

# **industrial health and safety**

## **Technical control of pollution in the iron and steel industry**

Research progress report: 1 January 1980



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## Introduction

This fourth summary of research progress reports continues the series of reports designed to give a brief survey of the ECSC's research activities in the field of pollution control in the iron and steel industry (\*).

The Commission of the European Communities has been an active campaigner for environmental protection: the first research work on protection of the environment in the steel industry subsidized by the ECSC was carried out as early as 1957.

Whereas the first research programmes were mainly concerned with air pollution and providing the appropriate protection at the place of work, later, particularly as part of the third programme (1974 - 1978), research aims were broadened to include the control of water pollution, noise and the re-utilization, or the environmentally safe elimination, of residues and waste matter.

Given the present extremely difficult situation in the European steel industry' the growing interest of all participants in these research programmes, can be explained

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- (\*) - Report "Technical control of atmospheric pollution in the iron and steel industry", June 1963
  - Report of 30 June 1972 (EUR 4921)
  - Report of 30 June 1977 (EUR 5977)

not least by the desire to provide better protection for the environment by means of cost-effective improvements in manufacturing and processing techniques or the introduction of new techniques without at the same time endangering the international competitiveness of the European iron and steel industry.

From this point of view, research in the field of environmentally safe re-use of residue materials deserves particular attention.

This brochure is intended to summarize in one compact volume the state of progress of the 68 research projects on 1 January 1980, the great majority of which come under the heading of the third research programme. In the case of one or two research projects, there was additional material to be included which was not all available at the time the report of 30 June 1977 was drawn up.

Attention is also drawn to the fact that the results, or partial results, of the research projects dealt with here have been discussed at conferences and round-table discussions and have been summarized in the appropriate reports (x).

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- (x) - Round-table discussion on coking plants, Luxembourg, 7 and 8 June 1977, 3 and 4 October 1978
  - Conference on waste and residues from the iron and steel industry, Luxembourg, 5 June 1978
  - Round-table discussion on coking plants, Luxembourg, 1 and 2 October 1979.

General summary  
(30.6.1977 to 1.1.1980)

The 68 research projects dealt with in this brochure are divided into four main groups of topics:

1. control of air pollution
2. control of water pollution
3. noise abatement
4. re-utilization or environmentally safe disposal of residues and wastes.

The aim of the following is to give a brief summary of the main results in each of these groups.

In order to give the interested reader further details relating to the research projects, the results of each individual research project, or the progress of the research project at 1 January 1980, are briefly summarized in the following four chapters.

1. Control of air pollution

1.1 Further development of general measurement methods.

A significant portion of the work carried out during the Second Programme consisted in improving and harmonizing measurement techniques. One or two of these research projects were not completed until after the publication of EUR 5977 of 1977 and there are consequently some results that have to be included here.

The lengthy research into the further development of the "Konitest" (PS 158) showed that this device could be used in an improved form for the continuous measurement of total dust quantities at the place of work, but only under specific conditions that were determined during the research.

There has been further progress in the techniques for counting dust particles (PS 175, 229). But the research work has also demonstrated that the measurements, e.g. determination of the quartz content of respirable dusts by X-ray diffraction, may be influenced by various test parameters.

A comparison of several devices designed to measure dustfall (PS 272) produced a wide range of variation, and consequently poor comparability of the measurement data. Nevertheless, the project was of value in demonstrating the conditions under which these measurement devices could make a useful contribution to the practical monitoring of dustfalls.

More recent areas of research are concerned with the planning and evaluation of measurements. The aim here is to obtain more accurate information relating to environmental pollution by setting up monitoring networks in and around steel works and, if possible, to detect correlations between immission and the emitting sources (PS 231, 283). The working methods developed during the course of the research work make it possible to optimize the positioning of measuring points on the monitoring networks, using a mathematical synthesis of measurement data, and thus to achieve reliable analyses for the purposes of comparison with the prescribed standards. On the other hand, the available results would indicate that monitoring networks of this kind are not very suitable for obtaining reliable evidence of the correlation between immission and emitting sources.

Measurement of the mean concentration of solid and gaseous materials at the place of work itself can also be improved by systematic large-scale measurement programmes followed by the development of a mathematical model, in such a way that only a few significant measurements are then required for further monitoring (PS 300).

#### 1.2 Research in the field of coke ovens, ore preparation and blast furnaces

The fundamentally important question of atmospheric pollution from coking plants was dealt with in three research projects (PS 285, 305, 319). The first of these research projects aimed to establish the personal exposures of coke oven personnel, as well as to investigate the efficiency of protective measures (PS 285). Distinct differences between the levels of dust and benzene soluble substances at different locations were discovered. Comparison with an American study showed that the levels measured were approximately 50% lower than in America.

The protective measures investigated, both individual respiratory protection in the form of respirator helmets and the provision of air-conditioned refuges, gave good results. The concentration of pollutants diminished by factors of between 6 and 11.

This research similarly made an important contribution to the development of sampling and analysis methods for pollutant measurement strategy.

The development of new methods of reducing emission sources or collecting pollutants from coke ovens constitutes a particularly difficult and multi-faceted problem, which may be approached in various ways. One option is to collect all the emissions from coke oven operation centrally, by totally enclosing the battery in a shed (PS 305). Experiments carried out on a 1: 10 scale model have already resulted in significantly improved understanding of the flow conditions in the individual sections of the shed and have yielded promising suggestions for solutions. The alternative solution of roofing over only parts of the shed, for example on the quenching track side, may also produce favourable results.

In order to reduce the relatively serious emissions from leaking oven doors, four different kinds of novel seals for coke oven doors are at present being tried out on seven-metre ovens (PS 319).

Three of the research projects subsidized by the ECSC deal with pelletizing and sintering plants (PS 248, 257, 297). Extensive measurements of atmospheric pollution at various work locations in a pelletizing plant showed that the concentrations of dust and fluoride were well below the MAC values. Working conditions may be further improved by implementing some of the possible improvements that resulted from the research work.

In the research at sintering plants, emissions of  $SO_2$  were given particular attention. One possible way of reducing these emissions could consist in reducing the proportion of solid fuels by preheating the sinter mix. On the other hand, it was established that the  $SO_2$  content of the waste gases was not constant over the whole length of the sintering strand, but reached a definite maximum at certain points (PS 257, 297).



Three research projects in the field of blast furnaces were concerned with investigating the possibility of improving working conditions during slag granulation, desulphurization and tapping (PS 237, 256, 288). Initial documentary material relating to the operational parameters affecting air pollution and the design of waste gas extraction plants was prepared.

### 1.3 Research in melting shops

Work in this field was mainly concentrated on electric melting shops. Particular attention was given to the design and the optimization of direct and secondary fume extraction systems in single-furnace and multi-furnace shops (PS 224, 302, 309). As may be expected, the design suggestions made for new, projected shops (e.g. furnace enclosure) are different from those for existing shops.

One of the achievements of this research is the fact that the present results of the experiments have yielded a mass of operational data on flow volumes of waste gases during individual stages of the process, i.e. melting, refining and tapping. As regards the tapping phase, special studies were carried out on direct traction of fume. This research work is still partially incomplete.

Further research has yielded new information on the collection of gaseous and particulate emissions using bag filters (PS 298, 309). Experiments on the entrapment of fluorine compounds in bag filters showed that it was possible to achieve an excellent collection rate for fluorine compounds in particulate form. 50% of hydrofluoric acid fume can be collected. In the case of heavy metal oxides, the collection rate is more than 99%. The properties of various filter materials and suitable testing methods were also investigated.

1.4 General investigations into the composition of air pollutants, the performance of dust collection systems and problems in the processing of steel.

One or two of the basic research projects concern the origin and composition of emissions containing fluorine in sinter plants, melting shops and electroslag remelting plants (PS 238, 255). Special sampling and analysis techniques were developed so that fluorine compounds of differing degrees of toxicity could be more precisely and more easily distinguished.

Several research projects were given over to investigating the emission of nitrogen oxides from industrial furnaces (PS 226, 295, 250). The principal parameters affecting the operation of industrial burners were established and provided the basis for drawing up practical approximation equations for  $\text{NO}_x$  emissions. The relationships that were established suggested one or two possible ways of reducing emissions of  $\text{NO}_x$ ; nevertheless, the practical opportunities for the implementation of these measures seem slight.

As regulations governing permitted emissions become stricter and stricter there is a danger that dust collection requirement will impede further development of steelmaking techniques. One piece of research was therefore given over to investigating performance in extreme cases and the flexibility of the overall system consisting of a production plant and a dust collection unit (PS 274). At sinter plants dust collection using electrofilters usually gives outstanding results. Certain operating conditions which differ from normal operation were investigated separately. In oxygen melting shops research is being carried out on the optimization of Venturi scrubbers.

In the steel fabrication sector, studies on workshop models provided useful pointers to ways of improving ambient conditions at the place of work (PS 253).

## 2. Control of water pollution

There were two main themes of research: on the one hand, the further development of analysis and control methods for improved monitoring of waste waters and, on the other hand, cleaning the waste waters from coking plants.

### 2.1 Analysis and monitoring methods

Efficient control of waste waters is in many cases only feasible using continuous analysis procedures, for which one of the fundamental preconditions is that the analysis should be carried out on an automated basis. In one of the research projects (PS 252) analysis processes for the most important substances were investigated and further developed. Particular attention was given, in so doing, to the suitability of these methods for continuous operation in steel-works.

In order to assess the toxicity of liquid wastes containing cyanide, those analysis methods that distinguish between free cyanides and non-toxic cyanide compounds were investigated and further developed (PS 273).

A series of optical measuring procedures for the monitoring of suspended solids in liquid wastes are at present available. The processes which were most suitable for continuous operation were determined (PS 243). An operational monitoring device designed to detect the presence of oil is at present being developed (PS 306).

Further research projects dealt with the design of liquid waste pipelines designed to discharge the pollutants into the sea without damage to the environment and the selection of environmentally safe conditioning products for industrial cooling circuits (PS 275, 303). Several products were identified which caused no damage when allowed to run away into the natural aquatic environment.

## 2.2 Liquid effluent from coking plants

The research project subsidized by the ECSC in this particular field and carried out during the period covered by this report produced a series of promising results.

Stripper columns operating on milk of lime produced technically sound results for the elimination of ammonia (PS 286, 279, 315), both for free ammonia and for fixed ammonium salts. This technology could be developed further and significantly improved in order to produce a self-clearing column. Creation of a weakly-acid zone in a two-section stripping also facilitates the removal of phenols and free cyanide. The Sidmar company is at present developing an industrial stripping column with a capacity of 45 m<sup>3</sup>/h.

The elimination of small residual quantities of ammonia from liquid coking plant effluent was obtained through a process of biological nitrification and denitrification in a pilot plant which was fed with industrial waste that had been subjected to biological pretreatment. Chlorination processes could also be used for this purpose; the appropriate research work has already begun (PS 315).

Two research projects (PS 260, 287) dealt with the biological purification of coking plant effluent, mainly with a view to removing phenols. First an attempt was made to establish the effects of changes in influent composition. No decisive correlation between these changes and the degree of efficiency of the plant were detected. The second research project resulted in a series of practical hints relating to the control of bio masses. In addition, some experiments in the physical-chemical treatment of effluent after stripping were carried out.

The CSM tried another avenue of approach to the problem of removing phenols and cyanide, in this case using activated carbon (PS 278). The main aim of the exercise was to reduce the cost of this process by activating semi-coke and carrying out adsorption in a fluidized bed which was continually fed with regenerated, activated carbon. Experiments in a pilot plant provided initial data on energy consumption and material loss.

Analysis methods for the detection of pollutants in coking plant effluents were tested and further developed in several other research projects.

### 2.3 Rolling mill effluent

In the rolling of steel a considerable quantity of oil and grease is consumed and these are partly removed in the waste water. In hot rolling mills the main problem is to remove oil from the circulating water, and also, if necessary, from the effluent discharged. Provisional results of a research project which is still under way (PS 304) show that 80 to 90% of the total oil present in the water is combined with suspended solids, mainly with solid particles of below 40  $\mu$ m.

The possibility of using flocculation by polyelectrolytes and various filtering techniques are being investigated.

In cold rolling mills emulsions of oil and water are used. Here the main problem is to remove the oil from the used emulsions and dispose of the residues. This latter aim can be achieved by adding the used emulsions to the heavy fuel oil which is injected into the tuyeres of blast furnaces (PS 236). Experiments have shown that this method is feasible.

### 3. Noise control

Community research carried out in this field is concerned almost exclusively with electric-arc furnaces. It is common knowledge that high performance electric-arc furnaces are sources of intense industrial noise. The electric-arc furnaces in use today are powered by 3-phase alternating current (50 Hz), which means that each of the three arcs is struck and then extinguished 100 times a second. This results in the typical crackling noise of an electric-arc furnace.

Carrying on where previous Community research had left off, the abatement of noise from electric-arc furnaces was further investigated in three co-ordinated projects (PS 289, 299, 301). Their aim was to broaden present knowledge of the mechanisms of noise generation and the main factors influencing it, and to improve safety precautions. The fundamental finding was that a significant proportion of the noise is attributable to the instability, both in time and in space, of the electric arc, a feature which is particularly marked during the melting

stage. At the moment experiments are going on to identify the main parameters of noise generation and to reduce the instability, for example, by introducing ionizing elements to the electric arc.

An essential part of this research, some of which will continue until the end of 1982, will entail the use of direct current to power the electrodes in order to reduce the noise emitted.

Another approach to noise abatement was to develop a new technique for electric-arc melting, based on continuous charging of the furnaces with pre-heating scrap (PS 296). With this procedure, there is a permanent bath of molten steel, and the very short arcs are struck beneath the slag cover, and as a result the noise levels recorded during these experiments were more satisfactory.

The aim of the research on industrial gas burners of the type used for heat treatment processes was likewise to find suitable ways of reducing the noise level in the vicinity of burners. The research project dealing with this topic (PS 251) yielded some suggestions for improvements.

#### 4. Re-utilization and environmentally safe elimination of residues and waste

By far the largest proportion of research projects in this category was concerned with investigations into the recovery or elimination of lead and zinc from dusts and sludges produced in the manufacture of pig iron and steel. Further research work was concerned with the beneficiation of LD slag and the storage, removal or recovery of other residues.

#### 4.1 Recovery or removal of lead and zinc

In an overall research programme consisting of several co-ordinated projects, various approaches were tried, so that when the research work was complete a range of different techniques was available and could be adapted to local conditions at individual steel works.

Experiments on sinter plants showed that removal of other metallic elements found with iron, such as lead and zinc, was only limited, although rather more efficient when volatilizing elements were present. The situation was similar in the cases of Cu, Sb and Sn (PS 225).

Reducing rotary kiln processes used in the treatment of dust and sludges (PS 271) seem promising. The volatilization of zinc, which was achieved in large scale experiments was more than 95% effective, producing final discharge quantities varying between 0.05 and 0.10%. In the case of the volatilization of lead, furnace discharge values of up to 0.10% of lead can be expected.

Similarly, initial experiments in the wet processing of sludges using caustic soda with subsequent cementation and electrolysis produced interesting results. The procedure to be adopted for a semi-technical plant was established (PS 313). Another promising approach could be the removal of zinc from blast furnace dusts with carbonic acid (PS 235). The process works under pressure, and the degree of extraction rises as the pH value of the leaching solution falls.

Preconcentration processes using particle separation have also been developed. The degree of effectiveness of processes of this sort, however, seems to be very much dependent on the origin and the chemical and physical properties of the materials being treated.



At the present time recovery techniques for lead and zinc are not being used on an industrial scale in European steel works. The economic feasibility of any new processes developed will be of decisive importance.

#### 4.2 Re-utilization of LD slags

Research carried out in this field (PS 281, 320) was fundamentally aimed at raising the  $P_2O_5$  content, in order to open up new opportunities for the disposal of such slags as calcareous phosphate fertilizers.

For this purpose an enrichment process using the following phosphatic waste or by-products was attempted: bonderized sludges, produced during the surface refinement of steels, washery residues, a waste product containing phosphoric acid and other phosphatic waste materials.

Various methods were investigated for incorporating these materials: blending or crushing, decomposition by adding to liquid slags, or before addition of other materials. The effectiveness of the final product was tested in crop-growing tests.

To judge by the results, the waste product containing phosphoric acid and some types of washery residue are suitable for the enriching process on condition that an appropriate blending technique is used. The thermal decomposition of calcium aluminium phosphate in a rotary kiln also results in a usable final product when combined with the slag.

Despite the possibilities demonstrated by these research projects, one should not overlook the following limitations:

- The products added must be largely free of elements such as zinc, boron and fluorine that are harmful to plants,
- materials which are added to promote thermal decomposition of the liquid slag must not contain any residual humidity (risk of accidents),
- thermal decomposition processes are not at present commercially viable,
- the phosphatic waste materials examined are usually generated in small quantities scattered over wide areas, and an economic solution would have to be found to the problem of transport.

#### 4.3 Environmental problems of storage on tips

Two research projects (PS 270, 291) were concerned with improving knowledge of the behaviour on tips of water-soluble steel works wastes and their effects on the environment.

With the help of leaching tests, it was established that, generally, sulphur is the most soluble component element of blast furnace slag, steel works slags, sludges and dusts. On contact with the air, the sulphur which has been leached out of the tip rapidly oxidizes to produce sulphate ions.

Altogether, taking due account of the results for fluorine, heavy metals etc., the danger of water pollution by run-off from slag heaps is very small.

Hydrological investigations on a slag heap have shown that there is no water-bearing layer within the heap and that, as the subsoil under the heap is relatively impermeable, the

ground water beneath is scarcely, if at all, affected by infiltration of pollutants. Run-off water from the slag heap no longer contains any sulphides.

#### 4.4 Pickling plants

The classic chemical pickling process for the descaling of steel presents a significant risk of environmental pollution. As part of the ECSC-sponsored research work, two different proposals for a solution of this problem were investigated (PS 262, 282).

The first solution approached the problem via the application of a mechanical descaling process to wire rod. One of the weak points of this process, which was not ultimately a new one, was remedied by eliminating the residual quantity of scale, which is normally between 0.5 and 1% of the total. This was done by final pickling in a phosphoric acid bath with activation by ultra-sound (sonication). The pickling acid can be regenerated and recycled by filtration.

The second solution entails the development of a new process - neutral electrolytic pickling - during which the creation of acidic wastes which are harmful to the environment is likewise avoided. In the course of the research the most favourable operating parameters were established and subsequently tested in a pilot plant. The trials were carried out principally with hot rolled strip made of Si-steel.

#### 4.5 Recycling of wastes with high Cr and Ni content

Wastes of this kind occur in the manufacture and processing of stainless steel. One research project (PS 307) was concerned with the re-use of these valuable metals in the manufacturing process, and thereby, at the same time, eliminating the need for dumping.

Of the large quantity of processes and waste materials which were investigated, the most promising were pelletizing and recycling back to the furnace of solids filtered out of furnace fume and briquetting of grinding swarf. In the latter case, however, the oil content of the briquette is still too high for recycling back to the furnace. Testing methods for removing or recovering the oil has not yet been concluded.

CHAPTER 1

Control of atmospheric pollution

Measurements and recording of concentrations of silicogenic, toxic and obnoxious dusts using the "Konitest".

(Bayerisches Landesinstitut für Arbeitsschutz,  
Munich, Research Project PS 158)

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Research using the "Konitest" has already been reported upon in the booklets published in 1972 (EUR 4921/Research Project 159) and 1977 (EUR 5977).

The quantity to be measured to determine the concentration of solid matter in a mixture of gas and dust using the "Konitest" is an energizer current. This current is produced by contact-electrical interactions between solid particles and an energizer tube, through which the gas-dust mixture under investigation is drawn. Contact between the solid particles and the energizer tube causes the charges to be separated. The charges that are deflected by the energizer tube produce an energizing current, which gives virtually instantaneous, continuous measurement of the dust concentration.

The aim of the research programme was to detect any health risk arising from the effects of dust at the place of work. The emphasis in this research programme lay on the further development of the "Konitest" device, with the aim of making direct measurements of concentrations of respirable fine dust in accordance with the Johannesburg Convention, as well as measuring the total dust concentration at various work places in a Bavarian steel works.

Two different approaches were tried for continuous measurement of fine dust:

1. Pre-separation of the coarser dust, using an axial separating cyclone
2. Use of an MPG-II sampler, involving the separation of coarser dusts in a horizontal elutriator, which was re-equipped for the purpose of continuous logging of the discharge current generated by the respirable dust.

Comparative measurements were carried out at the various work places with the filter-type samplers GRAVIKON VC 25 (Sartorius Company, Göttingen), and MPG-II (Wazau Company, Berlin).

Determination of the presence of harmful substances (free crystalline silicic acid, quartz and toxic components) was carried out using IR and emission spectroscopy, and with an electron beam micro-probe.

For the overall assessment of the results, total dust and respirable dust measurements are available for the following measurement places:

- scrap crusher, control pulpit,
- flue dust loading point,
- ladle lining,
- converter platform,
- electric steel conditioning,
- slag crusher, control pulpit,
- basic slag grinding plant,
- bagging of ground basic slag,
- stripping of hot-metal ladles.

The MAC value for inert respirable dust is not exceeded at any of the work places for very long, even if levels equal to the MAC value are occasionally achieved. High short-term values in excess of the MAC values for inert respirable dust were only recorded in the case of guniting, but respirators supplying fresh air were used during this work.

The highest respirable dust concentrations were measured at the basic slag grinding plant and during the breaking out of hot-metal ladles. The average respirable dust value was  $3.5 \text{ mg/m}^3$  at the basic slag grinding plant and  $2.3 \text{ mg/m}^3$  at the bagging station.

A qualitative examination of dusts collected from various work places showed that the MAC values for toxic dusts had not been exceeded anywhere.

The conclusion drawn from this work on the further development of the existing measuring devices is that for total dust measurements a device with a split energizing swirl tube for linear and logarithmic read-outs is particularly suitable for continuous measurement at work places where severely corrosive dusts are present. Limitations arise when there is high relative atmospheric humidity (flue dusts) and when work involves the processing of refractory materials (frequent reversal of polarity of the discharge current).

Preference was given to a modified MPG-II sampler for continuous respirable dust measurements because of its dust separation characteristics. But not even this device came up to expectations when used in work places where there is frequent reversal of the polarity of the discharge current.

Investigation of the effects on dust particle counts of overlapping particles and of the medium in which the particles are held during counting.

(Instituut voor Gezondheidstechniek TNO, Delft,  
Research Project PS 175)

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Some additional results are given for this research project that were not yet available when booklet EUR 5977 was compiled.

In the first part of the research, laboratory investigations were carried out with the aim of establishing the main factors affecting dust-particle counts, in order to achieve a final harmonization of counting methods.

For the counts an optical microscope, a scanning electron microscope and an image analyser linked with an optical microscope (Quantimet) were used.

The following conclusions may be drawn:

1. With subjective interpretation by the observer overlapping is not demonstrable up to a surface coverage density of 8%.
2. If counts are carried out according to the rules of the National Coal Board, coverage densities should not exceed 2.5%. Higher coverage densities entail a proportionally steeper increase in overlappings than Roach's theory indicates. Perhaps this can be attributed to the fact that the distribution of the particles on the surface of the filter is not, as usually accepted in theory, arbitrary.



In order to be sure of achieving low coverage densities of this type in practice, a rotating dust sampler was developed during the second part of the research work which can be used in fume ducts with a high dust concentration ( $250 \text{ mg/m}^3$ ), high gas flow rates (up to  $20 \text{ m/s}$ ) and a temperature of  $150^\circ\text{C}$ .

