-absorbing rollers were replaced by rubberized rollers, pressed against the strip by means of pneumatic jacks or a system of springs.

These modifications led to significant improvements in the level of noise (-20 dB (A)).

#### **7.8. REDUCTION OF NOISE PRODUCED BY TRANSPORT EQUIPMENT USED IN THE IRON AND STEEL INDUSTRY**

Within the research previously mentioned, three projects were devoted to the scope for reducing noise generated by handling equipment specific to the iron and steel industry.

- a) Project PS 353 - BFI - tackles noise emission in merchant bar finishing shops.

A new handling device has been designed which takes account of the lessons learned from this research. It can carry out operations involving the collection, assembly, storage, transport and stacking of section mill products with a minimum of noise. It is being built and, when completed, will be set up in an industrial situation.



- b) The BSC has undertaken research into the use of skids for the handling of products on the cooling, loading and transfer banks of beam and section mills (PS 378).

Four different types of auxiliary material were selected and tested in order to reduce noise caused by the movement of beams along the transfer rails.



## LIST OF PROJECTS COVERED BY THE FOURTH PROGRAMME

Project number	Institute	Subject of research
PS 308	IRH	Evaluation under simulated industrial conditions of formulations for the conditioning of water in cooling circuits without impact on the environment, developed in the context of project PS 303.
PS 310	IRH	Complementary research aiming at the valorization and the industrial use of the filtration process for oil-containing water, developed in the context of project PS 304. Process of filtration on a pre-conditioned sand bed.
PS 312	MANNESMANN	Improvement of dedusting systems by minimizing the amount of air to be extracted.
PS 313	GHFAB and CEBEDEAU	Pilot study of a caustic soda treatment process for reducing the zinc and lead content of waste products from iron- and steelmaking processes.
PS 314	GHFAB and CEBEDEAU	Development of a new method for determining the respirable dust and free silica levels at work-places in iron and steel works.
PS 316	CEBEDEAU and BECEWA	Development of a strategy for the uniform measurement of atmospheric pollutants at work-places in the EEC countries - Dust and gas sampling.
PS 318	LECES	Development of methods for sampling and measuring sulphuric aerosol emissions from steelworks and their environment.
PS 321	BFI	Development of a compact electrostatic filter for dust sampling and collection.
PS 324	MFI	Optimization of the sintering process with reference to the emission of pollutants, in particular SO <sub>2</sub> and CO.

PS 325	LECES	Improvements in the collection of secondary fume emissions.
PS 326	BFI	Noise radiation in high-roofed workshops in the steel industry.
PS 327	CREUSOT-LOIRE	Study of the lixiviation of foundry sand.
PS 328	LECES	Study of methods for reduction of noise generated by UHP arc furnaces.
PS 329	ITALSIDER	Measurement of atmospheric dust and gas concentrations using laser beams.
PS 330	BCRA	A study of the inhibitory organic material occurring in carbonization liquors and other chemical effluents.
PS 331	BSC	Measurement of the noise, particulate and gaseous emissions from a plasma steelmelting furnace, and to assess its impact on the working environment.
PS 332	LECES	Coking plant pollution - Measurement of benzene, toluene and xylene (BTX) in the atmosphere within and in the vicinity of coking plants.
PS 333	BSC	Development of continuous monitors for aqueous effluent analysis.
PS 334	BSC	Development of a new method for the quantification of respirable dust and free silica at workplaces in iron and steel works.
PS 335	GHFAB and CEBEDEAU	Combined treatment of municipal sewage and industrial effluents - Application to coking plant effluent.
PS 336	HOOGOSENS	Coking plant pollution - Measurement of benzene, toluene and xylene (BTX) in the atmosphere within and in the vicinity of coking plants.
PS 337	BF	Coking plant pollution - Measurement of benzene, toluene and xylene (BTX) in the atmosphere within and in the vicinity of coking plants.
PS 338	CSM	Study of advanced techniques for the treatment of steelworks effluent: magnetic clarification using high intensity fields.
PS 339	CSM	Improvement in the efficiency of biological treatment of coking plant effluent by the use of oxygen or enriched air.

PS 340	NCB and NSF	Pollution at coke works - Measurement of benzene, toluene and xylene (BTX) in the atmosphere within the environs and in the neighbourhood of coke works.
PS 341	GHFAB and INIEX	Pollution at coke works - Measurement of benzene, toluene and xylene (BTX) in the atmosphere, within and in the environment of coke works.
PS 342	NCB NSF and CRE	Pollution at coke works - Measurement of polycyclic aromatic hydrocarbons (PAH) in the atmosphere within and in the environment of coke works.
PS 343	TNO	Sampling of total dust at the workplace in the iron and steel industry.
PS 344	LECES	The behaviour of pollutants (F, Zn, Pb) in iron and steel works.
PS 345	BF	Atmospheric pollution at coking plants - Measurement of polycyclic aromatic hydrocarbons (PAH) in coking plants.
PS 346	LECES	Pollution at coking plants - Measurement of polycyclic aromatic hydrocarbons (PAH) in the atmosphere within and in the vicinity of coking plants.
PS 347	LECES	Research into the source of atmospheric pollution in an industrial environment.
PS 348	IRSID	Further reduction in noise generation from DC arc furnaces.
PS 349	BFI	Reduction of noise from pipes during bleeding and charging of blast furnaces.
PS 350	HOOGOVENS	Prevention of the tapping of pig iron containing zinc from a blast furnace.
PS 351	BSC	Remote monitoring of the properties of the waste gases from steelmaking processes (CO <sub>2</sub> + furnace dusts).
PS 352	BSC	A study of bag filter fabrics and filter operation on a full-scale plant cleaning fume from electric arc furnaces.
PS 353	BFI	Attenuation of noise emission in merchant bar finishing shops by modifying the handling and transport processes.