With the rotating filter probe (ROFIS) the dust accumulation time on a particular part of the filter can be pre-set to between 0.1 and 17 seconds. In this way it is possible to achieve very low densities of dust accumulation, whilst the higher dust accumulation times on the inner perimeter of the filter, which are four times greater than those on the outer perimeter, make further overlapping investigations possible.

Results of measurements carried out on fume from sinter plants:

1. Assessments of the number of conglomerates per surface unit suggest that approximately 5 to 10% of the particles are still present in the fumes as light agglomerates. If the speed of rotation of the filter is increased a part of these light agglomerates may disintegrate.
2. Clearly there are extreme variations in the "momentary" concentrations of particles in the fumes. They varied between 5 000 and 12 000 particles per  $\text{cm}^3$ . In order to determine the average concentration of particles on the filter, a larger number of filter sites would need to be analysed than was possible under the terms of this study.
3. The numerical distribution of particle-size yielded a figure of 66% of particles smaller than  $1 \mu\text{m}$ , with a standard deviation of 4.6%, rather than the previous figure of 80% below  $1 \mu\text{m}$  given by the plant operators.

Electron microscope investigation of respirable  
iron and steel industry dust  
(Musée d'Histoire Naturelle, Luxembourg,  
Research Project PS 229)

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Because their composition varies widely according to the place of work, the dusts present in the steel industry pose a series of problems for researchers attempting to determine the particle size distribution and composition.

This is particularly true of the respirable dust fraction. Work carried out by the Steinkohlenbergbauverein has shown the great influence that the density of the various dust particles has on particle-size analysis by sedimentation. Research by CEBEDEAU has shown how the particle composition of dusts of below 5  $\mu\text{m}$  can influence the quartz content as measured by X-ray diffraction.

This research project was intended to devise methods, using electron microscopy, to investigate the particle composition of respirable dust of below 5  $\mu\text{m}$  obtained by sedimentation of total dust samples, or from samplers equipped with a pre-separator.

First the electron microscope was equipped with a MICRO-VIDEOMAT image analyser and methods for the analysis of particle size were worked out. Magnifying the particles 8 400 times proved to be the most favourable approach, as it allowed a measuring range of between 0.5 and 5  $\mu\text{m}$  to be covered. Various ways of preparing samples were studied. The best dispersion was obtained with alcohol, although foundry dusts could not be adequately dispersed by alcohol. The contrast necessary for image analysis proved to be sufficient for all iron and steel works dusts.

Further investigations gave the following results:

1. The use of dust samplers with pre-separation of the coarser dusts for representative measurements of dust incidence in the steel industry is problematic.
2. When carrying out particle analysis on steel-work dusts, account must be taken of the differences in the densities of the components, which are of many different types.
3. It follows that these differences also influence the determination of the quartz content by X-ray diffraction.
4. Comparing measurements with and without a pre-separator is difficult, not to say impossible, since different separating methods are used: sometimes cyclone separation and sometimes sedimentation.
5. The measurement technique based on the use of the electron microscope is not yet simple enough for routine use. Nevertheless, it represents a useful aid in the development of sampling methods for respirable dusts.

Remote monitoring of the properties of untreated effluent gas from oxygen steelmaking processes

(British Steel Corporation, London, Research Project PS 254)

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In order to reduce dust emission in steel-works, detailed knowledge of the operating conditions during emission is required. This involves in particular the direct measurement of waste gas flow, composition and temperature.

The aim of the research was to develop suitable direct measurement methods which could replace the difficult and unreliable sampling methods using probes.

The following points should be noted from the results of the research:

1. Gas flow measurements:

The possibility of carrying out 'time of flight' measurements using optical pyrometers was investigated. For this purpose, pyrometers were sited at two points along the waste gas stream and the signals recorded were assessed by cross-correlation analysis. When due account is taken of the measurement parameters worked out during the tests, agreement with conventional flow measurements (with Pitot-static tubes, Venturis etc.) was good.

Waste-gas systems were studied on the following: An AOD-converter, an electric-arc furnace, a 1 - tonne experimental converter and an industrial converter with fume ducts measuring  $4 \times 5 \text{ m}^2$ . It was established that it is advisable to filter out the low-frequency component of the detector signal. The optimum distance between the two pyrometers is equal to the diameter of the fume duct.

2. Waste gas temperature:

Good measurements of the temperature of hot, dust-laden gases can be obtained with radiation pyrometers if the spectral response of the pyrometer is below  $1 \text{ /um}$ .

3. Analysis of waste gases:

An instrument for the measurement of water vapour concentrations in waste gases was developed which operates in the gas flow and therefore does not depend on the collection and processing of samples. It uses infra-red absorption techniques and is designed for water vapour

contents of up to 50% at temperatures below 500°C and a path length of up to 1 120 mm. Tests in the waste-gas duct of an electric-arc furnace gave satisfactory results and showed that it was possible to regulate the spraying of the water into the waste gases in such a way that they were cooled but not saturated.

A similar kind of instrument could be used to determine the CO<sub>2</sub> content. The spectral analysis requirements for such an instrument were investigated.

Monitoring of suspended particulate matter in the vicinity of iron and steel works  
(Laboratoire d'Etude et de Contrôle de l'Environnement Sidérurgique, Maizières-les-Metz, Research Project PS 261)

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Unlike gaseous pollutants, concentrations of particulate matter are particularly difficult to measure at source. This research work is designed to achieve predominantly pragmatic aims: to examine the efficiency of the various instruments at present available on the market for sampling dusts.

First of all, the devices were tested in the laboratory and a series of modifications was made with the aim of improving their reliability. The samplers examined were the following:  
Non-automated samplers : Hexhlet, High Volume Sampler, Turbo-Capteur, Collectron, Gravicon.  
Automated instruments : Saphimo beta ray analyser, Phoenix-Sinclair photometer.

During this phase of research particular attention was given to certain aspects of the measuring technique which are of great importance for this kind of measurement:

1. Beta-ray absorption as a measuring principle was investigated more closely. This method can provide reliable results if the instrument geometry is optimized. Otherwise the chemical composition of the dust can influence the results.
2. Control of the sampler air flow rate is of fundamental importance in all the devices tested. Four separate systems were examined. The Georgin control valve showed good regulating performance.
3. The stability of the filtering media may be affected during measurements by thermal, mechanical and humidity factors. Teflon membranes seem to provide constant results, but every filter material has its advantages and disadvantages. For this reason, it is always indispensable to check the calibration of instruments before they are put into operation, in order to eliminate the possibility of completely disparate results.

In the second phase of research in-plant experiments were carried out on a measuring rig equipped with a specialized meteorological centre.

It was established that trends in dust concentrations measured on the various instruments over a period of time showed some similarity whereas the absolute readings pointed to very considerable differences between the devices. The air flow rate plays an important role in this. It affects the absolute measurement result, as also the disparities in particle size composition.

The long-term reliability of the instruments was also variable and some of them are not recommended for routine operation.

Correlation of results provided by six devices  
for sampling settling dusts or 'dustfall'.  
(University of Liège, Research Project PS 272)

This research project complements and completes research carried out at the University of Liège in the years 1973 and 1974. The aim of this research was to compare the results obtained with four devices for sampling settling dust. As a continuation of this work, the present project was intended to investigate other devices in current use in Western Europe in sites with different characteristics and in strongly diversified climatic conditions.

The research work that has been carried out comprised the following:

- preliminary study of the technical characteristics of the devices : study of sensitivity and precision by blind tests, study of the effect of the period of sample storage on the results;
- main experiments with the following devices:

Bergerhoff dust counter

Hibernia dust counter

ISO dust counter

Owen dust counter

the Liège sphere

Vaseline and silicone-coated plates.

Results :

The investigations showed that the instruments tested were not very accurate and in many cases were not especially sensitive. This poor performance is attributable to the

devices themselves (different design and geometry) and also to the great heterogeneity of the environment in respect of coarser dust particles.

Comparability of the results obtained by these devices was also poor. They all exhibited substantial systematic and random errors.

These negative conclusions do not in any way detract from the value of the information provided by these devices : they are practical, economical, simple to use, require no special knowledge or chemistry and make it possible to monitor major changes in the level of pollution from month to month, provided that the results obtained are not too strictly interpreted.

On the basis of all the experimental findings of this study, the order of preference for the devices tested is as follows:

1. Owen counter
2. ISO counter
3. Hibernia counter.

The Bergerhoff counter is not recommended, (inadequate strength, very poor sensitivity) and neither are the Liège sphere and the dust measuring plates (saturation, rain damage).



Development of a method of analysing measurements of atmospheric pollution in the iron and steel industry

(Laboratoire d'Etude et de Contrôle de l'Environnement Sidérurgique, Maizières-lès-Metz, Research Project PS 231)

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Setting up monitoring networks in and around iron and steel works is generally agreed to be a useful means of tracking down the environmental pollution arising from these plants. But experience has shown that the typically large number of steel industry emissions of varying types and quantities considerably complicates the evaluation of measurement data.

The aim of the research carried out by LECES was, therefore, to upgrade the quality of the information provided by these measurements by improving the mathematical aids and using statistical modelling methods and multi-variate analysis.

In particular, the following evaluation procedures were examined and further developed:

1. Automated cartography:

The surface distribution of data is to be calculated automatically using computer programs. The STAMPEDE and CARTOLAB programs were examined to see whether they were appropriate for this purpose and once some operating parameters had been optimized, both proved to be useable.

2. Processing and synthesis of measurement results: the statistical analysis of measurements provides useful information e.g. for detecting unsuitable sampling points or defective probes. Frequency analysis also makes it possible to determine the effect of several different variables. It is indispensable for the purposes of

comparison with pollution standards. Particular programs were developed to determine correlations with individual emission sources.

3. Overall analysis of multi-dimensional data fields:

Various procedures were examined and further developed in order to assess and structure the totality of the data. The data show both pollution levels at individual sampling sites and meteorological parameters over periods of time. For the purposes of automatic classification and type-analysis, the algorithms DIDAY, SEGMENT and FORTIN proved to be extremely useful. They were successfully applied to examples of monitoring networks and pointed up causal connections between measurement data and emitters and/or weather conditions. Optimization of the networks is also possible.

In the last part of the research, an attempt was made to define strategies for an air pollution alert system. This work, which is closely tied up with the problems of weather forecasting, has led to some encouraging results but may not yet be considered concluded.

Basic planning for measuring the distribution of pollutants in air with a view to assessing the relationships between immission and emission sources.

(Betriebsforschungsinstitut des Vereins  
Deutscher Eisenhüttenleute, Dusseldorf,  
Research Project PS 283)

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In this project, which will shortly be completed, the basic planning of a network to measure the distribution of pollutants in the air is described, with particular reference to emissions specific to steel industry production.

The main emphasis of the research work lies on the following points:

1. Examination of the value and accuracy of the many methods of propagation calculation and the various meteorological parameters by comparing the results with measured data.
2. Development of a method of setting up networks with a minimum number of measuring points, so that the position, radius of action and even overlapping of emission sources can be assessed from the measured immission distribution.

First of all, the mathematical bases of five immission forecasting procedures

1964 Technical Directives for Air

September 1974 draft of German Engineers' Association  
Document 2289

Rhineland Technical Control Board

North-West Refinery Order of May 1975

Royal Netherlands Meteorological Institute

were programmed for a digital computer where necessary, and existing programs were reworked and further developed in order to calculate frequency distributions of pollutant concentrations.

During the further course of the research, emission data from a sinter plant were used and the SO<sub>2</sub> immission was measured using both fixed and mobile sampling stations. Evaluation of the measurement results (emission, immission and meteorological data covering a total of 123 hours) showed that it was very hard to prove the existence of a clear relationship between immission and emission, whether static or dynamic. Only in one case were the direction of the winds and the weather conditions such that it was possible to establish a clear correlation.

An estimation model to calculate the pollutant concentration field is being developed to work out a method of setting up measurement networks with a minimum number of measuring points. In this model the coefficients of the functions similar to the forecast procedure are expressed in terms of variable parameters which can be adapted to the measurements.

To judge by the provisional results of this research work, it would appear difficult to establish a reliable degree of correlation between immission and emitters. Only when all the measurements and calculations have been assessed for the final report can definitive statements be made. This is particularly true of the choice of initial values for the parameters and the choice of initial research aims, which are essential for optimization.

#### Measuring strategy

(TNO, Delft, Research Project PS 300)

Only a brief report will be given on the aims of this research project and the present state of progress, since the results available at the time this report was drawn up were still not conclusive.

The aim of the research is to develop a measuring strategy which will make it possible, using as small a number of concentration measurements as possible, to arrive at estimates of the average levels of pollution caused by solid and gaseous materials and the frequency of maximum concentrations in workplaces in the steel industry. In the last analysis, it is the average level of pollution during overall exposure and the frequency of peak concentrations which determine the health risk at the place of work.

The first investigation target chosen was a central workshop of a large works, and the following data were logged continuously:

- concentration of respirable dusts
- total dust concentration
- ambient temperature
- wind direction and velocity
- power consumption of each electric welding machine
- consumption of material during welding.

One or two of these parameters were measured in various places; at the same time, random sample measurements were also carried out using conventional devices.

A significant proportion of the research carried out concerned the development of adequate and rational data-processing systems. During these experiments approximately 100 000 items of data were collected per week. A system was developed to transfer these data onto magnetic-tape cassettes and then onto storage discs for subsequent computer processing.

The results available would indicate that mathematical models of atmospheric pollution in particular workplaces taking account of the conditions obtaining in those places can provide more accurate and more prompt results than the statistical measuring strategies which have hitherto been employed.

Measurement and analysis of airborne emissions  
from coke ovens with particular reference to  
worker exposure  
(British Steel Corporation, London,  
Research Project PS 285)

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The aim of this research programme was as follows:

- To establish standard methods of sampling and analysis for the routine monitoring of coke ovens.
- To monitor individual exposure levels of coke-oven personnel exposed to atmospheric pollution in several coke oven batteries and to compare the findings with the results of measurements in American coking plants.
- To investigate the efficiency of respiratory protection and air conditioning equipment.
- To provide environmental data for epidemiological studies.

Results:

Sampling and analysis: In order to obtain as representative a set of results for individual exposure as possible, only personal samplers carried by members of the workforce were used. The devices turned out to be easily usable and produced reliable results.

Methods for identifying and quantifying polycyclic aromatic hydrocarbons and benzene-soluble matter (BSM) were tested. Both thin-film and gas chromatography may be used, and particularly good results are produced by high performance liquid chromatography: this method was found to give quick, easily reproducible and reliable results. The sample separation time was reduced to ten minutes with the use of an ultrasonic process.

Monitoring of personal exposure levels: Clear differences were observed between exposure levels at different workplaces on the coke-oven battery. The highest levels of exposure for both dust and BSM are found on the top of the oven battery. Here the average level of dust pollution was close to the threshold limit of  $10 \text{ mg/m}^3$ , whilst the BSM values were distinctly higher than the threshold limit of  $0.2 \text{ mg/m}^3$ : on average, depending on the battery investigated, they were between 4 and 8 times higher. Nevertheless, these values are lower than those that were measured in American studies, where factors of between 5 and 16 times higher were recorded.

Improvements carried out on individual coke oven batteries produced appreciable decreases in occupational pollution levels, for both dust and BSM.

Measurements with static samplers were carried out on various coke-oven machines. In general, they resulted in lower values than those given by the personal samplers carried by operatives.

Efficiency of protective devices: Two topics were studied: the efficiency of personal protection provided by the Airstream respirator helmet, on the one hand, and, on the other hand, the use of air-conditioned refuges. In both cases satisfactory results were obtained. The average protection factor (concentration of pollutant in the air/concentration of pollutant in the protective device) with the Airstream helmet was 3 for dust and 11 for BSM. In the case of the refuge cabins, average protection factors of 6 for dust and 9 for BSM were calculated.

Epidemiology: It was not possible, on the basis of the data collected, to detect a clear relationship between individual occupational exposure and health risks. On the other hand, it was possible to make comparisons between the mortality rate of groups of workers and the average mortality rate of the male population of Great Britain.

The incidence of lung cancer was found to be approximately the same as that to be expected for the population working in industry as a whole. Comparison with the figures produced by the American study showed that the incidence of lung cancer observed in England was distinctly smaller.

Model tests with novel ventilation systems for  
coke-oven sheds  
(Bergbau-Forschung GmbH, Essen, Research  
Project PS 305)

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The aim of this research project is to provide guidelines for the planning and operation of coke-oven sheds which will guarantee optimum conditions for environmental protection, operational safety, occupational safety, protection against corrosion, energy consumption and running costs.

Research work was of two types, involving both model tests to determine the most favourable air-flow profiles throughout the area of the model shed and measurements of ambient fume concentrations in coke-oven batteries during operation.

The tests on the model battery shed showed that even the slightest cross-wind forces the fume over the oven top and out of the front of the battery shed. In the vicinity of the quenching track shed a cross-wind with a speed of more than 1 m/s has a negative effect on fume extraction. If the number of bulkheads in the quenching track shed is doubled the effect of the cross-wind is only noticeable at approximately 1.4 m/s.



The aim of this basic development work on the shed model was to collect for the first time all the emissions formed during coke-oven operation. The model was designed to enclose a battery 40 ovens 4 m high, 12 m long and 450 mm wide.

The experiments showed that the most fundamental factor was the construction of properly functioning fume deflectors to direct the air flows in the three main areas: the space above the quenching cars, the space above the coke guide and the space above the oven top. The free cross-sections of these three areas must be optimally adapted to each other.

By means of various reconstructions of the model a significant improvement in the flow relationship was achieved.

A further area of research was the development of usable sampling systems for the measurement during coke-oven operation of emissions from leaky service openings, such as coke-oven doors, stand pipes and charging holes. After one or two failures, a device for taking samples of emissions in the area of the coke-oven door was developed which gave good results. It consists of a flexible aluminium foil which is attached to buckstays in front of the coke-oven door. Initial measurements of leakage from coke-oven doors showed that emissions varied widely depending on the coking time, so that it is not yet possible to give a clear picture of fume collection quantities.

Development of novel seals for coke-oven doors  
(Bergbauforschung GmbH, Essen, Research  
Project PS 318)

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The aim of this research project is to examine novel seals for coke-oven doors which make it possible to eliminate more or less severe leakage emissions. The research project is being carried out on a battery with 48 7 m ovens.

First of all, several new developments for sealing coke-oven doors were examined in collaboration with four manufacturing firms. The discussions drew partly on research findings which had been obtained from a previous research project carried out by Bergbauforschung GmbH on 6 m coke ovens.

Four different door designs with novel seals were developed; practical testing of them on ten coke-ovens was begun in 1980.

Apart from the actual construction of the door, the shape and the material of the refractory lining of the body of the door have a decisive influence upon leakage from oven doors. Consequently, specially shaped, ready-made plugs of a quartz material will be tested first, in combination with membrane seals on large-scale ovens. Quartz blocks, because of their very limited expansion under the effect of heat, are not sensitive to sudden changes of temperature and are resistant to caking even when they have been in use a long time.

Research into possibilities of improving working conditions in the firing shop of the pelletizing plant at Hoogovens IJmuiden B.V. by studying the dispersion of air pollution in the plant under the influence of the air currents prevailing in the area

(TNO, Delft, Research Project PS 248)

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In the pelletizing plant a mixture of ore concentrates and fine ore is processed to produce pellets ( $\varnothing$  approx.12 mm). In the firing shop the wet pellets from the pellet-shaping plant are dried, pre-heated, fired and finally cooled with air. The atmospheric pollution arising from operations of this sort is propagated by the intense heat generated and the resulting air currents, both inside and outside the shop.

In order to follow the course of events throughout the workshop, the following measurements were taken at approximately 200 measuring points:

- air speed (direction and absolute value)
- temperature
- dust concentration
- fluoride concentration.

The results were as follows:

The pattern of air currents is determined primarily by the emission of heat from the firing plant. This heat emission causes upward convection above the firing unit. The supply of air through the slats on the side-walls is influenced by the wind, but the overall ventilation flow-rate is only affected by wind speeds of more than 4m/s. With lower wind speeds, the air is exchanged approximately 23 to 25 times per hour.

The highest air temperatures were found above the firing unit

in the convection currents. The lowest, on the other hand, were measured in the slats in the side walls, where the air flows in from the outside.

The highest dust concentrations were found in the screening zone and at the beginning and the end of the firing unit, where the pellets are loaded on to and off the grate.

Fluorides are given off at the input end of the firing unit; the highest concentrations were found in this area. From the input end of the firing unit to the discharge end the concentrations gradually decreased.

The study showed that nowhere in the shop is pollution so bad that urgent improvements are needed. Both the dust and fluoride concentrations are well below the MAC values. Nevertheless, these concentrations could probably be even further reduced in some places. To this end, the following measures should be considered:

1. The gap between the pellets on the firing grate and the front side of the wall of the firing unit could be almost completely closed off.
2. The side walls of the firing unit could be even more completely sealed at the level of the wheels. More sealing plates could be fitted along the sides of the firing unit.
3. The vibrating drains in the screening unit could be better enclosed.

Abatement of sulphur dioxide emissions from iron-ore sinter plants into the environment by reducing the amount of solid fuel in the sinter mix

(Centre de Recherches Métallurgiques, Liège, Research Project PS 257)

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The SO<sub>2</sub> in the waste gases from sinter plants derives mainly from the solid fuels used for the sintering of iron ores. Waste gas cleaning systems designed to eliminate SO<sub>2</sub> from the gases are now being developed and the results so far seem promising. It is, however, already clear that these processes will involve high investment costs.

For this reason the present aim is to reduce SO<sub>2</sub> emissions directly at source. This was the object of the present research project, which was concerned with reducing the proportion of solid fuels, the sulphur content of which is generally rather high (1.0 to 1.5% in coke breeze), and to replace it with low-sulphur or even sulphur-free gas fuels.

The most promising solution seemed to be to preheat the sinter mix before firing; the sinter mix was preheated by means of low-sulphur or sulphur-free waste gases, whose oxygen potential and temperature were regulated so that the quantity of solid fuel burned during pre-heating is minimal and the softening point of the sinter mix is not exceeded.

A series of preliminary tests was carried out in an experimental sintering pan, and it emerged that a temperature of 800°C was appropriate for the process.

Experimental production runs using a new experimental sintering rig with a pre-heater independent of the ignition unit were subsequently carried out with various ore mixtures.

Minette-based mix:

Given the same mechanical resistance, the pre-heating process saves approximately 50% of the solid fuels. The sulphur content of the waste gases declines from approx. 1.0 to 0.7 g/t sinter and the SO<sub>2</sub> content in the waste gases falls from 1.1 to approx. 0.6 g/Nm<sup>3</sup>.

On the other hand, although the sintering rate was increased by approximately 10%, the length of the pre-heating process did lead to a reduction in production. However, perforation of the mix before heating made it possible to bring production to a level which was virtually the same as the reference value.

These experiments were carried out using natural gas. Further experiments using blast-furnace gas resulted in a speeding-up of the sintering process. Pre-heating with fumes which do not contain steam is more satisfactory.

Haematite-based mixes:

Two different ore mixtures were tested. In both cases the proportion of solid fuels was reduced by 25%. Given the same sinter strength, the sulphur content of the waste gases fell from 0.6 to 0.3 - 0.4 g/tonne of sinter and the SO<sub>2</sub> content of the waste gases fell from 0.8 to 0.3 - 0.5 g/Nm<sup>3</sup>.

Continuous measurements of the SO<sub>2</sub> content in the waste gases during the sintering process yielded other interesting results: SO<sub>2</sub> is only given off for some 30 - 40% of the total sintering time, and principally in that zone where there is a rapid rise in the waste gas temperature. This discovery may be of interest for the design of waste gas desulphurizing plants, which could possibly be operated with a smaller

quantity of waste gases.

Investigation and control of the emissions of gaseous acid pollutants by iron-ore sinter plants and their effect on the environment (Laboratoire d'Etude et de Contrôle de l'Environnement Sidérurgique, Maizières-lès-Metz, Research Project PS 297)

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This research falls into two clearly distinct stages:

- the development and testing of a multi-stage monitoring system for acidic, gaseous pollutants to be used in a sinter plant, and
- continuous monitoring of the waste gases in order to obtain a better understanding of the cause of their emission and thereby to develop measures to reduce the quantity of gaseous pollutants.

The first part has been largely completed: a device designed to extract and dilute the fumes emitted was developed. Fume is aspirated using a diaphragm pump ( $2 \text{ m}^3/\text{h}$ ), filtered in a stainless steel frit filter and subsequently diluted (1/20 to 1/1000). They can then be transported at ambient temperatures along a Teflon duct. The analysis of the  $\text{SO}_2$  and the  $\text{NO}_x$  is carried out continuously by automatic measuring devices.

The multi-stage continuous measuring system was successfully used in two cases:

- continuous measurement in the wind boxes of an ore sinter plant,
- continuous gas analysis during the sintering process in an experimental sinter pan.

The first results of these measurements have already produced some interesting data:

The SO<sub>2</sub> content measured in a wind box at the beginning of the sintering strand varied between 21 and 148 ppm. In contrast, contents of 258 to 1 020 ppm of SO<sub>2</sub> were identified in a wind box in the region of the burn-through point. The NO<sub>x</sub> contents did not appear to be in any way dependent on the sampling point over the length of the sintering strand. They were between 30 and 310 ppm NO<sub>x</sub>. Naturally the type of fuel used, as well as the operating parameters of the sinter plant, must be taken into account in assessing these measurements in order to arrive at further conclusions.

In the case of the measurements carried out on the experimental sinter pan, a special drying process was developed for the aspirated gas sample. Initial measurements show a significant rise in the SO<sub>2</sub> content shortly before burn-through. The NO and NO<sub>2</sub> contents did not change markedly in the course of the sintering process.

Purification of toxic fumes produced during  
slag granulation  
(Centre Belge d'Etude et de Documentation des  
Eaux, Liège, Research Project PS 237)

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This research, which was mentioned in report No EUR 5977, has now been completed. Its aim was to develop processes to reduce the levels of gaseous pollutants produced during the granulation process.



For this purpose, fundamental research on the origin of the pollutants was carried out:

- in situ study of the nature and composition of gaseous emissions during slag granulation
- theoretical study and laboratory tests on the reactions between slag and water
- research into treatment of emissions.

It was established that with the reactions which occur,  $H_2S$  and  $SO_2$  emission is essentially dependent on the presence of oxygen (air) in the reaction zone and that the lower the temperature of the slag before quenching, the greater the reduction in the quantities of sulphur compounds.

In the vapours formed during granulation the concentrations of  $H_2S$  (approx. 180 ppm) are approximately 3 to 4 times higher than the concentration of  $SO_2$  (approx. 50 ppm). Fluorine compounds are present in far smaller concentrations than the sulphur compounds (approx. 2 ppm); the proportion of cyanide compounds is even lower (approx. 0.5 ppm).

In order to reduce the quantities of gaseous pollutants, the experiments suggested a number of possible developments promising some degree of success on condition that they can be adapted to the special features of the slag granulation process. There are two main ways of reducing sulphur emissions: neutralizing the  $H_2S$  as soon as it is formed or retarding the formation of  $H_2S$ .

The first method consists of neutralizing the  $SO_2$  with a sufficient quantity of basic quenching fluid. Large amounts of soda must be used for this process, and it requires a quenching system in a closed circuit. The soda consumption is estimated at 1 kg of soda per tonne of granulated slag, using  $9\text{ m}^3$  of water per tonne of granulated slag.

The second method entails the use of mechanical means to improve the contact between slag and air and aims at minimum water consumption at the lowest possible slag temperature. The liquid slag is converted into a foam and ejected into the surrounding air using rotating baffle drums. Not only are pollutant emissions reduced, but the product resulting from this process possesses good hydraulic and thermal characteristics.

Plants of this kind have been installed recently in French and Luxembourg steelworks.

Elimination of fumes emitted during desulphurization of pig-iron in the ladle which constitute a hazard to workers and the immediate environment.

(Centre de Recherches Métallurgiques, Liège, Research Project PS 256)

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The desulphurization of pig-iron between blast furnace and converter is carried out in a large number of European steel works by adding powdered soda ash when the pig-iron is poured into the transfer ladle. The subsequent reactions generate large quantities of fume, which are all the greater the higher the temperature of the pig-iron and the greater the quantity of soda added.

These fumes contain sodium compounds in quantities of approximately 5 to 8 g/Nm<sup>3</sup> and constitute an unpleasant form of pollution for the operatives. Other desulphurization products have been proposed and are to some extent in use. In general they are more expensive without having any less unpleasant effects on the environment.

In order to reduce fume generation during desulphurization with soda, the following aims were pursued in this research programme:

- to reduce the generation of soda fumes
- to improve the efficiency of the desulphurization process
- to collect and extract the desulphurization fumes.

As a solution to the first two problems, the incorporation of selected additives in the soda and changes in standard operating practice were investigated.

First of all, tests were carried out in a pilot plant; subsequently industrial tests were conducted in three different Belgian and Luxembourg steel works. The results may be summarized as follows:

1. Adding other substances to the soda, such as pitch, hydrocarbon polymers, NaOH etc. did not improve either the release of fumes involved in its use or its desulphurizing capability.
2. The use of soda briquettes and the lengthening of the reaction time (slow pouring of the pig-iron into the ladle) led to a substantial decrease in fume formation and improved desulphurizing. The fume emission is decreased by a third, thereby improving working conditions substantially.

The research on the collection of desulphurizing fume revealed that problems arose from the momentarily very high quantity of fume and the high temperatures; during the desulphurization process a great deal of heat is generated

through combustion of CO and results in temperatures of up to 900°C in the waste gases, even when there is a great excess of air. Research indicated that the most important parameters influencing the design of a fume extraction plant were the pig-iron pouring speed and the regulation of soda addition.

Development of plant for the removal of dust-laden waste gases arising during blast furnace tapping  
(Verein Deutscher Eisenhüttenleute, Düsseldorf, Research Project PS 238)

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This research work will not be concluded until 1981. For this reason only a short report will be given on the aims of the research project and the present state of progress.

Environmental factors such as dust, gases, vapours, sparking, heat radiation and draughts represent significant sources of annoyance and discomfort for the operatives working at the blast furnace. At the more modern large-scale blast furnaces, pig-iron is tapped from more than one tap hole and the number of tappings can be as high as 16 per day and per furnace.

As furnace tapping is accompanied by copious fume emission and intense heat generation, it seems desirable to collect the dust-laden waste gases at source and to remove them from the environment. The aims of the project were, accordingly, as follows:

- measuring dust and gas emission and correlating it with various factors at the following sources: furnace tap-hole, pig-iron and slag runners, pig-iron and slag ladle platform. The measurements are being carried out in several plants.

- calculation of generally valid characteristic values and criteria for the design of waste-gas extraction plants.
- trials using a pilot plant.

So far measurements of gas flow and volume and dust contents have been carried out during pig-iron pouring into the ladle and during tapping of a blast furnace with a hearth diameter of 4.5 metres.

Analysis of these figures shows a correlation between the specific quantity of dust per metre of runner length and both the mass flow of pig-iron and the ratio of sulphur to manganese (S/Mn). Theoretical calculations using mathematical models produced generally valid characteristic values which may be used in designing waste-gas extraction systems.

Development of technically and economically optimum processors for ventilation and dust extraction in steel-works shops  
(Betriebsforschungsinstitut des Vereins  
Deutscher Eisenhüttenleute, Düsseldorf,  
Research Project PS 224)

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This project has already been reported on in EUR 5977 (June 1977). Since then the research work has been completed.

The aim of this work was to produce technically and economically optimum solutions to the problem of direct and secondary fume extraction in steel-works shops which could be installed in new buildings and in old buildings undergoing conversion. The investigations were mainly concentrated on electric melting shops, because these pose particularly difficult problems of ventilation and pollutant propagation.

The traditional process of direct extraction from the furnace through a fourth hole in the furnace roof is satisfactory for collecting most of the dust arising during electric arc melting - that is to say, during the melt-down and oxygen refining stages. But the dust produced during charging, tapping and also, to some extent, refining, can not be collected properly by this method. The main emphasis of the in-plant investigations was therefore placed upon measuring emissions arising during charging and tapping; these are of great importance for the design of roof-hood extraction systems.

The research comprised the following subdivisions:

- in-plant studies and measurements in electric melting shops (roof-hoods, air-curtain pilot plants to collect tapping fumes)
- tests in the laboratory and on models (roof-hood shapes, permeability to gas of various filter media, hot-model test-rigs)
- design studies for fume collection in existing and future electric melting shops (roof-hood extraction, localized fume collection systems, furnace enclosure, capital and running costs).

These extensive studies yielded the following results of practical importance:

1. By means of studies carried out on air-flow models, a system of roof-hoods in three sections was developed. Separate sections were used for tapping or charging. Depending on the height of the shed, an extraction rate of 300 000 to 800 000 m<sup>3</sup>/h, corresponding to 6 - 14 times the quantities of fume produced, is necessary. The side panels and the inside dividing plates of the roof-hoods

should be set at an angle of 45 degrees, or more, and the lower perimeter should be flanged towards the centre of the hood. As a guide-line for the hood entry area, ten to twelve degrees can be taken as half the angle of propagation over the perimeter of the emission source.

2. A diminution of the extraction rates to about 50% with equal efficiency is only possible if the electric furnace is enclosed. Various designs for enclosures of this kind combined with secondary fume extraction were investigated. Thus, for example, the overall extraction rates required can be reduced to between 3 500 and 4 000 m<sup>3</sup>/h per tonne of crude steel for two 100-tonne furnaces working in tandem if they are operated in an enclosed section of the shop. With a specially designed system for secondary fume extraction above the ladle, the specific extraction volume can be reduced even further.
3. On the basis of measurements carried out during normal running, it was established that during tapping a maximum of between 1 000 and 1 200 m<sup>3</sup>/h of fume per tonne of crude steel are given off above the ladle. These quantities are within the extraction capacity of a direct extraction system. As an alternative to collecting hoods located above the ladle, a pilot air-curtain plant was constructed and tested in industrial trials. After optimizing the operating conditions, an average collection efficiency of 54% was achieved with an extraction capacity of 100 000 m<sup>3</sup>/h. Theoretical considerations, and calculations on the basis of test results, suggest that, depending on the size of the furnace and the ladle, the tapping time and the quality of the steel, an extraction capacity of 150 000 m<sup>3</sup>/h is necessary to achieve a satisfactory degree of fume collection of more than 80%.

Combustion-free collection of the smoke  
emitted by electric-arc furnaces and prospects  
for separating the dust thus collected  
(IRSID, Maizières-lès-Metz, Research Project  
PS 290)

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This project has not been completed; consequently this report will only give a brief account of the aims of the research and the work done so far.

The dust and gas emission of UHP electric arc furnaces with a high oxygen blowing rate is becoming increasingly similar to that of oxygen convertors. This suggests that the well known and successful technique of combustion-free fume collection used on oxygen convertors could also be adapted to electric arc furnaces. The advantages of this process are the significantly smaller quantity of waste gases and the efficient removal of dust and also, perhaps, in the possibility of recovering the energy contained in the waste gases. During an initial series of tests, the volume, temperature, composition and dust-content of electric arc fume were investigated. The measurements were carried out on a 6-tonne experimental oven and on a 70-tonne furnace, both with oxygen lance operation and with oxygen gas burners.

One central finding of these initial tests was that the H<sub>2</sub> and CO contents during melting are relatively high (25 to 40% H<sub>2</sub>, 35 - 45% CO), and as a result the originally planned process had to be abandoned and the pilot plant was designed, for safety reasons, on the following lines:

- fume collection through a fourth hole in the roof with appropriate sealing of the electrode entry points,



- subsequent stoichiometric combustion of the gases by pilot burners in a combustion chamber
- cooling to 600 - 800°C followed by wet de-dusting.

A process of this kind has a technical advantage over the current industrial practice, in that the volumes of waste gases to be treated are approximately 4 - 5 times smaller, which means that cheap and efficient de-dusting is possible.

Study of catching gaseous and particulate pollutants by bag filtration. Application to electric steel plants.

Extension to other steel plant shops.

(Laboratoire d'Etude et de Contrôle de l'Environnement Sidérurgique, Maizières-lès-Metz, Research Project PS 298)

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Apart from their good dust removal characteristics, bag filters have the advantage of being able to remove gaseous compounds that react with the dust coating on the filter materials. Hitherto, bag filters have been used primarily in electric arc melting shops, and the operational parameters and dust collection efficiency achieved are well known. Nevertheless, little is so far known regarding the efficiency of modern bag filters in respect of certain gaseous and particulate pollutants which are very harmful to the environment.

The aim of this research project is to investigate the filtering capacity of bag filters in two quite specific cases in electric melting shops:

- collection of gaseous emissions of fluorine compounds on the filtering material. Gases of this kind arise when fluorspar is used in steel production;

- collection of very fine dusts from metal compounds (ZnO  $\text{MoO}_3$  etc.), which arise during the oxidation of metallic vapours at high temperatures.

For this purpose a series of laboratory experiments was first of all carried out; they revealed a high degree of hydrofluoric acid removal by the steel-works dust caught on the cloth filters.

Next, a large pilot plant was erected which is being operated in parallel with an industrial de-dusting system at the Breuil electric melting shop (Creusot/Loire). The pilot plant is connected to the fourth hole in the furnace roof of a 60-tonne furnace and has a total filtering surface area of  $65\text{m}^2$ . The high efficiency filter system used consists of 48 'outside' bag filters with a diameter of 0.18 metres and a height of 2.4 metres. The volume treated can be adjusted to between 4 000 and 12 000  $\text{m}^3/\text{h}$ .

At the present stage of research, information is already available regarding the most efficient filter material and the collection of fluorine compounds and metallic oxides:

Optimum filtering efficiency is obtained using polyester filters with a porosity of  $1\ 000\ \text{m}^3/\text{h}/\text{m}^2$  at 20 mm WG and having a weight of 500 to 550  $\text{g}/\text{m}^2$ . They were monitored over a period of fifteen months and proved to be exceptionally durable. Extra-large, high efficiency filter plants are economical in terms of energy consumption and are less subject to breakdowns.

In the case of particulate fluorine compounds, an exceptional average removal efficiency of 99% was observed, i.e. equal to that observed for other dusts. Hydrofluoric acid fumes, on the other hand, were only filtered out to the extent of 50%. Further tests are planned.

The collection of heavy metal oxides was initially only

investigated in respect of molybdenum oxide. The filter system removes 99.8% of these dusts from the collected fume and may therefore be said to be exceptionally efficient. Emissions into the environment are thus mainly dependent on the collection efficiency of the fume extraction plant. The form in which the molybdenum is added (ferro-molybdenum pieces, oxide in powder form, etc.) and the shop's metal output play a role here. Optimizing fume extraction by modifying the shapes of the hoods and by direct extraction through the fourth hole in the furnace roof may produce significant improvements.

Improved fume control from electric arc furnaces  
(GKN Rolled and Bright Steel Limited, Cardiff,  
Research Project PS 302)

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The research work is still only in its early stages, so that at the moment only a brief report can be given on the project.

The aim of the research is to achieve an efficient and, at the same time, cheap method of cleaning fume in electric arc melting shops where two or more furnaces are in operation at the same time.

When the primary and secondary extraction systems are used in combination, as is often the case in connection with dry filter systems, relatively high extraction volumes are possible, usually designed for the brief period of maximum emission during charging and tapping. For 100-tonne furnaces, fan capacities of up to 750 000 m<sup>3</sup>/h are normal in the United Kingdom.

The fume cleaning plant in use at GKN's TREMORFA steel works

has provisions for running the extractor fans at full or half speed, and also for using the separate extraction systems of the two 100-tonne furnaces in conjunction with each other.

This means it is possible to obtain optimum performance using both systems in combined operation. For this purpose extensive dust measurements were carried out; sampling stations with the necessary probes were located in the ducting from the furnaces and hoods and at the intake and exit of the gas cleaning plant.

It is expected that the planned optimization will also yield information on the design of new combined systems for multi-furnace operation, which may lead, with lower ventilated performances, to more efficient fume cleaning at lower fan speeds and with lower levels of noise.

Optimum control of dust removal from waste  
gases in electric steel plants  
(Betriebsforschungsinstitut des Vereins  
Deutscher Eisenhüttenleute, Düsseldorf,  
Research Project PS 309)

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The purpose of this research project is to investigate the various options for fume collection and cleaning in electric arc melting shops employing several arc furnaces and adaptation to steelmaking operations at minimal running costs.

More and more electric-arc furnaces are being equipped with a secondary extraction system - e.g. by means of roof hoods - in addition to direct extraction through the fourth hole in the furnace roof to collect dust-laden fumes generated during charging, tapping, refining and fettling. In these systems

the fumes from various sources are usually brought together and cleaned in a single filter.

In a multi-furnace shop the extraction performance of fans and the filter areas of the dust removal plant cannot, for economic reasons, be designed to cope with the maximum fume emission levels but only for the average levels. In view of the limitations this imposes, and various problems linked with the difficulty of controlling and regulating direct extraction systems, the high energy consumption and the difficulty of adapting them to varying fume volume-flows, one is bound to wonder whether, and in what circumstances, an approach based on combining the direct and secondary extraction flows is justified and under what conditions separation of the two systems provides the better solution.

The work programme for this research topic can be summarized as follows:

- collection of the varying fume flows during multi-furnace operation through interconnected direct and roof hood extraction
- measurement of temperatures and dust contents
- measurement of pressure drop in the ducting and in the filter aggregates
- study of various filter media and testing of different cleaning systems
- transfer of filter plant control to an electric-arc furnace process-control computer
- optimization of fume volume control and fan regulation.

During this research work, which is expected to be completed by the end of 1980, considerable use was made of the findings

of research on individual furnaces in ECSC project PS 224 mentioned above.

The following results are at present available:

1. On a BFI hot-model test rig further tests were carried out to determine the effect of temperature and velocity on the angle of propagation of hot rising fumes. It was found that the angle of propagation is scarcely affected by the temperature, but mainly by the flow velocity. As the rate at which the gases rise increases, a total angle of propagation of approximately  $15^{\circ}$  is achieved. This figure was confirmed during industrial tests; hitherto almost twice as large an angle of propagation had been assumed in the design of roof hoods.
2. Comparative tests on 38 filter fabrics, and subsequent measurement on large-scale filter plants with filter bags made of eight of these materials, showed that the clean gas tests in accordance with the DIN standards gives no proper indication of operational performance. The pressure drop in a filter medium is not primarily dependent on the fabric used, but rather on the structure of the filter cake and the filter cleaning arrangements.
3. In a melting shop with three electric-arc furnaces, industrial measurements were made to establish volume flows, dust quantities and fume temperatures during several heats over certain periods of time. By simultaneous monitoring of the direct extraction system and the roof hood, the mutual influence of the volume flows was observed. Analysis of the data obtained showed that further measurements would have to be carried out to control the volume flows. To this end additional sampling points for the direct extraction system are being installed in the fume offtake elbow.

Fluorine precipitation in dry dust-extraction  
processes in carbon monoxide waste gases from  
steel production

(Krupp Forschungsinstitut, Essen, Research  
Project PS 180)

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Depending on the operating conditions, plant and metallurgical objectives, the addition of fluorspar may be necessary during steel making by the basic-oxygen process. The resulting emissions require adequate waste-gas cleaning plants.

The results of previous research work have shown that there is no environmental pollution by gaseous fluorine compounds when fume is treated by the wet dedusting plants that are most commonly used in basic-oxygen steel-making plants. Industrial measurements of fume cleaned in a wet dedusting plant working on the Venturi principle in a basic steel making plant, revealed fluorine concentrations in the clean gas of between 0.5 and 1.5 mg/Nm<sup>3</sup> were measured. The quantities of fluorspar added were between 4 and 5 kg per tonne of crude steel.

But for dry dedusting processes, emission levels of gaseous pollutants such as hydrogen fluoride are less well-known. Tests suggest that it may be possible to fix these compounds thanks to the high dust content of the waste gases, so that only small quantities of gaseous fluorine compounds are emitted.

Consequently, the aim of this research was, on the one hand, to investigate the emission of gaseous fluorine compounds as a function of operating conditions during the basic-oxygen process and, on the other hand, to determine the extent of fluorine precipitation in dry dedusting plant.

To this end, a continuous measuring process was first developed to log levels of gaseous fluorine compounds throughout the basic oxygen process. The waste-gas system of a 3-tonne experimental converter was used for the subsequent tests. The main flow of gases, which went to a wet dedusting plant, was connected via a bypass to a dry electric dust filter.

It was noted that, depending on the type of lime additive, there was a considerable increase in the emission of gaseous fluorine compounds coinciding with the usual sudden jump in decarbonization in the first third of the blowing phase, which subsequently subsided again.

With the addition of a considerable quantity of fine-grained soft-burnt lime - injected into the oxygen stream - at the beginning of the melt, fluorine emission can be greatly reduced. If lump lime is used, greater emission of gaseous fluorine compounds must be expected than with soft-burnt lime. The maximum level of emission is raised considerably if the proportion of hydrate in the lime additive is increased.

The investigations into the precipitation of fluorine in the dry dust extraction plants showed that approximately 70% of the fluorine emissions were trapped by fixing on the converter dust. Rising proportions of CaO in the dust further reduced the emission of gaseous fluorine compounds. As the CO content of the fume rises the receptivity of the converter dust for fluorine diminishes.



Investigation into particle size in brown smoke  
and factors influencing it

(Max-Planck Institut für Eisenforschung GmbH,  
Düsseldorf, Research Project PS 311)

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Oxygen blowing forms part of various processes by which pig-iron is made into steel. A common feature of all these processes is that large quantities of extremely fine-grained brown fume result, which have to be eliminated in de-dusting plants.

The aim of this research project is to investigate the way the fume is produced and to use this information to improve further the efficiency of dust extraction plants.

The laboratory tests were carried out using a levitation melting plant. In this process a steel sample is held in suspension solely by means of a high-frequency alternating electromagnetic field and is heated by induction. This permits a pure smelt, free from contact with the crucible material, and sample temperatures of up to 2 400°C may be reached.

Hitherto, mixtures of Co, CO<sub>2</sub> and O<sub>2</sub> have been mainly used as reaction gases, as is most common in practice. In order to establish the basic factors affecting the reactions, such as temperature and flow-rate, helium, nitrogen and mixtures of helium and oxygen were also used.

Particle-size analysis posed certain measurement problems, since the fume particles are of sub-microscopic size (approximately 10 to 500 nm); an electron microscope was used.

Results so far:

- The temperature of the sample is of great importance. As the temperature rises, the fume becomes coarser; the quantity of fume increases exponentially.
- As the gas flow volume increases, the size of the fume particles diminishes. The fume volume increases as the flow-rate increases.
- Particle size is higher in the case of pure iron samples than in the case of iron containing 4.5% carbon.
- As the CO<sub>2</sub> content rises, the fume volume increases.