PS 354	EDELSTAHLWERKE BUDERUS	Noise reduction at workplaces near blasting plant for narrow strip.
PS 355	FGES	Measures to reduce gaseous sulphur emission during trials for production of blast furnace lump slag.
PS 356	CRM	Optimization of the operation of electrostatic precipitators in sintering plant by continuous or sequential gravimetric measurement of dust content of the fume.
PS 357	BSC	Improvements in the detection and measurement of carbon monoxide for the safety of steelworks personnel.
PS 358	IRH	Complete purification or conditioning of ammoniacal liquor from coking plants by chemical oxidation, using in particular oxygen and ozone either separately or in combination.
PS 359	CVMP	Beneficiation of dust from the iron and steel industry (clarification sludge from blast furnace gases and converter dust) using physical methods.
PS 361	CHERCHAR	Study of possible improvements to the process for steam stripping of the ammonia present in coke-oven liquor.
PS 362	CHERCHAR	Formation of nitrogen oxides as a function of heating conditions in coke ovens.
PS 363	BF	Formation of nitrogen oxides as a function of heating conditions in coke ovens.
PS 365	LECES	Research into means of improving the operation of electrostatic precipitators in iron and steel works.
PS 366	CSM	Study of the generation of nitrogen oxides in the iron and steel industry. Investigation of possible means of limiting the quantities of NO <sub>x</sub> emitted.
PS 367	LECES	Investigation into the formation of nitric oxides in the iron and steel industry. Study of possible ways of limiting the quantities of NO <sub>x</sub> emitted.

PS 368	THYSSEN AG	Development of a process for the treatment and dezincification of LD dust in a sintering plant, using a gravel bed filter dedusting process with addition of calcium chloride.
PS 369	BCIRA	The selection of a suitable cristobalite standard to be used in the analysis of airborne dusts for cristobalite.
PS 370	MW and BFI	Development of flame cutting equipment incorporating mechanical ventilation and de-dusting facilities for cutting up steel and iron skulls.
PS 372	INIEX	Development of methods for determining the origin of dusts in the environment of iron and steel works and quantifying the responsibility of the principal emitters.
PS 373	BFI	Optimization of plant modifications to reduce noise and dust emission in electric arc furnaces.
PS 374	BFI	Use of high-power plasma burners to reduce the level of environmental nuisance in electric arc steelmaking.
PS 375	FIAT	Research relating to noise abatement by installing an enclosure hood over a 150 t electric arc furnace.
PS 376	ILFA	Reduction of noise levels during welding and flame cutting (including hot scarfing).
PS 378	BSC	The reduction of noise resulting from the traverse of steel sectional products across transfer skids on cooling, loading and transfer banks.
PS 379	IRH	Leaching of iron and steel industry wastes: variability of the results from one plant to another and over a period of time.
PS 380	BCRA	Investigation, inventory and control of odoriferous pollutants in the steel and carbonization industries: emissions at the workplace and in the general environment.
PS 381	LECES	Monitoring and prevention of malodorous emissions from iron and steel works and coking plants - Studies to be conducted at the source of pollution, at places of work and in the environment.

PS 382	SBF and UCL	Monitoring and prevention of malodorous emissions from iron and steel works and coking plants - Studies at the source of pollution, at places of work and in the environment.
PS 383	CEBEDEAU	Treatment of chromic wastes, with recovery of chrome and recycling of water.
PS 384	CREUSOT-LOIRE	Medium and long term changes occurring to heavy metals contained in dumped dusts.
PS 385	CEBEDEAU	Treatment of electric arc furnace dusts to remove zinc and lead.
PS 386	CSM	Study of techniques for the treatment of steelworks effluent: high-gradient magnetic clarification. Tests on the magnetic filtration of electric furnace fume cleaning liquors.
PS 387	DSM	Investigation into and demonstration of the removal of organic substances and nitrogen from coking plant effluents. Biological nitrification-denitrification process.
PS 388	BSC	Recovery of wastes produced during stainless steelmaking.
PS 389	GHFAB and CRM	Improved method of removing tar from coking plant effluent. Detarring by centrifuging.
PS 390	CSM	Pilot scale study of the interrelation between the operational parameters of the sintering process and the formation of nitrogen oxides.
PS 391	BRGM	Perfecting of methods for determining the origin of dusts in an iron industry environment and measuring how much responsibility goes to the main emission points.
PS 392	BSC	The treatment of coking plant liquors for the extraction of nitrogen: research leading to the industrial-scale demonstration of a single sludge system. Biological nitrification-denitrification process.
PS 393	GHFAB and CEBEDEAU	Anaerobic purification of coke oven liquids.
PS 394	LECES	Minimization of emissions of gaseous pollutants by optimum heat control during grate sintering.



PS 395	CSM	New passivation methods for tinfoil and galvanized sheet using baths without chromate.
PS 396	CSM	Removal of ammoniacal nitrogen from coking plant effluent by means of biological discs with simultaneous removal of organic pollutants (predenitrification-nitrification).
PS 397	KFI	Elimination of nitrogenous waste gases from mixed-acid pickling baths.
PS 398	IRSID	Design and installation of electrochemical sensors intended to reduce pollution caused by acid pickling.
PS 399	CSM	Recovery of pollutants of significant economic value from waste pickling liquor used with stainless and special steels along with elimination of the pollution caused by them.
PS 400	CRM	Disposal of the organic sludge resulting from the biological treatment of coking plant waste waters.
PS 401	BFI	Development and testing of an instrument for determining the concentration and droplet distribution of oil aerosols.
PS 402	TNO	Measuring strategy: follow-up investigation into the reduction of the scale of measurements required to achieve reliable pollution concentration monitoring at places of work.







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