Planned experiments:

- The influence of various kinds of gas on fume volume quantity and particle size
- Dependence of particle size and fume volume on alloying elements, compared with experiments on pure iron. Influence of the carbon content.

Study of a purification plant and of associated problems with the aim of perfecting its efficiency

(Italimpianti, Genoa, Research Project PS 276)

In this research project, a physical-mathematical model for the optimum design of an extraction hood for an LD converter was developed.

The model entails calculation of an overall energy balance in connection with the geometry of the hood. Input data include the gas volume, concentrations of solid matter, cooling water volumes, converter capacity, the air factor, fume temperature on leaving the hood etc. The computer program provides

design data for the size and shape of the extraction hood.

For optimization of the whole extraction system, it would, of course, be necessary for the program to include mathematical models for the Venturi scrubbers and for subsidiary plant.

Measurements carried out on existing plants provided information on the composition and behaviour of the particulate matter entrained by the gas.

Dust extraction from waste gases in open-hearth furnaces working with high scrap ratios  
(Edelstahlwerk Witten AG, Witten, Research  
Project PS 242)

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A report has already been published on the aims and the partial results of this research project, which was completed at the end of 1977, and this report appeared in booklet EUR 5977. For this reason, only a few points need to be added which have emerged from the final report.

For cleaning of the waste gases, the electrofilter process was used during this research work. The open-hearth furnaces, which were combined with waste-heat boilers, were equipped with an electrofilter by means of a common bus arrangement. It turned out that the 'dry' operating method developed after thorough tests gave optimum dust removal when operating between 350 and 400°C without gas conditioning. The official emission limit of 150 mg/m<sup>3</sup> was not exceeded. Of course, in the case of filter plants of this kind, operating at temperatures in the 300 to 400°C range, insulators with very high insulation values must be used.

In addition, various parameters affecting the efficiency of the filter were investigated:

When the plant is operating in the dry mode the degree of dust removal rises as the fume temperature rises. In the partly conditioned mode (high pressure water sprays) the reverse is true, and filter temperatures of 250°C should be observed.

Another important factor is the power input; it may be optimized for a particular degree of separation, in connection with the selected mode of operation. The most favourable power consumption is obtained with the dry mode of operation. Here a value of 0.2 kWh/1000 m<sup>3</sup> seems reasonably economic.

Study of the real composition of fluorinated substances emitted into the air from iron and steel works, for the purpose of devising a means of converting toxic fluorinated compounds into less harmful substances

(Centre Belge d'Etude et de Documentation des Eaux, Liège, Research Project PS 238)

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The work carried out in the course of this project has made it possible to determine the chemical and physical properties and, in certain cases, the exact nature, of the fluorinated compounds emitted in electric arc melting shops, oxygen-process steelworks, and sinter plants.

When alloy steels are produced in an electric-arc furnace using fluorspar, the fluorinated compound discharged into the atmosphere consists mainly of CaF<sub>2</sub>, as a solid, insoluble fluoride, for which the environmental pollution standards are less strict.

Almost all the fluorine emitted in spray form during ingot

casting of rimming steel (powdered mould additions with a high  $\text{CaF}_2$  and  $\text{Na}_2\text{CO}_3$  content) is in the form of  $\text{NaF}$ , a solid soluble fluoride. These fumes, which are rich in 'solid fluorine' (approximately 25% F in the dust), contain very little gaseous fluorine (less than 0.5% of the total F content).

The fluorinated compounds emitted during the sintering of high-phosphorus ore are essentially  $\text{HF}$  and  $\text{SiF}_4$ , gaseous, soluble fluorides, but it has proved impossible to determine the proportions in which these substances are present. Gaseous fluorine accounts for at least 90% of the total fluorine emitted when the dedusting system is of the dry type, and ensures that dust-emission does not exceed  $150 \text{ mg/m}^3$ .

During this research work, the sampling methods and analysis techniques necessary for the tests were also further developed.

Investigation of physical-chemical transport processes in the emission of fluorine-containing gases from liquid slags and solid phases, with a view to finding possible ways to reduce fluorine contamination of the environment  
(Max-Planck-Institut für Eisenforschung GmbH,  
Düsseldorf, Research Project PS 255)

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The development of the electroslag refining process (ESR) in recent years has led metallurgists to devote more and more attention to slags whose main component is calcium fluoride. Although the physical and chemical properties of these slags make them particularly suitable for ESR, fluorine volatilization can pollute the environment with noxious and toxic fluorine compounds.

In order to understand what happens when fluorine-containing compounds from fluorspar slags are volatilized, the measurements outlined below were taken.

Using the entrainment method, the vapour pressure of pure  $\text{CaF}_2$  was measured in the relevant range for pyrometallurgy of 1 500 to 1 600°C, and the equation of the vapour pressure curve and thermodynamic data for  $\text{CaF}_2$  were calculated.

The  $\text{CaF}_2$  vapour pressure is greatly reduced by  $\text{CaO}$ .  $\text{Al}_2\text{O}_3$  added to pure  $\text{CaF}_2$  reacts to form gaseous aluminium fluoride ( $\text{AlF}_3$ ).  $\text{CaO}$  addition greatly inhibits the formation of  $\text{AlF}_3$ . In addition, the reactions of the oxides  $\text{TiO}_2$ ,  $\text{MgO}$  and  $\text{SiO}_2$  with liquid  $\text{CaF}_2$  were examined thermogravimetrically. The addition of  $\text{TiO}_2$  to  $\text{CaF}_2$  greatly reduces the weight of the slag by virtue of the volatilization of a titanium fluoride. The volatilizing compound is either  $\text{TiF}_4$ , or an oxyfluoride of the composition  $\text{TiOF}_2$ .

$\text{MgO}$  additions do not accentuate volatilization, whereas  $\text{SiO}_2$  additions greatly increase the rates of volatilization through the formation of silicon tetrafluoride.

Under gaseous atmospheres' with defined humidity, increasing water vapour partial pressures led to increased volatilization through the formation of hydrogen fluoride. Calculations showed the formation of  $\text{SiF}_4$  was only of significance at the beginning, immediately after the addition of  $\text{SiO}_2$ .

The emission of fluorine-containing compounds from fluorspar

slags is reduced with increasing CaO activity. The lowest volatilization rates are found in lime-saturated slags. Provided other metallurgical conditions are met (metal/slag reaction, hydrogen absorption, operating conditions etc.), the slags should have high CaO contents (if possible, to saturation).

Investigation of total nitrogen oxide emissions from industrial gas furnaces with a view to the development of burners with waste gases having a low nitrogen oxide content  
(Betriebsforschungsinstitut des VDEH,  
Düsseldorf, und Ruhrgas AG, Essen, Research  
Project PS 226)

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This research work has already been reported on in booklet EUR 5977. The measurements carried out during the subsequent part of the research on semi-technical trial furnaces and on production plants may now be summarized as follows:

The main parameters affecting the formation of  $\text{NO}_x$  are the following:

- the air factor ( $\text{O}_2$  content in the waste gases)
- average combustion air temperature
- average furnace temperature
- the mixing method.

The formation of nitrogen oxide in combustion processes reaches its maximum at air factors of  $\lambda = 1.05$  to  $1.20$ . In industrial plants, as a rule, the combustion processes run at air factors of between  $1.1$  and  $1.2$ , which corresponds to 2 to 4% volume of oxygen in the waste gases.

An essential parameter affecting the formation of nitrogen oxide is the combustion air temperature. As the  $\text{NO}_x$  formation

depends upon the temperature of the flame, a high combustion air temperature, which brings perceptible heat into the combustion chamber, raises the temperature of the flame and consequently the emission of  $\text{NO}_x$ .

Evaluation of the industrial tests showed that with the usual mode of operation of industrial reheating and heat-treatment furnaces, the method of mixing in practice only plays a subordinate role.

An approximation equation for  $\text{NO}_x$  emission was worked out as a basis for emission and immission forecasting, and as a possible means of optimizing the performance of plant in service. The criterion for the  $\text{NO}_x$  emission is not the heat-flow in the plant, as has been stated in the literature hitherto, but the average furnace temperature and the average temperature of the combustion air. The oxygen concentration in the flue gases is a less important factor in most cases.

In industrial plant, nitrogen dioxide,  $\text{NO}_2$ , accounted for less than 10% of the various  $\text{NO}_x$  concentrations measured at furnace temperatures of over  $1\ 000^\circ\text{C}$ . As the furnace temperature drops,  $\text{NO}_x$  formation is increasingly affected by the oxygen content of the flue gases. At such temperatures, the method of furnace operation determines whether, and in what quantities,  $\text{NO}_2$  is formed and emitted.

Preventive measures for reducing  $\text{NO}_x$  emission from reheating and heat-treatment furnaces would include lowering the combustion air temperature, close-to - stoichiometric combustion, combustion in stages and recycling combustion gases back into the combustion air upstream of the burner. But several of these suggestions would probably not be feasible in technical practice. The most promising approach seems to be the recycling of the flue gases through the burner. Here, however, the heat transfer question must also be taken into account; only a concerted effort at optimizing all the parameters



Promises success.

Avoidance or distruction of  $N_xO_y$  clusters in  
industrial exhaust gases  
(Technische Hochschule, Aachen, Research  
Project PS 295)

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The applicants, in a preceding research project financed by the Commission of the European Communities, have made the surprising discovery that, in addition to the numerous reactions of  $N_xO_y$  with oxidic solids, a polymerization of the gaseous molecules up to molecular weights of 1 800 also takes place, as compared with the molecular weight of the monomer  $NO$  of 30.

It is fairly probable that the macro-molecular  $N_xO_y$  clusters, because of their high local concentrations, are more toxic than monomers. For this reason it must also be accepted that the biological danger of emission and/or immission of  $NO_x$  could be lowered if a way could be found, through improved knowledge of the way they are formed, of avoiding or destroying the polymer species.

Investigations of the following are planned:

- chemical reactions of the gaseous nitrogen oxides with dust particles in the waste gases and oxides in refractory brick linings, leading to the formation of nitrates, nitrites and complex gaseous  $N_xO_y$  compounds as a function of temperature, light irradiation, oxygen concentration and contact time;
- identification and analysis of the gaseous macro-molecules

(clusters) formed during the reactions of the nitrogen oxides with the dust in waste gases, furnace lining, etc.:

- destruction of the clusters by thermal, ion and electron impacts, corresponding to electrostatic dust precipitation.

As part of the research work, an improved ultra-high vacuum apparatus was constructed and the adsorption, desorption and the reactions of  $N_xO_y$  with CaO and  $Na_2O$  were studied by quadrupole mass spectrometry. Several previously unknown  $N_xO_y$  species were identified and evidence of heavy  $N_xO_y$  clusters up to  $(NO)_{64}$  was provided.

Tests with both  $N_xO_y$ /air mixtures and also with the  $NO_2$  gas commercially available, showed that these gases also contain some heavy  $(N_xO_y)$  and/or  $(NO_2)$  complexes.

Reduction of pollutant emission from and  
conservation of energy in industrial flames  
and furnaces

(International Flame Research Foundation,  
IJmuiden, Research Project PS 250

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One of the most efficient ways of reducing pollutant emission is to optimize combustion processes, heat transfer and total fuel consumption. The aim of this research project was therefore to obtain data on the relationship between heat transfer, operational variables and combustion parameters with a view to optimizing furnace operation.

The research programme comprised four furnace studies. Three of these (Part I) were carried out on the same furnace under similar conditions, during which a variety of different burners and operational variables were tested. The test furnace operated with a type of flame-firing commonly found in reheating furnaces in the steel industry.

The fourth experiment (Part II) was concerned with the special application of high-intensity natural gas oxygen flames, and was designed to measure the extremely high temperature convection heat transfer from flames impinging vertically on the heat sink.

The principal results were the following:

#### Part I

- The use of different burner and/or flame types led to changes in the thermal furnace efficiency of up to 25% with a low-temperature - heat sink. With a high-temperature - heat sink this effect was even greater.
- A 5% reduction of the excess air results in an average 3% improvement in furnace efficiency.
- If blast furnace gas is used ( 1 200 kcal/kg) instead of natural gas, furnace efficiency falls by 30% at the same thermal input.
- Under identical input conditions, it is possible to change the peak heat flux by 40% when the swirl intensity is increased from  $S = 0$  to  $S = 1.7$ .
- When heavy fuel oil is used,  $SO_3$  emission can be reduced by a factor of 10 and  $NO$  emission by approximately 20% by reducing the excess air from 30% to 5%.

- The application of staged combustion can reduce the NO emission from heavy fuel oil flames at low air preheat by between 30 and 60%.

## Part II

- Typical convective heat transfer coefficients obtained using natural gas/oxygen flames were  $0.3 \text{ kW/m}^2 \text{ }^\circ\text{C}$ , compared with  $0.07 \text{ kW/m}^2 \text{ }^\circ\text{C}$  from natural gas/air flames. Interesting data, of use in furnace design, were obtained from the measurements of the convection heat-flow in relation to the combustion chamber load and burner heat sink spacing.
- As a consequence of the higher combustion temperatures, the  $\text{NO}_x$  emissions measured for natural gas/oxygen flames were higher by approximately one order of magnitude than for natural gas/air flames. Here, of course, air infiltration played a particularly significant part.

As part of this research, a series of noise measurements was also carried out. The effect of burner parameters on the intensity of the noise can be adequately predicted, though of course allowance must be made for the fact that the noise emission data obtained for the burners cannot easily be applied to the overall complex of burners and furnaces.

Correlation between the operating characteristics of steelworks plant and the efficiency of its dedusting equipment

(Laboratoire d'Etude et de Contrôle de l'Environnement Sidérurgique, Maiyières-lès-Metz, Research Project PS 274)

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The tendency towards increasingly stringent national standards for pollution means that the existing dust extraction systems must be operated within extremely narrow margins in order to comply with the regulations. Every technological advance in a steel-making process can therefore only be successful if the plant's dedusting capacity can cope with it. Dust extraction plants may therefore act as obstacles in the way of better and more competitive steel-making techniques.

The aim of this research is to detect obstacles of this kind in the interface between production and dedusting plants, and to eliminate them.

The results at the present stage of research are as follows:

Sinter plants:

Normally the fume cleaning with electrofilters gives excellent results. During regular operation, emission levels are often significantly below the permitted limits, e.g.  $25 \text{ mg/Nm}^3$  instead of  $150 \text{ mg/Nm}^3$ .

One or two special cases were looked at in greater detail: when the burn-through point diverges from the most favourable position there may be a slight increase in dust formation. When the plant is restarted or shut off, there are wide variations in the burn-through point and, at the same time, increased production of dust, which over a short period - for about one minute - may rise to  $200 \text{ mg/Nm}^3$ . Samples taken over a period of 10 minutes, however, remained below  $100 \text{ mg/Nm}^3$ .

Dust removal efficiency was highest with fume humidity levels in the medium range (approximately  $40 \text{ g/Nm}^3$ ) at higher or lower levels it was less satisfactory.

The sulphur content falls as the moisture content rises.

Oxygen converters: (with wet dedusting)

During tests to improve measurement techniques on a converter with combustion-free fume collection, IKOR probes were inserted with an electro-static measurement system. If the technology of this type of probe can be successfully improved, they may become an important monitoring instrument for wet dedusting. First of all, a droplet separator was developed for the measuring probe, designed to make it possible to identify the quantity of dust both in the collected water and in the fume.

Tests carried out on the converter with fume collection featuring post-combustion showed that during the second blowing stage the quantity of dust was 40% higher than during the first stage. It must be noted here that crude iron rich in phosphorus was blown with powdered lime; the quantities of lime injected are normally between two and three times higher in the second stage than in the first stage.

The well-known dependence of dedusting efficiency on the pressure drop in the Venturi scrubbers was confirmed. Of course, the volume flow, which normally falls as the pressure drop increases, also plays a role. Here an optimum compromise must be found.

The quantity of water has a decisive influence. Optimizing the ratio between water quantity and gas flow-rate may also produce favourable results here.

### Electric arc melting shops

It was established that bag filters have no selective effect vis-à-vis the various components of the dusts. The zinc and lead contents of the dusts discharged into the atmosphere were however somewhat lower than in the total dust before de-dusting.

There was no clear correlation between the quantity of dust and the mode of operation (use of oxygen lance, oil-oxygen burners, etc.), although dust make was somewhat higher at the beginning of the melting stage when oil-oxygen burners were used.

The filtering efficiency in the case of fluorine-containing dusts is more than 99% and is absolutely comparable with that for total dusts. The collection efficiency for molybdenum oxide was examined with various addition methods.

In addition, further volume flow measurements were carried out during fume collection through the fourth hole in the furnace roof and through the roof hoods in order to devise criteria for the optimization of control parameters. The results will be reported on at a later date.

Examination of the airflow pattern, temperature dispersion and concentration dispersion of air pollution in models of the 'S-hall' of the Hoogovens IJmuiden B.V. tin plating shops  
(TNO, Delft, Research Project PS 253)

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Workplace pollution and heat can often be irritating or even dangerous for the health of the personnel working in the shops concerned.

In order to avoid full-scale studies of the environment in workshops, which entail complex and expensive measurements, it is worth considering whether examinations carried out on models could not produce serviceable results more quickly and more cheaply. Such a study was carried out as part of this research project, on a 1:20 scale model. Air speed, temperature and concentrations were measured at approximately 200 different points, and compared with the findings of measurements from previous tests carried out in the actual workshop.

The 'S-hall' has two electrolytic strip tin-plating plants. The two melting furnaces constitute the main sources of heat, while the main source of air pollution is the oil mist given off by the lubrication system of the plant.

Results of the tests on models and comparisons with the full-scale tests:

1. the air-flow patterns in the workshop and in the model are in close agreement. They are determined by free convection, due to the warmth generated by the plant;
2. the air temperatures in the workshop may be predicted with satisfactory accuracy from the measurements carried out on the model;
3. the accuracy of prediction of the pollutant concentrations is distinctly less reliable and in the case of the air velocities prediction is not possible on the basis of the measurements carried out on the model.

It would seem possible, given precise information about the geometry of the shop, the sources of heat, heat loss etc., to make useful forecasts of the rates of air exchange that may be expected in a workshop of this kind, and in addition, to obtain indications of the average temperature gradient between the interior of the shop and the outside. Model



tests and computer programs constitute useful aids for this.

Fume and dust abatement in a slab conditioning  
yard  
(ITALSIDER, Taranto, Research Project PS 322)

The development of flame scarfing by automatic means has brought with it increased pollution of the workplace through dust and gases. In particular, the latest generation of these machines (spot scarfers) causes pollution, the extent and nature of which is not yet fully known.

The purpose of this research, therefore, is to

- determine the quantity and nature of the dusts and gases arising during slab scarfing in relation to the operating conditions
- to design and manufacture the necessary plant for optimum collection, extraction and cleaning of the fumes from the new machines and to test them in operational conditions.

Initial tests and measurements carried out on the extraction plant attached to the scarfing machine had demonstrated the need for design alterations to improve environmental conditions.

At the present stage of research, plans for a newly designed extraction hood are available, and an improved solution for attaching the hood to the scarfing machine has also been devised: the hood is mounted on a bogie in order to guarantee optimum collection of the fumes.

Total water consumption for dedusting and removal of solids is estimated to be 350 m<sup>3</sup> per hour. But for the practical implementation of the design, water availability may present problems, so that at present alternative solutions based on a system in which the water is circulated in a closed circuit are being prepared.

## CHAPTER 2

### Control of water pollution

Research aimed at the preparation, improvement and development of methods for the control and the automatic and continuous supervision of the degree of waste-water pollution in the iron and steel industry, with initial reference to water with a high level of dissolved salts. (Centro Sperimentale Metallurgico, Rome, Research Project PS 252)

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The main emphasis in this research lay on the testing, development and improvement of automatic and continuous analysis techniques capable of standing up to continuous use in a steelworks. The results for the various substances analysed are summarized below:

Ammonium ions (phenol-hypochlorite method); the automatic method gives good results, even in very complex waste waters such as those from coking plants.

Nitrates and nitrites (colorimetric method with sulphanilamide and N [1-naphthyl-ethylene-diamene] after the reduction of the nitrate): satisfactory results obtained in the laboratory were not confirmed during industrial use.

Nitrites: the above-mentioned automatic colorimetric test reaction may also be employed under all industrial conditions.

Total phenols (foline-ciocaltene method): the automatic technique only gives good results if no sulphides are present.

Simple cyanides (pyridine-barbituric acid method): even in the most difficult cases, for example effluent coming directly from the coking plant, this automatic method may be used without any interference.

Total cyanides (pyridine-barbituric acid method): ultraviolet irradiation causes the separation of the complex cyanides, and also of sulphur cyanide.

Sulphur cyanide (iron nitrate method): the automatic method gives satisfactory results for final waste waters from steel-works. In the case of coking plant effluent, disturbances were noted.

Sulphides (methylene-blue method): if the sample is sufficiently diluted, the automatic method gives satisfactory results, at least for high (100 to 500 mg/l) and average contents (20 - 100 mg/l).

Total organic carbon (T.O.C.): The automatic analyzing device used gave good results over a longish period of time, even in the case of complex waste waters. Problems of corrosion, however, persist with some of the pneumatic valves. This is particularly true of alkaline effluent with a high salt content.

Total oxygen demand (T.O.D.): the automatic analyzing device which was examined gave rise to a series of problems, which occurred when waters with a high salt content were used. There were blockages caused by the formation of crystals, corrosion problems and problems connected with calibration using standard solutions.

The research further showed that it is usually necessary, in the case of automatic analysis techniques to reduce the content of suspended particles to a residual level of less than 50 mg/l. This could be done with, for example, sand-filter columns that can be regenerated.

Determination of free cyanides in liquid and solid wastes.

(Centre Belge d'Etude et de Documentation des Eaux, Liège, Research Project PS 273)

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To assess the toxicity of waste waters or sludges containing cyanides, analytical determination of the total cyanide content is not enough; it may give erroneous indications, both of the risk to the environment and of the treatment procedures to be used.

This fact is connected with the marked tendency of the cyanide ion to form non-toxic complexes with heavy metal cations, and with cyanide conversion, which depends on the pH value: the result is dissociation of metallic complexes on the one hand, and conversion of the cyanide into prussic acid on the other hand.

The aim of this research is to select the best procedure from the variety of existing ones and, in particular, to compare processes for the determination of free cyanide with each other.

Results:

1. Determination of free cyanide:

Amongst the colorimetric methods, the pyridine-barbituric acid method turned out to be superior to the pyridine-pyrazolone process. The standard deviation was 0.78%, as compared with 2.70%.

The processes using cyanide-specific electrodes produced results which were more difficult to reproduce.

A coulometric method was also tested. It was reasonably accurate, but had some practical disadvantages, so that, out of all the processes tested, the pyridine-barbituric acid method would appear to be the most advantageous.

2. Determination of total cyanide:

The Wanschura distillation method entails the decomposition of all the heavy metal complexes under investigation, with the exception of  $\text{Co}^{3+}$ . In practice, however, this does not constitute any great disadvantage, as complex cobalt cyanides are relatively rare.

During photochemical decomposition using ultraviolet irradiation, the  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Co}^{3+}$  compounds were not completely split. What is more, the irradiation period needed was significantly longer than is indicated in the literature.

3. Determination of partial cyanide:

The Bucksteeg and Dietz distillation method at a pH value of 4 entails total decomposition of the  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  complexes and therefore makes it possible to arrive at a quantitative determination. The degree of dissociation for  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Co}^{3+}$  is small.

The exchange resin separation process was also studied. The very stable complexed cyanides, such as those of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$  and also  $\text{Ni}^{2+}$ , do not respond to this process. It is not a completely satisfactory method, but it represents a good compromise between the value of the information obtained and the simplicity of application which is imperative for monitoring processes.

4. Determination by means of calculation :

A calculator program was devised, by means of which the  $\text{CN}^-$  and  $\text{HCN}$  concentrations of solutions with a known total concentration of cyanides and heavy metal cations and a known pH value can be established.

Monitoring of suspended solids in iron and  
steelwork water and effluents  
(British Steel Corporation, London, Research  
Project PS 243)

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Many iron and steel-works processes produce effluent containing suspended solids. These may be separated out and reclaimed or they may be allowed to flow away into rivers or the sea. In both cases the concentration of solid suspended matter must be determined, whether for technical reasons or for reasons of environmental safety.

The instruments available for this purpose may be divided into separate categories according to the optical measuring principle they are based on. The purpose of the present research project was to discover which types of device and which optical measuring principle were best suited for the measurement of suspended solids concentrations in various types of steelworks effluents.

The following instruments were selected:

1. Shandon Southern WPRL Suspended Solids Meter (side scatter at  $90^{\circ}$  to the incident beam)
2. Monitek 215/130 (forward scatter at  $5^{\circ}$  to the incident beam)
3. Anacon 303 R (backward scatter, i.e. reflectance, at  $180^{\circ}$  to the incident beam)
4. Hach Surface Scatter 4 (scatter from the surface region of the effluent, the incident beam impinging on the surface at a small angle)
5. Anacon 303 T (transmittance of the incident beam through the effluent). In the course of the research this device was replaced by the Partech Suspended Solid Monitor HP/LP.

The results of tests carried out on various kinds of effluent may be summarized as follows:

- In the case of blast furnace effluent great difficulty was experienced in attempting to prevent serious fouling of the instruments, that is to say, the optical surfaces and in the sampling system. In the case of one blast furnace, the effluent from which was already partially treated and clarified, the situation was somewhat easier.
- Oxygen converter effluent certainly caused fouling of the optical surfaces of the measuring instruments, but this was readily removed with dilute hydrochloric acid.
- Fouling was not a significant problem with rolling mill effluent; the problem here was more the presence of finely dispersed air bubbles, which have scattering properties like particles and caused false high readings. A bubble remover was constructed and used but was not completely effective all the time.
- Coking-plant effluent was corrosive to copper and brass parts of the measuring instruments.

The practicalities of instrument operation far outweighed theoretical considerations. Side scatter and forward scatter principles were consistently the best, the back scatter principle the worst. Transmission and surface scatter principles were about equal, but the effectiveness of the transmission principle was reduced by poor flow-cell design. Surface scatter instruments may prove most useful as indicators of malfunctional trends in the operation of water treatment plants.



Development and testing of an oil detection device for monitoring pollution of bodies of water

(Betriebsforschungsinstitut des Vereins Deutscher Eisenhüttenleute, Düsseldorf, Research Project PS 306)

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There is a danger in the steel industry of unacceptably high levels of oil contamination of effluent, particularly rolling mill effluent. Because stricter legal requirements are expected to be imposed, appropriate monitoring instruments suited to industrial use must be developed in steel works.

The oil detection device that is to be developed with the help of this research project, which is expected to be completed by the end of 1981, must first of all be of a strong and durable design, simple to use and suitable for reliable long-term use in the steel works. The oil analyzing or detecting devices available on the market at present do not fulfil these requirements.

During initial tests it was established that the principle of ultraviolet radiation-induced fluorescence had good prospects of success for the detection of oil on water.

Previous work had shown that modulation of the ultraviolet light and selective use of particular frequencies during the measurements was the most practical way of eliminating the influence of outside light. The exact position of the fluorescence spectra of the oils in question was plotted. A system of operating the sources of ultraviolet light using a pulse generator was developed.

Process of dispersion of pollutants discharged into the sea, in relation to their concentration and temperature, to marine currents and their temperature, to winds and to the shape of the coast

(Italimpianti, Genoa, Research Project PS 275)

Steel works located near the coast are allowed to discharge their effluent into the sea. In so doing, however, it is essential to avoid concentrations of pollutants dangerous to health and damage to marine fauna and flora.

When planning to discharge effluent into the sea, or when planning any purification or treatment stations upstream it is necessary to know the extent to which the pollutants will become diluted in certain areas at various distances from the point of discharge.

The purpose of the present research project was to identify the dispersion parameters, using a mathematical simulation model and to conduct practical tests to test the model and obtain further material for the planning of optimum discharge plants.

In the course of the research work, a simulation model was constructed based on the dispersion models of Joseph-Sendner and von Kulleberg, as also on the statistical diagrams of Okubo. The model consists of two parts:

- one part designed to simulate the sea currents caused by the tides, air pressure gradients and winds,

and

- another for the dispersion of the pollutants discharged through an outlet into the area under investigation.

In this way, depending on the particular concentration of pollutants, the quantity of effluent and the local conditions, it is possible to choose the most favourable position and the optimum dimensions for the discharge plant.

The necessary initial data that must be included in the model are: shape and size of the bay (not more than 50 km), astronomical forces in the area in question, air-pressure gradient in relation to time, wind direction and wind force, quantity of effluent and concentration of pollutants. The results obtained include figures for the direction and strength of the sea currents which are easy to represent graphically, and the concentrations of pollutants as a function of the data entered for a given simulation period.

During the experimental part of the research, tests were carried out in the Gulf of La Spezia. Various discharge points were selected and the characteristics of the discharge were varied. In addition, a series of tests were carried out in the Gulf of Genoa using Rhodamin B in order to measure the changes in the maximum concentration over time. The experimental results confirmed the accuracy of the mathematical simulation model.

Evaluation and reduction of nuisances caused  
by the discharge into the natural environment  
of conditioning products for industrial  
cooling circuits  
(Institut de Recherches Hydrologiques, Nancy,  
Research Project PS 303)

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The choice of conditioning products for industrial cooling water circuits should be based on accurate knowledge of their

efficiency and of the consequences of their discharge into the natural environment. Such knowledge, however, is not fully available at the present moment. This research project was therefore based on the following plan:

- selection of 39 reagents for the purpose of examining their efficiency in inhibiting scale formation and corrosion,
- selection and identification of waters suitable for use in the iron and steel industry, with a wide range of characteristics for the purposes of the tests of conditioning products,
- installation of 5 pilot cooling circuits for the purpose of testing the conditioning products
- a study of their effects on the natural environment.

Results so far:

1. Of the products that were examined in respect of their ability to inhibit the corrosion of copper, two reagents, benzotriazole and tolyltriazole, were particularly effective. They were both the most active products and the least harmful to the environment. When discharged into open water, benzotriazole degrades faster than tolyltriazole.
2. There are several products for inhibiting iron corrosion, which are not harmful to the environment. The most efficient ones are low molecular weight polyacrylic acid, the gluconates and sodium glucoheptanate used in conjunction with zinc salts and HEDP (hex-ethylene-diphosphate).
3. Tests carried out on products to inhibit scale formation showed that various harmless materials were usable: polyacrylic acid, HEDP and polymaleic acid.

So far, it has been established that there are products

available which are both extremely efficient and are, at the same time, without any risk for the natural environment.

The experimental work is being continued to investigate a small number of particularly interesting products more closely.

Elimination of volatile pollutants from coking plant waste water in a stripping column featuring automatic and continuous cleaning (Centre de Recherches Métallurgiques, Liège, Research Project PS 286)

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The aim of treating coking-plant effluent in stripper columns is to remove the ammonia, HCN, H<sub>2</sub>S and a maximum of phenol compounds. Stripping columns using lime produce good results, both for free and fixed ammonia. This is, however, a relatively expensive process which cannot easily be maintained in continuous operation because of fouling.

This is the origin of the attempt to improve and to optimize the technology of this treatment process. The CRM and the Sidmar company undertook this venture, which has been successfully completed.

The degree of fouling in stripping columns using lime is a function (apart from the nature of the liquors to be treated) of the type of plate used, the quality of the milk of lime, and the carbonate ion content when the lime is added.

The work has shown that the fixed perforated plates chosen for the experiments are more efficient than the traditional bubble-cap or tunnel plates and have greater resistance to fouling. The plates tested had a small perforated area and small diameter holes, thus assuring very turbulent conditions in the bubbling zone.

Fixed perforated plates, because of their excellent resistance to fouling, are easy to clean and provide a simple solution to the problem of clogging of the columns by precipitated calcium salts.

The use of moveable plates, however, may provide a more complete solution, but one which is technically more complicated. Here some technical improvements are still necessary.

As a result of the tests at Sidmar coking-plant, using a semi-industrial plant with 8 perforated plates and treating, on average, four  $4 \text{ m}^3/\text{h}$  of residual amoniactal liquor, the performance of the perforated plates may be summarized as follows:

- under optimum conditions, the overall efficiency of ammonia removal was about 25% better than with a conventional bubble-cap column.
- The hydraulic capacity was between 8 and  $22 \text{ m}^3/\text{h}/\text{m}^2$  of solution (optimum 12.5), which corresponds to an operating flexibility of 1: 3;
- The average specific steam consumption can vary between 170 and  $210 \text{ kg}/\text{m}^3$  of water to be treated (non-lagged column).
- The loss of pressure in each plate was less than 100 mm water-gauge under optimum operating conditions.

For certain liquors heavily charged with pyridine, aniline and quinoline, it was necessary to inject an anti-foaming agent, which would, however still be active during biological cleaning.

The work has also shown that the provision of a weakly acid zone (pH 5-6) in two-section stripping columns favours the removal of phenols and free cyanide. This weakly acid zone may be obtained by increasing the number of plates in the first stripping section of a conventional column (stripping of free ammonia). In this way, about 84% of the phenols present in the waste water from the Sidmar coke-ovens were removed by lime stripping (including the dilution effect). In the same way, the injection of lime may be done at a position where the quantity of carbonate ions in the water is very small. Of course, the capital costs rise if more plates are used.

Significant relationships were also found between the pH of the stripped water and its residual contents of both fixed and free ammonia. Here there are prospects of monitoring the efficiency of the stripping on a continuous basis.

Considerable importance is also attached to the effect of the type of lime used (quick-lime or slaked-lime), and its quality (degree of firing, grain size) on the physico-chemical properties of the lime milk. The quality of the water used for the lime milk is also important.

In addition, methods of measuring and regulating the flow of milk and automatic equipment for the preparation of the milk of lime were tested and improved.

Sidmar is at present developing an industrial stripping column with a capacity of 45 m<sup>3</sup>/h, based mainly on the results of these investigations.

Further research on biological treatment of chemical pollutants in waste waters from coke plants. Biological nitrification and denitrification

(Centro Sperimentale Metallurgico, Rome,  
Research Project No PS 279)

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At the present stage of technological progress the cleansing of coking plant effluent is usually so arranged that during the first stage the effluent is stripped with steam in order to separate as large a quantity as possible of ammonium salts and eliminate them in the form of gas.

The residual quantities of ammonia salts, which often occur in quantities of between 200 - 300 mg/l (indicated as NH<sub>4</sub>), remain unchanged in the subsequent biological treatment. The main aim of this cleaning stage is to make harmless or eliminate a large proportion of the remaining chemical substances, which include widely varying organic compounds (phenols, cyanides, sulphides, etc.).

In order to reduce the harmfulness of this effluent for animal and plant life in seas, rivers and lakes, there is an ever-growing need also to eliminate the residual quantities of ammonia from the coking plant waste water. This is particularly so in the case of discharge of the effluent into the sea, as the toxicity of ammonia is increased by an alkaline pH (approximately 8.4).



The aim of the research was to develop a procedure for biological nitrification of the residual ammonia compounds and subsequent biological elimination of the nitrates formed.

The development work was successfully completed: after extensive laboratory investigations a biological pilot plant with two nitrification and denitrification tanks of approximately 500 litres, as well as a clarification basin of appropriate size, were put into operation at Italsider's Trieste works.

The rate of ammonia elimination and the Michaelis - Menten constant were measured for the nitrification process. Because the process took place extremely rapidly, and because the formation of sludge was equally fast, this was not possible in the case of the denitrification process.

During the final stage of the research the pilot plant was charged with industrial coking-plant effluent which had been subjected to industrial biological pretreatment. The nitrogen content present as ammonia, namely 600 mg/l, was reduced to 1 mg/l in the form of nitrate.

Elimination of moderate concentrations of ammonia and other chemicals that can be oxidized by active chlorine (sulphides, phenol compounds, cyanides) in the presence of catalysts

(BECEWA, Ghent, Research Project PS 315)

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To comply with the requirement that even small residual quantities of ammonia be eliminated from coking-plant effluent, various chlorination procedures are examined in this research project, which comprises the following stages:

- Development of analysis techniques for measuring ammonia, chloramines and free and fixed chlorines.
- Investigation of the use of active chlorine for the oxidation of ammonia to produce various intermediate and final products in relation to the pH and the reaction time.
- Investigation of chlorine consumption in relation to any cyanides, sulphides, phenols, etc. that may be present.
- Combined chlorination and dechlorination in the presence of activated carbon.
- Experiments with industrial coking-plant effluent.

Results so far:

1. During tests designed to evaluate analytical methods to measure residual chlorine, the applicability and the advantages and disadvantages of the following processes were compared: iodometry, amperometry, two orthotolidine processes, leuco-crystal violet, syringaldazine, diethyl-p-phenylenediamine, specific chlorine electrodes and differential pulse polarography of arsenosobenzene.
2. The chlorination of ammonia is affected by the pH value. The optimum pH is between 6.5 and 7.

Outside this optimum range chlorine consumption rose rapidly, and even under optimum conditions chlorine requirements were higher than quoted in the literature. The breakdown of ammonia and chloramine to produce nitrogen took place in 15 minutes. When the pH was above 8, no more dichloroamines were found.

3. When activated carbon is included in the chlorination process, account must be taken of the acclimatization of this carbon. The reaction of hypochlorous acid with activated carbon takes place in two stages, and the speed of the reaction depends on the surface oxides formed, some of which are released in the form of CO or CO<sub>2</sub>.
4. Acclimatized activated carbon is not necessary for the dichloroamine to break down. The carbon monoxide layers formed can be used to break the monochloroamines down. With a pH of 5.4, equivalent amounts of mono- and dichloroamines are formed. The corresponding chlorine consumption can be reduced to a Cl/N-mole ratio of 1.58.
5. The degree of acidity has a clear influence on the chlorination of phenol. With a Cl/phenol mole ratio of 9, a pH of 7 was found to be the optimum figure. The reaction proceeds much more slowly than during the chlorination of ammonia. The phenol was not fully oxidized until two and a half hours had gone by.
6. The reaction between chlorine and sulphides takes place very rapidly. Whilst a Cl/S mole ratio of 1 led to an incomplete reaction, a ratio of 4 oxidized all the sulphides. The chlorine consumption is smallest in the pH range of 8 to 9.
7. The first results of chlorination experiments on coking plant effluent in laboratory pilot plants point to high

chlorine consumption. The coking-plant effluent contains a great number of other substances, apart from ammonia, which also consume chlorine. It was also established that the results are influenced by the type of activated carbon used. An examination of various chlorination methods, with or without activated carbon, will be continued on a laboratory pilot-plant scale.

Performance of a microbiological treatment  
plant for coke-oven liquors with variability  
of input  
(British Steel Corporation, London, Research  
Project PS 260)

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The aim of this programme was to determine the long-term and short-term effects of variations in the influent composition on the effluent from a treatment plant under different operating conditions. The research work was principally carried out by the British Carbonization Research Association on behalf of the BSC.

The attempt to set up a large-scale treatment plant working in normal conditions for the purpose of this programme had to be abandoned because of a series of technical difficulties. It was therefore decided to carry out the research programme in a 50 l pilot plant at the BCRA laboratories.

The effluent to be treated came from the Orgreave coking-plant. Two mobile laboratories were used for the purpose of carrying out routine analysis of samples taken at intervals of two hours from the influent and effluent, and also for more complex analyses. The chemical data were then processed

at the BSC laboratories in Battersea.

No clear connection was found between chemical composition of the influent liquor and inhibition of treatment efficiency or of plant operation.

One essential advance achieved through this research programme, however, is the development and refining of analysis techniques for rapid analyses of coking-plant effluent. Automated colorimetric analysis methods for thiocyanate, total ammonia, phenols and COD (chemical oxygen demand) were developed. The total organic carbon content was determined using a Tocsin Mark II apparatus. Other methods for determining quantities of chloride, fluoride, cyanide, sulphide, sulphate, thiosulphate, nitrate, nitride, phosphate, boron and vanadium were tested. In addition, atom absorption spectrometry was used for determining the presence of trace elements, mercury and calcium, and gas chromatography to detect the presence of phenols, organic bases and high-molecular-weight inhibitory compounds.

Improvement of coke-plant waste water purification by controlling the operation parameters of the treatment plants. Application to assisted biological purification.

(Centre Belge d'Etude et de Documentation des Eaux, Liège, Research Project PS 287)

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In the light of the progress made very recently (see Research Project PS 286) in the treatment of coking-plant effluent in stripper columns, the original aim of this research project was modified, so that biological after treatment became

the main topic. It can be assumed that in modern stripping plants of this kind most of the sulphide and the free cyanide will have been removed, which means that one of the problems for biological purification is also eliminated.

In the course of the research work, tests were first of all carried out on a laboratory scale in order to develop the most favourable cycles and techniques.

During a later stage, tests were made on a pilot plant with a capacity of 1 000 litres in semi-continuous operation. The volume of air blown in was  $1.2 \text{ m}^3/\text{h}$ .

Next, tests were carried out in the physico-chemical pre-treatment of the waters after stripping. Backing up the biological treatment by ozone oxidation does not seem advisable. On the other hand, the combination of extensive stripping with automatic purification, and complementary ozone treatment to bring phenol levels to the standards is an interesting solution which has advantages over traditional biological treatment. The cyanide would have to be subsequently oxidized using chlorine.

A range of findings emerge from these tests:

- the biomass which has adapted to coking-plant liquor contains two populations which are biologically distinct but may coexist in varying proportions. One decomposes the thiocyanates, while the other removes the other substances (mainly phenols and their derivatives).
- Generally, such a biomass flocculates without difficulty; anomalies may arise through the formation of very small flocs or huge cohesive masses which are inactive.

- The most reliable and rapid indicators of overloading are pH values exceeding 7.4 and the appearance of thiocyanates in the effluent at concentrations in excess of 2 mg/l.
- A biomass of at least 1 g/l is required to ensure satisfactory and stable treatment in a single stage with complete mixing of the liquor.
- Dilution of the crude liquor in a ratio of 3 or more parts to 1 ensures trouble-free purification.
- The addition of growth factors is useful to restore a biomass in a reaction tank whose sludge has become weakened, or to develop a biomass in the start-up phase.
- Action to restore a sludge which has been weakened must be taken as quickly as possible. (Dilution of the crude liquor, reduction or cessation of intake).
- The biomass can tolerate a phenol concentration of 300 mg/l in the diluted influent. As soon as this concentration reaches or exceeds 435 mg/l, thiocyanate removal ceases.
- Under satisfactory operating conditions compliance with the standards for phenoles (<5 mg/l) and 5-day BOD (<100 mg O<sub>2</sub>/l) will be ensured. The COD standard (<500 mg O<sub>2</sub>/l), on the other hand, will be very difficult to satisfy on a continuous basis.
- Nitrification contributes considerably to the 5-day BOD of the treated liquor, accounting for 50% or over.

Pilot scale removal of phenols and cyanides  
from the waste water of coking plants using  
activated carbon

(Centro Sperimentale Metallurgico, Rome,  
Research Project PS 278)

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Alongside biological treatment - probably the commonest method for eliminating phenols and other organic compounds from coking-plant effluent - treatment with activated carbon may also be of technical and economic interest depending on the local industrial situation.

The purpose of this research project was to investigate the overall problem, i.e. the economic manufacture of activated carbon, the treatment of coking-plant waste waters and the regeneration of the spent carbon.

The results of the experiments may be summarized as follows:

Activation of semi-cokes

Preliminary tests have shown that semi-cokes can be activated by partial carbon gasification in  $\text{CO}_2$  at  $900^\circ\text{C}$ .

The following are the conditions for the activation of three substances (a commercial semicoke ( $S_1$ ), a semicoke produced at CSM ( $S_2$ ) and an intermediate product of the semicoking process, the so-called "Carbonizzato" ( $C_2$ ) produced at CSM):

- temperature:  $850^\circ\text{C}$
- activating gas:  $\text{CO}_2 + \text{H}_2\text{O}$  ( $\sim 70\% \text{N}_2$ ,  $20\% \text{H}_2\text{O}$ ,  $10\% \text{CO}_2$ )
- weight loss: 50%
- particle size: 0.8 to 1.5 mm.



In these conditions, although the ash content of the activated products was high (10 - 15%), the adsorption capacity was comparable to that of specific commercial activated carbon.

In a pilot reactor with a capacity of 12 kg of semicoke, further activation experiments were carried out in order to test the working hypotheses developed in laboratory work and in order to obtain information relating to the use of the activation gases.

The quality of the activated coke obtained with this pilot reactor was practically identical to that of laboratory-scale activated coke. The quality of the activated coke obtained in  $\text{CO}_2 + \text{H}_2\text{O}$  was similar and sometimes slightly lower than that obtained in simulated combustion fumes, regardless of the starting material, while semi-coke.  $\text{S}_2$  and Carbonizzato  $\text{C}_2$  produced the same quality of activated coke.

Two industrial processes may therefore be envisaged:

1. recycling of reaction gases with oxygen and water vapour injection
2. use of combustion fumes.

Calculations show that if the first process is to be self-sustaining oxygen consumption of  $1 \text{ Nm}^3 \text{ O}_2 / \text{ kg}$  activated carbon is necessary, while thermal self-sufficiency of the combustion fumes process calls for approx.  $2.8 \text{ Nm}^3 \text{ CH}_4 / \text{ kg}$  activated carbon.

#### Adsorption process

The adsorption process was studied in the laboratory while the behaviour of CSM-produced and commercially available activated carbon was followed in a pilot plant installed near the coke oven plant of the ITALSIDER iron and steel complex at Trieste. The water was taken directly from coke oven collecting mains and filtered through sand before being fed into the pilot plant. The pilot plants consisted of three columns of

4.5 m total length and 220 mm diameter.

The input water contained between 700 and 1600 ppm of total phenols, 1600 to 2500 ppm total aromatics, 900 to 2000 ppm TOC, and 5000 ppm  $\text{NH}_3$ ; during the period of the experiment the pH value was between 9.5 and 9.7, whilst the temperature was between 22 and 35°C.

The output water contained  $\leq 5$  ppm total phenols,  $\leq 250$  ppm TOC, regardless of the activated carbon employed, but results showed that different amounts of activated carbon are necessary per  $\text{m}^3$  of water treated, according to their respective adsorption capacities.

For commercial activated carbon (COMM<sub>1</sub>) this amount was 5.95  $\text{kg}/\text{m}^3$ , for COMM<sub>2</sub> 10.53  $\text{kg}/\text{m}^3$ , for CSM S<sub>1</sub> 10.53  $\text{kg}/\text{m}^3$  and for S<sub>2</sub> 7.24  $\text{kg}/\text{m}^3$ .

#### Regeneration of spent activated carbon

Because of the high cost of activated carbon, the regeneration and recycling of spent or saturated carbon is imperative.

Several chemical methods for regenerating of spent activated carbon have been tried, but the results obtained were not satisfactory. Thermal regeneration in conditions similar to activating conditions was found completely satisfactory on a laboratory scale when the activated carbon was saturated with monohydric phenols. Some problems arose, however, at the pilot plant in Trieste during the thermal regeneration of commercial activated carbon and activated coke produced by CSM.

During a 25-minute treatment in simulated combustion fumes under fluidized bed conditions at 820°C, there was a decrease in adsorptive capacity of the order of 5 to 7%. A mathematical study was made of the relationship between loss of adsorption and loss of weight of the activated carbon recycled, with restoration of initial weight with fresh activated carbon, as this is of key importance for the commercial viability of the

process. Of course, such estimates of the commercial viability of the total treatment chain can only be based on the pilot plant data for energy consumption, material loss and efficiency, and therefore cannot yield conclusive results.

#### Cyanide elimination

In an initial series of laboratory tests, various methods of oxidization of cyanide were investigated. Starting from an initial concentration of 120 ppm of cyanide, the best result obtained after six and a half hours of treatment was 48 ppm, obtained by aeration plus activated carbon plus hydroquinone. The process cannot, however, be considered satisfactory.

Much better results were obtained in the pilot plant by adding formaldehyde or butylaldehyde to the water before feeding it into the adsorption column. The cyanide content decreased from 60 ppm to 8 - 10 ppm. The addition of aldehyde does not increase the TOC of the effluent; this latter may even be reduced by a further 6 to 22%, in addition to the reduction caused by cyanide removal. The conclusion to be drawn from this is that other pollutants react with the aldehydes to form adsorbable compounds.

Study of the removal of non-emulsified oils in circulating water and especially in discharges from steel works possessing hot-rolling mills. (Institut de Recherches Hydrologiques, Nancy, Research Project PS 304)

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The hot-rolling of steel entails consumption of mineral oil and grease estimated at 0.4 l of oil per tonne of final product in 1975. In spite of continually improving plants and monitoring of the lubricant circuits, a significant proportion of the lubricants is entrained in the circulating water or in the effluent. The problem to be tackled in this research project was therefore the following:

- removal of oils from the circulating water
- treatment of total effluent discharged from the works, where the high degree of dilution by the considerable quantities of effluent discharged makes existing treatment processes uneconomic.

To tackle both these problems, new treatment methods must be investigated which will facilitate the operation of water circulation in hot-rolling mills and which will reduce the quantities of oil discharged to the environment.

The results achieved so far may be summarized as follows:

1. The total oil concentration in industrial circuits at various melting shops and hot-rolling mills hardly ever exceeds 20 mg/l. The concentrations vary according to the point in the circuits at which samples are taken, but remain fairly constant at each sampling point.
2. 80-90% of the total oil content of the water is adsorbed onto the surface of suspended matter, mainly solid particles below 40  $\mu$ m. Most of the remainder is found in dissolved condition (average concentration approximately 1 mg/l).
3. Possible ways of using polyelectrolytes for flocculation of oil-bearing small solid particles and colloids prior to separation of suspended matter by physical means were investigated. Tests on over 100 products gave varying results: in the case of melting-shop effluent, anionic polyelectrolytes gave the best results. The nature and characteristics of the most appropriate reagents differ sharply according to the circuit. The combined use of different products does not improve the flocculation results.

4. Gravitation separation has an efficiency of between 40 and 80%, according to the conditions under which it is used. It may be used as the first stage, for the separation of solid particles onto which the oil has been adsorbed.

Various types of filtration test are planned.



### CHAPTER 3

#### Noise control

Reduction at source of arc-furnace noise  
(Laboratoire d'Etude et de Contrôle de  
l'Environnement Sidérurgique, Maizières-lès-  
Metz, Research Project PS 289)

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Research designed to reduce the noise produced by electric-arc furnaces has two aims:

- reduction of noise produced by traditional furnaces operating on alternating current
- the use of direct current in order to reduce noise emission from the electric arc.

Results so far:

#### Alternating current

It was considered appropriate to simulate the behaviour of electric arcs and related noise generation in tests on small-scale models before proceeding to large-scale experiments. For this purpose an experimental plant was set up which produced electric arcs of 30-50 volts and 30-100 amps, between two graphite electrodes or between an electrode and steel filings.

The results of the experiments provide information on the influence of graphite composition, the power supply and the length of the electric arc. It turned out that the arc striking conditions were of great importance: they affect

the brief variations in power, which more than the overall power level itself, have a decisive influence on the production of noise. At the same power level, a short electric arc produces less noise than a long one.

Initial industrial tests were carried out on a scrap-charged 70-tonne furnace with a diameter of 5.5 m (39/47 MVA) and on a 70-tonne furnace with a diameter of 5.8 m (46 MVA).

Thanks to these tests, the measurement technique was further developed. The results showed that the level of noise was related in a relatively complex manner to the electric power level. Apart from significant sound emission at the basic frequency of 100 Hz, there was also a high degree of sound emission in the frequency range above 1 000 Hz, which are connected with the instability of the electrode on the one hand, and of the furnace charge on the other.

If oxygen-gas burners are used, the frequency spectrum is broadened and the noise intensity is generally higher. At the present stage of research, it is not yet possible to indicate the principal causes for this fact.

A further series of tests were carried out on a 45-tonne UHP furnace with a diameter of 4.8 m (25/30 MVA). During the melting stage the electric arcs are extremely unstable, which causes a high emission of sound, equal to approximately 100 decibels. Once the metal bath has been formed, the electric arcs are more stable, but small disturbances are enough to cause high sound emission of approximately 100-110 decibels even at that stage.

The aim of this research to reduce the noise generated - could not be achieved by improving the stability of the electric arc, and experiments were therefore conducted on the possibility of introducing ionizing elements (Ce, La, Li, Ti, K, Na) into the electric arc. The results of experiments so far available are not conclusive.



### Direct current

Tests carried out on a pilot plant have shown that sound emission can be reduced if the traditional alternating current power supply is replaced by direct current. Once the metal bath has been formed, the noise intensity measured was approximately 5-10 decibels lower. Power supply was 1 MVA.

As a result of these encouraging results, this solution was pursued further with the following research programme:

- development of technology: installation of suitable power supply facilities and an electrode in the furnace hearth to pass electric current through the bath;
- construction of a regulatory system for the electrodes designed to minimize the instability of the electric arc and thus optimize direct current operation.

At present this work is still going on.

Attempts to reduce the noise and circuit effects of electric-arc furnaces using direct current.

(Betriebsforschungsinstitute des Vereins  
Deutscher Eisenhüttenleute, Düsseldorf,  
Research Project PS 290)

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The emphasis of the work carried out hitherto in this project was, on the interpretation and explanation of physical effects at the electric arc in respect of noise emission, and on the evaluation of measurements carried out on a series of industrial arc furnaces.

An essential aspect of the programme, the research work carried out on a fairly large experimental furnace operating on direct current (approx. 5 tonnes capacity) has had to be postponed for various reasons. The experimental furnace

will probably not be operational before the end of 1980.

Experiments to investigate the physical processes that take place in the electric arc in connection with noise generation indicate that magnetic fields have a decisive influence on the movement of the electric arc, which is particularly irregular during the scrap meltdown stage. The magnetic forces produce rotation of the arc in the liquid bath, which is responsible for the higher frequency components of the noise spectrum.

A further possible source of noise may be vaporizing at the electrodes, and account must therefore be taken of the electrode material and its possible influence.

Industrial measurements were carried out on a 50-tonne UHP production furnace with a power supply of 34.5 MVA. This furnace has water-cooled side walls and a water-cooled ceiling. Separate measurements of the noise emitted from the interior of the furnace (airborne noise 5 m from the furnace slag door) and from the shell of the furnace itself (body noise), showed that in both cases pronounced frequency components of 50 Hz, 100 Hz, 150 Hz and 200 Hz were present.

Analysis of the results of extended series of measurements on several production furnaces points to some typical characteristics of the noise patterns:

- the highest noise levels were noted usually at the beginning of meltdown of each scrap basket. Throughout the melting stage the noise level does not normally sink below 90 dB (A).
- With continuous charging of directly-reduced ore (sponge iron) there is a 12 dB (A) reduction in noise level, similar to that when fine scrap is used. At the moment,

however, no use can be made of this discovery in industrial practice because not enough sponge iron is available for it to be economic.

- The size of the furnace does not have a decisive effect on noise generation. On the other hand, it was established that the average noise level during meltdown was related to the specific installed capacity of the transformer (MVA per tonne of tap weight).

Comparison with the results of research carried out in other countries, shows that correlations cannot be made without careful consideration if a uniform measuring methodology was not abided by.

Investigations into the mechanisms of noise generation from electric arc furnaces.  
(British Steel Corporation, London, Research Project PS 301)

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This research programme, which was approved at the same time as the previous two projects, also takes the results of laboratory tests as a basis for subsequent large-scale tests on a series of production furnaces designed to identify the decisive factors in the emission of sound.

Alternating-current electric arcs of up to 9kA were produced in a single-phase experimental furnace between a 150 mm graphite electrode and a slag-covered steel pool. Comparisons between the cine film pictures of the shape and movement of the arc and the noise measurements showed that harmonic noise is always associated with current controlled pulsations of the arc diameter and periodic movement of the arc. Broadband

noise is due to random movement and the rotation of the arc column.

Large-scale tests were carried out on 7 industrial furnaces of between 3 and 170 tonnes. Noise emission increased directly with:

- furnace power
- size of the scrap charged
- sinking slag depth.

The use of continuously-charged granulated pig-iron seems to have a dampening effect on the noise.

Noise control and fume elimination in an  
electric arc steel making plant  
(Ceretti, Villadossola, Research Project PS 296)

It is a well known fact that the latest generations of electric furnaces (HP and UHP furnaces) have aggravated the problems of noise and fumes. The aim of this research project was to ascertain which forms of noise and fume pollution are associated with a new electric furnace technology developed and put into operation at the Ceretti company.

The melting plant consists mainly of two electric furnaces of 90 tonnes nominal capacity with transformers having nominal power of 30 MVA, and a pre-heating furnace fuelled by natural gas with a throughput of 100 tonnes/hour.

Both furnaces are continuously charged with pre-heated scrap (or pre-reduced ore) from this ring-shaped pre-heating furnace and operate on the basis of a residual melt which remains in the furnace. As a consequence of difficulties that

arose during the research the capacity of the furnace was increased to 130 tonnes, so that 100 tonnes could be tapped and 30 tonnes remained in the furnace as the residual melt.

To ensure even distribution of the scrap during charging the furnace rotates slowly around its vertical axis. The furnace roof remains stationary and is sealed off from the main body of the furnace by a sand seal.

Half of the heat energy to fire the ring-shaped pre-heating furnace comes from the hot furnace gases; the other half is provided by natural gas burners.

The noise measurements at a distance of 15 m and with two open doors gave a maximum sound level of 92 dB(A) when two furnaces were in operation with a total power of 28 MW. This favourable result can be attributed to the following improvements:

- Reduction of electric power while maintaining the same level of productivity. Given a tap-to-tap time of 3 hours and an average tap weight of 95 tonnes, the melting power was of the order of 270 kVA/tonne of liquid steel. The scrap was pre-heated to approximately 1000°C.
- Reduction of the arc length as a consequence of the very low reactance of the furnace transformer circuit. This makes it possible to operate the furnaces with low secondary tensions (maximum 298 volts) at acceptable power factors (0.82 to 0.85).
- Elimination of arcing between the electrodes and the solid scrap. A liquid bath of molten steel is always present and the electric arcs, which are only very short, are always submerged beneath a covering of slag which damps the noise emission. During continuous charging of pre-heated scrap into a molten pool, the melting process is completed very quickly.

In exceptional cases noise levels higher than 92 dB(A) were recorded. This is the case during start-up with solid scrap at the beginning of the week, or after down time. But these are only short periods which are of no serious consequence for conditions during normal operation.

Significant improvements were also noted in dust levels. Charging the furnaces takes place on a continuous basis through the fourth hole in the furnace roof, and at the same time the fumes are piped away to the pre-heating furnace. The pre-heating furnace is connected to an efficient extractor system with a capacity of 800 000 Nm<sup>3</sup>/h and dry dedusting in bag filters. Before this the waste gases are passed through a heat exchanger, in which they heat up the combustion air for the natural gas burner to approximately 300°C.

In addition, various sources of dust emissions were eliminated, for example at the furnace doors, at charging devices (which are of the closed-container type), by optimizing of the pressure regulation in the flow of waste gases etc.

An improvement in pollutant emission is to be expected in view of the fact that certain metals with a low melting point (Zn, Pb, etc.) are already melted down in the pre-heating furnace and accumulate at the bottom of the furnace.

The overall result is that only a low level of dust emission was noted around the furnaces; however, no adequate solution has yet been found to the problem of reducing dust emission during tapping.

Investigation of the causes of noise and pulsation produced by gas burners for industrial furnaces.

(Betriebsforschungsinstitut des Vereins Deutscher Eisenhüttenleute, Düsseldorf, Research Project PS 251)

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The aim of the research project is to discover the causes of noise generation by industrial burners of the type used in the steel industry, and take measures to protect persons working in the vicinity of these from noise.

The research relates in the first instance to high-speed burners, where the exit speed of the hot combustion gases at the burner orifice is above 60 m/s, as are frequently preferred for heat-treatment processes.

In this research project, different types of burner were investigated: blower burners with a relatively low exit speed, swirling-stream and parallel-stream burners, nozzle-mix and long and short-flame burners of various kinds.

A free-jet test rig and two furnace chambers were available for the experiment. In order to keep the number of experimental variables as low as possible, all the investigations, once the appropriate initial tests had been concluded, were carried out with an air factor of  $\lambda = 1$  and with natural gas.

Some of the main conclusions of the extensive experimental findings are given here; the final report will have to be consulted for a complete evaluation.

- In several cases it was possible to achieve an improvement of approximately three dB in the noise level by minor design modifications.

For example, an improvement of this kind was achieved on the nozzle-mix burners by reducing the gas nozzle diameter, using a larger number of air nozzles and a higher angle of attack. In other nozzle-mix burners, the improvement was achieved by enlarging the nozzle diameter.

It was established that as a general rule the sound pressure level can be reduced if the mixing of the combustion gas and the combustion air along the burner axis is as intensive as possible, thus leading to stable combustion.

- On a certain type of swirl-type burner installed on a pusher furnace, minor design modifications did not result in any lowering of the sound level. Only when the basic burner design was modified (to incorporate stabilization of the flame deflector) was a noise reduction of 12 dB achieved.
- Investigations carried out on another swirl-type burner showed that there was a relatively favourable frequency composition. On an A-weighted scale the value was approximately 90 dB(A). Modified gas lances gave an improvement of 2 dB.
- The sound pressure levels measured in the furnace chamber were generally 30 dB lower than the values measured on the free-jet test bench.
- Sound emission is very closely dependent on the load factor. Use can only be made of this possibility in special cases, however, e.g. by using a larger burner at 50% nominal load.



Development of an array of microphones for  
directional sound measurement.

(Hoogovens, IJmuiden, Research Project PS 323)

When carrying out sound measurements in an industrial environment where there are several sources emitting noise at the same time, it is interesting to establish the connection, if any, between the noise level and the direction.

It is hoped that this aim can be achieved by developing a special array of microphones designed specifically for this purpose. The proposed arrangement, consisting of a series of identical microphones placed at equal distances from each other, was tested in the laboratory with various types of microphones. Once the appropriate model had been selected and the electrical switching system had been further developed in order to add up the signals, initial measurements using artificial noise source were carried out on unbuilt-up ground.

The results are so satisfactory that we can now pass on to the next phase of research. This will entail installing the system to detect the location of sound sources in an industrial complex.



CHAPTER 4

Reutilization and environmentally safe  
elimination of residues and wastes.

Investigation into the treatment and processing  
of waste matter from iron and steelworks.  
(Verein Deutscher Eisenhüttenleute, Düsseldorf,  
Research Project PS 225)

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The majority of the results obtained from this research have  
already been reported upon in brochure EUR 5977. Research  
results relating to the following topics remain to be reported  
on.

- Investigation of residues and waste materials used in  
sinter plants in respect of environmental protection.
- Research on the treatment and processing of residues from  
iron and steelworks by means of reverse osmosis.

The work on the former topic can be subdivided into the  
following main experiments:

1. Laboratory sinter trials to trace components of residues  
and wastes charged in sinter plants.
2. Measurements on a full-scale sinter plant to study  
pollutants.
3. Research on ways of reducing sintering fumes.

The results of ladle sinter tests on the behaviour of the  
tramp elements frequently present in sinter blends may be  
summarized as follows:

In all tests the sulphur was almost completely expelled from the sinter mix. It was shown that there was a sulphur-rich layer 3 to 7 cm-wide, which moved along just ahead of the point of combustion. As the basicity rose, sulphur enrichment of this area increased. This means that the peak levels of  $\text{SO}_2$  occur in the sinter waste gas along the sinter machine, before the flame front reaches the grate. As the basicity rises this peak becomes more pronounced.

Chlorine was expelled until only a few traces remained, independently of the form in which it was present in the mix.

Only small amounts of the metallic elements associated with iron (Pb, Zn, Cu, Sb and Sn) were expelled during sintering, but rather more when volatilizing agents were present, in this case compounds containing chlorine.

The tests carried out yielded little information about the behaviour of sodium and potassium. For the most part they remained in the mix, and expulsion was only slightly increased by adding chlorine.

Measurements carried out on an industrial sinter plant confirmed the results indicated above only in part, though the difficulty of carrying out the experiments must be taken into account. The following rough figures were obtained: approximately 70% of the sulphur, 60% of the chlorine, and 36% of the fluorine were expelled during sintering. A comparison of the total quantities in the collected gas and in the fumes upstream of the fan showed that 32% of the sulphur, and 35% of the chlorine were filtered out of the fume in the dust cyclone and must be precipitated in the cyclone dusts. This reduces the quantities recycled and hence the air pollution caused, on condition that at least part of this cyclone dust can be evacuated from the system.

Investigations into the possibility of recycling hot fume components showed that this solution had a certain chance of technical success and environmental improvement. Theoretical calculations of various gas control options indicated that in one case the volume of sinter fume discharged into the atmosphere could be reduced by up to 40%. At the same time, there were definite savings in fuel, although only at the cost of some sintering efficiency.

The second theme of research concerns the treatment and processing of residues from steelworks by the process of reverse osmosis. All in all, the results of the tests were not very promising. The quality of the extracts obtained from top gas dusts and sludges by ammoniacal leaching of zinc and lead elution with acetic acid and the quantity of washing water generated were such that no reasonable economic use can be made of reverse osmosis. This was due partly to the fact that high osmotic pressures are necessary in most cases for reverse osmosis treatments, and partly to the lack of durability of the membranes at present available, which would create problems and extra costs if they were to be used in regular operation. The permeation capacity required would demand large membrane surfaces, which would also entail high capital and running costs.

Reutilization and preparation for release into the environment of dust and sludge containing Fe, Zn and Pb produced in the manufacture of iron and steel.

(Verein Deutscher Eisenhüttenleute, Düsseldorf,  
Research Project PS 271)

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Taking due account of the results achieved in research project PS 225 in industrial tests on Wälz (rotary kiln) furnaces,

which were reported upon in brochure EUR 5977, further in-plant tests were continued as part of this research project.

In the Wälz process the charge materials, which are mainly mixtures of blast furnace sludge, LD sludge and LD dust, are subjected to reducing volatilization of the zinc and lead component. Retreatment and reutilization of the residual materials mean that the quantities of waste which have to be dumped can be reduced, and in this way damage to the environment can be avoided.

For these tests a mixture of recycled materials was chosen corresponding to the composition to be expected in the 1980s. The mixture was composed as follows:

12% blast furnace sludge  
64% partly dried LD sludge  
24% LD dust.

Mill sludge was also added for two short tests.

The tests were carried out in a 41-m long Wälz furnace in the Berzelius Metalhütten GmbH plant and lasted, divided into four stages, for a total of 29 days.

It was found that the simplest method of pretreatment was to combine the individual constituents and feed them into an impact crusher and roll the ensuing mixture on a disc pelletizer.

The nature of the reducing agents used also played a very important role. These included coke breeze, Emscher coal, high temperature coke from brown coal, brown coal briquettes and lean coal. The choice of additives and the conditions under which they were added also had a vital influence on the

temperature variations in the furnace, the pattern of operations and the degree of volatilization achieved.

On average, throughout the four stages of tests, a reducing agent consumption of 307 kg/per tonne of charging material was recorded. The highest and lowest figures for reducing agent consumption were 240 and 390 kg per tonne. The tests were carried out with 5% to 10% carbonized material in the form of excess breeze coke. By treating the material discharged from the kiln using magnetic separation, carbon contents in the 'sponge iron' of less than 2.3% were achieved.

In the case of zinc and lead, contents of approx. 0.1% in the furnace discharge material were noted. Often, however, even lower figures were recorded. This corresponds to volatilization of more than 95%.

The metallization of the iron never presented any problem. Samples taken straight from the kiln were 98% metallized, whilst in the cooled material the proportion was on average more than 90%. The precondition for a high degree of metallization and satisfactory volatilization is always, of course, the application of high basicity. The ratio of CaO + MgO to SiO<sub>2</sub> in the charge material should be at least 1:2.

The Wälz oxide in the fume was separated out by treatment in, in turn, the cooling tower, staggered conduction and electrical gas cleaning plant, during which processes the separated dust became richer and richer in lead and zinc throughout the sequence. The chemical composition of the Wälz oxide from the first, third and fourth series of tests was as follows:

	Average	ranging from:
Zn%	21.3	19.8 to 22.1
Pb%	9.6	8.4 to 11.4
Fe%	27.7	24.9 to 28.5
C %	4.5	3.7 to 5.3

The wälz oxide constituted 17.5% of the total discharge material from the kiln collected throughout the test.

The agglomeration of the fine constituents of the kiln discharge material was accomplished most easily by cold briquetting with a 3% sulphite leaching mixture. Attempts to use direct hot briquetting methods were unsatisfactory.

Study of the reduction of the zinc and lead contents of materials used in the production of pig iron in order to eliminate air and water pollution.

(ARBED, Esch-sur-Alzette, and Centre Belge d'Etude et de Documentation des Eaux, Liège, Research Project PS 235)

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This research project has already been reported on in detail in booklet EUR 5977 but there are still some findings of tests carried out mainly at ARBED to be reported.

1. Tests in a pilot plant on the combined leaching of Zn (with ammoniacal solutions of ammonium carbonate) and Pb (with acetic acid) did not confirm the very promising results of the laboratory tests. Technical difficulties and doubts about the economic viability of the process suggested that the process is not very promising for industrial purposes.
2. Rotary furnace tests to expel Zn and Pb using a process of dry chlorination were abandoned in view of the results already obtained elsewhere.
3. Similarly, the processes for the enriching of Zn and Pb based on air separation of the zinc and lead-rich fines, or by addition of milk of lime to the blast furnace gas cleansing water in order to precipitate the dissolved zinc, were also discontinued because of the difficulties



encountered during the process.

4. On the other hand, zinc removal from the dusts by dissolution with carbonic acid solution and recovery as zinc carbonate seemed promising. The process works under pressure, and the degree of extraction rises as the pH value of the leaching solution falls and as the solid/liquid ratio declines.  
Data relating to the economic viability of the process will not be available until trials have been carried out on a pilot plant.
5. Studies of the levels of zinc and lead in recycling circuits in sinter plants and blast furnaces provided the information that non-recycling of the blast furnace dusts mainly affects the zinc content of the blast furnace sludges.

Pilot study of a caustic soda treatment process for reducing the zinc and lead content of waste products from iron and steel making processes.  
(Centre Belge d'Etude et de Documentation des Eaux, Liège, Research Project PS 313)

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The first part of this research project, which is to be carried out in two stages, has been completed.

It was shown in a previous research project (PS 235, see booklet EUR 5977) that wet treatment - in soda lye - of sludge-like steel industry residues to remove zinc and lead was technically possible and had good prospects from the economic point of view.

The objects of the first stage of this follow-up research project were:

- Further investigation of the various stages of the treatment process. Final decision on the choice of pilot plant, preparation of the plans and determination of the size of the reactors.
- Construction of the actual pilot plant.

Results:

Extraction by leaching: It was decided that a two-stage process of extraction be leaching in counterflow conditions would be undertaken.

Solid/liquid separation: Of the various possible separation processes (filtering, decantation, centrifuging) the decantation process was chosen, as it provides satisfactory results when carefully selected, non-ionic flocculation agents are used.

Cementation: The best conditions for this operation, by which the lead is recovered prior to electrolysis, were determined. At a high reaction speed, yields approaching 100% were achieved.

Electrolysis: The critical current densities and the other process conditions for technically and commercially satisfactory separation of zinc were established.

Washing of leaching residues: Planning and design criteria for the construction of the cylindro-conical decanters were prepared.

Filtration and dehydration of sludge: Filter presses and a solid-bowl centrifuge were used for this purpose.

On the basis of the findings of this research, a pilot plant was constructed which is now available for carrying out semi-technical tests.

Recovery of valuable materials from sludge produced during the retreatment of blast furnace waste gases.

(Centre de Recherches sur la Valorisation des Minerais, Nancy. Laboratoire de Chimie du Solide de l'Université de Nancy, Research Project PS 258)

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A number of results must be included here to supplement the data given in booklet EUR 5977. These results relate in particular to investigations into the various pre-treatment processes for the separation of zinc and lead:

- Flotation tests by means of carrier minerals; depending on the pH conditions, the carrier mineral was calcite or quartz grains. The results obtained are very mediocre and the technique unwieldy and complicated for industrial application.
- Recovery tests by means of wet high-current and low-current magnetic separation. These tests gave only moderate results owing to the excessive fineness of the grains constituting the crude ore.
- Selective flocculation and dispersion test; the selective flocculation tests did not give good results. The reagents used were not selective owing to the poor crystallinity of the phases containing the zinc and the lead.

From the extensive dispersion tests carried out, however, a simple and economic method of pre-concentration was developed.

Results obtained with the pre-concentration method:

It was established following phase dispersion tests, that zinc and lead were concentrated predominantly in the small grain-size fractions of the sludges. For grain separation at

37  $\mu$ m the pre-concentration process gave the following results:

When the lead and zinc content of the crude ore is between:

- 3 and 4% concentrates assaying between 7 and 10% are obtained, with a recovery rate of around 80% for lead and 60% for zinc.
- 4.5 and 8.5% concentrates assaying between 10 and 20% are obtained, the recovery rates then being around 80% for both elements.
- 10 and 15% concentrates assaying between 22 and 33% are obtained, the recovery rate then being over 80%.

These results can be improved from the point of view of the lead and the zinc content, but this would be to the detriment of the recovery rate, especially in the case of zinc.

Beneficiation of secondary clarification sludge  
from blast furnace gases and convertor dusts.  
Recovery of lead and zinc.  
(Laboratoire de Chimie du Solide, Nancy,  
Research Project PS 317)

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During previous research (PS 258) it was possible, on the basis of a series of samples all taken from the same place (Hayange, Lorraine) to study the phases of zinc and lead, to determine and demonstrate the distribution of zinc throughout its various phases, and to show that both elements occur in concentrated form in fine dust. A pre-concentration process using grain separation was developed by the Centre de Recherches et de Valorisation des Minerais.

It was through necessary to extend the investigations to include samples of differing origin and this is the subject of this research project. So far the following samples have

been examined:

- |  |         |                            |
|--|---------|----------------------------|
| - blast furnace                            | sludge  | Sacilor (France, Joeuf)    |
| - blast furnace                            | sludge  | Arbed (Luxembourg, Esch)   |
| - blast furnace                            | sludge  | Cockerill (Belgium, Liege) |
| - blast furnace                            | sludges | Thyssen (Germany, Hamborn) |
| - LD converter                             | dust    | Thyssen (Germany)          |
| - LD converter                             | dust    | Thyssen (Germany)          |
| - 1/3 blast furnace +<br>2/3 LD converter. | mixture | Thyssen (Germany)          |

The first result of this research was the basic observation that no generally valid rules for the composition of the samples in respect of their zinc or lead content could be established. This is particularly true of the distribution of these elements throughout the various grain fractions.

In the case of the Lorraine blast furnace sludges sample, metallic Zn was principally present in particle fractions of more than 250  $\mu\text{m}$ , zinc oxide and wurtzite were present in all fractions of below 500  $\mu\text{m}$ , and PbS in all fractions.

In the Luxembourg blast furnace sludge sample, the zinc was distributed in the form of oxides and hydroxides on an equal basis throughout practically all fractions. Wurtzite is only found to a limited extent. Lead is found in all fractions as a carbonate.

Because of their high zinc contents, both the sludges could be used for zinc recovery without any prior treatment. In the sample provided by the Cockerill company, on the other hand, the lead and zinc content was too small for recovery of these metals through simple treatment.

In the case of the blast furnace sludges from Germany, lead was present as a sulphide and as a carbonate in the fine

particle proportions ( $\leq 30 \mu\text{m}$ ), which were most predominant. Zinc was present as wurtzite ( $\text{ZnS}$ ) and oxide.

The samples from the LD shops had high iron oxide and calcite contents. Zinc and lead were mainly present in the fine particles; the corresponding phases were not identified.

The enriching tests which were subsequently carried out with the blast furnace and LD samples received from Germany were unsatisfactory. This was partly because of the extremely high proportion of fine particles in the sample. In the case of the LD samples particles of below  $38 \mu\text{m}$  accounted for between 74 and 79%, whilst the blast furnace samples had fine particle proportions  $\leq 38 \mu\text{m}$  of 82% in the case of the blast furnace + LD mixture and 92 to 99% in the case of the blast furnace fine sludge or the filter cake.

Further tests are planned.

Manufacture of phosphatic fertilizers.

(Verein Deutscher Eisenhüttenleute, Dusseldorf,  
Forschungsgemeinschaft Eisenhüttenschlacken,  
Duisburg, Research Project PS 281)

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For every tonne of pig iron produced, an average of 350 kg of slag is formed, and in steel production, an additional 150 kg of slag per tonne of crude steel (approx.) must be disposed of. Whereas blast furnace slags can be completely beneficiated, this is not true of steelworks slags, in spite of the continuous development of completely new areas of use.

During the smelting of ores rich in phosphorus this problem does not arise as the resulting steelworks slags, which are also rich in phosphorus (12-18%  $P_2O_5$ ), constitute an excellent fertilizer. During recent years, however, steel manufacture has been increasingly switching over to the use of ores with a low phosphorus content; because of their relatively low phosphate content (1-3%  $P_2O_5$ ), the saleability of the resulting steelwork slags is limited.

Increasing the  $P_2O_5$  content of this slag to a level of 3 to 7% will open up new commercial outlets for this slag as a calcareous phosphatic fertilizer. The aim of the present research project was to investigate whether steelworks slag could be enriched as regards its  $P_2O_5$  content, which is of great value to plants, by adding chemically or thermally decomposed waste or by-products containing phosphates, so that it could then be used as a calcareous phosphatic fertilizer.

For the enriching process bonderized sludges produced during the surface refinement of steels, washery wastes, a waste product containing phosphoric acid and some phosphatic waste materials deriving from other industries were investigated.

Bonderized sludge or washery wastes were mixed or crushed with steel works slag and crop-growing tests showed that the maximum phosphatic effect for bonderized sludge was 76%, and for washery wastes 83% as compared with the standard Thomas phosphates. Crushing the washery wastes with steelworks slags is not possible because some of the material adheres to the walls of the crushing mill.

Liquid waste from the chemical industry which contains phosphoric acid cannot be added to either solid or liquid steelworks slag for reasons of operational safety. After neutralization with lime, a powdery phosphatic substance results which is well suited for enrichment with full phosphatic effect.

Phosphates can be thermally decomposed by molten calc-silicate slags (steelworks slags). However thermal decomposition of bonderized sludge by blending with liquid steelworks slags is not safe, since the residual moisture causes slag ejection. In addition, industrial tests showed that the sludge was not sufficiently decomposed and that the phosphate was very unevenly distributed. The available heat in the slags is such that the phosphates can only be enriched by a maximum of 5% with washery wastes.

Crop-growing tests with these artificially enriched slags are only of limited reliability in the case of bonderized sludge enrichment, because the enrichment level was too low. When washery wastes are used it is quite clear that the boron contents of these substances depresses plant growth. As a general principle, it was established that waste and by-products used for this purpose must be as free as possible of elements that are harmful to plant life such as zinc, boron and elements that produce apatites, in particular fluorine.

These phosphatic waste products are produced in small quantities in many areas scattered throughout the country and an economic solution must be found to the problem of transport if the possibilities of using these products for phosphatic enrichment that have been demonstrated by this research are to be put to practical use.



Thermal fusion of phosphates, especially a Ca-Al phosphate, in a rotary kiln processing material at a rate of 800 kg/h.

(Verein Deutscher Eisenhüttenleute, Düsseldorf, Forschungsgemeinschaft Eisenhüttenschlacken, Duisburg, Research Project PS 320)

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The fundamental problem tackled in the previous research project, PS 289, is the same as that dealt with in this project: that is to say, increasing the  $P_2O_5$  contents of LD slags to between 3 and 7% in order to create new sales outlets for these slags as phosphatic fertilizers.

Following a successful series of laboratory tests, thermal fusion in a rotary kiln of a calcium aluminium phosphate with lime and soda, and ashed sludge with soda was studied under semi-technical conditions.

Pelletizing the mixture of Ca-Al phosphate, soda and various calcareous substances ( $CaO$ ,  $Ca(OH)_2$ ,  $CaCO_3$ ) resulted in the formation of deposits on the pelletizing disc, which suggests that long-term use of this process would not be feasible. The most reliable pellets were those which were produced using  $Ca(OH)_2$ . The problem cannot be solved by charging powdery mixtures into the rotary kiln; when this was done accretions on the wall of the kiln resulted. Briquetting these mixtures does not raise any problem.

Initial tests to investigate combustibility showed that the Ca-Al phosphate in the form of pellets was only suitable for the rotary kiln process when  $Ca(OH)_2$  was used, whilst it can be used in the form of briquettes when  $CaCO_3$  or  $Ca(OH)_2$  are used. From the point of view of cost, the mixture containing

$\text{CaCO}_3$  is more attractive. The ashed sludge and sodium carbonate mixture is only suitable in briquette form.

In the semi-industrial trials a phosphate fusion  $\gg 95\%$  was achieved in pellets of Ca-Al-phosphate/soda/ $\text{Ca}(\text{OH})_2$ , in briquettes of Ca-Al-phosphate/soda/ $\text{CaCO}_3$ , and in ashed sludge/soda at 1150 and 1050°C respectively. During two-year crop-growing tests the efficiency of the phosphates in the resulting products was equal to that of the standard Thomas phosphate fertilizer used for comparison.

A profitability analysis shows that the costs of thermal fusion of phosphates in a rotary kiln are still higher than those of comparable phosphates, above all because of the high energy and manpower requirements of the process.

Research into the causes of the pollution of surface and underground water and means of its control during the preparation, storage and use of blast-furnace slag.

(ARBED, Luxembourg, Research Project PS 270)

Any contact between blast-furnace slag and water can lead to leaching and subsequent discharge into the environment of the soluble compounds it contains. Such contact can occur when the slag is being spray-cooled as it is drawn off into pits, when it is dumped on slag heaps and when the slag is used on building sites.

The substances leached out of blast furnace slag consist mainly of sulphur compounds (sulphides, thiosulphates and polysulphides) and alkaline salts (sodium and potassium), of which the former may fix the oxygen dissolved in the water whilst the latter may raise the pH of the water and thus lead to the formation of deposits and scale.

In order to obtain a better understanding of the complex leaching processes, leaching experiments were carried out on a pilot scale and in the laboratory, and large-scale investigations were carried out on slag heaps.

#### Leaching tests

Laboratory tests, tests in a 3-tonne tank and large-scale tests on a 40 t slag pit with slags of various textures demonstrated that the quantities of leached sulphur varied considerably (0.022 to 1.174 g sulphur per kg of slag).

The main parameter affecting the quantity of sulphur was the age, the particle-size and the porosity of the slags. The majority of the soluble compounds are dissolved during the first 24 hours.

#### Investigations on slag heaps

As part of a hydrological investigation at a slag heap (at Ehlerange), the following facts were established:

- there is no aquiferous layer within the slag heap;
- the water-flow within the heap is not equally distributed; water finds its way out through particular channels;
- the seepage takes between two and three weeks;
- given the almost impermeable basis upon which the slag heap is built, the ground water located beneath it is scarcely affected by the infiltrations from the slag heap;
- the run-off water evacuated from the slag heap via drains into the main water course does not contain any sulphides.

Measurements carried out on a slag heap after the blast furnaces supplying it had been closed down, showed that once additional dumpings of slags cease the temperature and concentration of pollutants rapidly decline.

Oxygenation and precipitation of sulphur compounds

During laboratory and large-scale tests with run-off water, oxygenation with air and sulphide precipitation using ferrous sulphate appeared to be the most promising from the technical and economic points of view.

Interaction between wastes and water  
(IRSID, Maizières-lès-Metz, Research Project  
PS 291)

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This project also dealt, in a more general way, with the effect on surface and ground water of the disposal of waste products on dumps. In order to determine the potential extent of leaching, approximately 150 leaching tests were carried out in the laboratory on waste products from the iron and steel industry.

The tests showed up several fundamental tendencies:

1. All in all, the dissolution kinetics obey laws of the first order.
2. Leaching affects only the surface of the product.
3. The pH values recorded are mainly the result of interaction between calcium and water.
4. Dissolution of most of the elements is limited by the very low solubility of their hydroxides.

5. Generally speaking, sulphur is in relative terms the most soluble element in blast-furnace and steel-making slags, as well as in the dust and sludge from the two types of plant. When leached, this sulphur oxidizes rapidly on contact with the air and turns into sulphate ions.
6. In the case of dust from electric-arc furnaces, the solubility of lead increases as a function of the free lime content. It ought to be possible to arrest this phenomenon by rational use of lime in electric steel-making plant.
7. The fluorine ion proved to have very low solubility in the treated sludge downstream of the alloy steel fluoronitriding process and also in other by-products with a low fluorine content.
8. All in all, the risk of water pollution by steel-making waste dumps is very limited.

The results of the laboratory tests were cross-checked by analysing sample solutions taken from the bottom of dumps. It is important not to forget that a natural dilution coefficient of at least 10 has to be applied to the flow of water from refuse dumps, as an American study carried out by the Environmental Protection Agency has shown. Under these conditions, fluorine and heavy metals do not cause pollution of the surface or ground water.

As a follow-up to this study, a standard leaching procedure prepared and implemented at the European level would be useful in that it would enable operators in the sector to appraise the pollution risk and also to make plant-to-plant comparisons.

Elimination from rivers and beauty spots of pollution from wire-drawing plants by developing a new mechanical descaling process for steel wire.

(Centre de Recherches de Pont-à-Mousson,  
Pont-à-Mousson, Research Project PS 262)

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It is usual to descale hot-rolled steel wire by a chemical pickling process. The pickling baths are neutralized with lime, and the resulting calcium salts are discharged into water courses. The ferric hydroxide which also results from the process has to be disposed of on waste dumps.

This environmental pollution can be eliminated by mechanical descaling, during which the steel wire is normally cleaned of its scale by plastic deformation of the wire rod on two planes. Of course, this process also has disadvantages, as it leaves small amounts of residual scale which have an unfavourable effect on the drawing qualities and the appearance of the wire.

The aim of this research is to examine the possibility of descaling wire rod by a new mechanical process, in which the rod is subjected to plastic elongation applied by a tensioning device.

#### Results:

By means of static elongation tests, it was established that during the early stages of deformation in all cases the initial effect is for a significant amount of scale to be freed from the wire rod. Subsequently, descaling slows down, but even after very extreme deformation there is still a certain amount of scale on the wire, the exact amount of which depends on the original scale thickness and, above all, on the roughness of the wire rod. The optimum degree of deformation is 8%; the corresponding percentage of residual

scale is between 0.5 and 1%.

Tests carried out on wire rod that had been stored in the open air and was slightly rusty did not yield significantly different results.

These results obtained with elongation are absolutely comparable with those obtained with bending in two directions. It was therefore decided that it was pointless to build a special descaling machine working on the elongation principle.

Further research was carried out on the removal of the residual scale by an ecologically acceptable pickling process. 7% phosphoric acid was used at a temperature of 70°C in a plant with ultrasonic vibration facilities (1 kW, 20 kHz). A certain degree of phosphatization of the wire was observed, which would facilitate high-speed drawing of the wire without any need for lime or borax treatment. By filtering the pickling fluid, the acid can be directly recycled. Using this process it was possible to remove the residual scale almost completely.

Definition of a continuous neutral electrolytic pickling process for the radical solution of noxious industrial effects.

(Centro Sperimentale Metallurgico, Rome,  
Research Project PS 282).

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The traditional chemical pickling process for the descaling of steel constitutes a significant source of environmental pollution. The neutral electrolytic pickling process proposed by CSM (NED = neutral electrolytic descaling) obviates the use of acid. The latter is replaced by neutral salts, which may be regenerated or eliminated without danger to the environment, as may also the resulting pickling sludges.

The aim of this research is to establish the process parameters for such a plant for the descaling of hot-rolled strip of non-alloy, low-alloy and Si-steel for electric sheet.

Results so far:

It was noted that the main electrolytic reactions, that is to say those which result in the electrolytic decomposition of the water, took place during the activation stage; for this reason electric voltage necessary in practice for the reaction in the NED process is virtually independent of parameters such as temperature, bath movement, concentration and current density. Operating conditions were satisfactory at an electrolysis voltage of 3 volts.

The conductivity of the  $\text{Na}_2\text{SO}_4$  solutions used as the electrolyte was measured as a function of the salt concentration and the temperature; in addition, methods were developed for calculating important operating parameters.

Studies of the characteristics of wire-rod scale subjected to pre-treatment (mechanical scale removal) showed that pre-treatment had a very strong influence on the pickling process. It was found that the NED process would only be feasible if the reduction in diameter as the scale was removed during re-rolling was over 2%.

The results of experiments on the treatment and/or reuse of the resulting sludges are not yet complete, and as they were obtained with laboratory-produced sludges they ought to be checked using industrial sludges, or sludge from a pilot plant. No particular difficulties are, however, expected.

Tests carried out on hot-rolled Si-steel showed that it reacted more readily than non-alloy steel.



The characteristics of the resulting surface film depend on the subsequent passivation process and the Si content of steel. In practical applications of the NED process to Si-steel, it is desirable that there should be a sequence of cathodic and anodic polarization of the steel strip.

After the completion of the pilot plant, operating tests were carried out in order to optimize the process. The initial tests were carried out using shot-blasted coils made of Si steel with current densities of between 20 and 60 A/dm<sup>2</sup>. It was confirmed that mechanical pre-treatment had a fundamental influence on the surface quality and hence on the required current density. Given a thickness of steel strip of 2.5 mm, power of between 25 and 70 kWh/t was required, according to the nature of the pre-treatment.

Study of the combustion of used emulsions from cold rolling mills without air-polluting residues.

(Centre Belge d'Etude et de Documentation des Eaux and Centre de Recherches Métallurgiques, Liège, Research Project PS 236)

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The aim of the research work was to develop devices for the elimination of the oil residues and oil sludges produced during the regeneration of emulsions used in cold-rolling mills. A two-stage process was suggested as a way of solving the problem:

- separation and precipitation of the oil residues out of the emulsions and effluent,
- ecologically safe combustion of the residues.

The first stage was successfully completed in 1977; the

results were summarized briefly in booklet EUR 5977. The flow-chart developed for the treatment of the effluent comprises the breakdown and flocculation of the emulsions with subsequent electrostatic flotation. The clarification treatment using electrostatic flotation must be carried out with the addition of a non-ionic polyelectrolyte. The rates of cleansing achieved in this way are excellent, though they are only guaranteed if the characteristics of the emulsion that is being treated remain reasonably constant.

The task of carrying out the second part of the research was taken on by the Centre de Recherches Métallurgiques in Liège. Tests were designed to examine the possibility of burning the emulsions in the tuyeres of blast furnaces using existing fuel oil injection systems. On the basis of CEBEDEAU's findings, oily rolling mill effluent that could not be cleaned using the separation process developed was used for these experiments.

Comparisons with the FOG injection system developed by the CRM showed that the use of this rolling mill effluent instead of the water normally used for the atomization process did not affect the tuyeres in any significant way. High combustion rates were achieved.

This method can therefore be used for ecologically safe elimination of used emulsions, on condition, of course, that an efficient atomization system is also used. Since the injection of water raises coke consumption in the blast furnace, the quantity injected should be limited to approximately 10% of the fuel oil consumption.

Recycling of wastes produced during stainless steel making.

(British Steel Corporation, London, Research Project PS 307)

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The manufacture of stainless steels creates waste products, including furnace fumes, mill scale, metallic swarf, semi-metallic sinter and pickling liquors. If the wastes could be recycled, not only would the problem of pollution be solved, but there would be a saving of the valuable metals, chromium and nickel.

The research work concerned with this particular aim will not be completed until 1981. The partial results so far available are as follows:

1. Solids contained in fume

Pelletized fume products were returned to a 15-t arc furnace (between 1.0% and 4.5% of the tap weight of the furnace). The tests show that the recycled nickel component of the products was taken up by the molten bath, whereas the chromium was lost in the slag. A slight increase in the phosphorus and sulphur contents of the steel was noted. The process would seem to be technically feasible and interesting from the economic point of view, though the operational problems involved must be further investigated in a larger production plant.

Furnace fume products pelletized together with coke were charged to a high-carbon melt, for the purpose of reducing the metal oxides, in a test furnace. The reduction was completed by addition of ferrosilicon. The resulting product, however, is not considered economic because of its low alloy content and the high production costs.

Further reduction tests were carried out with pelletized solids in an experimental-scale rotary kiln. Iron oxide was

reduced readily, but chromic oxide could only be reduced at a very high temperature. The quantity of carbon needed for the reduction is high, but the process still seems to be economically viable.

An alternative way of re-using solids could be the process of briquetting. Initial tests using various briquetting presses showed that the addition of a binder is necessary. Operational tests using cement as a binder may well succeed, but have not yet been completed. Further tests using rolling briquetting machines and bitumen as a binder are planned.

## 2. Neutralized pickling residues

Tests designed to make the sludge arising from the pickling of stainless steel re-usable were principally concentrated on filter processes. In particular, the use of high-pressure filter presses and the effect of filtering aids such as slaked lime, steelworks dusts and fine ash were investigated.

Tests using an Alfa Laval piston press at pressures of up to 138 bar resulted in filtration times of more than 10 minutes; between 4 and 5 minutes is considered an acceptable filtration time. The addition of filtering aids had scarcely any effect on the result. The filter cake still has a certain residual moisture content which is too high for it to be used in the furnace. All in all, filtration is not at present considered very promising. Tests are still under way on the vaporization of the residual moisture.

## 3. Grinding residues

During grinding, waste products consisting of metallic swarf and semi-metallic sinter are produced containing approximately 20% oil.

Recovery of this extremely valuable waste product was tried,

using a briquetting process. The briquettes produced still contained approximately 7% oil; for safety reasons, however, an oil content of below 2% is required for use in electric furnaces. For the further research work several firms were contacted to investigate the possibility of separating and recovering the oil before briquetting.



I. CONTROL OF AIR POLLUTION

I

1	2	3	4	5
Project Reference	Research undertaken by	Subject of research	Dates for commencement and completion of research	Maximum aid as % of research cost in u.a.
PS 158	Bayerisches Landes - institut für Arbeits- schutz Pfarrstrasse, 3 D- 8 MÜNCHEN 22	Measurement and recording of con- centrations of silicogenic, toxic and obnoxious dusts at working places using the "Konitest".	01.09.1971 31.08.1978	75,00 % 32.786,88 R.E.
PS 175	Institut voor Milieu- hygiene en Gezondheids- techniek T.N.O. Schoemakerstraat, 97 NL- 2628 DELFT VK Wijk 8	Investigation of the effects on dust particle counts of overlap- ping particles and of the medium in which the particles are held during counting.	01.07.1971 31.12.1976	65,00 % 8.618,79 R.E.
PS 229	Musée d'Histoire Naturelle Marché aux Poissons LUXEMBOURG	Electron microscope investigation of respirable dusts in the iron and steel industry.	01.11.1973 30.06.1976	60,00 % 23.500,00 R.E.

PS 254	British Steel Corporation 14e, Battersea Park Road LONDON SW 11 4 LZ	Remote monitoring of the properties of untreated effluent gas from oxygen steelmaking processes	01.08.1974 31.10.1977	60,00 % 124.608,00 R.E.
PS 261	Laboratoire d'Etude et de Contrôle de l'Environnement Sidérurgique LEGES B.P.36 F57210 MAIZIERES-LES-METZ	Monitoring of suspended particulate matter in the vicinity of iron and steel works.	01.04.1975 30.09.1977	60,00 % 11.500,00 R.E.
PS 272	Université de Liège 2, rue Armand Stévant B- 4000 LIEGE	Correlation of results provided by six devices for sampling settling dusts, or "dustfall".	01.04.1976 31.03.1978	60,00 % 35.904,00 R.E.
PS 231	Laboratoire d'Etude et de Contrôle de l'Environnement Sidérurgique LEGES B.P.36 F- 57210 MAIZIERES-LES-METZ	Development of a method of analyzing measurements of atmospheric pollution in the iron and steel industry.	01.01.1975 31.03.1978	60,00 % 178.167,40 R.E.
PS 283	Betriebsforschungs- institut des Vereins Deutscher Eisenhütten- leute VDEh Breite Strasse, 27 D- 4 DUESSELDORF	Basic planning for measuring the distribution of pollutants in the air with a view to assessing the relationship between immission and emission sources.	01.04.1977 31.03.1980	60,00 % 157.200,00 R.E.



PS 300	Institut voor Milieuhygiene en Gezondheidstechniek Schoemakerstraat, 97 NL-2628 VK DELFT Wijk 8	Measuring strategy.	01.01.1978 01.01.1981	60,00 % 234.300,00 R.E.
PS 285	British Steel Corporation 140, Battersea Park Road GB-LONDON SW 11 4LZ	Measurement and analysis of airborne emissions from coke-ovens, with particular reference to worker exposure.	23.07.1976 22.06.1979	60,00 % 271.200,00 R.E.
PS 305	Bergbau-Forschung GmbH Postfach 130 140 D - 4300 ESSEN 13	Model tests with novel ventilation systems for coke-oven sheds.	01.04.1977 01.10.1979	60,00 % 224.700,00 R.E.
PS 319	Bergbau-Forschung GmbH Postfach 130 140 D - 4300 ESSEN 13	Development of novel seals for coke-oven doors.	01.10.1978 01.10.1981	60,00 % 579.000,00 R.E.
PS 248	Institut voor Milieuhygiene en Gezondheidstechniek Schoemakerstraat, 97 NL- 2628 VK DELFT Wijk 8	Research into possibilities of improving working conditions in the firing shop of the pelletizing plant at Hoogovens IJmuiden B.V. by studying the dispersion of air pollution in the plant under the influence of the air currents prevailing in the area.	01.08.1974 31.12.1976	60,00 % 58.500,00 R.E.

PS 257	Centre de Recherches Métallurgiques C.R.M. Abbaye du Val-Benoit B - 4000 LIEGE	Abatement of sulphurdioxide emissions from iron ore sinter plants into the environment, by reducing the amount of solid fuel in the sinter mix.	01.01.1975 31.12.1976	60,00 % 73.500,00 R.E.
PS 297	Laboratoire d'Etude et de Contrôle de l'Environnement Sidérurgique LECES B.P. 36 F-5721e MAIZIERES-LES- METZ	Investigation and control of the emission of gaseous acid pollutants by iron ore sinter plants and of their effect on the environment.	01.08.1977 01.08.1979	60,00 % 89.100,00 R.E.
PS 237	Centre d'Etude et de l'Environnement CEBEDEAU 2, rue Armand Stévant B - 4000 LIEGE	Purification of toxic fumes produced during slag granulation.	01.05.1975 30.06.1978	60,00 % 20.635,85 R.E.
PS 256	Centre de Recherches Métallurgiques C.R.M. Abbaye du Val-Benoit B - 4000 LIEGE	Elimination of fumes emitted during desulphurization of pig-iron in the ladle which constitute a hazard to workers and the immediate environment.	01.10.1974 30.09.1976	60,00 % 78.200,00 R.E.
PS 288	Betriebsforschungs- institut des Vereins Deutscher Eisenhütten- leute VDEh Breite Strasse, 27 D- 4 DUESSELDORF	Development of plant for the removal of dust-laden waste gases arising during blast furnace tapping.	01.05.1977 30.04.1981	60,00 % 330.600,00 R.E.

PS 224	Betriebsforschungs- institut des Vereins Deutscher Eisenhütten- leute VDEh Breite Strasse,27 D- 4 DUESSELDORF	Development of technically and economically optimum processes for ventilation and dust extrac- tion in steelworks shops.	01.12.1972 31.12.1977	60,00 % 159.016,00 R.E.
PS 290	Institut de Recherches de la Sidérurgie Française IRSID 78105 SAINT-GERMAIN/LAYE 185,rue Président Roosevelt (FRANCE)	Combustion-free collection of the smoke emitted by electric-arc fur- naces and prospects for separating the dust thus collected.	01.12.1977 01.12.1980	60,00 % 371.100,00 R.E.
PS 298	Laboratoire d'Etude et de Contrôle de l'Environ- nement Sidérurgique LEGES B.P. 36 F- 57210 MAIZIERES-LES- METZ	Study of catching gaseous parti- culate pollutants by bag filtra- tion. Application to electric steel plants; extension to other steelplant shops.	01.10.1977 01.10.1979	60,00 % 75.900,00 R.E.
PS 302	G.K.N. Rolled & Bright Steel LTD Sub-Groups Head Office P.O. Box 3 CF 1 1TF CASTLE WORKS CARDIFF U.K.	Improved fume control from elec- tric-arc furnaces.	01.08.1977 01.08.1979	60,00 % 166.800,00 R.E.
PS 309	Betriebsforschungs- institut des Vereins Deutscher Eisenhütten- leute VDEh Breite Strasse,27 D- 4 DUESSELDORF	Optimum control of dust removal from waste gases in electric steel plants.	01.01.1978 01.01.1981	60,00 % 249.000,00 R.E.

PS 180	Fried. Krupp GmbH Forschungsinstitut Münchener Strasse 100 D - ESSEN	Fluorine precipitation in dry dust extraction processes in carbon monoxide-containing waste gases in steel production.	01.03.1971 30.06.1977	65,00 % 85.500,00 R.E.
PS 311	Max Planck Institut für Eisenforschung GmbH Postfach 14e 14e Max Planck Strasse 1 D - 4 DUESSELDORF	Investigation into particle size in brown fume and factors influencing.	01.07.1978 01.07.1981	60,00 % 181.800,00 R.E.
PS 276	Italmimpianti Piazza Piccopietra, 9 I - 16121 GENOVA	Study of a purification plant and of associated problems with the aim of perfecting its efficiency.	01.05.1976 31.01.1978	60,00 % 19.800,00 R.E.
PS 242	Thyssen Edelstahlwerke AG, Werk Witten Auestrasse 4 D - 5810 WITTEN 1 Postfach 1369	Dust extraction from waste gases in open-hearth furnaces working with high scrap ratios.	01.11.1973 31.12.1977	60,00 % 373.302,94 R.E.
PS 238	Centre Belge d'Etude et de Documentation des Eaux ( CEBEDEAU ) 2, rue Armand Stévant B - 4000 LIEGE	Study of the real composition of fluorinated substances emitted into the air from iron and steel works for the purpose of devising a means of converting toxic fluorinated compounds into less harmful substances.	01.06.1975 31.05.1977	60,00 % 39.860,00 R.E.

PS 255	Betriebsforschungs - institut des Vereins Deutscher Eisenhütten - leute VDEh Breite Strasse 27 D - 4 DUESSELDORF	Investigation of physical-chemical transport processes in the emis- sion of fluorine-containing gases from liquid slags and solid phases with a view to finding possible ways to reduce fluorine contami- nation of the environment.	01.04.1975 31.12.1977	60,00 % 56.789,00 R.E.
PS 226	Betriebsforschungs - institut des Vereins Deutscher Eisenhütten - leute VDEh Breite Strasse 27 D - 4 DUESSELDORF	Investigation of total nitrogen oxide emissions from industrial gas furnaces with a view to the development of burners with waste gases having a low nitrogen oxide content.	01.11.1974 31.13.1977	60,00 % 134.585,53 R.E.
PS 295	Reinisch-Westfaelische Technische Hochschule Aachen 16, Kopernikusstrasse D - 51 AACHEN 16	Avoidance or destruction of N <sub>2</sub> O - clusters in industrial exhaust gases.	01.09.1976 31.08.1979	60,00 % 168.900,00 R.E.
PS 250	International Flame Research Fondation Hoogovens NL - IJMUUDEN	Reduction of pollutant emission from and conservation of energy in industrial flames and furnaces.	01.01.1975 30.09.1977	60,00 % 197.500,00 R.E.
PS 274	Laboratoire d'Etude et de Contrôle de l'Environ- nement Sidérurgique LECES B.P. 36 F- 57210 MAIZIERES-LES- METZ	Correlation between the operating characteristics of steel works plant the efficiency of its dedusting equipment.	01.06.1976 31.12.1978	60,00 % 109.200,00 R.E.

PS 253	Instituut voor Milieuhygiene en Gezondheidstechniek T.W.O. Schoemakerstraat, 97 NL- 2628 DELFT Wijk 8	Examination of the airflow pattern, temperature dispersion and concentration dispersion of air pollution in models of the S-hall of the Hoogovens IJmuiden B.V. tin-plating shop.	01.12.1975 30.06.1978	60,00 \$ 51.500,00 R.E.
PS 322	Italsider S.P.A. Via Appia KM 648 I - TARANTO	Research on fume and dust abatement at a slab-conditioning yard.	01.07.1978 01.07.1981	60,00 \$ 121.800,00 R.E.

II. CONTROL OF WATER POLLUTION

IX

1	2	3	4	5
Project Reference	Research undertaken by	Subject of research	Dates for commencement and completion of research	Maximum aid as % of research cost in u.a.
PS 252	Centro Sperimentale Metallurgico S.p.a. C.S.M. Via di Castel Romano I - ROMA	Research aimed at the preparation, improvement and development of methods for the control and the automatic continuous supervision of the degree of waste-water pollution in the iron and steel industry, with initial reference to water with a high level of dissolved salts.	01.02.1975 28.02.1978	60,00 % 129,500,00 R.E.
PS 273	Centre Belge d'Etude et de Documentation des Eaux " CEBEDEAU " 2, rue Armand Stévert B- 4000 LIEGE	Determination of free cyanides in liquid and solid wastes.	01.06.1976 31.05.1978	60,00 % 54.000,00 R.E.
PS 243	British Steel Corporation Head Office 140, Battersea Park Road GB-LONDON SW 11 4LZ	Monitoring of suspended solids in iron and steel works water and effluent.	01.07.1975 31.12.1978	60,00 % 101.408,00 R.E.

PS 306	Betriebsforschungs- institut des Vereins Deutscher Eisenhütten- leute VDEh Breite Strasse, 27 D- 4 DUESSELDORF	Development and testing of an oil- detection device for monitoring pollution of bodies of water.	01.08.1978 01.08.1981	60,00 % 183.300,00 R.E.
PS 275	Italmiimpianti Piazza Piacapietra 9 16121 GENOVA Italia	Process of dispersion of pollu- tants discharged into the sea, in relation to their concentration and temperature, to marine currents and their temperature, to winds and to the shape of the coast.	01.05.1976 31.01.1978	70,00 % 22.050,00 R.E.
PS 303	Institut de Recherches Hydrologiques 10, rue Ernest Bichat F - 54000 NANCY	Evaluation and reduction of nui- sances caused by the discharge into the natural environment of conditioning products for indus- trial cooling circuits.	01.07.1978 01.07.1980	60,00 % 70.200,00 R.E.
PS 286	Centre de Recherches Metallurgiques C.R.M. Abbaye du Val-Benoit B -4000 LIEGE	Elimination of volatile pollutants from coking-plant waste water in a stripping column between automatic and continuous clearing.	01.07.1976 31.07.1978	60,00 % 175.800,00 R.E.



<p>PS 279</p>	<p>Centro Sperimentale Metallurgico S.p.A.CSM Via di Castel Romano I- 00129 ROMA</p>	<p>Further research on biological treatment of chemical pollutants in waste waters from coking plants Biological nitrification and denitrification.</p>	<p>01.01.1977 31.12.1978</p>	<p>60,00 % 151.800,00 R.E.</p>
<p>PS 315</p>	<p>Centre Belge d'Etude et de Documentation des Eaux " CEBEDEAU " 2,rue Armand Stévant B- 4000 LIEGE</p>	<p>Elimination of moderate concentrations of ammonia and other chemicals that can be oxidised by active chlorine (sulphides, phenol compounds, cyanides) in the presence of catalysts.</p>	<p>01.09.1978 31.08.1979</p>	<p>60,00 % 172.200,00 R.E.</p>
<p>PS 260</p>	<p>British Steel Corporation Head Office 140,Battersea Park Road GB-LONDON SW 11 4LZ</p>	<p>Performance of a micro-biological treatment-plant for coke-oven liquors with variability of input</p>	<p>01.04.1975 30.09.1978</p>	<p>60,00 % 120.060,00 R.E.</p>
<p>PS 287</p>	<p>Centre Belge d'Etude et de Documentation des Eaux " CEBEDEAU " 2,rue Armand Stévant B- 4000 LIEGE</p>	<p>Improvement of coke plant waste water purification by controlling the operation parameters of the treatment plants. Application to assisted biological purification.</p>	<p>02.01.1977 31.12.1978</p>	<p>60,00 % 288.000,00 R.E.</p>

PS 278	<p>Centre Sperimentale Metallurgico S.p.A. C.S.M. Via di Castel Romano I- ROMA</p>	<p>Pilot-scale removal of phenol and cyanides from the waste water of coking plants using activated carbon.</p>	<p>01.10.1976 31.03.1979</p>	<p>60,00 % 189.300,00 R.E.</p>
PS 304	<p>Institut de Recherches Hydrologiques 10, rue Ernest Bichat F- 54000 NANCY</p>	<p>Study of the removal of non-emulsified oils in circulating water and especially in discharges from steelworks possessing hot rolling mills.</p>	<p>01.07.1978 01.07.1980</p>	<p>60,00 % 100.800,00 R.E.</p>

## III. NOISE CONTROL

XIII

1	2	3	4	5
Project Reference	Research undertaken by	Subject of research	Dates for commencement and completion of research	Maximum aid as % of research cost in u.a.
PS 289	Institut de Recherches de la Sidérurgie Française IRSID 185, rue Président Roosevelt, 78105 SAINT-GERMAIN-EN-LAYE	Reduction at source of arc-furnace noise.	01.10.1977 01.10.1980	52,28 % 436,015,00 R.E.
PS 299	Betriebsforschungs-institut des Vereins Deutscher Eisenhüttenleute, VDEh, Breite Strasse, 27 D- 4 DUESSELDORF	Attempts to reduce the noise and circuit effects of electric-arc furnaces using direct current.	01.12.1977 31.12.1982	60,00 % 361,200,00 R.E.
PS 301	British Steel Corporation Head Office Battersea Laboratory, 140 Battersea Park Road LONDON SW11 4LZ	Investigations into the mechanisms of noise generation in electric-arc furnaces.	01.01.1978 01.01.1980	60,00 % 84,900,00 R.E.
PS 296	P.M. Ceretti S.p.A. Corso Italia 27 I- 28029 VILLADOSSOLA	Reduction of noise and elimination of fumes from electric-arc furnaces in steel making plants.	01.01.1977 01.01.1979	21,02 % 382,669,00 R.E.

PS 251	Betriebsforschungs- institut des Vereins Deutscher Eisenhütten- leute VDEh Breite Strasse, 27 D- 4 DUESSELDORF	Investigation of the causes of noise and pulsation produced by gas bur- ners for industrial furnaces.	01.05.1976 30.04.1979	60,00 % 113.966,00 R.E.
PS 323	Hoogovens IJmuiden BV Postbus 461 NL- 1970 AL IJMUIDEN	Development of an array of micro- phones for directional sound measu- rement.	01.07.1978 01.07.1980	60,00 % 25.200,00 R.E.

IV. RE-UTILIZATION AND ENVIRONMENTALLY SAFE  
ELIMINATION OF RESIDUES AND WASTE MATTER.

XV

1	2	3	4	5
Project Reference	Research undertaken by	Subject of research	Dates for commencement and completion of research	Maximum aid as % of research cost in u.a.
PS 225	Betriebsforschungs- institut des Vereins Deutscher Eisenhütten- leute VDEh Breite Strasse, 27 D- 4 DUESSELDORF	Investigation of the treatment and processing of waste matter from iron and steel works.	01.11.1973 31.07.1977	68,34 % 555.042,52 R.E.
PS 271	Betriebsforschungs- institut des Vereins Deutscher Eisenhütten- leute VDEh Breite Strasse, 27 D- 4 DUESSELDORF	Re-utilization and preparation for release into the environment of dust and sludge containing Fe, Zn and Pb produced in the manufac- ture of iron and steel.	01.09.1975 31.08.1978	60,00 % 589.478,00 R.E.
PS 235	ARBED-Division d'Esch Belval - C.P. 142 L- ESCH-SUR-ALZETTE	Study of the reduction of the zinc and lead content of materials in the production of pig iron in order to eliminate air and water pollution.	01.11.1973 31.07.1976	64,54 % 242.628,00 R.E.

PS 258	Laboratoires de Réfractaires et Minerais 71, avenue Général Leclerc F- 54012 NANCY Cedex B.P.3013	Recovery of valuable materials from sludge produced during the retreatment of blast furnace waste gases.	01.04.1975 31.03.1977	60,00 % 113.314,46 R.E.
PS 317	Université de Nancy Laboratoire de Chimie Minérale Case postale 140 F- 54037 NANCY Cedex	Beneficiation of secondary clarification sludge from blast furnace gases and converter dusts.	01.11.1978 01.09.1980	60,00 % 81.600,00 R.E.
PS 281	Betriebsforschungs- institut des Vereins Deutscher Eisenhütten- leute VDEh Breite Strasse,27 D- 4 DUESSELDORF	Manufacture of phosphatic fertilizers.	01.08.1976 31.07.1979	60,00 % 81.900,00 R.E.
PS 320	Betriebsforschungs- institut des Vereins Deutscher Eisenhütten- leute VDEh Breite Strasse,27 D- 4 DUESSELDORF	Thermal fusion of phosphates, especially a Ca-Al phosphate, in a rotary kiln processing material at a rate of 800 kg/hour.	15.07.1978 01.07.1980	60,00 % 70.200,00 R.E.
PS 270	ARBED-Division d'Esch Belval - C.P. 142 L- ESCH-SUR-ALZETTE	Research into the causes of the pollution of surface and underground water and means of its control during the preparation, storage and use of blast furnace slag.	01.06.1976 31.12.1978	60,00 % 157.623,00 R.E.

PS 291	Institut de Recherches de la Sidérurgie Française IRSID P- SAINT-GERVAISE-EN-LAYE B.P. 2129	Interaction between wastes and water.	01.07.1976 30.06.1978	60,00 % 99.900,00 R.E.
PS 262	Centre de Recherches de Pont-à-Mousson Maisières 54700 B.P. 28 P- PONT-A-MOUSSON	Elimination from rivers and beauty- spots of pollution from wire-dra- wing plants by developing a new mechanical descaling process for steel wire.	01.03.1976 30.04.1977	60,00 % 68.963,00 R.E.
PS 282	Centro Sperimentale Metallurgico C.S.M. Via di Castel Romano Casella post. 10747 I- 00129 ROMA	Definition of a continuous electro- lytic pickling process (DEN) for the radical solution of noxious industrial effects.	01.06.1976 31.05.1979	30,00 % 165.000,00 R.E.
PS 236	Centre Belge d'Etude et de Documentation des Eaux " CEBEDEAU " 2, rue Armand Stévert B- 4000 LIEGE	The combustion of used emulsions from cold-rolling mills without air polluting residues.	01.01.1975 31.12.1977	75,00 % 125.009,00 R.E.
PS 307	British Steel Corpora- tion Head Office 140, Battersea Park Road GB-LONDON SW 11 4LZ	Recycling of wastes produced during stainless steel making.	20.07.1977 20.07.1980	60,00 % 59.400,00 R.E.

1	2	3	4	5
PS 313	Centre Belge d'Etude et de Documentation des Eaux " CEREDAU " .. 2, rue Armand Stévant B- 4000 LIEGE	Pilot study of caustic soda treatment process for reducing the zinc and lead content of waste products from iron and steel making processes.	01.08.1978 30.06.1981	60,00 % 360.000,00 R.E.



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This report is the fourth drawn up since the beginning of the ECSC's research activities in the field of pollution control in the iron and steel industry.

The interest which this work has aroused in the industrial world and in the most varied circles has not ceased to increase along with the need to improve the environment of people in general and that of industrial centres in particular. Like many others, the iron and steel industry has been faced with the essential task of controlling the pollution which it causes.

The European Commission has thus quite naturally been involved in these efforts and has made its contribution in accordance with the Treaty, particularly in the research sector.

The aim of the Commission of the European Communities in publishing this brochure is to summarize in a compact volume the essential data enabling interested readers to note recent research projects and the relevant references permitting them to trace the progress of these projects if they wish. Further information is given in the regular 'Euro-abstracts' publications.

Reports follow on a total of 68 research projects, divided up into different thematic groups and arranged within these in alphabetical order. Most of them still come under the 3 programme, but they do also include - in particular in connection with the residue and waste problem - projects from the 4 programme.



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